Lecture Notes in Statistical Mechanics and Mesoscopics

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(`arXiv:1107.0568`)

These are the lecture notes for quantum and statistical mechanics courses that are given by DC at Ben-Gurion University. They are complementary to *Lecture Notes in Quantum Mechanics* [arXiv:quant-ph/0605180]. Some additional topics are covered, including: introduction to master equations; non-equilibrium processes; fluctuation theorems; linear response theory; adiabatic transport; the Kubo formalism; and the scattering approach to mesoscopics.

Thermal Equilibrium

Systems with interactions

Fluctuations and Response

System interacting with a bath

Additional topics

Detailed table of contents is available in the last two pages.

Thermal Equilibrium

[1] The statistical picture of Mechanics

Before we start discussing the *canonical formalism* of statistical mechanics, we would like to dedicate the first lecture for some preliminaries regarding: Random variables and probability functions; The statistical picture of classical dynamics in phase space; The notion of chaos; Stationary states in general; and the canonical state in particular.

This lecture is quite terse, and possibly will be expanded in the future.

[1.1] Random variables

Here is a list of topics that should be covered by a course in probability theory:

$$\text{Random variable/observation} \qquad \hat{x} \tag{1.1}$$

$$\text{Distribution function} \qquad \rho(x) \tag{1.2}$$

$$\text{for discrete spectrum} \qquad \rho(x) \quad \equiv \quad \text{Prob}\,(\hat{x} = x) \tag{1.3}$$

$$\text{for continuous spectrum} \qquad \rho(x)dx \quad \equiv \quad \text{Prob}\,(x < \hat{x} < x + dx) \tag{1.4}$$

$$\text{Changing variables} \qquad \hat{y} = f\,(\hat{x})\,, \quad \tilde{\rho}\,(y)\,dy = \rho(x)dx \tag{1.5}$$

$$\text{Expectation value of the random variable} \qquad \langle \hat{x} \rangle \equiv \sum_x \rho(x)x \tag{1.6}$$

$$\text{Expectation value of some other observable} \qquad \langle \hat{A} \rangle \equiv \sum_x \rho(x)A(x) \tag{1.7}$$

$$\text{Variance} \qquad \text{Var}(\hat{x}) = \langle (\hat{x} - \langle \hat{x} \rangle)^2 \rangle = \langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2 \tag{1.8}$$

$$\text{Moment generating function} \qquad Z(\lambda) = \langle \mathrm{e}^{\lambda \hat{x}} \rangle \tag{1.9}$$

$$\text{Comulant generating function is defined through} \qquad Z(\lambda) \equiv \exp[g(\lambda)] \tag{1.10}$$

$$\text{Gaussian distribution, definition} \qquad \rho(x) \propto \exp\left[-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right] \tag{1.11}$$

$$\text{Gaussian distribution, comulant} \qquad g(\lambda) = \mu\lambda + \frac{1}{2}\sigma^2\lambda^2 \tag{1.12}$$

Legendre transform.– We can write the probability function as $\rho(x) = \exp(-F(x))$, and redefine the comulant generating function as $G(\lambda) = -g(\lambda)$. We have by definition

$$e^{-G(\lambda)} \quad = \quad \int_{-\infty}^{\infty} e^{-F(x)\ +\ \lambda x}\ dx \tag{1.13}$$

If we are allowed to use a saddle point approximation, it follows that $G(\lambda)$ is related to $F(x)$ by a Legendre transform:

$$G(\lambda) \quad \approx \quad \min_x \Big\{F(x) - \lambda x\Big\} \quad = \quad F(\bar{x}) - \lambda\bar{x} \tag{1.14}$$

where the most probable value $\bar{x}$ is determined by solving $\lambda = F'(x)$. We shall see that this is formally the same mathematics as going from the Helmholtz to Gibbs free energy. Below we explain that the inverse of this relation is the large deviation theory.

[1.2] Several random variables

In classical probability theory we can define a joint distribution function for random variables, and then characterize this distribution by correlation functions.

$$\text{Joint distribution function of two variables} \quad \rho\,(x,y) \tag{1.15}$$

$$\text{Correlation between two variables} \quad C_{xy} = \langle \hat{x}\hat{y}\rangle - \langle \hat{x}\rangle\langle \hat{y}\rangle \tag{1.16}$$

In the quantum framework, known as "measurement theory", it is not possible in general to define joint distribution function. Instead one defines a probability matrix. See the lecture regarding the first and the second quantum postulates in quant-ph/0605180

If we have a sequence of random variable $\{\hat{x}_j\}$ it is called a stochastic process, and the common notation for the correlation function is C_{ij}. For time-continuous process the notations is $C(t',t'')$ where t' and t'' are the two "sampling" times of the "signal".

Adding random variables.–
Adding two independent random variables:

$$\begin{aligned}
\hat{S} &= \hat{x}+\hat{y} \\
\langle \hat{S}\rangle &= \langle \hat{x}\rangle + \langle \hat{y}\rangle \\
\mathrm{Var}(\hat{S}) &= \mathrm{Var}(\hat{x}) + \mathrm{Var}(\hat{y}) \\
g_s(\lambda) &= g_x(\lambda) + g_y(\lambda)
\end{aligned}$$

Adding N independent and identically distributed random variables:

$$\begin{aligned}
\hat{S} &= \sum_{j=1}^{N} \hat{x}_j \\
\langle \hat{S}\rangle &= N\mu \\
\mathrm{Var}(\hat{S}) &= N\sigma^2 \\
g_s(\lambda) &= Ng(\lambda)
\end{aligned}$$

The are two useful results for large N. One is the central limit theorem and the other is the large deviation theory.

Central limit theorem.– We define the scaled variable

$$\hat{y} \equiv \frac{\sum_j \hat{x}_j - N\mu}{\sqrt{N}\ \sigma} \tag{1.17}$$

The statement is that in the large N limit it has a normal distribution with zero average and unit dispersion. This follows by taking the limit of

$$g_y(\lambda) = N\left[g\left(\frac{\lambda}{\sqrt{N}\sigma}\right) - \frac{\lambda\mu}{\sqrt{N}\sigma}\right] \tag{1.18}$$

Large deviation theory.– Define the scaled variable $\hat{x} = (1/N)\sum \hat{x}_j$. Accordingly

$$g_x(\lambda) = Ng\left(\frac{\lambda}{N}\right) \tag{1.19}$$

The sloppy statement regarding its distribution is

$$\rho(x) \sim e^{-Nf(x)}, \qquad f(x) = \max_{\lambda}\{\lambda x - g(\lambda)\} \tag{1.20}$$

In order to prove this result note that $\Theta(x) < e^{\lambda x}$ for any positive λ. Consequently

$$\mathrm{Prob}(\hat{x} > x) = \left\langle \Theta\left[\left(\sum \hat{x}_j\right) - Nx\right]\right\rangle < \left\langle e^{\lambda[(\sum \hat{x}_j)-Nx]}\right\rangle = e^{N(g(\lambda)-\lambda x)} \tag{1.21}$$

A lowest bound is obtained by optimizing the value of $\lambda \in [0, \infty]$. A complementary inequality is obtained for $\text{Prob}(\hat{x} < x)$, where the value of $\lambda \in [-\infty, 0]$ is optimized to get the lowest bound. Thus, the unconstrained optimization provides a lowest bound for $\tilde{\rho}(x) \equiv \min\{\text{Prob}(\hat{x}{<}x), \text{Prob}(\hat{x}{>}x)\}$, which is asymptotically similar to $\rho(x)$. Note that the optimization parameter λ is formally like λ/N, where λ is conjugate to the random variable $\hat{x}$.

[1.3] The statistical description of a classical particle

The statistical state of a classical particle with one degree of freedom is described by a probability function:

$$\rho(x,p)\frac{dxdp}{2\pi\hbar} \quad \equiv \quad \text{PROB}\left(x < \hat{x} < x+dx, p < \hat{p} < p+dp\right) \tag{1.22}$$

where the normalization is

$$\iint \frac{dxdp}{2\pi\hbar}\ \rho\left(x,p\right) \quad = \quad 1 \qquad\qquad [\text{in the next lectures } \hbar = 1] \tag{1.23}$$

The generalization of this definition to the case of d freedoms is straightforward with Planck cell volume $(2\pi\hbar)^d$. The expectation values of observables are defined in the usual way:

$$\langle A \rangle \quad = \quad \iint \frac{dxdp}{2\pi\hbar}\ \rho\left(x,p\right)\ A(x,p) \tag{1.24}$$

We note that in the quantum context one can define a quasi distribution that corresponds to $\rho(x,p)$, known as the *Wigner function*. Furthermore with any observable $\hat{A}$ we can associate a phase apace function $A(x,p)$ such that the expectation value can be calculated using classical look-alike formulas. This is known as the *Wigner-Weyl formalism*. This formalism can be regraded as generalization of WKB: Roughly speaking one may say that each Planck cell in phase space can be regarded as representing a quantum state. The volume of Planck cell is $(2\pi\hbar)^d$ where d is the number of freedoms. Above we have assumed $d = 1$. Note that the normalization convention allows a sloppy interpretation of $\rho\left(x,p\right)$ as the probability to occupy a Planck cell in phase space. We also remark that the quantum requirement $\mathsf{trace}(\rho^2) \leq 1$ implies that a wavepacket in space space cannot occupy a volume that is less than a Planck cell. The probability function of x is

$$\rho(x) \quad = \quad \int \frac{dp}{2\pi}\rho\left(x,p\right) \tag{1.25}$$

The "spreading" of a wavepacket is characterize by

$$\sigma_x^2 \quad \equiv \quad \text{Var}(\hat{x}) \quad = \quad \langle(\hat{x} - \langle\hat{x}\rangle)^2\rangle \quad = \quad \langle\hat{x}^2\rangle - \langle\hat{x}\rangle^2 \tag{1.26}$$

$$\sigma_p^2 \quad \equiv \quad \text{Var}(\hat{p}) \quad = \quad \langle(\hat{p} - \langle\hat{p}\rangle)^2\rangle \quad = \quad \langle\hat{p}^2\rangle - \langle\hat{p}\rangle^2 \tag{1.27}$$

In the quantum context $\sigma_x\sigma_p > (\hbar/2)$. The "energy" of the system is defined as follows:

$$E \quad = \quad \langle\mathcal{H}\left(\hat{x},\hat{p}\right)\rangle \quad = \quad \iint \frac{dxdp}{2\pi\hbar}\ \rho\left(x,p\right)\ \mathcal{H}(x,p) \tag{1.28}$$

Later we shall define some other "spectral" functions that are related to $\mathcal{H}$. Those can be written as an expectation value of functions of $\mathcal{H}$.

[1.4] Dynamics in phase space

The difference between "classical mechanics" and "classical statistical mechanics" parallels the distinction between "Heisenberg picture" and "Schrodinger picture" in quantum mechanics. The former describes the evolution of the system using a set of dynamical variables that obey some equations of motion, while the latter describe the evolution of the associated probability function. In order to make the above distinction clear we consider the simplest example: a free particle. The Hamiltonian is

$$\mathcal{H} = \frac{p^2}{2\mathsf{m}} + V(x), \qquad \text{for free particle } V(x)=0 \tag{1.29}$$

Say that at $t=0$ the particle is at (x_0, p_0). The equations of motion are

$$\dot{x} = \frac{\partial \mathcal{H}}{\partial p} = \frac{p}{\mathsf{m}} \tag{1.30}$$

$$\dot{p} = -\frac{\partial \mathcal{H}}{\partial x} = 0 \tag{1.31}$$

The solution is $x(t) = x_0 + (t/\mathsf{m})p_0$ and $p(t) = p_0$. In the Heisenberg picture we regard $\hat{x}_0$ and $\hat{p}_0$ as random variables that have some probability function $\rho\,(x,p)$. Then we define new random variables

$$\hat{x}_t = \hat{x}_0 + \frac{t}{\mathsf{m}}\hat{p}_0 \tag{1.32}$$

$$\hat{p}_t = \hat{p}_0 \tag{1.33}$$

It follows from the composition law of random variables that there is spreading in space as a function of time:

$$\sigma_x\,(t) = \sqrt{\sigma_x^2 + \left(\frac{t}{\mathsf{m}}\right)^2 \sigma_p^2} \sim \frac{\sigma_p}{\mathsf{m}} t \tag{1.34}$$

where (σ_x, σ_p) is the initial spreading. It should be clear that "spreading" is a classical effect that originates if we assume that there is some dispersion in the momentum. In quantum mechanics this effect is unavoidable because preparations with zero dispersion are non-physical.

In the optional Schrodinger picture we define $\rho_t\,(x,p)$ as the probability distribution of $\hat{x}_t$ and $\hat{p}_t$. So instead of talking about the time evolution of $\hat{x}$ and $\hat{p}$ we talk about the time evolution of $\rho\,(x,p)$. In statistical mechanics we prefer the latter point of view. Evolution takes place in phase space. Liouville theorem applies. Let us see how we use the "Schrodinger picture" in the above example. Assume that the free particle has been prepared at (X_0, P_0), namely,

$$\rho_{t=0}\,(x,p) = \frac{1}{\sigma_x \sigma_p} \exp\left(\frac{(p-P_0)^2}{2\sigma_p^2}\right) \exp\left(\frac{(x-X_0)^2}{2\sigma_x^2}\right) \tag{1.35}$$

After time t the state is

$$\rho_t\,(x,p) = \frac{1}{\sigma_x \sigma_p} \exp\left(\frac{(p-P_0)^2}{2\sigma_p^2}\right) \exp\left(\frac{(x-\frac{t}{\mathsf{m}}p-X_0)^2}{2\sigma_x^2}\right) \tag{1.36}$$

If the preparation is not a "classical pure state", but say a Gaussian wave-packet that has some finite momentum spread σ_p, then one observes spreading as explained previously. More generally we can discuss the spreading of a wavepacket in the case of a non-linear oscillator. In such case $V(x)$ has either *sub-quadratic* or *super-quadratic* variation, and consequently the oscillation frequency $\omega(E)$ depends on the energy: decreases or increases with energy respectively. If the initial distribution has some finite spread σ_E in energy, there will be angular spreading that leads to a quasi-ergodic distribution within the energy shell. It is not really ergodic because if we started with a mono-energetic distribution ($\sigma_E = 0$) it would not fill uniformly the energy surface: here the energy surface is merely a one-dimensional "ellipse". For graphical illustrations see figures in the next section.

[1.5] The route to ergodicity

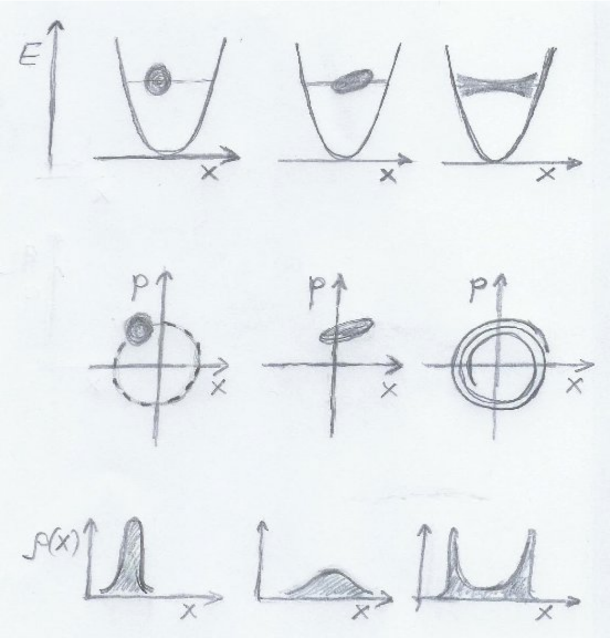
Let us outline some major observations with regard to the dynamics of classical Hamiltonian systems.

Simple 1D system:– The student is expected to be familiar with the dynamics of harmonic oscillator; potential well; pendulum. In the case of non-linear oscillations we have the *spreading* effect. In the case of a pendulum we have a multi-component phase space with separatrix. The dynamics is not chaotic. One can define the oscillation frequency $\omega(E)$ as a function of energy. In the quantum case $\omega(E)$ corresponds to the level spacing at the vicinity of the energy E.

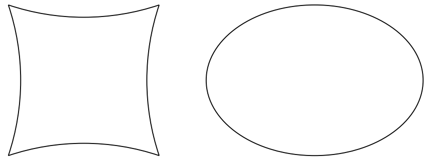
Chaotic system:– The student is expected to be familiar with the dynamics in simple billiards. The visualization can be achieved using a Poincare section. In the case of a Sinai billiard (motivated by the discussion of Lorentz gas) the dynamics is fully chaotic, leading to ergodization. More generally we might have *mixed phase space* that contains "chaotic sea" as well as "islands".

Ergodization:– The evolution of a chaotic system leads to an ergodization on the energy shell. This can be mathematically described using the Boltzamnn approach: course graining of phase space by dividing it into cells; definition of Boltzamnn entropy. Eventually the system will become stationary-like, as if it were prepared in a state that has maximum entropy.

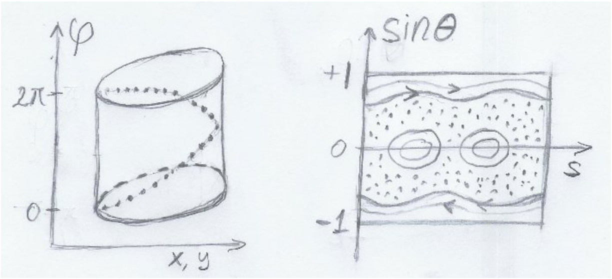
Driven system:– There is a complicated route to chaos in the case of driven integrable (1D) systems. In contrast to that in the case of driven globally chaotic systems the picture is qualitatively simple: if we prepare the system initially within an energy shell, it will "evolve" with this energy shell, along with diffusion transverse to the energy shell. This diffusion leads in general to increase of the average energy (heating).



Spreading illustration. – We consider the evolution of an initial Gaussian distribution (left panels) in the case of a non-linear oscillator. After a short time (middle panels) the spreading is like that of a free particle. After a long time (right panels) one observes an ergodic-like distribution within the energy shell. However, this is not really ergodic: if we started with a mono-energetic distribution, it would remain localized on the energy shell, as in the case of an harmonic oscillator.



Convex Billiard Concave Billiard



Phase space illustration. – The dynamics of a particle in a convex (Sinai) Billiard is completely chaotic. In contrast to that, in the case of a concave billiard, we have a mixed phase space that contains both quasi-integrable regions and chaotic sea. The phase space is 3-dimensional (x, y, φ) where φ is the direction of the velocity. It is illustrated in the left lower panel. The dotted line indicates the normal direction on the boundary. The reflections are specular with regard to this direction. The right lower panel is the two-dimensional (s, θ) Poincare section of phase space: each trajectory is represented by a sequence of points that indicate successive collisions with the boundary, where s is the boundary coordinate, and θ is the collision angle (relative to the normal).

[1.6] Stationary states

The evolution of a statistical state is determined by the Lioville equation of classical mechanics, which becomes the von-Neumann Lioville equation in quantum mechanics.

$$\frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho]_{\text{PB}} \tag{1.37}$$

We consider non-driven bounded systems, and focus our attention on *stationary* states that do not change in time. This means $\partial\rho/\partial t = 0$. In the classical language ρ can be regarded as a mixture of "energy shells", while in the quantum language it means that $\rho \mapsto \text{diag}\{p_r\}$ is a mixture of energy eigenstates labelled by r. In particular the classical microcanonical state corresponds to an energy eigenstate, and is formally written as

$$\rho(x,p) = \frac{1}{\mathsf{g}(\mathcal{E})}\delta(\mathcal{H}(x,p) - \mathcal{E}) \tag{1.38}$$

The canonical state is

$$p_r = \frac{1}{Z(\beta)}\,\mathrm{e}^{-\beta E_r} \tag{1.39}$$

and in a classical context it is written as

$$\rho(x,p) = \frac{1}{Z(\beta)}\,\mathrm{e}^{-\beta\mathcal{H}(x,p)} \tag{1.40}$$

The density of states and the partition function are defined as

$$\mathsf{g}(E) = \mathsf{trace}(\delta(E - \mathcal{H})) = \sum_r \delta(E - E_r) \tag{1.41}$$

$$Z(\beta) = \mathsf{trace}(\mathrm{e}^{-\beta\mathcal{H}}) = \sum_r \mathrm{e}^{-\beta E_r} = \int \mathsf{g}(E)dE\,\mathrm{e}^{-\beta E} \tag{1.42}$$

We note that the probability distribution of the energy can be written as $\rho(E) = \mathsf{g}(E)\,f(E)$, where the occupation probability function is $f(E) \propto \delta(E - \mathcal{E})$ and $f(E) \propto \mathrm{e}^{-\beta E}$ in the microcanonical and canonical cases respectively. If we have a many body system of non-interacting participles we can re-interpret $f(E)$ as the occupation function, and accordingly $\rho(E)$ becomes the energy distribution of the particles (with normalization N).

[1.7] The microcanonical and canonical states

Let us assume the following total Hamiltonian for a universe that consists of system and environment:

$$\mathcal{H}_{\text{total}} = \mathcal{H}(Q) + \mathcal{H}_{\text{env}}(Q_\alpha) + \mathcal{H}_{\text{int}}(Q, Q_\alpha) \tag{1.43}$$

For sake of presentation we do not write the conjugate momenta, so Q stands for (Q,P) or it may represent spin freedoms. If one neglect the interaction the eigenenergies are written as $E_{r,R} = E_r + E_R$, where r labels system states and R labels environmental states.

It is argued that the weak interaction with the environment leads after relaxation to a canonical state which is determined by the parameter

$$\beta = \frac{d}{dE}\log(\mathsf{g}_{\text{env}}(\bar{E})) \tag{1.44}$$

where $\mathsf{g}_{\text{env}}(\bar{E})$ is the density of states of the environment, and $\bar{E}$ is the total energy of the universe. The argument is based on the assumption that the universe (system+environment) is a closed system with some total energy $\bar{E}$. This microcanonical assumption can be relaxed (more generally β can be some averaged value), but for sake of clarity we take it as a starting point. This means that after ergodization all the states with energy $\bar{E} < E_{r,R} < \bar{E} + dE$ have equal probability. It follows that the probability to find the system with energy E_r is proportional to the number of states such that $(\bar{E}{-}E_r) < E_R < (\bar{E}{-}E_r) + dE$. The number of such states is $\mathsf{g}_{\text{env}}(\bar{E}{-}E_r)dE$ and therefore we conclude that

$$p_r \quad \propto \quad \mathsf{g}_{\text{env}}(\bar{E}{-}E_r) \quad \approx \quad \mathsf{g}_{\text{env}}(\bar{E})\mathrm{e}^{-\beta E_r} \tag{1.45}$$

Accordingly

$$p_r \quad = \quad \frac{1}{Z}\mathrm{e}^{-\beta E_r} \tag{1.46}$$

where the so-called partition function provides the normalization

$$Z(\beta) \quad = \quad \sum_r \mathrm{e}^{-\beta E_r} \tag{1.47}$$

The partition function may depend on parameters that appear in the system Hamiltonian. Therefore we use in general the notation $Z(\beta, X)$.

[1.8] Mathematical digression

Sometimes is is more appropriate to expand the log of a function. Specifically this would be the case if the function is definite positive and span many decades. Let us see what is the error which is involved in such an expansion:

$$f(x) = x^N \tag{1.48}$$

$$f\left(x+\delta x\right) = x^N + Nx^{N-1}\delta x + \frac{1}{2}N(N-1)x^{N-2}\delta x^2 \tag{1.49}$$

$$\delta x \ll x/N \tag{1.50}$$

Optionally we expand the log of the function:

$$S(x) \equiv \ln f(x) = N\ln(x) \tag{1.51}$$

$$S\left(x+\delta x\right) = N\ln(x) + \frac{N}{x}\delta x - \frac{1}{2}\frac{N}{x^2}\delta x^2 \tag{1.52}$$

$$\delta x \ll x \tag{1.53}$$

Thus we have the recipe:

$$f\left(x+\delta x\right) \quad \approx \quad f(x)\mathrm{e}^{\beta\delta x} \qquad\qquad \text{where} \quad \beta \quad \equiv \quad \frac{\partial \ln f(x)}{\partial x} \tag{1.54}$$

In complete analogy we have:

$$\mathsf{g}\left(E_0 + \epsilon\right) \quad \approx \quad \mathsf{g}\left(E_0\right)\mathrm{e}^{\beta\epsilon} \tag{1.55}$$

where β is the log derivative of the density of states.

[2] Spectral functions

Various types of spectral functions are defined in mathematical physics. In the quantum context they characterize the spectrum $\{E_n\}$ of energies of as given Hamiltonian $\mathcal{H}$. In the continuum or classical limit it is essential to define a *measure*. Below we focus on the most popular spectral functions in statistical mechanics: the density of states $\mathsf{g}(E)$, and the partition function $Z(\beta)$. We shall see later that the state equations of a system in equilibrium can be derived from, say, the partition function. Hence the spectral function serves as a *generating function*.

In the section below we define $\mathsf{g}(E)$ and $Z(\beta)$, and show how they are calculated using standard examples: Two level system; Harmonic oscillator; Particle in a box; Particle with general dispersion relation; The effect of $A(x), V(x)$ potential; Several particles; Identical classical particles, the Gibbs factor; Particles with interactions; In particular two quantum particles; Molecules of type AA and AB (exercise).

[2.1] The definition of counting and partition functions

We consider a time independent bounded system which is described by a Hamiltonian $\mathcal{H}$ whose eigenvalues are E_r. We can characterize its energy spectrum by the functions

$$\mathcal{N}(E) \equiv \sum_r \Theta(E - E_r) = \sum_{E_r<E} 1 \tag{2.1}$$

$$Z(\beta) \equiv \sum_r \mathrm{e}^{-\beta E_r} \tag{2.2}$$

If we have a large system we can smooth $\mathcal{N}(E)$, and then we can define the density of states as

$$\mathsf{g}(E) \equiv \frac{d\mathcal{N}(E)}{dE} = \overline{\sum_r \delta(E - E_r)} \tag{2.3}$$

Note that

$$Z(\beta) = \int \mathsf{g}(E) dE \ \mathrm{e}^{-\beta E} \tag{2.4}$$

For a classical particle in 1D we can use the above definitions with the prescription

$$\sum_r \longmapsto \iint \frac{dxdp}{2\pi\hbar} \tag{2.5}$$

Each "Planck cell" in phase space represents a state. Accordingly

$$\mathcal{N}(E) = \iint \frac{dxdp}{2\pi} \Theta(E - \mathcal{H}(x,p)) = \iint_{\mathcal{H}(x,p)<E} \frac{dxdp}{2\pi} \tag{2.6}$$

$$Z(\beta) = \iint \frac{dxdp}{2\pi} \mathrm{e}^{-\beta\mathcal{H}(x,p)} = \int \mathsf{g}(E) dE \ \mathrm{e}^{-\beta E} \tag{2.7}$$

In what follows the Gaussian integral is useful:

$$\int \mathrm{e}^{-\frac{1}{2}ax^2} dx = \left(\frac{2\pi}{a}\right)^{\frac{1}{2}} \tag{2.8}$$

[2.2] Two level system or spin

The Hamiltonian of spin 1/2 in magnetic field is

$$\mathcal{H} \;=\; \frac{1}{2}h\sigma_z \tag{2.9}$$

The eigenstates are $|+\rangle$ and $|-\rangle$ with eigenvalues $E_{\pm} = \pm h/2$. Accordingly

$$Z(\beta) \;=\; \mathrm{e}^{-\beta\left(-\frac{h}{2}\right)} + \mathrm{e}^{-\beta\left(\frac{h}{2}\right)} \;=\; 2\cosh\left(\frac{1}{2}\beta h\right) \tag{2.10}$$

Optionally we can write the energies of any two level system as $E_r = \epsilon n$ with $n = 0, 1$ then

$$Z(\beta) = \left(1 + \mathrm{e}^{-\beta\epsilon}\right) \tag{2.11}$$

[2.3] Two spins system in interaction

If we have N is interacting spins the sum over states can be factorized and we simply get

$$Z_N(\beta) \;=\; \Big(Z_1(\beta)\Big)^N \tag{2.12}$$

For two spins in the absence of magnetic field we get $Z_2 = 2^2 = 4$. Let us see what happens if there is an interaction:

$$\mathcal{H} \;=\; \varepsilon\sigma^a\cdot\sigma^b \;=\; \left(2S^2 - 3\right)\varepsilon, \qquad S = \frac{1}{2}\sigma^a + \frac{1}{2}\sigma^b \tag{2.13}$$

The energy levels are $E_{singlet} = -3\varepsilon$ and $E_{triplet} = \varepsilon$. With and added magnetic field the partition function is

$$Z(\beta) \;=\; \mathrm{e}^{3\beta\varepsilon} + \left[\mathrm{e}^{\beta h} + \mathrm{e}^{-\beta h} + 1\right]\mathrm{e}^{-\beta\varepsilon} \tag{2.14}$$

which factorized for $\varepsilon = 0$, but not in general.

[2.4] Harmonic oscillator

The Hamiltonian of Harmonic oscillator is

$$\mathcal{H} = \frac{p^2}{2\mathsf{m}} + \frac{1}{2}\mathsf{m}\omega^2 x^2 \tag{2.15}$$

The eigenstates are $|n\rangle$ with eigenvalues $E_n = \left(\frac{1}{2} + n\right)\omega$. Accordingly

$$Z(\beta) \;=\; \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\left(\frac{1}{2}+n\right)\omega} \;=\; \frac{1}{2\sinh\left(\frac{1}{2}\omega\beta\right)} \tag{2.16}$$

Note that if we write the energies as $E_r = \epsilon n$ with $n = 0, 1, 2, 3, 4, ...$ then

$$Z(\beta) = \frac{1}{1 - \mathrm{e}^{-\beta\epsilon}} \tag{2.17}$$

Now let us see how the classical calculation is done.

$$\mathcal{N}(E) \quad = \quad \frac{1}{2\pi}\ \text{ellipse area} \quad = \quad \frac{1}{2\pi}\,\pi\left(\frac{2E}{\mathsf{m}\omega^2}\right)^{\frac{1}{2}}(2\mathsf{m}E)^{\frac{1}{2}} \quad = \quad \frac{E}{\omega} \tag{2.18}$$

$$Z(\beta) \quad = \quad \int dx\ \mathrm{e}^{-\beta\frac{1}{2}\mathsf{m}x^2}\int\frac{dp}{2\pi}\ \mathrm{e}^{-\beta\frac{p^2}{2\mathsf{m}}} \quad = \quad \left(\frac{2\pi}{\beta\mathsf{m}\omega^2}\right)^{\frac{1}{2}}\left(\frac{\mathsf{m}}{2\pi\beta}\right)^{\frac{1}{2}} \quad = \quad \frac{T}{\omega} \tag{2.19}$$

One can verify the validity of WKB quantization.

[2.5] Particle in a 1D box

The simplest is to assume periodic boundary conditions

$$\mathcal{H} \quad = \quad \frac{p^2}{2\mathsf{m}} \qquad x\in[0,L] \quad \text{(ring)} \tag{2.20}$$

The eigenstates are the momentum states $|p\rangle$ with

$$p \quad = \quad \frac{2\pi}{L}n \qquad \text{where } n = 0, \pm1, \pm2... \tag{2.21}$$

Hence the eigenvalues are

$$E_n \quad = \quad \frac{1}{2\mathsf{m}}\left(\frac{2\pi}{L}n\right)^2 \tag{2.22}$$

The number of states up to energy E is

$$\mathcal{N}(E) \quad = \quad 2\frac{L}{2\pi}(2\mathsf{m}E)^{\frac{1}{2}} \quad \equiv \quad \frac{1}{\pi}k_E L \quad \equiv \quad 2\frac{L}{\lambda_E} \tag{2.23}$$

The density of states is

$$\mathsf{g}(E) \quad = \quad \frac{L}{\pi v_E} \tag{2.24}$$

The 1D case here is pathological because in general the density of states grows rapidly with energy. Nevertheless in the limit of ”infinite volume” we may treat the spectrum as a continuum:

$$Z(\beta) \quad = \quad \sum_{n=-\infty}^{\infty}\mathrm{e}^{-\beta E_n} \quad \approx \quad \int_{-\infty}^{\infty}dn\ \mathrm{e}^{-\beta\frac{1}{2\mathsf{m}}\left(\frac{2\pi}{L}\right)^2 n^2} \quad = \quad L\left(\frac{\mathsf{m}}{2\pi\beta}\right)^{\frac{1}{2}} \quad \equiv \quad \frac{L}{\lambda_T} \tag{2.25}$$

Let us see how the calculation is carried out classically. We can still consider a ring, or optionally we can write the Hamiltonian with a box potential $V_L(x)$. Then we get

$$\mathcal{N}(E) \quad = \quad \text{rectangle area} \quad = \quad \frac{1}{2\pi}\times L\times 2\,(2\mathsf{m}E)^{\frac{1}{2}} \quad = \quad 2\frac{L}{\lambda_E} \tag{2.26}$$

$$Z(\beta) \quad = \quad \int dx\int\frac{dp}{2\pi}\ \mathrm{e}^{-\beta\frac{p^2}{2\mathsf{m}}} \quad = \quad L\left(\frac{\mathsf{m}}{2\pi\beta}\right)^{\frac{1}{2}} \quad = \quad \frac{L}{\lambda_T} \tag{2.27}$$

One can verify the validity of WKB quantization (but without the 1/2 shift).

[2.6] A particle in 3D box, or higher dimensions

Consider a particle in a d=3 box of volume $\mathsf{V} = L^d$.

$$\mathcal{H} \;=\; \sum_{i=1}^{3} \frac{p_i^2}{2\mathsf{m}} \;+\; \text{[implicit boundary conditions with volume } L^d\text{]} \tag{2.28}$$

The eigenstates are

$$\vec{p} \;=\; \frac{2\pi}{L}\,(n_1, n_2, n_3) \tag{2.29}$$

$$E_{n_1 n_2 n_3} \;=\; \frac{1}{2\mathsf{m}}\left(\frac{2\pi}{L}\right)^2 \left(n_1^2 + n_2^2 + n_3^2\right) \tag{2.30}$$

The summation over the states factorizes:

$$Z(\beta) \;=\; \sum_{n_1 n_2 n_3} \mathrm{e}^{-\beta E_{n_1 n_2 n_3}} \;=\; \left(\sum_{n} \mathrm{e}^{-\beta E_n}\right)^3 \;=\; \frac{\mathsf{V}}{\lambda_T^3} \tag{2.31}$$

The above calculation gives $Z = (L/\lambda_T)^d$ in d dimensions. For the counting function we get:

$$\mathcal{N}(E) \;=\; \frac{1}{(2\pi)^d}\frac{\Omega_d}{d}\,(k_E L)^d \;=\; \begin{Bmatrix} 2 \\ \pi \\ 4\pi/3 \end{Bmatrix} \left(\frac{L}{\lambda_E}\right)^d \tag{2.32}$$

and accordingly

$$\mathsf{g}(E) \;=\; \frac{\Omega_d}{(2\pi)^d}\,(k_E L)^{d-1}\,\frac{L}{v_E} \;\;\propto\;\; E^{(d/2)-1} \tag{2.33}$$

The factor $(k_E L)^{d-1}$ can be interpreted as the number of open modes. For $d = 2$ the DOS is independent of energy and reflects the mass of the particle.

As far as the *classical* calculation is concerned, N particle systems is formally like one particle system with $d \mapsto Nd$. In the quantum treatment the Fermonic or Bosonic nature of identical particles should be taken into account: see later how the calculation is done e.g. for two particles).

[2.7] Classical particle in magnetic field

For a particle in an arbitrary scalar potential $V(r)$ in 3D we get

$$Z(\beta) \;=\; \int \frac{dr\;dp}{(2\pi)^3}\,\mathrm{e}^{-\beta\mathcal{H}} \;=\; \left(\frac{1}{\lambda_T}\right)^3 \int dr\;\mathrm{e}^{-\beta V(r)} \tag{2.34}$$

Let us include also a vector potential:

$$\mathcal{H} = \frac{1}{2\mathsf{m}}\,(p - A(r))^2 + V(r) \tag{2.35}$$

$$Z = \int \frac{dr\,dp}{(2\pi)^3}\,\mathrm{e}^{-\beta\left[\frac{1}{2\mathsf{m}}(p-A(r))^2+V(r)\right]} = \int \frac{dr\,dp'}{(2\pi)^3}\,\mathrm{e}^{-\beta\left[\frac{1}{2\mathsf{m}}(p')^2+V(r)\right]} \tag{2.36}$$

The result does not depend on $A(r)$. The energy spectrum is not affected from the existence of $A(r)$. The energies are $E = (1/2)\mathsf{m}v^2 + V(r)$ irrespective of $A(r)$. This is no longer the case upon quantization. Note the implicit assumption of having background relaxation processes that make the dynamics irrelevant.

[2.8] Gas of classical particles in a box

Let us consider N particles:

$$\mathcal{H} = \sum_{\alpha=1}^{N}\left[\frac{\vec{p}_\alpha^{\,2}}{2\mathsf{m}} + V(r_\alpha)\right] + U(r_1,...,r_N) \tag{2.37}$$

In the absence of interaction the partition function is

$$Z_N(\beta) = \Big(Z_1(\beta)\Big)^N = \left[\frac{1}{\lambda_T^3}\int d^3r\,\mathrm{e}^{-\beta V(r)}\right]^N \tag{2.38}$$

From now on we assume gas of identical particles and therefore include the Gibbs factor:

$$Z_N(\beta) \mapsto \frac{1}{N!}Z_N(\beta) \tag{2.39}$$

For N interacting particles we get

$$Z_N(\beta) = \frac{1}{N!}\left(\frac{1}{\lambda_T^3}\right)^N \int dr_1...dr_N\,\mathrm{e}^{-\beta U(r_1,...,r_N)} \tag{2.40}$$

[2.9] Two quantum identical particles

Let us see what is the partition function for a system that consists of two identical particles, say in a box. The total energy is written as $E_{ab} = E_a + E_b$. The partition function is

$$Z(\beta) = \frac{1}{2}\sum_{a\neq b}\mathrm{e}^{-\beta(E_a+E_b)} + \begin{Bmatrix}1\\0\end{Bmatrix}\sum_a \mathrm{e}^{-\beta(2E_a)} \tag{2.41}$$

$$= \frac{1}{2}\left(\sum_{a,b}\mathrm{e}^{-\beta(E_a+E_b)} \pm \sum_a \mathrm{e}^{-2\beta E_a}\right) = \frac{1}{2}\Big[Z_1(\beta)^2 \pm Z_1(2\beta)\Big] \tag{2.42}$$

For a particle in a d dimensional box

$$Z_1 = \left(\frac{L}{\lambda_T}\right)^d \tag{2.43}$$

$$Z_2 = \frac{1}{2}\left(Z_1^2 \pm 2^{-d/2}Z_1\right) \tag{2.44}$$

Note that for $d = 3$ we get

$$Z_2(\beta) = \frac{1}{2}Z_1^2 \times \left[1 \pm \frac{1}{2^{3/2}}\left(\frac{\lambda_T^3}{\text{volume}}\right)\right] \tag{2.45}$$

The Fermi case is similar to hard sphere:

$$Z_2(\beta) \quad = \quad \frac{1}{2}Z_1^2 \times \left[1 - \left(\frac{\text{sphere volume}}{\text{box volume}}\right)\right] \tag{2.46}$$

[2.10] Two quantum particles in a box with interaction

The calculation of the partition function Z_2 for two identical quantum particle in a box, is both interesting and later on useful for the purpose of calculating the second virial coefficient of an N particle gas. The Hamiltonian is:

$$\mathcal{H} = \frac{P^2}{4\mathsf{m}} + \frac{p^2}{\mathsf{m}} + V(r) \tag{2.47}$$

In order to be able to do the calculation using separation of variables we cheat with the boundary conditions as follows: The center of mass motion is confined to a box of volume $\mathsf{V} = (4\pi/3)R^3$, and the relative motion is confined by $|r| < R$ independently. Accordingly the partition function is factorizes as follows:

$$Z_2 \quad = \quad \left(2^{3/2}\frac{\mathsf{V}}{\lambda_T^3}\right)\left[\sum_{n\ell m}^{\prime} \mathrm{e}^{-\beta E_{n\ell m}}\right] \quad = \quad \left(2^{3/2}\frac{\mathsf{V}}{\lambda_T^3}\right)\left[\sum_b \mathrm{e}^{-\beta E_b} + \int_0^\infty \mathsf{g}(k)dk\ \mathrm{e}^{-(\beta/\mathsf{m})k^2}\right] \tag{2.48}$$

where (n, ℓ, m) are the good quantum numbers for the relative motion. Ignoring the possibility of spin, the sum is over *even* or *odd* values of ℓ, for Bosons or Fermions respectively. In the second equality we separate the bond states from the scattering (continuum) states. In order to determine the DOS of the latter we recall that the radial wave functions are phase shifted spherical Bessel functions. Accordingly the box quantization condition for the allowed k_n values is

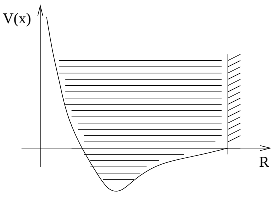
$$kR - \frac{\pi}{2}\ell + \delta_\ell \quad = \quad n\pi \tag{2.49}$$

From here one deduce a formula for the effect of the phase shifts on the DOS:

$$\mathsf{g}(k) - \mathsf{g}^{(0)}(k) \quad = \quad \frac{1}{\pi}\sum_{\varrho}^{1}(2\ell+1)\,\frac{\partial\delta_\ell}{\partial k} \tag{2.50}$$

Using this result we get after integration by parts the following expression for the interaction effect on the partition function:

$$Z_2 - Z_2^{(0)} \quad = \quad \left(2^{3/2}\frac{\mathsf{V}}{\lambda_T^3}\right)\left[\sum_b \mathrm{e}^{-\beta E_b} + \frac{\lambda_T^2}{\pi^2}\sum_{\ell}^{\prime}\int_0^\infty kdk\ \delta_\ell(k)\ \mathrm{e}^{-(\beta/\mathsf{m})k^2}\right] \tag{2.51}$$



[3] The canonical formalism

[3.1] The energy equation of state

Consider some system, for example particles that are confined in a box. The Hamiltonian is

$$\mathcal{H} \ = \ \mathcal{H}(\boldsymbol{r}, \boldsymbol{p}; X) \tag{3.1}$$

where X is some control parameter, for example the length of the box. Assuming that we are dealing with a *stationary* state, the energy of the system is

$$E \ \equiv \ \langle \mathcal{H} \rangle \ = \ \mathsf{trace}(\mathcal{H}\rho) \ = \ \sum_r p_r E_r \tag{3.2}$$

If the system is prepared in a canonical states, then it is a mixture of energy eigenstates with probabilities

$$p_r = \frac{1}{Z} \mathrm{e}^{-\beta E_r} \tag{3.3}$$

where the partition function is

$$Z(\beta, X) \ = \ \sum_r \mathrm{e}^{-\beta E_r} \tag{3.4}$$

One observes that the energy of a system that is prepared in a canonical state can be derived from the partition function as follows:

$$E \ = \ \langle \mathcal{H} \rangle \ = \ -\frac{1}{Z}\frac{\partial}{\partial \beta} Z \ = \ -\frac{\partial}{\partial \beta} \ln Z \tag{3.5}$$

Also one can find expressions for the higher moments, for example

$$\langle \mathcal{H}^2 \rangle \ = \ \frac{1}{Z}\frac{\partial}{\partial \beta}\frac{\partial}{\partial \beta} Z \tag{3.6}$$

In particular one deduces the relation

$$\mathrm{Var}(E) \ = \ \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 \ = \ \frac{\partial^2}{\partial \beta^2} \ln Z \ = \ T^2 \frac{\partial E}{\partial T} \ = \ T^2 C \tag{3.7}$$

where in the latter equality we have defined the temperature as $T = 1/\beta$ and the heat capacity as $C = dE/dT$. The notion of temperature will be discussed further below.

[3.2] The Equipartition theorem

In the classical context the Hamiltonian might be a sum of quadratic terms

$$\mathcal{H} \ = \ \sum_j c_j q_j^2 \tag{3.8}$$

where q_j are either coordinates of conjugate momenta. The partition function factorizes, where each quadratic term contributes a $\propto T^{1/2}$ term. It follows that each quadratic term contributes $T/2$ to the energy, and hence $1/2$ to the heat capacity.

This observation can be applied to the analysis of "balls connected by springs". We can always go to normal coordinates. The center of mass degree of freedom contributes $T/2$ to the energy, while each vibrational mode contributes T.

A formal extension of this so-called "Equipartition Theorem" is as follows:

$$\left\langle q_i \frac{\partial \mathcal{H}}{\partial q_j} \right\rangle \;=\; T\delta_{ij} \tag{3.9}$$

The proof is as follows: The measure of integration over phase space can be written as $dq_i dq_j dq'$, where q' represents all the other coordinates. Applying integration by parts we have

$$\int dq_i dq_j dq' \; q_i \; \frac{\partial \mathcal{H}(q)}{\partial q_j} \mathrm{e}^{-\beta\mathcal{H}(q)} = -\frac{1}{\beta}\int dq_i dq_j dq' \; q_i \; \frac{\partial}{\partial q_j}\left[\mathrm{e}^{-\beta\mathcal{H}(q)}\right] = \delta_{ij}\frac{1}{\beta}\int dq_i dq_j dq' \mathrm{e}^{-\beta\mathcal{H}(q)} \tag{3.10}$$

and form here follows the Equipartition Theorem. This generalized version is useful in discussing particles that have interaction $u(x_i - x_j) \propto |x_i - x_j|^\alpha$, which constitutes a generalization of the harmonic ($\alpha = 2$) case.

[3.3] Heat capacity

From the Equipartition Theorem one deduce that the heat capacity of an "ideal" system equals to the effective number of freedoms: Each independent quadratic term in the Hamiltonian contributes 1/2 to the heat capacity. This simple prescription should be refined for two reasons: (i) Degrees of freedom can "freeze" in the quantum treatment; (ii) In general a many body system is not ideal due to interactions. We first discuss the quantum issue referring to spins and oscillators.

Spin and oscillator.– For spin (+) or oscillator (-) with level spacing ω we have

$$\ln(Z(\beta)) \;=\; \pm\ln(1 \pm \mathrm{e}^{-\beta\omega}) \tag{3.11}$$

$$E \;=\; -\frac{\partial \ln Z}{\partial \beta} \;=\; \frac{\omega}{\mathrm{e}^{\beta\omega} \pm 1} \tag{3.12}$$

$$C(T) \;=\; \frac{dE}{dT} \;=\; \frac{1}{\left[2\text{csnh}\left(\frac{\omega}{2T}\right)\right]^2}\left(\frac{\omega}{T}\right)^2, \qquad \text{"csnh" is cosh or sinh} \tag{3.13}$$

In both case the low temperature behavior of C is identical, namely, for $T \ll \omega$ it is dominated by the Boltzmann factor $\mathrm{e}^{-\beta\omega}$. At high temperature C of the spin drop down because energy reaches saturation, while C of the oscillator approaches unity reflecting the classical prediction $E \approx T$. Since $E = \omega n$ it is more illuminating to re-write the above results as follows:

$$\langle n \rangle \;=\; \frac{1}{\mathrm{e}^{\beta\omega} \pm 1} \;\equiv\; f(\omega) \tag{3.14}$$

$$\mathrm{Var}(n) \;=\; [1 \mp f(\omega)]f(\omega) \tag{3.15}$$

where $f(\omega)$ is known as the occupation function. In the case of an oscillator the result for the number variance can be regarded as a sum of a shot-noise particle-like term $\mathrm{Var}(n) = \langle n \rangle$, and a classical term $\mathrm{Var}(n) = \langle n \rangle^2$. In the case of a spin the fluctuations go to zero in both the "empty" and "full" occupation limits. It is customary in quantum-optics to characterize the fluctuations by $g^{(2)} = (\langle n^2 \rangle - \langle n \rangle)/\langle n \rangle^2$ and to say that the bosonic (oscillator) result $g^{(2)} = 2$ corresponds to bunching, while the fermionic (spin) result $g^{(2)} = 0$ corresponds to anti-bunching. The value $g^{(2)} = 1$ reflects Poisson statistics and would apply in the case of coherent state preparation.

Debye model.– Let us refer further to a system that can be described as consisting of many harmonic freedoms, e.g. modes of vibrations. The spectral density of the modes might be $\propto \omega^{\alpha-1}$. For example in Debay model $\alpha = d = 3$, with some cutoff frequency ω_c. Then we get for the heat capacity

$$C(T) \;=\; \text{const} \int_0^{\omega_c} \frac{1}{\left[2\sinh\left(\frac{\omega}{2T}\right)\right]^2} \left(\frac{\omega}{T}\right)^2 \omega^{\alpha-1} d\omega \;=\; \text{const}\; T^{\alpha} F\left(\frac{\omega_c}{T}\right) \tag{3.16}$$

where

$$F(\nu) \;\equiv\; \int_0^{\nu} \frac{\mathrm{e}^x}{(\mathrm{e}^x-1)^2} x^{\alpha+1} dx \tag{3.17}$$

The quantum result can be described as emerging from "freezing" of freedoms due to the quantization of energy. This phenomena has lead to the birth of quantum mechanics in the context of blackbody radiation (Planck law).

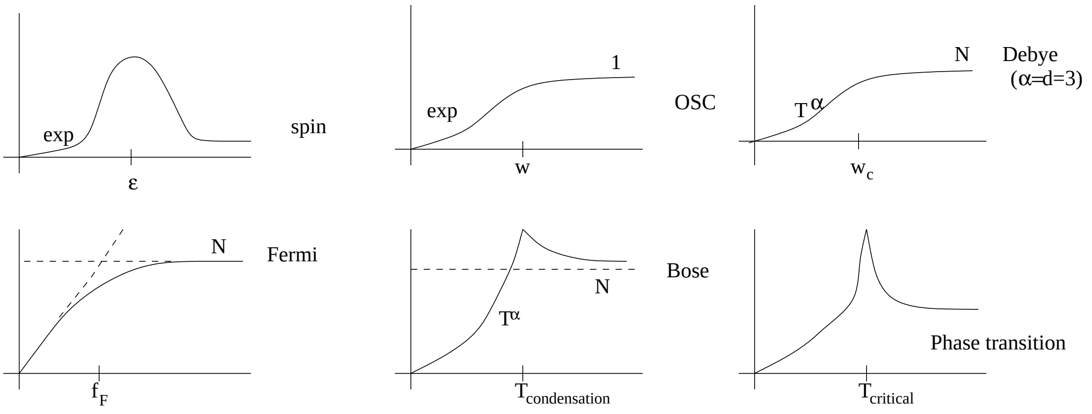
Glasses.– The standard model for glasses regard them as a large collection of "two level" entities with splitting ω that has roughly uniform distribution. Hence the calculation of the heat capacity is formally as in the Debye model model with sinh replaces by cosh, and $\alpha = 1$, leading to a linear dependence $C(T) \propto T$.

Quantum gases.– In the classical treatment, disregarding prefactors of order unity, a gas of N particles have total energy $E \sim NT$, hence the heat capacity is $C \sim N$. If we have a gas of Fermions in low temperatures, then the number of excited particles is $N_{\text{eff}} \propto T$, hence the energy is $E \propto T^2$, and the heat capacity is $C(T) \propto T$. In contrast to that Bosons in 3D condense into the ground states. Hence the occupation of an excited state of energy ϵ_r is formally the same as the occupation of an oscillator with the same frequency. Consequently one observes $C(T) \propto T^{\alpha}$ as in Debye model.

Phase transitions.– We shall discuss phase transitions in later lectures. As the temperature is lowered towards a critical temperature T_c the system becomes "correlated", which means that the effective number of freedoms is reduced. We assume $T > T_c$ and note that similar picture applies if one approaches T_c from below. We can easily explain why the heat capacity diverges as T_c is approached. For an ideal gas, or better to think about a collection of non-interacting oscillators, the partition function is $Z = g^N$, where N is the number of freedoms, and $g \propto T$ is the number of accessible states for a single freedom at temperature T. For a correlated system $Z = g^{N_{\text{eff}}}$, where $N_{\text{eff}} = N/\xi^d$ is the effective number of independent regions, and ξ is called the correlation length. The prototype Ising model consist of spins ($g = 2$) rather than oscillators and $\xi \propto |T - T_c|^{-\nu}$ where $\nu \approx 1/2$. Either way we can write the expression for the heat capacity as follows:

$$C(T) \;=\; \beta^2 \frac{d^2 \ln Z}{d\beta^2} \;\equiv\; C_g(T) + C_{\xi}(T) \tag{3.18}$$

where the non-singular $C_g(T)$ originates from the temperature dependence of g, and equals N for non-interacting oscillators, reflecting the effective number of freedoms. The singular term $C_{\xi}(T)$ originates from the temperature dependence of ξ. For an Ising system its divergence near the critical temperature is described by $|T - T_c|^{\nu d-2}$. Note the significance of the space dimension d.



[3.4] Generalized forces

Assume that X is a parameter that appears in the Hamiltonian. We define the generalized force $\mathcal{F}$ which is associated with the parameter X as

$$\mathcal{F} = -\frac{\partial \mathcal{H}}{\partial X} \tag{3.19}$$

This definition will be motivated later on when we discuss the notion of *work*. We shall explain that for an isolated system that undergoes a quasi-static adiabatic process the change in energy is $dE = -\langle \mathcal{F} \rangle \, dX$, meaning that the work that has been dome by the system is $dW = \langle \mathcal{F} \rangle \, dX$. Here are some examples for generalized forces:

parameter	**generalized force**
piston displacement in cylinder with gas	Newtonian force
volume of a box with gas	Newtonian pressure
length of a polymer	Newtonian force (tension)
homogeneous electric field	total polarization
homogeneous magnetic field	total magnetization
magnetic flux through a ring	electric current

Flux and Current.– We would like to better clarify why the magnetic flux and the electrical current are conjugate variables. Note that for an homogeneous magnetic field the flux through a ring is $\Phi = \mathsf{A}\mathcal{B}$, and the magnetization is ad-hock defined as $\mathcal{M} = \mathsf{A}\mathcal{I}$, where A is the area of the ring. Using the notation $X = \Phi$, the direct identification of the conjugate force as the current, is rationalized in a simple-minded manner as follows: If we make a change dX of the flux during a time dt, then the electro-motive force (EMF) is $-dX/dt$, leading to a current $\mathcal{I}$ in the ring. The energy increase of the ring is the EMF times the charge, namely $dE = (-dX/dt) \times (\mathcal{I}dt) = -\mathcal{I}dX$. Optionally, if we set $X = \mathcal{B}$, the conjugate force is the magnetization, and we get $dE = -\mathcal{M}d\mathcal{B}$.

Magnetic field.– Usually we shall denote the *applied* magnetic field not by $\mathcal{B}$ as above, but by the letter h, possibly absorbing into it the coupling constant. For example we write the interaction of a spin with a vertical magnetic field as $-h\sigma_z$. But there are circumstance in which the sample affects the the magnetic field in a way that cannot be ignored. For example: if we place a typeI superconductor inside a solenoid, it expels sideways the magnetic field, such that the *total* magnetic field is $\mathcal{B} = 0$ inside the sample. We therefore have to be careful in how we write the Hamiltonian. Schematically we write

$$\mathcal{H}_{\text{total}} = \sum_{j \in \text{system}} \frac{1}{2\mathsf{m}_j}(p_j - e_j A)^2 + U(r_1, r_2, ...) \tag{3.20}$$

$$+ \Big[\text{similar expression for the solenoid}\Big] + \frac{1}{8\pi}\int \mathcal{B}(x)^2 \, d^3x \tag{3.21}$$

Our focus is on the system, so we keep only the interaction of the system with the solenoid:

$$\mathcal{H}_{\text{total}} = \mathcal{H}_{\text{system}}(r_j, p_j; A) + \frac{1}{8\pi}\int \mathcal{B}(x)^2 \, d^3x - \int A \cdot J_{\text{solenoid}} \, d^3x \tag{3.22}$$

The current density of the solenoid defines the *applied* magnetic field through the relation

$$\nabla \times h = 4\pi \, J_{\text{solenoid}} \tag{3.23}$$

Substitution of this definition into the last term, and doing integration by parts, the Hamiltonian that described the interaction of the system with the *applied* magnetic field takes the following form:

$$\mathcal{H}_{\text{total}} \; = \; \mathcal{H}_{\text{system}}(r_j, p_j; \mathcal{B}) \; + \frac{1}{8\pi}\int \mathcal{B}(x)^2 \, d^3x \; - \frac{1}{4\pi}\int h(x)\mathcal{B}(x) d^3x \tag{3.24}$$

For pedagogical clarity we write $\mathcal{B}$ instead of A in $\mathcal{H}_{\text{system}}$. Schematically the interaction with the external field h is described by a term that looks like $-h\mathcal{B}$. We emphasize that h is the control parameter, while $\mathcal{B}$ is the conjugate dynamical variable. The expression for the work takes the form

$$dW \; = \; \frac{\mathsf{V}}{4\pi}\mathcal{B}(h)\, dh \; \equiv \; \frac{\mathsf{V}}{4\pi} h\, dh \; + \; \tilde{M}(h)\, dh \tag{3.25}$$

Note that the electromagnetic field is regarded as part of the sample. If we excluded the electromagnetic field, and regarded $\mathcal{B}$ as a control parameter, we would define the magnetization as $\tilde{M} \equiv \langle -d\mathcal{H}_{\text{system}}/d\mathcal{B}\rangle$. This is consistent with the above, because the equilibrium value of $\mathcal{B}$ is determined by the equation $\langle -d\mathcal{H}_{\text{total}}/d\mathcal{B}\rangle = 0$, leading to $\mathcal{B} = h + 4\pi\tilde{M}$. In the next lecture, regarding thermodynamics, $\mathcal{H}_{\text{total}}$ will be identified as a "grand Hamiltonian" with which a "Gibbs" free energy can be associated.

[3.5] Susceptibility and fluctuations

Given X and assuming that the system is prepared in a canonical state characterized by some β, we can derive the average value y of the generalized force $\mathcal{F}$ from the partition function as follows:

$$y(X) \; \equiv \; \langle \mathcal{F} \rangle_X \; = \; \sum_r p_r \left(-\frac{dE_r}{dX}\right) \; = \; \frac{1}{\beta}\frac{\partial \ln Z}{\partial X} \tag{3.26}$$

The generalized susceptibility describes the dependence of $y(X)$ on the the parameter X, namely,

$$\chi(X) \; \equiv \; \frac{\partial y}{\partial X} \; = \; \frac{1}{T}\text{Var}(\mathcal{F}) \tag{3.27}$$

The second equality requires few lines of algebra. Let us illuminate this relation, and re-derive it, by considering a prototype example: the dependence of of the length of a polymer, or the volume of a gas, on the applied tension or pressure. In this example the total Hamiltonian can be written as

$$\mathcal{H}(\lambda) \; = \; \mathcal{H} - \lambda V \tag{3.28}$$

where the parameter λ is the applied field, and V is the conjugate dynamical variable (length or volume in the above mentioned examples). Consequently we get in the presence of the applied field

$$\langle V \rangle_\lambda \; = \; \frac{\mathsf{trace}\left[V \exp\left(-\beta\mathcal{H}(\lambda)\right)\right]}{\mathsf{trace}\left[\exp\left(-\beta\mathcal{H}(\lambda)\right)\right]} \; = \; \langle V \rangle + \beta\lambda\left[\langle V^2\rangle - \langle V\rangle^2\right] \; + \; \text{higher orders} \tag{3.29}$$

where both numerator and denominators have been expanded, without much caring about commutation relations. From the above we deduce the following *classical* relation between the compressiblility and the fluctuations:

$$\kappa \; \equiv \; \left[\frac{\partial\langle V\rangle_\lambda}{\partial\lambda}\right]_{\lambda=0} \; = \; \frac{1}{T}\text{Var}(V) \tag{3.30}$$

In a later lecture we shall introduce generalizations of this relation that are known as the "Onsager regression theorem" and as the "Fluctuation dissipation relation".

The relation $\kappa = (1/T)\text{Var}(V)$ parallels the relation $C = (1/T^2)\text{Var}(E)$ between the heat capacity and the fluctuations in energy. It automatically implies that these constants have to be positive. Another way of looking on it is to say that $C > 0$ and $\kappa > 0$ are stability conditions. Negative value means that that the system will undergo a "phase separation" process. See discussion of the "Maxwell construction" is the "Interactions and phase transitions" lecture.

[3.6] Empirical temperature

In practice we would like to be able to probe the β of the environment. For this purpose we use a thermometer. The simplest thermometer would be an ideal gas in a box, for which the partition function is

$$Z(\beta,\mathsf{V}) = \mathsf{V}^N \left(\frac{\mathsf{m}}{2\pi\beta}\right)^{\frac{3N}{2}} \tag{3.31}$$

$$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathsf{V}} = \frac{N}{\mathsf{V}}\beta^{-1} \tag{3.32}$$

The empirical temperature is defined as follows:

$$\theta = \frac{P\mathsf{V}}{N} = \frac{1}{\beta} \tag{3.33}$$

We can of course define different thermometers. The idea is simply to identify a measurable quantity that reflects the parameter β.

[3.7] The Virial theorem

Somewhat related to the equipartition theorem, is the Virial theorem. It is used to relate the expectation value of the "kinetic" and "potential" terms in Hamiltonian of the type $\mathcal{H} = K(p) + U(r)$.

Consider any observable G. It is clear that if the system is prepared in a *stationary* (not necessarily canonical) state, then the expectation value $\langle G\rangle$ is constant in time. By the rate of change equation of motion it follows that

$$\Big\langle [\mathcal{H}, G] \Big\rangle = 0 \tag{3.34}$$

In particular let us consider the generator of dilations

$$G = \frac{1}{2}\sum_j (r_j \cdot p_j + p_j \cdot r_j) \qquad \text{[the symetrization is required in the quantum case]} \tag{3.35}$$

For the Hamiltonian $\mathcal{H} = K(p) + U(r)$ we get

$$\left\langle p \cdot \frac{\partial K}{\partial p} \right\rangle - \left\langle r \cdot \frac{\partial U}{\partial r} \right\rangle = 0 \tag{3.36}$$

with implicit summation over j. If the classical equipartition theorem applies, each term equals T multiplied by the number of freedoms. For quadratic $K(p)$ and $U(r)$ the first term equals $2\langle K\rangle$, and the second term equals $-2\langle U\rangle$. More generally, for two-body interaction of the type

$$U(r) = \sum_{\langle ij\rangle} u(r_i - r_j) = \sum_{\langle ij\rangle} |r_i - r_j|^\alpha \tag{3.37}$$

the second term in the Virial theorem equals $-\alpha\langle U\rangle$. This is a meaningful statement for $\alpha > 0$, otherwise there should be a "box" that confines the particles. Writing the full Hamiltonian as $\mathcal{H} = K(p) + U(r) + V_L(r)$ we deduce that

$$\left\langle p \cdot \frac{\partial K}{\partial p} \right\rangle - \left\langle r \cdot \frac{\partial U}{\partial r} \right\rangle - \left\langle r \cdot \frac{\partial V_L}{\partial r} \right\rangle = 0 \tag{3.38}$$

In the next section we shall see how this relation helps us to derive an expression for the "pressure" on the walls of the box.

[3.8] Pressure on walls

Possibly the simplest point of view about pressure is to regard it as arising from collisions of particles with the walls. This is the so called the *kinetic picture* point of view. However, within the framework of the *canonical formalism* the pressure is defined as the generalized force that is associated with the volume, such that $đW = P d\mathsf{V}$. It is quite puzzling that in the formal classical calculation the kinetic part factors out and the mass of the particles does not appear in the result:

$$\ln(Z(\beta,\mathsf{V})) = -\frac{3N}{2}\ln\beta + N\ln\mathsf{V} + \text{const} \tag{3.39}$$

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2}NT \tag{3.40}$$

$$P = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mathsf{V}} = \frac{NT}{\mathsf{V}} \tag{3.41}$$

With interactions we have to calculated a complicated configuration $(dr_1 dr_2 ... dr_N)$ integral. This calculation will be discussed in later sections. In the absence of interactions we see that the pressure is related to the kinetic energy, namely $P = (2/3)E/\mathsf{V}$. Below we generalize this relation using the Virial theorem: we shall see that quite generally, both classically and quantum mechanically, the pressure is related to the kinetic and potential energy of the gas.

The volume deformation of a box is represented by a deformation field $D(r)$. To be specific let us write the Hamiltonian of N gas particles in a box as follows:

$$\mathcal{H} = K(p) + U(r) + V_L(r - \lambda D(r)) \tag{3.42}$$

Here $K(p)$ is the kinetic term, and $U(r)$ are the interactions, and $V_L(r)$ is box defining potential, and λ is the deformation parameter. We want λ to equal the extra volume due to the deformation, such that $\mathsf{V} = \mathsf{V}_0 + \lambda$. We therefore normalize the displacement field such that

$$\oiint D \cdot ds = 1, \qquad \text{standard choice: } D(r) = \frac{1}{3\mathsf{V}_0}\, r \tag{3.43}$$

Accordingly the definition and the expression for the pressure are

$$P = \left\langle -\frac{\partial \mathcal{H}}{\partial \mathsf{V}} \right\rangle = \left\langle -\frac{\partial \mathcal{H}}{\partial \lambda} \right\rangle_{\lambda=0} = \frac{1}{3\mathsf{V}}\left\langle r \cdot \frac{\partial V_L}{\partial r} \right\rangle = \frac{1}{3\mathsf{V}}\left[\left\langle p \cdot \frac{\partial K}{\partial p}\right\rangle - \left\langle r \cdot \frac{\partial U}{\partial r}\right\rangle\right] \tag{3.44}$$

where in the last equality we have used the Virial theorem. Note that this extends the discussion of the Virial theorem in previous section. The case of inter-atomic interactions with $\alpha > 0$ (bounded system with no walls) can be regarded formally as a special case of the above relation with $P = 0$. If $\alpha < 0$ there is non-zero pressure. We can use the equipartition theorem to obtain in the classical case

$$P = \frac{1}{\mathsf{V}}\left[NT - \frac{1}{3}\left\langle r \cdot \frac{\partial U}{\partial r}\right\rangle\right] \tag{3.45}$$

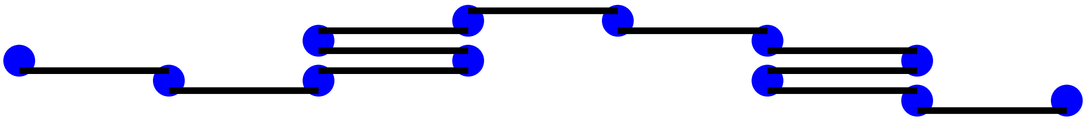
where the first term is the same as in the law of ideal gases, while the second is due to the interactions, and can be expressed using moments of the inter-particle separation.

[3.9] Tension of a polymer

The calculation of a tension of a polymer is very similar to the calculation of pressure. The parameter in the Hamiltonian is the length X of the polymer, which is analogous to the length or the volume of the box that contains the gas particles. In both cases the formal result depends only on the configuration integral, while the kinetic term factors out. Thus in both cases the result does not depend on the mass of the particles. The partition function for a polymer that is composed of N monomers is

$$Z(\beta, X) \;=\; [\text{kinetic term}] \times \sum_{\text{conf.}} \delta(X-(r_1+r_2+...+r_N))\; \mathrm{e}^{-\beta U(\text{configuration})} \tag{3.46}$$

For simplicity we assume a one-dimensional configuration, such that each monomer is like a link of a chain or small spring with potential energy $u(r)$, such that the total potential energy is $U = u(r_1)+u(r_2)+...+u(r_N)$. For hard-links, in analogy with the case of hard-spheres, the potential energy merely restricts the space of allowed configurations. A one-dimensional chain that is composed of hard-links is illustrated in the figure below. For this ring $u(r) = 0$ for $r = \pm a$, and $u(r) = \infty$ otehrwise.



Without the extra X restriction the summation would give a value $Z(\beta)$. One observes that the ratio $Z(\beta,X)/Z(\beta)$ would be the probability of observing length X if the polymer were unconstrained at its endpoints. According to the central limit theorem, for toy model that is illustrated in the figure

$$\mathrm{P}(X) \;=\; \frac{Z(\beta,X)}{Z(\beta)} \;\propto\; \exp\left[-\frac{1}{2}\left(\frac{X}{L_0}\right)^2\right] \tag{3.47}$$

Above we assumed that the polymer can stretch either sides, hence its average algebraic length is $\langle X\rangle = \sum\langle r_j\rangle = 0$, while the RMS average is $L_0 = \sqrt{\langle X^2\rangle} = \sqrt{N}a$. From the partition function $Z(\beta,X)$ we can derive the force that is exerted on the endpoint, aka Hooke's law:

$$\langle \mathcal{F}\rangle_X \;=\; \frac{1}{\beta}\frac{\partial \ln Z}{\partial X} \;=\; -(T/L_0^2)\; X \tag{3.48}$$

Considering the more general case, with arbitrary $u(r)$, one would like to have a procedure for the calculation of the partition function. Technically this can be done as follows:

$$Z(\beta,X) \;=\; \int\frac{dk}{2\pi}\int dr_1dr_2...dr_N\; \mathrm{e}^{i(X-(r_1+r_2+...+r_N))k}\; \mathrm{e}^{-\beta U(r_1,r_2,...,r_N)} \;\equiv\; \int\frac{dk}{2\pi}\,\mathrm{e}^{i\,k\,X}\;\tilde{Z}(\beta,k) \tag{3.49}$$

Above the we have omitted the irrelevant kinetic term. The integral over all possible configurations factorizes Notably for hard-links it is the "volume" of the possible configurations that have zero potential energy. In the rest of this section we expalin how to carry out this calculation in a more physically appealing way.

Gibbs procedure.– Assume that a tension f is applied on the polymer: this can be regarded as an "electric" field that is applied on the endpoint of the polymer, or as an applied "weight". The Hamiltonian becomes

$$\mathcal{H}_G(\hat{r};f) \;=\; \mathcal{H}+f\hat{X} \;=\; \text{KineticTerm}+\sum_{j=1}^{N}[u(r_j)+fr_j] \tag{3.50}$$

where $\hat{X} = \sum r_n$. In the new configuration $\hat{X}$ is an un-constrained dynamical variable, and the equilibrium point X_{eq} is determined by the condition $\mathcal{F}(X) = f$. Note that in order to keep sign consistency we have defined the applied field in the negative direction. If fluctuations are neglected we expect $\langle X\rangle_f = X_{\text{eq}}$ that is derived from $\mathcal{H}_G$, to be consistent with $\langle\mathcal{F}\rangle_X = f$ that is derived from $\mathcal{H}$. If we blur the distinction between the tension $\langle\mathcal{F}\rangle$ in the sense of expectation value, and the tension f in the sense of an external parameter (applied force), then, under the same assumption, the relation $dE_G = Xdf$ is consistent with $dE = -fdX$. In other words: if the conjugate of X is f, then in the Gibbs-Hamiltonian framework the conjugate of f is $-X$. The Gibbs partition function is

$$Z_G(\beta,f) \;=\; \int dr_1 dr_2 ... dr_N \ \mathrm{e}^{-\beta[U(r_1,r_2,...,r_N)+(r_1+r_2+...+r_N)f]} \;=\; \left[\int dr \mathrm{e}^{-\beta[u(r)+fr]}\right]^N \tag{3.51}$$

The factorization of this partition function implies that the total length $\langle X\rangle$ of the polymer, for a given applied field f, is the sum of lengths of the monomers for the same field (the field determines the tension of the polymer).

We realize that $Z(\beta,X)$ and $Z_G(\beta,f)$ are related by a Fourier transform.

$$Z_G(\beta,f) \;=\; \int Z(\beta,X)\ \mathrm{e}^{-\beta f X}\ dX \tag{3.52}$$

In a formal mathematical perspective the former is like the probability function, and the latter is like the associated moment generating function. What we were doing is in fact a generalization of the "convolution theorem", as used in the derivation of the central limit theorem.

Finally, in the large N limit the relation between $Z_G(\beta,f)$ and $Z(\beta,X)$ can be formulated as a Legendre transformation. We shall encounter the Legendre transformation in the next section, in a formally identical context, as the relation between the Gibbs free energy $G(T,P)$ and the Helmholtz free energy $F(T,\mathsf{V})$. Later we use the same trick in the analysis of quantum gases, when we go from the canonical to the so called “grand-canonical” framework.

[3.10] Polarization

The polarization is the generalized force that is associated with electric field. Let us assume that we have a bounded system of particles with an added uniform electric field:

$$\mathcal{H} \;=\; \sum_\alpha \frac{p_\alpha^2}{2\mathsf{m}_\alpha} + \text{interactions} + \text{potential} - \sum_\alpha q_\alpha \mathcal{E} x_\alpha \tag{3.53}$$

$$\hat{P} \;=\; -\frac{\partial\mathcal{H}}{\partial\mathcal{E}} \;=\; \sum_\alpha q_\alpha \hat{x}_\alpha \tag{3.54}$$

The polarization $\tilde{P}$ is the expectation value of $\hat{P}$. One simple example is the calculation of the polarization of an "atom", where we have (say) a negative particle that is bounded by a "spring" to a positive charge. Another simple example concerns a diatomic molecule that has a permanent dipole moment μ. Here the Hamiltonian is

$$\mathcal{H}(\theta,\phi,p_\theta,p_\phi) \;=\; \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2(\theta)} - \mu\mathcal{E}\cos(\theta) \tag{3.55}$$

where I is the moment of inertia. For the polarization we get

$$\tilde{P} \;=\; \frac{1}{\beta}\frac{\partial \ln Z}{\partial\mathcal{E}} \;=\; \mu\left[\coth\left(\frac{\mu\mathcal{E}}{T}\right) - \left(\frac{\mu\mathcal{E}}{T}\right)^{-1}\right] \tag{3.56}$$

Note that expansion for weak field implies the electric susceptibility $\chi = (1/3)\mu^2/T$.

[3.11] Magnetization

The magnetization is the generalized force that is associated with magnetic field. It is either due to having spin degree of freedom (Pauli) or due to the orbital motion. Here we clarify the definition using the three simplest examples.

Pauli magnetism.– Consider a collection of N spins. We denote the magnetic filed by h. The Hamiltonian is

$$\mathcal{H} = -\sum_{\alpha=1}^{N} g_\alpha h S_z^\alpha \tag{3.57}$$

$$\hat{M} = -\frac{\partial \mathcal{H}}{\partial h} = \sum_{\alpha=1}^{N} g_\alpha S_z^\alpha \tag{3.58}$$

The magnetization $\tilde{M}$ is the expectation value of $\hat{M}$. For a single spin 1/2 entity we get the following result:

$$\tilde{M} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial h} = \frac{g}{2}\tanh\left(\frac{gh}{2T}\right) \tag{3.59}$$

Note that expansion for weak field implies the magnetic susceptibility $\chi = (1/4)g^2/T$. Note also that in the classical limit ("large spin") the problem becomes formally identical to that of calculating polarization of electric dipoles.

Orbital magnetism (classical).– In the following we shall identify what is the magnetization $\hat{M}$ for charged spinless particles, using the formal definition $-\partial\mathcal{H}/\partial h$. In the 1D case (ring) it is identified as arising from a circulating current. In the 2D case it is more convenient to bypass the question what is $\hat{M}$ and to go directly to the $\tilde{M}$ calculation via the partition function. In the classical case one obtains $\tilde{M} = 0$. But in the quantum calculation one obtains finite result. The classical result is puzzling because we would like to interpret $\hat{M}$ as arising from circulating currents as in the 1D case. Indeed such interoperation is possible. The point to realize that within the bulk we indeed have circulating electrons that give rise to a diamagnetic response. But this is compensated by "Hall currents" that flow along the boundary. The exact cancellation of these two contributions is spoiled upon quantization, instead we get the de Haas van Alphen (dHvA) oscillations. Details below.

Orbital magnetism (1D).– Consider a spinless particle in a ring of length L, and area A. The magnetic flux is $\Phi = h\mathsf{A}$. The Hamiltonian, the velocity-operator, the current-operator and the magnetization-operator are

$$\mathcal{H} = \frac{1}{2\mathsf{m}}\left(p - e\frac{\Phi}{L}\right)^2 + V(x) \tag{3.60}$$

$$\hat{v} = i[\mathcal{H}, x] = \frac{1}{\mathsf{m}}\left(p - e\frac{\Phi}{L}\right) \tag{3.61}$$

$$\hat{I} = -\frac{\partial \mathcal{H}}{\partial \Phi} = \frac{e}{L}\hat{v} \tag{3.62}$$

$$\hat{M} = -\frac{\partial \mathcal{H}}{\partial h} = \mathsf{A}\hat{I} \tag{3.63}$$

The magnetization $\tilde{M}$ is the expectation value of $\hat{M}$, or optionally we can refer to the circulating current I, which is the expectation value of $\hat{I}$.

Orbital magnetism (2D).– The more interesting case is the magnetization of electrons in a 2D box (3rd dimension does not play a role) due to the formation of Landau levels. We recall again that classically the energy spectrum of the system is not affected by magnetic field. But quantum mechanically Landau levels are formed (see "Lecture notes in Quantum mechanics"). Let us consider a box of area A that contains N spinless electrons. In the *bulk*, the energy of a Landau state that belongs to the ν level is $\varepsilon_\nu = (\nu + (1/2))\omega_B$ where $\omega_B = e\mathcal{B}/\mathsf{m}$ is the cyclotron frequency. The degeneracy of each Landau level is $g_B = e\mathcal{B}\mathsf{A}/2\pi$. The calculation of the single particle partition function is the same as that of harmonic oscillator (multiplied by the degeneracy). Assuming N electrons that can be treated as an ideal

Boltzmann gas we get

$$\tilde{M} \;=\; -\frac{N}{12}\left(\frac{e}{\mathsf{m}}\right)^2\frac{\mathcal{B}}{T} \;+\; \mathcal{O}(\mathcal{B}^3) \tag{3.64}$$

This result does not hold for a low temperature electron gas, because the Fermi statistics of the occupation becomes important. Assuming zero temperature we define $\mathcal{B}_n$ with $n = 1, 2, 3, ...$ as the threshold value for which n Landau levels are fully filled. This values are determined by the equation $ng_B = N$. Considering first strong field $\mathcal{B} > \mathcal{B}_1$, the energy of the system is $E_0^{(N)} = N\omega_B/2$ and hence

$$\tilde{M} \;=\; -\frac{\partial E_0^{(N)}}{\partial \mathcal{B}} \;=\; -N\frac{e}{2\mathsf{m}}, \qquad\qquad \text{for } \mathcal{B} > \mathcal{B}_1 \tag{3.65}$$

This result has a simple interpretation using "Bohr picture" of an orbiting electron: each electron performs a minimum energy cyclotron motion with unit angular momentum L, and associated magnetic moment $-(e/2\mathsf{m})L$. If the magnetic field is $\mathcal{B}_{n+1} < \mathcal{B} < \mathcal{B}_n$, one has to sum the energy of the electrons in n filled Landau levels, where the upper one is only partially filled. One obtain a quadratic expression from which it follows that the magnetization grows linearly from $-N(e/2\mathsf{m})$ to $+N(e/2\mathsf{m})$. Hence there is saw-tooth dependence of $\tilde{M}$ on the field, which is known as the de Haas van Alphen (dHvA) oscillations.

Semiclassical interpretation.– There is a simple way to understand the dHvA result. For this purpose assume that A looks like a circle. Each "Landau state" occupies a thin *strip* that has a finite width. Within each strip there is a diamagnetic cyclotron motion whose net effect is like having an inner anticlockwise current ($I^{\circlearrowleft} > 0$), and an outer clockwise current ($I^{\circlearrowright} < 0$). In the bulk the net current of a strip is zero, but nevertheless it has a diamagnetic contributions to the magnetization, because $I^{\circlearrowright}$ encloses a larger area compared with $I^{\circlearrowleft}$. As we come close to the boundary, near the potential wall, the net current of the strip becomes positive, and its value is determined by the potential gradient. This is known as Hall effect. In the case of hard wall there is a nice semi-classical illustration of the trajectories that bounce along the boundary. Upon quantization the "strips" support so-called "edge states". When $\mathcal{B}$ crosses $\mathcal{B}_n$ we get a jump in the magnetization that corresponds to the occupation of an additional edge states: The total Hall conductance of n Landau levels is $G_H = (e/2\pi)n$, residing in a region that experiences a potential difference ω_B. Hence the drop in the magnetization is $(G_H\omega_B) \times \mathsf{A} = N(e/\mathsf{m})$. It is now easy to understand why in the classical limit we do not have magnetization: the Hall current along the edges compensates the diamagnetic currents of the bulk. It is only upon quantization that the balance is violates, and instead we have the dHvA oscillations as a function of $\mathcal{B}$.

[4] Thermodynamics

[4.1] Absolute temperature and entropy

Let us *formally* vary the parameters X and β. The implied change in the energy is

$$dE \;=\; \sum_r dp_r E_r + \sum_r p_r dE_r \;=\; \left[\left(\sum_r \frac{dp_r}{d\beta}E_r\right)d\beta + \left(\sum_r \frac{dp_r}{dX}E_r\right)dX\right] \;+\; \left[\left(\sum_r p_r\frac{dE_r}{dX}\right)dX\right] \tag{4.1}$$

The second term in the formal dE expression is identified as the work $đW$ that would be done on the system during a reversible quasi-static process:

$$\sum_r p_r dE_r \;=\; \left(\sum_r p_r \frac{dE_r}{dX}\right)dX \;=\; -y(X)\;dX \tag{4.2}$$

In the next section we shall identify the first term in the formal dE expression as the heat $đQ$ that would be absorbed during a reversible quasi-static process. This expression is not an "exact differential", but it has an *integration factor* that depends only on the empirical temperature. In fact this integration factor turns out to be β, hence we define the the *absolute temperature*:

$$T \;=\; \text{inverse integration factor} \;=\; \frac{1}{\beta} \tag{4.3}$$

such that $(1/T)đQ$ is the differential of a so-called entropy function:

$$\sum_r dp_r E_r \;=\; \left(\sum_r \frac{dp_r}{d\beta}E_r\right)d\beta + \left(\sum_r \frac{dp_r}{dX}E_r\right)dX \;=\; TdS \tag{4.4}$$

The implied *definition* of the thermodynamic entropy is

$$S \;=\; -\sum p_r \ln p_r \tag{4.5}$$

Note that the thermodynamic entropy is an extensive quantity in the thermodynamic limit. It should not be confused with other types of "entropy". In particular we shall discuss the "Boltzmann entropy" in a later section with regard to the 2nd law of thermodynamics.

We see that the formal expression for dE can be written as follows:

$$dE \;=\; TdS - ydX \tag{4.6}$$

It is important to emphasize that the above formal expression is a valid mathematical identity that holds irrespective of whether it reflects an actual physical process. However, it is only for a reversible quasi-static process that ydX is identified as the work, and TdS as the heat. For a non-reversible process these identifications are false.

[4.2] The Thermodynamic potentials

From the basic relation $dE = TdS - ydX$ one concludes that if E is formally expressed as a function of S and X, then we can derive from it the state equations $T(S,X)$ and $y(S,X)$. Accordingly ee say that $E(S,X)$ is a *thermodynamic potential.* At this stage it is convenient to define also the Helmholtz thermodynamic potential:

$$F(T,X) \;\equiv\; -\frac{1}{\beta}\ln Z(\beta;X) \tag{4.7}$$

Within the framework of the canonical formalism the energy is obtained taking to the derivative of Z with respect to β. This translates to the relation $E = F + TS$. The relation between $F(T,X)$ and $E(S,X)$ is formally a Legendre transform. Consequently $dF = -SdT - ydX$ and the associated state equations are

$$S = -\frac{\partial F}{\partial T}, \qquad y = -\frac{\partial F}{\partial X}, \tag{4.8}$$

Within the framework of the thermodynamic formalism *state equations* that describe physical systems are derived from *thermodynamic potentials*. The latter should be expressed using their canonical variables. The common thermodynamic potentials are:

$$E\left(S,X\right) \qquad dE = TdS - ydX \tag{4.9}$$

$$F\left(T,X\right) = E - TS, \qquad dF = -SdT - ydX \tag{4.10}$$

$$G\left(T,y\right) \equiv F + yX, \qquad dG = -SdT + Xdy \tag{4.11}$$

$$S\left(E,X\right), \qquad dS = \frac{1}{T}dE + \frac{y}{T}dX \tag{4.12}$$

The derivatives of the state equations are know as the "thermodynamic constants" though they are not really constant...

$$C \equiv T\frac{\partial S}{\partial T} \qquad \chi \equiv \frac{\partial y}{\partial X} \tag{4.13}$$

In the context of gases

$$\text{Compressibility} \equiv -\frac{1}{\mathsf{V}}\frac{\partial \mathsf{V}}{\partial P} \qquad \text{[common notation - "beta" or "kappa"]} \tag{4.14}$$

$$\text{ExpansionCoeff} \equiv \frac{1}{\mathsf{V}}\frac{\partial \mathsf{V}}{\partial T} \qquad \text{[common notation - "alpha"]} \tag{4.15}$$

[4.3] The Gibbs Hamiltonian approach

It is customary in thermodynamics to define "thermodynamic potentials" that are obtained from the Helmholtz free energy by means of Legendre transform. This can be regarded as a formal mathematical trick for switching the role of conjugate variables, but it also can be motivated physically. It is the same procedure that we had discussed regarding the calculation of the tension of a polymer. Here we repeat it with regard to a gas in a box with piston.

Let us regard the position of the piston (the parameter X) as a dynamical variable (let us call it x). We can apply force, say "electric" field f on the piston. Accordingly the "Gibbs Hamiltonian" of the system is

$$\mathcal{H}_G = \mathcal{H}(\cdots, x) + fx + \text{[optional kinetic term]} \tag{4.16}$$

The optional kinetic term is required if the piston has finite mass, but its inclusion will not affect the analysis because it factors out of the calculation. Given $x = X$ the force that the system exerts on the piston is $y(X) = \langle -\partial\mathcal{H}/\partial x\rangle_X$. Once x becomes a dynamical variable, and f is introduced, the equilibrium point of the piston is determined by the equation $f = y(x)$, hence the sign convention for the second term in $\mathcal{H}_G$.

The partition function of $\mathcal{H}_G$ is related to that of $\mathcal{H}$ by Laplace transform:

$$Z_G(\beta, f) = \sum_{x,r} \mathrm{e}^{-\beta E_{x,r}} = \sum_{x} Z(\beta, x)\ \mathrm{e}^{-(\beta f)x} \tag{4.17}$$

This can be written as

$$e^{-G(T,f)/T} \;=\; \sum_x \exp\left[-\frac{F(T,x)+fx}{T}\right] \tag{4.18}$$

In the thermodynamic limit fluctuations can be neglected, and a saddle point approximation implies

$$G(T,f) \;\approx\; \min_x \Big\{F(T,x)+fx\Big\} \;=\; F(T,\bar{x})+f\bar{x} \tag{4.19}$$

where the most probable value $\bar{x}$ is determined by solving the state equation $f=-F'(x)$. Accordingly we realize that $G(T,f)$ is the Legendre transform of $F(T,X)$. The roles of the conjugate variable X and f have been switched. If X and f are the volume V and the pressure P, then $G(T,P)$ is known as the Gibbs function.

[4.4] The chemical potential

Consider a gas that consists of N *identical* particles. This can be either *classical* or *quantum* gas (contrary to prevailing misconception, quantum mechanics is irrelevant to this issue - this will be explained in the "chemical equilibrium" lecture). Within the framework of the canonical formalism we define the chemical potential as follows:

$$\mu\left(T,\mathsf{V},N\right) \;\equiv\; \frac{\partial F}{\partial N} \tag{4.20}$$

Accordingly we have

$$dF \;=\; -SdT-Pd\mathsf{V}+\mu dN \tag{4.21}$$

$$dG \;=\; -SdT+\mathsf{V}dP+\mu dN \tag{4.22}$$

The above definition of the chemical potential can be motivated by adopting a "grand Hamiltonian" perspective. Let us define a "grand system" that consists of the system and of a reservoir of particles. This reservoir consists of a huge collection of sites that hold a huge number of particles with binding energy μ. If we transfer N particle from the reservoir to the system the energy of the "grand system" becomes

$$\mathcal{H}_G \;=\; \mathcal{H} \;-\; \mu N \tag{4.23}$$

The so called grand partition function $Z_G(\beta,\mu)$ of the Grand system will be discussed in future lecture.

[4.5] The extensive property

At this stage it is appropriate to remark on a relation between the Gibbs function and the chemical potential that holds is the so-called thermodynamic limit. In this limit the system acquires an *extensive* property that can be formulated mathematically. Relating to the Gibbs function $G(T,P;N)$, one observes that if N is multiplied by some factor, then the volume V and the entropy S for the same (T,P) are expected to be multiplied by the same factor, and hence also G should be multiplied by the same factor. We therefore write

$$G(T,P,N) \;=\; N\;G(T,P,1) \tag{4.24}$$

From $\mu=-dG/dN$ we deduce that the chemical potential is merely the Gibbs energy per particle. Consequently from the expression for dG it follows that

$$d\mu \;=\; -\frac{S}{N}dT \;+\; \frac{\mathsf{V}}{N}dP \tag{4.25}$$

[4.6] Work

In the definition of work the system and the environment are regarded as one driven *closed* unit. If we change X in time then from the "rate of change formula" we have the following exact expression:

$$\frac{dE}{dt} \;=\; \left\langle \frac{\partial \mathcal{H}}{\partial t} \right\rangle \;=\; -\langle \mathcal{F} \rangle_t \, \dot{X} \tag{4.26}$$

it follows that

$$\mathcal{W} \;\equiv\; \text{work done on the system} \;=\; E_{\text{final}} - E_{\text{initial}} \;=\; -\int \langle \mathcal{F} \,\rangle_t \, dX \tag{4.27}$$

This is an exact expression. Note that $\langle \mathcal{F} \rangle_t$ is calculated for the time dependent (evolving) state of the system. In a quasi-static adiabatic process one replaces $\langle \mathcal{F} \rangle_t$ by $\langle \mathcal{F} \rangle_{X(t)}$, where the notation $\langle \mathcal{F} \rangle_X$ implies that the system is assumed to be in a canonical state at any moment. More generally, within the framework of linear response theory

$$\langle \mathcal{F} \rangle_t \;\approx\; \langle \mathcal{F} \rangle_X \, - \eta \dot{X} \;=\; y(X) - \eta \dot{X} \tag{4.28}$$

The first terms is the conservative force, which is a function of X alone. The subscript implies that the expectation value is taken with respect to the instantaneous adiabatic state. The second term is the leading correction to the adiabatic approximation. It is the "friction" force which is proportional to the rate of the driving. The net conservative work is zero for a closed cycle while the "friction" leads to irreversible dissipation of energy with a rate

$$\dot{\mathcal{W}}_{\text{irreversible}} \;=\; \eta \dot{X}^2 \tag{4.29}$$

More generally it is customary to write

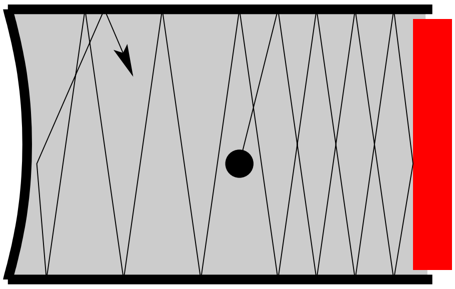
$$\mathcal{W} \;=\; -W + \mathcal{W}_{\text{irreversible}} \tag{4.30}$$

where the first term is the conservative work, or so to say "the work which is done by the system"

$$W \;=\; \int \langle \mathcal{F} \rangle_X \, dX \;=\; \int_{X_A}^{X_B} y(X) \, dX \tag{4.31}$$

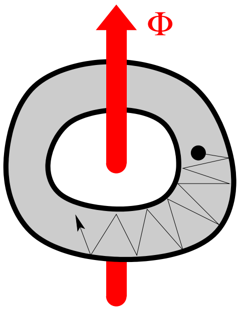
The two main examples that illustrate the above discussion are:

Example 1: box with piston



X = position of a wall element (or scatterer)
$\dot{X}$ = wall (or scatterer) velocity
$\langle \mathcal{F} \rangle$ = Newtonian force
$-\eta \dot{X}$ = friction law
$\eta \dot{X}^2$ = rate of heating

Example 2: ring with flux



X = magnetic flux through the ring
$-\dot{X}$ = electro motive force
$\langle \mathcal{F} \rangle$ = electrical current
$-\eta \dot{X}$ = Ohm law
$\eta \dot{X}^2$ = Joule law

In the first example instead of having a displaceable wall (”piston”) we can have a moveable object *inside* the box (”scatterer”). In the latter case there is friction while the conservative force is zero (because the volume of the box is not changing).

[4.7] Heat

In order to understand which type of statements can be extracted form the canonical formalism we have to discuss carefully the physics of work and heat. We distinguish between the system and the environment and write the Hamiltonian in the form

$$\mathcal{H}_{\text{total}} = \mathcal{H}(\boldsymbol{r},\boldsymbol{p};X(t)) + \mathcal{H}_{\text{int}} + \mathcal{H}_{\text{env}} \tag{4.32}$$

It is implicit that the interaction term is extremely small so it can be ignored in the calculation of the total energy. The environment is characterized by its temperature. More generally we assume that the environment consists of several “baths” that each has different temperature, and that the couplings to the baths can be switched on and off. Below we consider a *process* in which both the initial and the final states are equilibrated with a single bath. This requires that at the end of the driving process there is an extra waiting period that allows this equilibration. It is implied that both the initial and the final states of the system are canonical. Now we define

$$\begin{aligned}
\mathcal{W} = \text{work} \ &\equiv \ \Big(\langle\mathcal{H}_{\text{total}}\rangle_B - \langle\mathcal{H}_{\text{total}}\rangle_A\Big) && (4.33)\\
\mathcal{Q} = \text{heat} \ &\equiv \ -\Big(\langle\mathcal{H}_{\text{env}}\rangle_B - \langle\mathcal{H}_{\text{env}}\rangle_A\Big) && (4.34)\\
E_{\text{final}} - E_{\text{initial}} \ &\equiv \ \langle\mathcal{H}\rangle_B - \langle\mathcal{H}\rangle_A \ = \ \mathcal{W} \ + \ \mathcal{Q} && (4.35)
\end{aligned}$$

It is important to emphasize that the definition of work is the same as in the previous section, because we regard $\mathcal{H}_{\text{total}}$ as describing an isolated driven system. However, E is redefined as the energy of the system only, and therefore we have the additional term $\mathcal{Q}$ in the last equation.

Note.– It is possible to treat work and heat on equal footing. For this purpose one should define “work agents” in analogy to “heat baths”. The work agent is described by an Hamiltonian $\mathcal{H}_{\text{agent}}(X,P)$, and $\mathcal{W}$ is defined as the change of its energy. For example, a piston is described by $[1/(2M)]P^2 + fX$, where f is a weight. Assuming a large mass M, the work is stored in the form of potential energy of the weight.

[4.8] Quasi static process

In general we have the formal identity:

$$dE \ = \ \sum_r dp_r E_r + \sum p_r dE_r \tag{4.36}$$

We would like to argue that for an ideal (reversible) quasi-static process we can identify the first term as the heat $đQ$ and the second term is the work $-đW$. One possible scenario is having no driving. Still we have control over the temperature of the environment. Assuming a *volume preserving* quasi-static process we have

$$\begin{aligned}
dX \ &= \ 0 && (4.37)\\
dE \ &= \ \sum dp_r E_r = TdS && (4.38)\\
đQ \ &= \ TdS && (4.39)\\
đW \ &= \ 0 && (4.40)\\
\mathcal{Q} \ &= \ [E(B) - E(A)] && (4.41)\\
W \ &= \ 0 && (4.42)
\end{aligned}$$

A second possible scenario is having an isolated system going through an adiabatic process:

$$\begin{aligned} dp_r &= 0 && (4.43)\\ dE &= \sum_r p_r dE_r = -ydX && (4.44)\\ \text{đ}Q &= 0 && (4.45)\\ \text{đ}W &= ydX && (4.46)\\ \mathcal{Q} &= 0 && (4.47)\\ W &= -[E(B) - E(A)] && (4.48) \end{aligned}$$

Any general quasi-static process can be constructed from small steps as above, leading to

$$\begin{aligned} \mathcal{Q} &= \int_A^B TdS && (4.49)\\ W &= \int_A^B y(X)dX && (4.50) \end{aligned}$$

In particular for *isothermal* process we get

$$\begin{aligned} \mathcal{Q} &= T \times [S(B) - S(A)] && (4.51)\\ W &= -[F(B) - F(A)] && (4.52) \end{aligned}$$

If a process is both isothermal (constant T) and isobaric (constant P) we can still get work being done by changing some other parameter X. For example X might be a "reaction coordinate". Then we get

$$\begin{aligned} \mathcal{Q} &= T \times [S(B) - S(A)] && (4.53)\\ W &= -[G(B) - G(A)] && (4.54) \end{aligned}$$

[4.9] The reversibility of a quasistatic process

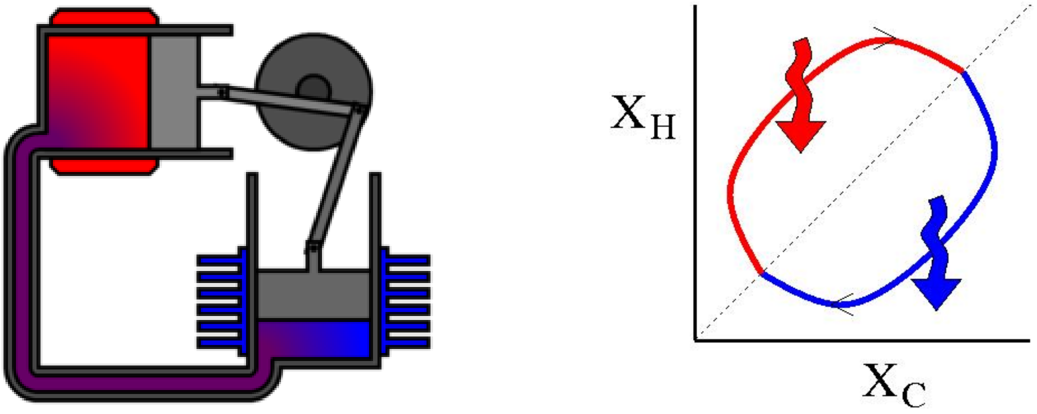
Consider for a gas in an isolated box with a movable piston. During a cyclic process the piston is displaced from X_A to X_B and then back to X_A. For a microcanonical preparations, assuming that the system is quasi-ergodic at any moment, the final state of the system is similar but not identical to the initial state, namely it will have larger dispersion in energy. In a future lecture we shall use the "Boltzmann entropy" as a measure for this dispersion, and we shall argue that the entropy tend to increase. Considering a *canonical* preparation the same observation holds, but now we can identify the "Boltzmann entropy" with the "Thermodynamic entropy". Accordingly we deduce a change $\Delta E = T\Delta S$ in the energy of the system. aka dissipation. Within the framework of linear response theory the dissipation rate is $\eta\dot{X}^2$, and therefore $\Delta E = 2\eta|X_B - X_A|\dot{X}$. In the quasi-static limit $\dot{X} \to 0$ this dissipation effect vanishes. We therefore conclude that a cyclic process becomes reversible in the quasistatic adiabatic limit.

We now turn to the process of heat exchange. We fix X and would like to change the temperature from T_C to T_H. Here we should regard the system and the baths as one closed unit. We first note that if we couple weakly a system that has temperature T with a bath that has temperature T_C, then, assuming $T = T_C$, the coupled system remains in the same equilibrium state. Note that this assumes *canonical* states and use the property $\exp[-\beta(E_{\text{sys}} + E_{\text{bath}})] = \exp[-\beta E_{\text{sys}}]\,\exp[-\beta E_{\text{bath}}]$. If we couple the cold system to the hot bath, we initiate a relaxation process towards the temperature T_H, that involves heat transfer $Q = C \cdot (T_H - T_C)$, where for simplicity we assume constant heat capacity C. To get a full cycle we connect again the system to the cold bath. The same amount Q flows from the system to the cold bath. Accordingly, the net outcome of the cycle is the transfer of energy Q from the hot bath to the cold bath, which is associated with an entropy change $\Delta S = [(1/T_C) - (1/T_H)]Q$. This is clearly irreversible. If the rate of heat flow is $\dot{Q} = K \cdot (T_H - T_C)$, the time of the cycle is $t = 2C/K$.

In order to change the temperature of the system in a reversible way, we have to assume that we have a set of baths $(n = 0, 1, 2, ..., N)$, with temperatures $T_n = T_C + ndT$, where $dT = (T_H - T_C)/N$. Each step of the cycle involves infinitesimal heat transfer $dQ_n = CdT$, and hence an entropy change $dS_n = C(dT/T_n)^2$. The total entropy change per cycle is $\Delta S = [(1/T_C) - (1/T_H)]CdT$. This residual irreversibility diminishes for $N \to \infty$. In this limit the process become quasistatic because the time required for the heat exchange with all the baths is $t = 2N \cdot (C/K)$.

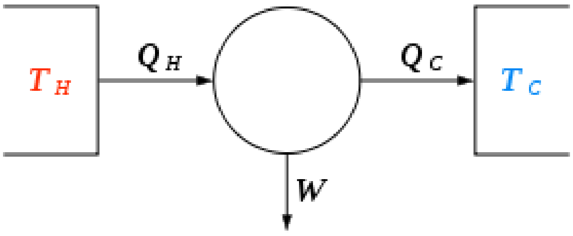
[4.10] Cycles

It is possible to design cycles in (X, T) space, such that the net effect is to convert heat into work (engine) or in reverse (heat pump). Consider for example a gas in a cylinder with a piston. If there is no restriction on the availability of baths the simplest engine could work as follows: Allow the gas to expand at high temperature; Lower the temperature; Compress the gas back by moving the piston back to its initial position; Raise back the temperature. The net effect here is to convert heat into work. This is known as the *Stirling cycle*. A traditional version of a *Stirling engine* is displayed in the following figure [left panel taken from Wikipedia]:

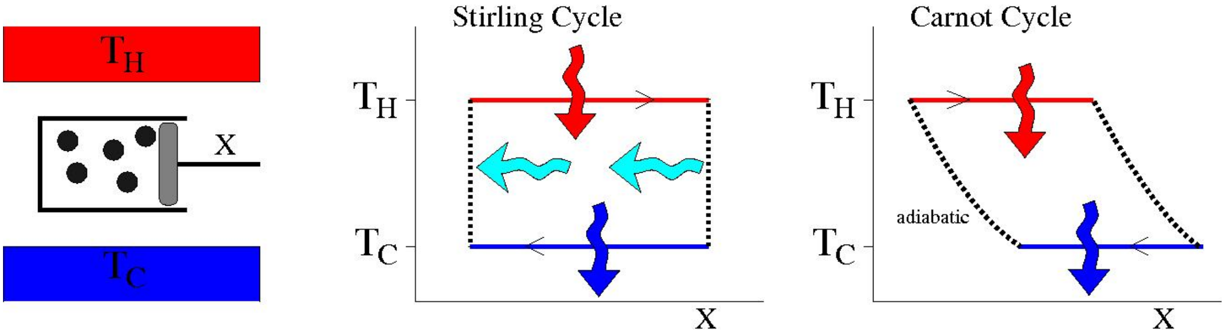


In order to see the relation between the engine and the cycle it is proposed to analyze the operation as follows. Denote by X_H and X_C the volumes of the hot and cold cylinders. As the wheel is rotated it defines a cycle in $(X_\mathrm{C}, X_\mathrm{H})$ space. The $X_\mathrm{H} > X_\mathrm{C}$ segment of the cycle represents expansion of gas during the stage when most of it is held in high temperature. The $X_\mathrm{H} < X_\mathrm{C}$ segment represents the compression of the gas during the stage when most of it is held in low temperature.

The disadvantage of the Stirling cycle is that in order to realize it in a reversible manner we need infinitely many intermediate baths in the heating and cooling stages. The way to do it in practice is to use a "heat exchange" device. This device can be regarded as layered structure that is attached in one end to the hot bath and in the other end to the cold bath. As a result each layer is held in a different temperature. We assume that the layers are quesi-isolated from each other. The trick is to couple the pipes that lead the gas between the hot and the cold cylinders to this layered structure, such that they can exchange heat with the layers without net effect on the temperature of the layer.



If we want to use a reversible cycle that uses two baths only, we can consider the Carnot cycle. See block diagram above [taken form Wikipedia]. Note that if we operate this cycle in reverse we get a heat pump instead of an engine. Let us analyze what happens during a Carnot cycle. Assuming that the levels become more dense as X is increased, it follows that the result of an adiabatic process would be a lower temperature (adiabatic cooling). To make this point clear consider just two levels E_1 and E_2 with occupation probabilities p_1 and p_2 respectively. The implied temperature is $T = (E_2 - E_1)/[-\ln(p_2/p_1)]$. In an adiabatic process the probabilities do not change, hence as the level get closer the implied temperature become lower. If the process is isothermal rather than adiabatic there will be heat absorption (isothermal absorption) and re-distribution of the probabilities such that $p_2/p_1 = \exp[-(E_2 - E_1)/T_0]$. These "rules of thumb" allow to gain intuition with regard to the operation of engines and heat-pumps.



Besides the piston example, the other simplest example for a thermodynamic cycle concerns spin $S \gg 1$ in magnetic field. In order to be consistent with the piston example we define $X = -|h|$, so larger X is like larger volume, i.e. higher density of states. We consider a cycle that consists of 4 stages: adiabatic cooling to lower temperature; isothermal absorption stage ($Q_{\mathrm{C}} > 0$); adiabtic heating to higher temperature; and isothermal emission stage ($Q_{\mathrm{H}} < 0$). The net effect is is to transfer heat from the cold bath to the hot bath, which requires to invest work.

At each stage the work W is positive or negative depending on whether the occupied levels go down or up respectively. The inclination is to say that during the adiabatic cooling stage the work is positive. This is true in the piston example, but not in general, as can be verified with the spin example. It should be clear that doing work on the system does not imply that its temperature becomes higher: the simplest demonstration would be to take an isolated container with gas to the top of Eifel Tower: it requires work but the temperature is not affected. What is essential for the operation of the cycle is the variation in the *density* of the levels, irrespective of whether they go up or down during the cycle.

[5] Chemical equilibrium and the Grand Canonical state

[5.1] The Gibbs prescription

In this lecture we are going to discuss chemical equilibrium. We shall see that the condition of chemical equilibrium involves the chemical potentials of the participating gases. For the purpose of calculating μ it is essential to find how the partition function depends on the number of particles. Classically the calculation of Z_N for a gas of *identical* particles is done using the Gibbs prescription:

$$Z_N[\text{Gibbs}] \;=\; \frac{1}{N!}\mathbb{Z}_N[\text{distinguishable particles}] \tag{5.1}$$

We shall motivate this prescription in the following discussion of chemical equilibrium. For an ideal gas we get

$$Z_N = \frac{1}{N!}Z_1^N, \qquad \text{where } \; Z_1 = \frac{\mathsf{V}}{\lambda_T^3}\sum \mathrm{e}^{-\beta\varepsilon_{\text{bound}}} \equiv g_0\frac{\mathsf{V}}{\lambda_T^3} \tag{5.2}$$

The summation is over the non-translational freedoms of the particle. Hence we get

$$\mu \;=\; \frac{\partial F}{\partial N} \;=\; T\ln\left(\frac{N}{Z_1}\right) \;=\; \varepsilon_0 + T\ln\left(\frac{N}{\mathsf{V}}\lambda_T^3\right) \tag{5.3}$$

where in the last equality we have assumed that the particle has a single well defined binding energy. The inverse relation is

$$N \;=\; Z_1\,\mathrm{e}^{\beta\mu} \;=\; \frac{\mathsf{V}}{\lambda_T^3}\,\mathrm{e}^{-(\varepsilon_0-\mu)/T} \tag{5.4}$$

The notion of identical particles:– The notion of *identical* particles does not require extra explanations if they are *indistinguishable* as in the quantum mechanical theory. Still we can ask what would happen if our world were classical. The answer is that in a classical reality one still has to maintain the Gibbs prescription if one wants to formulate a *convenient* theory for Chemical equilibrium. Namely, the condition for "chemical equilibrium" that we derive below has a simple form if we adopt the Gibbs prescription. Without the Gibbs prescription one would be forced to formulate an equivalent but non-friendly version for this condition.

[5.2] Chemical equilibrium

Consider the following prototype problem of chemical equilibrium:

$$A[a] \rightleftharpoons A[b] \tag{5.5}$$

where "a" and "b" are two phases, say to be in one of two regions in space, or to be either in the bulk or on the boundary of some bounded region. Given N identical particles we characterize the macroscopic occupation of the two phases by a reaction coordinate n, such that $N-n$ particles are in phase [a] and n particles are in phase [b]. The partition function is

$$\mathbb{Z}_N^{ab} \;=\; \sum_n \left\{\frac{N!}{(N-n)!\;n!}\right\}\,\mathbb{Z}_{N-n}^{a}\mathbb{Z}_n^{b} \tag{5.6}$$

The combinatorial "mixing" factor in the curly brackets counts the number of possibilities to divide N particles into two groups. It should be excluded if the particles are *indistinguishable*, as in the quantum theory. In the classical theory, where the particles are *distinguishable* it should be included, but it can be absorbed into the definition of the partition function. This is what we call the “Gibbs prescription”. Using the Gibbs prescription the above sum can be re-written as follows:

$$Z_N^{ab} \;=\; \sum_n Z_{N-n}^a Z_n^b \tag{5.7}$$

The probability to have $(N{-}n, n)$ occupation is proportional to the nth term in the partition sum:

$$p(n) \;=\; \left\{\frac{N!}{(N-n)!n!}\right\} \times \frac{\mathbb{Z}_{N-n}^a \mathbb{Z}_n^b}{\mathbb{Z}_N^{ab}} \;=\; \frac{Z_{N-n}^a Z_n^b}{Z_N^{ab}} \;=\; C\exp\left[-\beta\left(F^a(N-n)+F^b(n)\right)\right] \tag{5.8}$$

One should appreciate the usefulness of the Gibbs prescription. It is thanks to this prescription that the Free Energy is *additive*. If we did not use the Gibbs prescription we would be compelled to add in F a term that reflects *”mixing entropy”*. The most probable value $\bar{n}$ is determined by looking for the largest term. This leads to the Chemical equilibrium condition:

$$F^a(N-n)+F^b(n) \;=\; \text{minimum} \tag{5.9}$$

$$\rightsquigarrow \qquad -\mu^a(N-n)+\mu^b(n) \;=\; 0 \tag{5.10}$$

Let us consider the case of ideal gases. Using the expression for μ we get

$$\frac{n}{N-n} = \frac{Z_1^b}{Z_1^a} \qquad \rightsquigarrow \qquad \bar{n} = N\frac{Z_1^b}{Z_1^a+Z_1^b} \tag{5.11}$$

This example is simple enough to allow a determination of the average value $\langle n\rangle$ too. The probability distribution of the reaction coordinate is

$$p(n) \;=\; \frac{N!}{(N-n)!n!}\frac{(Z_1^a)^{N-n}\left(Z_1^b\right)^n}{(Z_1^a+Z_1^b)^N} \tag{5.12}$$

leading to

$$\langle n\rangle \;=\; \sum_n p(n)\, n \;=\; \bar{n} \tag{5.13}$$

We see that the expectation value of n coincides with its typical (most probable) value. In the more general case of chemical equilibrium, as discussed below, this is an approximation that becomes valid for $N \gg 1$ in accordance with the central limit theorem.

[5.3] The law of mass action

This procedure is easily generalized. Consider for example

$$2C \rightleftharpoons 5A + 3B \tag{5.14}$$

Given that initially there are N_A particles of type A, N_B particles of type B, and N_C particles of type C we define a macroscopic reaction coordinate n such that $N_C{-}2n$ is the number of particles of type C, and $N_\text{A}{+}5n$ is the number of particles of type A, and $N_\text{B}{+}3n$ is the number of particles of type B. Accordingly

$$Z^{abc} \;=\; \sum_n Z_{N_C-2n}^c Z_{N_\text{A}+5n}^a Z_{N_\text{B}+3n}^b \tag{5.15}$$

and

$$p(n) \;=\; \text{const}\ \mathrm{e}^{-\beta\left(F^c(N_C-2n)+F^a(N_\mathrm{A}+5n)+F^b(N_\mathrm{B}+3n)\right)} \tag{5.16}$$

leading to the equation

$$-2\mu^c(N_C-2n) + 5\mu^a(N_\mathrm{A}+5n) + 3\mu^b(N_\mathrm{B}+3n) \;=\; 0 \tag{5.17}$$

which with Boltzmann/Gibbs approximation becomes

$$\frac{(N_\mathrm{A}+5n)^5(N_\mathrm{B}+3n)^3}{(N_C-2n)^2} \;=\; \frac{(Z_1^a)^5\,\left(Z_1^b\right)^3}{(Z_1^c)^2} \tag{5.18}$$

or, assuming that [a],[b],[c] are all *volume* phases,

$$\frac{\left(\frac{N_\mathrm{A}+5n}{\mathsf{V}}\right)^5\left(\frac{N_\mathrm{B}+3n}{\mathsf{V}}\right)^3}{\left(\frac{N_C-2n}{\mathsf{V}}\right)^2} \;=\; \kappa(T) \tag{5.19}$$

where the reaction rate constant $\kappa(T) \propto \mathrm{e}^{-\varepsilon/T}$ depends on the reaction energy $\varepsilon = 5\varepsilon_a + 3\varepsilon_b - 2\varepsilon_c$. In this sign convention $\varepsilon < 0$ means exotermic reaction.

[5.4] Equilibrium in pair creation reaction

Consider the reaction

$$\gamma+\gamma \;\rightleftharpoons\; \mathrm{e}^+ \;+\; \mathrm{e}^- \tag{5.20}$$

This can be analyzed like a chemical reaction $C \rightleftharpoons A+B$, which is of the same type as considered in the previous version. The important point to notice is that Z^c is independent of n, and therefore the chemical potential of the electromagnetic field is formally $\mu^c = 0$. The electromagnetic field is like a "bath", and we can regard it as part of the environment, hence we could have written vacuum $\rightleftharpoons \mathrm{e}^+ + \mathrm{e}^-$. In any case we get at equilibrium

$$\mu^{\mathrm{e}^+}(n_1) \;+\; \mu^{\mathrm{e}^-}(n_2) \;=\; 0 \tag{5.21}$$

where in the Boltzmann/Gibbs approximation

$$\mu(n) \;\approx\; \mathsf{m}c^2 + T\ln\left(\frac{n\lambda_T^3}{\mathsf{V}}\right) \tag{5.22}$$

leading to

$$n_1 n_2 = \left(\frac{\mathsf{V}}{\lambda_T^3}\right)^2 \mathrm{e}^{-2\mathsf{m}c^2/T} \tag{5.23}$$

This problem is formally the same as that of a semiconductor where e^+ and e^- are the holes and the electrons, and $2\mathsf{m}c^2$ corresponds to the energy gap between the valance and the conduction bands. Accordingly, an optional derivation of the latter equilibrium condition can be based on a grand-canonical perspective (see next lecture) with regard to the occupation of the electrons.

[5.5] Equilibrium in liquid-gas system

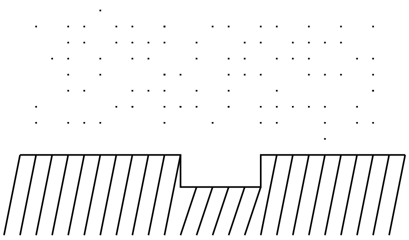
The equilibrium between a liquid phase and a gaseous phase is just another example for a chemical equilibrium. We can write the equation that determines the coexistence curve in (T, P) diagram as $[\mu_a(T,P) - \mu_b(T,P)] = 0$. By implicit differentiation of this equation with respect to T we get the Clausius-Clapeyron relation

$$\left.\frac{dP}{dT}\right|_{\text{coexistence}} = -\frac{\partial_T[\mu_a - \mu_b]}{\partial_P[\mu_a - \mu_b]} = \frac{\Delta S}{\Delta V} = \frac{1}{T}\,\frac{[\text{Latent heat}]}{[\text{Volume change}]} \tag{5.24}$$

Outside of the coexistence curve either μ_a or μ_b are smaller, and accordingly all the particles occupy one phase only.

[5.6] Site system

The chemical potential can be calculate easily for a system of N identical particles that occupy a set of M sites (or modes) that have the same binding energy ε. Since we assume that the biding energy is the same for all sites, it follows that estimating Z_1 is essentially a combinatorial problem. We assume $n \gg 1$ so we can approximate the derivative of $\ln(n!)$ as $\ln(n)$. We also write the result for the most probable n which is obtained given μ. Note that the result for $\bar{n}$ is meaningful only for large M.



Fermionic site:– Each site can have at most one particle

$$\begin{aligned} Z_n &= \frac{M!}{n!(M-n)!}\mathrm{e}^{-\beta\varepsilon n} && (5.25)\\ \mu &= \varepsilon + T\ln\left(\frac{n}{M-n}\right) && (5.26)\\ \bar{n} &= M(\mathrm{e}^{\beta(\varepsilon-\mu)}+1)^{-1} && (5.27) \end{aligned}$$

Bosonic site:– Each site can have any number of particles. The combinatorial problem is solved by asking how many ways to divide n particles in a row with $M-1$ partitions. If the particles were distinct the result would be $(n+(M-1))!$. Taking into account that the particles are indistinguishable we get

$$\begin{aligned} Z_n &= \frac{(n+M-1)!}{n!(M-1)!}\mathrm{e}^{-\beta\varepsilon n} && (5.28)\\ \mu &= \varepsilon + T\ln\left(\frac{n}{(M-1)+n}\right) && (5.29)\\ \bar{n} &= (M-1)(\mathrm{e}^{\beta(\varepsilon-\mu)}-1)^{-1} && (5.30) \end{aligned}$$

Electromagnetic mode:– Each mode of the electromagnetic field can be regarded as a Bosonic site that can occupy photons with binding energy ω. Since n is not constrained it follows formally that

$$\begin{aligned} \mu &= 0 && (5.31)\\ \bar{n} &= (\mathrm{e}^{\beta\omega}-1)^{-1} && (5.32) \end{aligned}$$

Boltzmann approximation:– Assuming dilute occupation ($1 \ll n \ll M$) we get a common approximation for both Fermi and Bose case:

$$Z_n = \frac{M^n}{n!} \mathrm{e}^{-\beta\varepsilon n} \tag{5.33}$$

$$\mu = \varepsilon + T \ln\left(\frac{n}{M}\right) \tag{5.34}$$

$$\bar{n} = M \mathrm{e}^{-\beta(\varepsilon-\mu)} \tag{5.35}$$

General system of sites:– If we want to consider the partition function of N particles in M sites that have different binding energies we have to calculate

$$Z_N(\beta) = \sum_{n_1+\ldots+n_M=N} \mathrm{e}^{-\beta(\varepsilon_1 n_1+\ldots+\varepsilon_M n_M)} \tag{5.36}$$

Because of the constraint the sum cannot be factorized. We therefore adopt the "Grand Hamiltonian" strategy and calculate the Grand partition function $\mathcal{Z}(\beta,\mu)$ that corresponds to $\mathcal{H}_G = \mathcal{H} - \mu N$. In principle we can get $Z_N(\beta)$ from $\mathcal{Z}(\beta,\mu)$ via an inverse transform, but in practice it is more convenient to stay with the Grand Hamiltonian framework.

[5.7] The grand canonical formalism

We can regard the grand canonical formalism as a special case of the canonical formalism, where the Grand Hamiltonian $\mathcal{H}_G = \mathcal{H} - \mu N$ describes a Grand system that consists of the gas particles and a hypothetical reservoir. Optionally we can motivate the introduction of a the grand canonical formalism following the same justification strategy as in the case of the canonical formalism. First we have to specify the many body eigenstates R of the system:

$$\hat{N}|R\rangle = N_R|R\rangle \tag{5.37}$$

$$\hat{H}|R\rangle = E_R|R\rangle \tag{5.38}$$

Then we assume that the system can exchange particles as well as energy with the environment. The probability of a many body eigenstate R is

$$p_R = \frac{\mathrm{e}^{-\beta E_R} Z^{\mathrm{env}}_{\bar{N}-N}}{Z^{\mathrm{sys+env}}}, \qquad \text{with} \quad Z^{\mathrm{env}}_{\bar{N}-N} \propto \mathrm{e}^{\beta\mu N} \tag{5.39}$$

We deduce that

$$p_R = \frac{1}{\mathcal{Z}} \mathrm{e}^{-\beta(E_R-\mu N_R)} \tag{5.40}$$

where the normalization constant is

$$\mathcal{Z}(\beta,\mu) \equiv \sum_R \mathrm{e}^{-\beta(E_R-\mu N_R)} \tag{5.41}$$

The Grand Canonical $\mathcal{Z}(\beta,\mu)$ is defined in complete analogy with the canonical case as sum over the many body states "R". For some purposes it is convent to write is as a function $\mathcal{Z}(z;\beta)$ of the fugacity:

$$z \equiv \mathrm{e}^{\beta\mu}, \qquad \frac{1}{\beta}\frac{\partial}{\partial\mu} = z\frac{\partial}{\partial z} \tag{5.42}$$

The Grand Canonical $\mathcal{Z}(\beta,\mu)$ can serve as a generating function as follows:

$$N \equiv \langle \hat{N} \rangle = \sum_R p_R N_R = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mu} \tag{5.43}$$

$$E - \mu N = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} \tag{5.44}$$

$$P \equiv \left\langle -\frac{\partial H}{\partial \mathsf{V}} \right\rangle = \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}}{\partial \mathsf{V}} \tag{5.45}$$

Equivalently

$$F_G(T,\mathsf{V},\mu) \equiv -\frac{1}{\beta}\ln \mathcal{Z} \tag{5.46}$$

$$N = -\frac{\partial F_G}{\partial \mu} \tag{5.47}$$

$$P = -\frac{\partial F_G}{\partial \mathsf{V}} \tag{5.48}$$

$$S = -\frac{\partial F_G}{\partial T} \tag{5.49}$$

$$E = F_G + TS + \mu N \tag{5.50}$$

In the thermodynamic limit F_G is extensive, also in the case of non ideal gas. Consequently

$$F_G(T,\mathsf{V},\mu) \;=\; -\mathsf{V}P(T,\mu) \tag{5.51}$$

$$dP \;=\; \frac{S}{\mathsf{V}}dT + \frac{N}{\mathsf{V}}d\mu \tag{5.52}$$

In other words rather then using the notation F_G, we can regard $P(T,\mu)$ as the generating function. Note that this is the "Grand canonical" version of the "canonical" Gibbs function relation

$$d\mu \;=\; -\frac{S}{N}dT + \frac{\mathsf{V}}{N}dP \tag{5.53}$$

For constant T, a variation in the chemical potential is related to a variation $dP = nd\mu$ in the pressure, where $n = N/\mathsf{V}$ is the density. In the canonical setup N is fixed, while in the grand-canonical setup V is fixed. The compressibility of the gas can be expressed as follows:

$$\kappa_T \;=\; -\left.\frac{1}{\mathsf{V}}\frac{d\mathsf{V}}{dP}\right|_N \;=\; \left.\frac{1}{N}\frac{dN}{dP}\right|_{\mathsf{V}} \;=\; \frac{1}{n}\frac{dn}{dP} \;=\; \frac{1}{n^2}\frac{dn}{d\mu} \tag{5.54}$$

[5.8] Fermi occupation

A site or mode can occupy $n = 0, 1$ particles. The binding energy is ϵ. the site is in thermochemical equilibrium with a gas in temperature β and chemical potential μ.

$$N_n \;=\; n \tag{5.55}$$

$$E_n \;=\; n\epsilon \tag{5.56}$$

$$p_n \;=\; \frac{1}{\mathcal{Z}}\mathrm{e}^{-\beta(\epsilon-\mu)n} \tag{5.57}$$

and accordingly,

$$
\begin{aligned}
\mathcal{Z}(\beta,\mu) &= \left(1+\mathrm{e}^{-\beta(\epsilon-\mu)}\right) & (5.58)\\
N(\beta,\mu) &= \langle \hat{n} \rangle = \sum_n p_n n = \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}+1} \equiv f(\epsilon-\mu) & (5.59)\\
E(\beta,\mu) &= \langle \hat{n}\epsilon \rangle = \epsilon f(\epsilon-\mu) & (5.60)
\end{aligned}
$$

We have defined the Fermi occupation function $0 \le f(\epsilon-\mu) \le 1$

[5.9] Bose occupation

A site or mode can occupy $n = 0, 1, 2, 3...$ particles. The binding energy is ϵ. the site is in thermochemical equilibrium with a gas in temperature β and chemical potential μ.

$$
\begin{aligned}
N_n &= n & (5.61)\\
E_n &= n\epsilon & (5.62)\\
p_n &= \frac{1}{\mathcal{Z}}\mathrm{e}^{-\beta(\epsilon-\mu)n} & (5.63)
\end{aligned}
$$

and accordingly,

$$
\begin{aligned}
\mathcal{Z}(\beta,\mu) &= \left(1-\mathrm{e}^{-\beta(\epsilon-\mu)}\right)^{-1} & (5.64)\\
N(\beta,\mu) &= \langle \hat{n} \rangle = \sum_n p_n n = \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}-1} \equiv f(\epsilon-\mu) & (5.65)\\
E(\beta,\mu) &= \langle \hat{n}\epsilon \rangle = \epsilon f(\epsilon-\mu) & (5.66)
\end{aligned}
$$

We have defined the Bose occupation function $0 \le f(\epsilon-\mu) \le \infty$. If $\epsilon < \mu$ then $\langle n \rangle \to \infty$. If $\epsilon = \mu$ then the site may have any occupation. If $\epsilon < \mu$ then $\langle n \rangle$ is finite.

[5.10] Bosonic mode occupation

The occupation of a mode of vibration, say the number photons in an electromagnetic mode, or the number of phonons in a vibration mode, are described by the canonical ensemble, by can be optionally regarded as described by the grand-canonical ensemble with $\mu = 0$. With slight change in notations we have:

$$
\begin{aligned}
N_n &= n & (5.67)\\
E_n &= n\omega & (5.68)\\
p_n &= \frac{1}{Z}\mathrm{e}^{-\beta\omega n} & (5.69)
\end{aligned}
$$

and accordingly,

$$
\begin{aligned}
Z(\beta) &= \left(1-\mathrm{e}^{-\beta\omega}\right)^{-1} & (5.70)\\
N(\beta) &= \langle \hat{n} \rangle = \sum_n p_n n = \frac{1}{\mathrm{e}^{\beta\omega}-1} \equiv f(\omega) & (5.71)\\
E(\beta) &= \langle \hat{n}\omega \rangle = \omega f(\omega) & (5.72)
\end{aligned}
$$

[6] Quantum ideal gases

[6.1] Equations of state

In what follows, unless written otherwise $\epsilon = 0$ is the ground state and

$$\sum_r \rightarrow \int_0^\infty \mathsf{g}(\epsilon) d\epsilon \tag{6.1}$$

The stationary states of the multi particle system are occupation states

$$|\boldsymbol{n}\rangle \;=\; |n_1, n_2, n_3, ..., n_r, ...\rangle \tag{6.2}$$

where $n_r = 0, 1$ for Fermi occupation and $n_r = 0, 1, 2, 3, 4, ...$ for Bose occupation. For these states we have

$$N_{\boldsymbol{n}} = \sum_r n_r \tag{6.3}$$

$$E_{\boldsymbol{n}} = \sum_r n_r \epsilon_r \tag{6.4}$$

$$p_{\boldsymbol{n}} \propto \mathrm{e}^{-\beta \sum_r (\epsilon_r - \mu) n_r} \tag{6.5}$$

which can be factorized. This means that each site or mode can be treated as an independent system. We use E and N without index for the expectation values in an equilibrium state. For the Fermionic and Bosonic case we have respectively ($\pm$)

$$\ln \mathcal{Z} = \pm \sum_r \ln(1 \pm \mathrm{e}^{-\beta(\epsilon_r - \mu)}) = \beta \int_0^\infty \mathcal{N}(\epsilon) d\epsilon \; f(\epsilon - \mu) \tag{6.6}$$

$$N = \sum_r \langle \hat{n}_r \rangle = \sum_r f(\epsilon_r - \mu) = \int_0^\infty \mathsf{g}(\epsilon) d\epsilon \; f(\epsilon - \mu) \tag{6.7}$$

$$E = \sum_r \epsilon_r \langle \hat{n}_r \rangle = \sum_r f(\epsilon_r - \mu) \epsilon_r = \int_0^\infty \mathsf{g}(\epsilon) \epsilon d\epsilon \; f(\epsilon - \mu) \tag{6.8}$$

$$P = \frac{1}{\beta} \frac{\ln \mathcal{Z}}{\mathsf{V}} = \frac{1}{\mathsf{V}} \int_0^\infty \mathcal{N}(\epsilon) d\epsilon \; f(\epsilon - \mu) \tag{6.9}$$

It is good to remember that $P(T, \mu)$ can serve as a generating function for all other state equations. This would be true also if the gas were not ideal. In particular $N/\mathsf{V} = dP/d\mu$ relates the density to the chemical potential, which implies a relation between the the pressure P and the density N/V.

[6.2] Explicit expressions for the state equations

We assume one particle states $|r\rangle$ that have the density

$$\mathsf{g}(\epsilon) = \mathsf{V} c\, \epsilon^{\alpha - 1}, \qquad \mathcal{N}(E) = \frac{1}{\alpha} \epsilon \, \mathsf{g}(\epsilon) \tag{6.10}$$

For a particle in d dimensional box $\alpha = d/\nu$ where ν is the exponent of the dispersion relation $\epsilon \propto |p|^\nu$, and c is a constant which is related to the mass m. For example, in the case of spin $1/2$ particle in $3D$ space we have

$$\mathsf{g}(\epsilon) = 2 \times \mathsf{V} \frac{(2\mathsf{m})^{3/2}}{(2\pi)^2} \epsilon^{\frac{1}{2}} \tag{6.11}$$

The following integral is useful (upper sign for Bose, lower sign for Fermi):

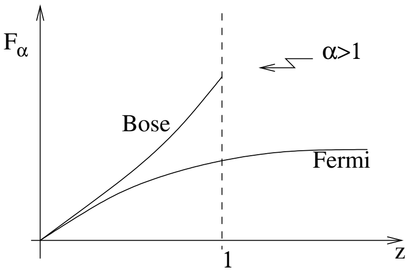
$$F_\alpha(u) \;\equiv\; \int_0^\infty \frac{x^{\alpha-1}\,dx}{\mathrm{e}^{x-u} \mp 1} \;\equiv\; \pm\Gamma(\alpha)\mathrm{Li}_\alpha(\pm z), \qquad z \equiv \mathrm{e}^u \tag{6.12}$$

where the upper/lower sign refers to the Bose and the Fermi case respectively. Details of the *Polylogarithm function* $\mathrm{Li}_\alpha(z)$ can be found in Wikipedia. In the physics community it is commonly denoted as $g_\alpha(z)$. Note that

$$\mathrm{Li}_\alpha(z) \;\equiv\; \sum_{\ell=1}^{\infty}\frac{1}{\ell^\alpha}z^\ell \;=\; z+..., \qquad \mathrm{Li}_\alpha(1)\equiv\zeta(\alpha), \qquad \frac{d}{dz}\mathrm{Li}_\alpha(z) = \frac{1}{z}\mathrm{Li}_{\alpha-1}(z) \tag{6.13}$$

As u becomes larger the function $F_\alpha(u)$ grows faster in the case of a Bose occupation, and it either diverges or attains a finite value as $u \to 0$. The finite value $F_\alpha(0) = \Gamma(\alpha)\zeta(\alpha)$ is attained for $\alpha > 1$. In particular we have $\Gamma(3/2) = \sqrt{\pi}/2$ and $\zeta(3/2) \approx 2.612$. For $\alpha = 1$ one obtains $\mathrm{Li}_1(z) = -\ln(1-z)$, which has logarithmic divergence as $z \to 1$. For $\alpha < 1$ it is easily shown that $F_\alpha(u) \sim [1/(1-\alpha)](-u)^{-(1-\alpha)}$ as u approach zero from below. In the Fermi case the integral is always finite. Using the step-like behavior of the Fermi occupation function we obtains for $z \gg 1$ the so-called Sommerfeld expansion:

$$F_\alpha(u) \;=\; \frac{1}{\alpha}u^\alpha\left[1+\alpha(\alpha-1)\frac{\pi^2}{6}\left(\frac{1}{u}\right)^2+...\right] \tag{6.14}$$



We can express the state equations using this integral, where z is identified as the fugacity. We get

$$\frac{N}{\mathsf{V}} \;=\; cT^\alpha\; F_\alpha\left(\frac{\mu}{T}\right) \tag{6.15}$$

$$\frac{E}{\mathsf{V}} \;=\; cT^{\alpha+1}\; F_{\alpha+1}\left(\frac{\mu}{T}\right) \tag{6.16}$$

while P is related trivially to the energy:

$$P \;=\; \frac{1}{\beta}\left(\frac{\ln\mathcal{Z}}{\mathsf{V}}\right) \;=\; \frac{1}{\alpha}\left(\frac{E}{\mathsf{V}}\right) \tag{6.17}$$

The grand-canonical free-energy is $F_G = -VP$, from which one can derive the entropy $S = -(dF_G/dT)_\mu$. Optionally the canonical free energy for N particles can be calculated via Legendre transform $F = F_G + \mu N$. The specific results in the case of a spinless non-relativistic Bose particles are [see also Huang p.231-232;242]:

$$\frac{N}{\mathsf{V}} \;=\; \frac{1}{\lambda_T^3}\,\mathrm{Li}_{3/2}(z) \tag{6.18}$$

$$\frac{E}{\mathsf{V}} \;=\; \frac{3}{2}\,\frac{T}{\lambda_T^3}\,\mathrm{Li}_{5/2}(z), \qquad P = \frac{2}{3}\left(\frac{E}{\mathsf{V}}\right) \;=\; \frac{T}{\lambda_T^3}\,\mathrm{Li}_{5/2}(z) \tag{6.19}$$

[6.3] Ideal gases in the Boltzmann approximation

We take $\epsilon = 0$ as the ground state energy of the one-particle states. The Boltzmann approximation is

$$f(\epsilon-\mu) \quad \approx \quad \mathrm{e}^{-\beta(\epsilon-\mu)} \tag{6.20}$$

It holds whenever the occupation is $f() \ll 1$. If it is valid for the ground state $\epsilon = 0$, then it is valid globally for all the higher levels. Accordingly the validity condition is $z \ll 1$, meaning $\mathrm{e}^{\beta\mu} \ll 1$. Under such condition one can make the approximation $\mathrm{Li}(z) \approx z$. In the case of standard 3D gas the Boltzmann approximation condition can be rewritten as

$$N\lambda_T^3 \quad \ll \quad \mathsf{V} \qquad \rightsquigarrow T \gg \frac{1}{\mathsf{m}\ell^2} \qquad \rightsquigarrow T \gg T_c \text{ (Bosons)}, \qquad \rightsquigarrow T \gg T_{\mathrm{F}} \text{ (Fermions)} \tag{6.21}$$

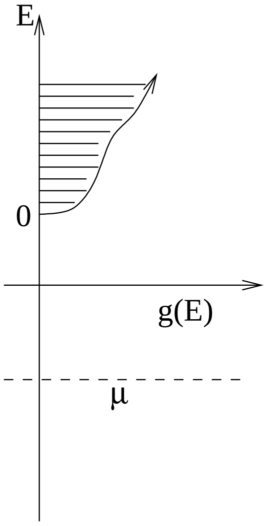
where $\ell = (V/N)^{1/3}$ is the typical distance between particles. Is later sections we shall defined the condensation temperature (T_c) and the Fermi energy (T_{F}). Within the framework of the Boltzmann approximation we can re-derive the classical equation of an ideal gas:

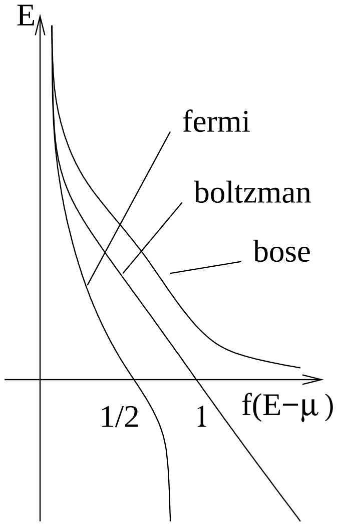
$$\frac{N}{\mathsf{V}} \; = \; \frac{1}{\lambda_T^3}\, z \; = \; \frac{1}{\lambda_T^3}\, \mathrm{e}^{\mu/T} \tag{6.22}$$

$$\frac{E}{\mathsf{V}} \; = \; \frac{3}{2}\frac{T}{\lambda_T^3}\, z \; = \; \frac{3}{2}\frac{N}{\mathsf{V}}T \tag{6.23}$$

$$P \; = \; \frac{T}{\lambda_T^3} z \; = \; \frac{N}{\mathsf{V}}T \tag{6.24}$$

Note that within this approximation E and P do not depend on the mass of the particles.



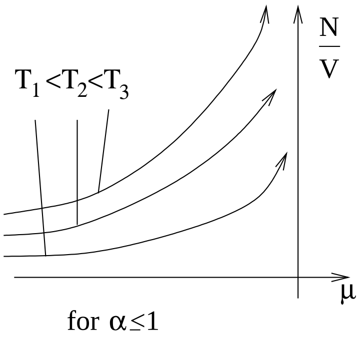


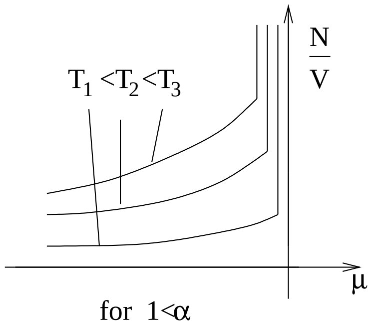
[6.4] Bose Einstein condensation

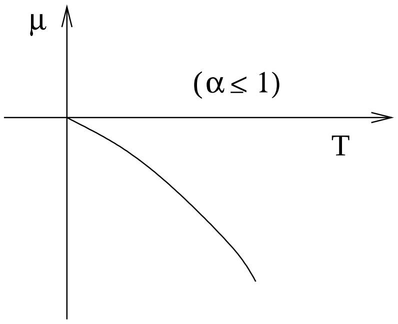
Let us write again the general expression for the occupation of the orbitals:

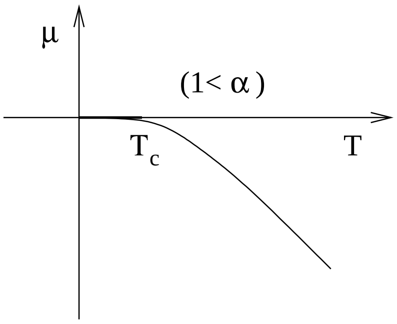
$$N(\beta,\mu) \quad = \quad \langle n_0 \rangle + \sum_{r>0} \langle n_r \rangle \quad = \quad \frac{1}{\mathrm{e}^{-\beta\mu}-1} \; + \; c\mathsf{V}\int \epsilon^{\alpha-1} d\epsilon \left(\frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}-1} \right) \tag{6.25}$$

In the limit $\mu \to 0^-$ this expression always diverges, so we can invert it and find μ as a function of N. But the physics is more illuminating if the ground-orbital occupation (n_0) is *dropped* from the above expression. Then we realize that for $\alpha > 1$, notably for $\alpha = 3/2$, the total occupation remains finite, namely $N(\mu \to 0^-) = c\mathsf{V}\Gamma(\alpha)\zeta(\alpha)T^\alpha$. It is implied that the excited states can accommodate only a *finite* fraction N/V of particles in the thermodynamic limit ($\mathsf{V} \rightarrow \infty$). Any additional amount of particles forces $\mu = 0$, and has to condense into the ground state orbital. The conclusion if different for $\alpha < 1$. For clarity we change notation to $\mathsf{V} = L^d$ and $\alpha = d/2$. The integral is dominated by the implicit lower cutoff $k \sim 1/L$. Hence we get $N(\mu \rightarrow 0^-) \propto L^d(L^2)^{1-(d/2)}T$. It is implies that the excited states can accommodate *any* fraction N/L^d of particles in the thermodynamic limit ($L \rightarrow \infty$). So in the latter case condensation is not forced. The figure below illustrates the reasoning of extracting μ versus T for a given N in both cases .









Considering $\alpha > 1$, having "$\mu = 0$" implies that

$$N = n_0 + c\mathsf{V}\Gamma(\alpha)\zeta(\alpha)T^{\alpha} \tag{6.26}$$

$$E = c\mathsf{V}\Gamma(\alpha{+}1)\,\zeta(\alpha{+}1)\,T^{\alpha+1} \tag{6.27}$$

$$P = \frac{1}{\alpha}\left(\frac{E}{\mathsf{V}}\right) \tag{6.28}$$

In particular the standard results for condensation in 3D are

$$N = n_0 + \mathsf{V}\zeta\left(\frac{3}{2}\right)\left(\frac{m}{2\pi}\right)^{\frac{3}{2}}T^{\frac{3}{2}} \tag{6.29}$$

$$P = \zeta\left(\frac{5}{2}\right)\left(\frac{\mathsf{m}}{2\pi}\right)^{\frac{3}{2}}T^{\frac{5}{2}} \tag{6.30}$$

The pressure P is independent of the total number of particles, because the condensate does not have any contribution. Hence the compressibility $\kappa \propto (\partial P/\partial \mathsf{V})^{-1} = \infty$. If we change the volume the extra/missing particles just come from the ground state, which is like a reservoir of $\mu = 0$ particles.

Given T, if we push N particles into a box, the condition to have condensation is $N > N(\beta, \mu \rightarrow 0^-)$. The condensation temperature, below which $\mu = 0$, is

$$T_c = \left(\frac{1}{c\Gamma\,(\alpha)\,\zeta\,(\alpha)}\frac{N}{\mathsf{V}}\right)^{1/\alpha} \sim \frac{1}{\mathsf{m}\ell^2} \tag{6.31}$$

where ℓ is the average distance between the particles. Given N, if one tries to eliminate μ, and writes it as a function of T, then one observes that below the condensation temperature μ is forced to become zero. Under such circumstances all the particles that cannot be occupied in the excited states have to condense in the ground state:

$$\langle n_0 \rangle \;=\; N \;-\; N\left(\beta, \mu \to 0^-\right) \;=\; \left(1 - \left(\frac{T}{T_c}\right)^{\alpha}\right) N \tag{6.32}$$

The common phrasing is that a macroscopic fraction of the particles occupies the ground state. This fraction is determined by $(T/T_c)^\alpha$ or equivalently by $[\mathsf{V}/\lambda_T^3]/N$. Note that $T \gg T_c$ is an optional way to write the Boltzmann condition.

[6.5] Fermi gas at low temperatures

At zero temperatures the Fermi function is a step function. At finite temperatures the step is smeared over a range T. In order to find explicit expressions for the state functions we have to perform an integral that involves the product of $f(\epsilon)$ with a smooth function $g(\epsilon)$. The latter is the density of states $\mathsf{g}(\epsilon)$ if we are interested in N, or $\epsilon\mathsf{g}(\epsilon)$ if we are interested in E. The Sommerfeld expansion is a procedure to get an approximation, say, to second-order in T. For this purpose we first define the zero temperature result

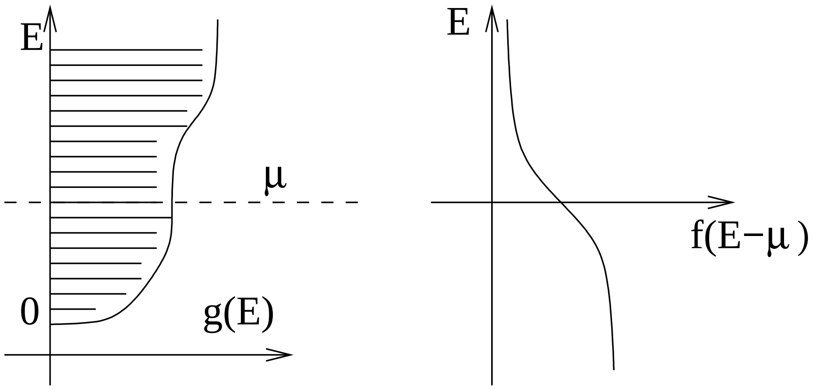
$$G(\mu) \;\equiv\; \int_{-\infty}^{\mu} g(\epsilon) d\epsilon \tag{6.33}$$

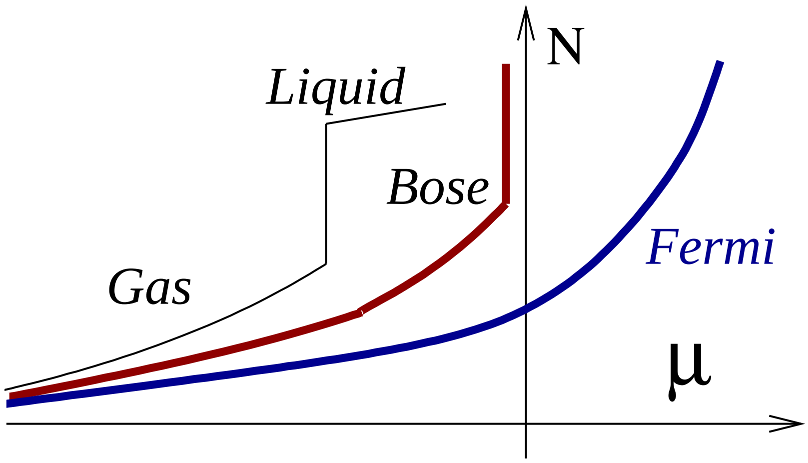
And then proceed with the finite temperature calculation using integration by parts:

$$\begin{aligned}
\int_{-\infty}^{\infty} d\epsilon \; g(\epsilon)\; f(\epsilon-\mu) \;&=\; \int_{-\infty}^{\infty} d\epsilon \; G(\epsilon)\; [-f'(\epsilon-\mu)] \;\equiv\; \int_{-\infty}^{\infty} d\epsilon \; G(\epsilon)\; \delta_T(\epsilon-\mu) && (6.34)\\
&=\; \int_{-\infty}^{\infty} d\epsilon \; \left[G(\mu) + G'(\mu)(\epsilon-\mu) + \frac{1}{2}G''(\mu)(\epsilon-\mu)^2 + ...\right] \; \delta_T(\epsilon-\mu) && (6.35)\\
&=\; G(\mu) \;+\; \frac{\pi^2}{6}T^2 G''(\mu) \;+\; \mathcal{O}(T^4) && (6.36)
\end{aligned}$$

We can apply this formula to the $N = \mathcal{N}(\mu)$ calculation. First we do the zero temperature integral, and from it eliminate μ as a function of N. This zero temperature result is known as the Fermi energy $\mu = \epsilon_F$. Then we substitute $\mu = \epsilon_F + \delta\mu$ in the above second order expression, expand $G(\mu) \approx G(\epsilon_F) + \mathsf{g}(\epsilon_F)\delta\mu$, and find

$$\mu(T) \;\approx\; \epsilon_F \;-\; \frac{\pi^2}{6}\frac{\mathsf{g}'(\epsilon_F)}{\mathsf{g}(\epsilon_F)}T^2 \;+\; \mathcal{O}(T^4) \tag{6.37}$$





The specific result for N fermions in system with $\epsilon^{\alpha-1}$ density of orbitals, and in particular for spinless non-relativistic fermions in 3D box is:

$$N \;=\; \frac{1}{\alpha}c\mathsf{V}\mu^{\alpha}\left[1+\alpha\left(\alpha-1\right)\frac{\pi^2}{6}\left(\frac{T}{\mu}\right)^2+...\right] \;=\; \mathsf{V}\frac{1}{6\pi^2}\left(2m\right)^{\frac{3}{2}}\mu^{\frac{3}{2}}\left[1+\frac{\pi^2}{8}\left(\frac{T}{\mu}\right)^2+...\right] \tag{6.38}$$

leading after elimination to

$$\epsilon_F \;=\; \left(\frac{\alpha}{c}\frac{N}{\mathsf{V}}\right)^{\frac{1}{\alpha}} \;=\; \frac{1}{2\mathsf{m}}\left(6\pi^2\frac{N}{\mathsf{V}}\right)^{\frac{2}{3}} \tag{6.39}$$

$$\mu \;=\; \left[1-(\alpha-1)\frac{\pi^2}{6}\left(\frac{T}{\epsilon_F}\right)^2+...\right]\epsilon_F \;=\; \left[1-\frac{\pi^2}{12}\left(\frac{T}{\epsilon_F}\right)^2+...\right]\epsilon_F \tag{6.40}$$

For the energy we get

$$E \;=\; \mathsf{V}\frac{3}{5}\frac{1}{6\pi^2}\left(2m\right)^{\frac{3}{2}}\mu^{\frac{5}{2}}\left[1+\frac{5\pi^2}{8}\left(\frac{T}{\mu}\right)^2+...\right] \;=\; \left[1+\frac{5\pi^2}{12}\left(\frac{T}{\epsilon_F}\right)^2+...\right]\frac{3}{5}N\epsilon_F \tag{6.41}$$

The pressure is given by the equation

$$P \;=\; \frac{2}{3}\left(\frac{E}{V}\right) \;=\; \frac{1}{5}\left(6\pi^2\right)^{\frac{2}{3}}\frac{1}{\mathsf{m}}\left(\frac{N}{\mathsf{V}}\right)^{\frac{5}{3}} \;+\; \mathcal{O}(T^2) \tag{6.42}$$

The grand-canonical free-energy is $F_G = -VP$ from which one can derive the entropy $S = -(dF_G/dT)_\mu \propto T$. The canonical free energy for N particles can be calculated via Legendre transform $F = F_G + \mu N$ leading to

$$F(T,V,N) \;=\; \left[1-\frac{5\pi^2}{12}\left(\frac{T}{\epsilon_F}\right)^2+...\right]\frac{3}{5}N\epsilon_F \tag{6.43}$$

From here one can recover the expression for the entropy $S = -(dF/dT)_N$, and additionally calculate the heat capacity $C_V = T(dS/dT)_{V,N} \propto T$ for a closed system of fermions.

Systems with interactions

[7] Interactions and phase transitions

Energy scales:– With regard to the prototype models of systems with interactions there are generically two energy scales. One is the interaction strength ε, and the other is the temperature T. For $T \gg \varepsilon$ a perturbative treatment is appropriate. See below the cluster expansion. For $T \ll \varepsilon$ it is advised to re-model the system with Hamiltonian that describes its collective excitations. The interesting regime is $T \sim \varepsilon$ where the phase transition takes place.

Models of interest:– It is natural to start with the discussion with the phenomenology of the gas-liquid phase transition, as implied by the Van-der-Waals equation of state. Later one realizes that the essential physics is captured by the "lattice gas" version, which is formally equivalent to the "Ising model" that describes a ferromagnetic phase transition. Its generalization is known as the "Potts model". The system consists of $\mathcal{N}$ sites. At each site there is a "spin" that can be in one of s possible states. The Ising model is a special case with $s = 2$, and the interaction is $\sigma_i\sigma_j$, where $\sigma = \pm 1$. The "Ising model" has a discrete up/down symmetry. Its Field theory version is known as the Landau model. The Heisenberg model is a different lattice model that has $S_i \cdot S_j$ interaction. This interaction has a continuous symmetry with respect to rotations. Its 2D version is known as the XY model. There are also corresponding Field theory models that are known as non-linear sigma models.

First order phase transition.– There are systems where there are (say) two families of states, such that each family has different DOS with different minimum. In such case a control parameter (call it h) might induce a crossover from the dominance of one family to the dominance of the second family. This crossover is reflected in the partition function and hence in the heat capacity and in the state equations. In the thermodynamic limit the crossover might be abrupt. In such case it is a "first order phase transition". If a change in a parameter leads to a *bifurcation* in the calculation of the partition function, it is called a "second order phase transition". The prototype example for phase transition is ferromagnetism where the magnetization might be "up" or "down".

Order parameter.– In order to analyze a second order phase transition it is useful to identify the "order parameter", which is a field $\varphi(x)$ that describes the coarse grained state of the system. In the prototype example of ferromagnetism it is the magnetization density in the sample. Defining an entropy functional $S[\varphi]$ that reflects the number of microscopic states that have the same field configuration, we can express the partition function as

$$Z = \sum_{\varphi} \mathrm{e}^{-A[\varphi]}, \qquad A[\varphi] = \frac{1}{T}\Big[E[\varphi] - TS[\varphi]\Big] \tag{7.1}$$

Symmetry breaking.– Second order phase transition is due spontaneous symmetry breaking leading to long range order. At $T = 0$ the definition of symmetry breaking is very simple. It means that $E[\varphi]$ attains (say) two distinct minimum that are described by different field configurations (different "order"). However, at finite temperature the canonical state is not the minimum of the energy functional $E[\rho]$ but of the free energy functional $F[\rho] = E[\rho] - TS[\rho]$. Accordingly entropic contribution may wash away the broken symmetry.

There is an implicit assumption with regard to the possibility to observe "symmetry breaking". It is assumed that $\varphi(x)$ has slow dynamics. If a magnet is prepared (say) with "up" magnetization then it takes a huge time until it flips to the quasi degenerate "down" magnetization.

Long range order.– In the prototype examples at high temperatures there is no "order" meaning that the correlation function $g(r) = \langle \varphi(r)\varphi(0) \rangle$ decays exponentially. As the critical temperature is approached from above the correlation length diverges. Below the critical temperature there is "long range order" and the correlation function should be re-defined with respect to the new order. There is a possibility to witness "infinite order phase transition" where below the critical temperature there is no long range order, but instead the correlation function become powerlaw. See discussion of the XY model.

Formal analysis.– Disregarding a few models that possess exact solutions, the analysis of the partition function can be done by adopting the following stages: **(1)** Primitive mean field theory evaluates the partition function by calculating $A[\varphi]$ for the field configuration that minimizes it. This corresponds mathematically to an inferior saddle point approximation. **(2)** Proper mean field theory is based on proper saddle point approximation, which means that the calculation takes into account the Gaussian fluctuations around the minimum. **(3)** Renormalization Group

(RG) treatment is required in the critical regime, whenever the Gaussian approximation in not valid. It explains the scaling anomalies that are witnessed in the vicinity of the critical temperature.

[7.1] Gas of weakly interacting particles

Consider a classical gas of interacting particles:

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2\mathsf{m}} + \sum_{\langle ij \rangle} u\left(\vec{x}_i - \vec{x}_j\right) \tag{7.2}$$

The partition function without the Gibbs factor is

$$\mathsf{Z}_N(\beta, \mathsf{V}) = \left(\frac{1}{\lambda_T^3}\right)^N \int dx_1 ... dx_N \ \exp\left[-\beta \sum_{\langle ij \rangle} u\left(x_{ij}\right)\right] \tag{7.3}$$

$$\equiv \left(\frac{1}{\lambda_T^3}\right)^N \int dx_1 ... dx_N \ \prod_{\langle ij \rangle} \left(1 + f\left(x_{ij}\right)\right), \qquad f(r) \equiv \mathrm{e}^{-\beta u(r)} - 1 \tag{7.4}$$

Note that the configuration space integral has the dimensions of V^N. It equals V^N if there are no interaction. If there are interactions we can regard the $f(r)$ as a perturbation. Then we can expand the product and perform integration term by term. The result can be organized as an expansion:

$$\mathsf{Z}_N(\beta, \mathsf{V}) = \left(\frac{\mathsf{V}}{\lambda_T^3}\right)^N \left[1 + \mathrm{coef}_2\left(\frac{N}{\mathsf{V}}\right) + \mathrm{coef}_3\left(\frac{N}{\mathsf{V}}\right)^2 + ...\right]^N \tag{7.5}$$

Note that we have raised an N using $(1+NS) \approx (1+S)^N$, such that S is an expansion in powers of the density (N/V). From here we can derive the so called Virial expansion for the pressure:

$$P = \frac{NT}{\mathsf{V}}\left[1 + a_2\left(\frac{N}{\mathsf{V}}\right) + a_3\left(\frac{N}{\mathsf{V}}\right)^2 + ...\right] = T\sum_{\ell=1}^{\infty} a_\ell(T)\left(\frac{N}{\mathsf{V}}\right)^\ell \tag{7.6}$$

The a_ℓ are known as the virial coefficients. From the above it is implied that

$$a_2 = -\frac{1}{2}\int f(r) d^3r = \frac{1}{2}\int\left[1 - \mathrm{e}^{-\beta u(r)}\right] d^3r \qquad \text{[classical]} \tag{7.7}$$

More generally it is implied from the discussion in the next sections that in order to get a_2 we just have to calculate the two-body partition function Z_2. Namely:

$$a_2 = -\frac{(\lambda_T^3)^2}{\mathsf{V}}\frac{1}{2!}\left[\mathsf{Z}_2 - \mathsf{Z}_1^2\right] \qquad \text{[general, no Gibbs prescription here!]} \tag{7.8}$$

The calculation of Z_2 for two interacting quantum particles, given the scattering phase-shifts, has been outlined in a past lecture. In the classical case it is standard to assume that the gas particles are like hard spheres, each having radius R, with some extra attractive part that has depth $\sim \epsilon_0$, similar to Lenard-Jones potential. Using high temperature expansion in β we get in leading order

$$a_2 \approx \frac{1}{2}\left[1 - \frac{\epsilon_0}{T}\right]\frac{4\pi}{3}(2R)^3 \equiv \bar{b} - \frac{\bar{a}}{T} \qquad \text{[Van-der-Waals]} \tag{7.9}$$

The coefficients $\bar{a}$ and $\bar{b}$ appear in the phenomenological Van-der-Waals equation of state that we shall discuss in a later stage. They are related to the attraction between the particles, and to their hard-core radius. Note that $\bar{b}$ is the excluded volume per particle multiplied by 2^{d-1}, where $d = 3$. Contrary to a common misconception it is only in 1D that $\bar{b}$ equals the excluded volume.

[7.2] The grand canonical perspective

It is simplest to deduce the Virial expansion from the grand canonical formalism. From now on the dependence on the temperature is implicit, and we emphasize the dependence on the fugacity z. The grand canonical partition function using the Gibbs prescription is

$$\mathcal{Z}(z) \ = \ \sum_{N=0}^{\infty} \frac{1}{N!} \mathsf{Z}_N z^N, \qquad \text{[Here } \mathsf{Z}_N \text{ is defined without Gibbs factor]} \qquad (7.10)$$

For an ideal classical gas all the Z_N are determined by the one-particle partition function, namely $\mathsf{Z}_N = \mathsf{Z}_1^N$. Accordingly $\ln(\mathcal{Z})$ includes a single term, namely $\ln(\mathcal{Z}) = \mathsf{Z}_1 z$. It makes sense to assume that interactions and quantum effects will add higher order terms. Hence we postulate an expansion

$$\ln \mathcal{Z}(z) \ = \ \sum_{n=1}^{\infty} \frac{1}{n!} \mathsf{B}_n z^n \qquad (7.11)$$

The relation between the B_n and the Z_n is formally the same as the relation between commulants and moments in probability theory:

$$\mathsf{Z}_1 \ = \ \mathsf{B}_1 \qquad (7.12)$$
$$\mathsf{Z}_2 \ = \ \mathsf{B}_1^2 + \mathsf{B}_2 \qquad (7.13)$$
$$\mathsf{Z}_3 \ = \ \mathsf{B}_1^3 + 3\mathsf{B}_1\mathsf{B}_2 + \mathsf{B}_3 \qquad (7.14)$$

Or backwards:

$$\mathsf{B}_1 \ = \ \mathsf{Z}_1 \qquad (7.15)$$
$$\mathsf{B}_2 \ = \ \mathsf{Z}_2 - \mathsf{Z}_1^2 \qquad (7.16)$$
$$\mathsf{B}_3 \ = \ \mathsf{Z}_3 - 3\mathsf{Z}_2\mathsf{Z}_1 + 2\mathsf{Z}_1^3 \qquad (7.17)$$

We can use these relations both directions: First we can evaluate a few Z_N, typically Z_1 and Z_2, in order to get the leading order B_n coefficients, say B_1 and B_2. Once the leading order B_n coefficients are known, we can generate from them a generalized Gibbs approximation for all(!) the Z_N.

[7.3] The cluster expansion

Our objective is to calculate the B_n coefficients in the expansion of $\ln(\mathcal{Z})$. For convenience we define their scaled versions b_n through the following substitution:

$$\frac{1}{n!}\mathsf{B}_n \ \equiv \ \mathsf{V} \left(\frac{1}{\lambda_T^3}\right)^n b_n(T) \qquad (7.18)$$

We turn to outline a general diagrammatic procedure to evaluate the b_n for a classical gas of interacting particles. A graph (network, diagram) is a set of vertices (nodes) that are connected by edges (connectors, bonds). In the present context each diagram represents an integral. The sum over all the connected diagrams that have n nodes gives the expansion coefficient B_n of the "comulant" generating function $\ln(\mathcal{Z})$, while the sum over all diagrams (including reducible diagrams) gives the expansion coefficient Z_N of the moments generating function $\mathcal{Z}$. Formally we write

$$\mathsf{Z}_N \quad = \quad \left(\frac{1}{\lambda_T^3}\right)^N \int dx_1 ... dx_N \prod_{\langle ij \rangle} (1 + f\left(x_{ij}\right)) \quad = \quad \left(\frac{1}{\lambda_T^3}\right)^N \sum [\text{diagrams with } N \text{ nodes}] \tag{7.19}$$

In this expression a diagram represents an integral of the type

$$C[3', 1, 2, 3] \times \int [f(x_{12}) f(x_{23})] \; [f(x_{56})] \; [f(x_{78}) f(x_{89}) f(x_{97})] \; dx_1 ... dx_9 \tag{7.20}$$

where C is a combinatorial factor that arise because we identify diagrams that differ only in the labelling of the vertices. One should realize that if a diagram is reducible, say $N = n_1 + n_2 + n_3$, then $C[n_1, n_2, n_3] = [N!/(n_1! n_2! n_3!)] C[n_1] C[n_2] C[n_3]$. In the above example $C[3'] = 3$ is the number of ways to have a triangle with 2 bonds, while $C[3] = 1$. Using this observation it is not difficult to prove that

$$\mathsf{B}_n \quad = \quad \left(\frac{1}{\lambda_T^3}\right)^n \sum [\text{connected diagrams with } n \text{ nodes}] \tag{7.21}$$

The implied expression for the b_n is the same diagrammatic sum, but the prefactor is replaced by $1/(n!\mathsf{V})$. The expressions for the leading coefficients are:

$$b_1 \quad = \quad \frac{1}{\mathsf{V}} \int dx \quad = \quad 1 \tag{7.22}$$

$$b_2 \quad = \quad \frac{1}{2!\mathsf{V}} \int f(x_{12}) \; dx_1 dx_2 \quad = \quad \frac{1}{2!} \int f(r) \; dr \tag{7.23}$$

$$b_3 \quad = \quad \frac{1}{3!\mathsf{V}} \int [3 f(x_{12}) f(x_{23}) + f(x_{12}) f(x_{23}) f(x_{31})] \; dx_1 dx_2 dx_3 \tag{7.24}$$

[7.4] The Virial coefficients

Having found the b_n the grand canonical partition function is

$$\ln \mathcal{Z}(z) \quad = \quad \mathsf{V} \sum_{n=1}^{\infty} b_n(T) \left(\frac{z}{\lambda_T^3}\right)^n \tag{7.25}$$

where $b_1 = 1$, and b_n has the dimension of length^{n-1}. Note that for an ideal Bose or Fermi gas one obtains $b_n = (\pm 1)^{n+1} n^{-5/2} (\lambda_T^3)^{n-1}$. We would like to find a procedure to determine these coefficients if there are weak interactions between the particles. Once they are known we get the state equations from

$$N \; = \; z \frac{\partial}{\partial z} \ln \mathcal{Z} \tag{7.26}$$

$$P \; = \; \frac{T}{\mathsf{V}} \ln \mathcal{Z} \tag{7.27}$$

leading to

$$\frac{N}{\mathsf{V}} \; = \; \sum_{n=1}^{\infty} n b_n(T) \; \left(\frac{z}{\lambda_T^3}\right)^n \tag{7.28}$$

$$\frac{P}{T} \; = \; \sum_{n=1}^{\infty} b_n(T) \; \left(\frac{z}{\lambda_T^3}\right)^n \tag{7.29}$$

It is customary to eliminate z/λ_T^3 from the first equation and to substitute into the second equation, thus getting the virial expansion with the coefficients

$$
\begin{aligned}
a_1 &= b_1 = 1 && (7.30)\\
a_2 &= -b_2 && (7.31)\\
a_3 &= 4b_2^2 - 2b_3 && (7.32)
\end{aligned}
$$

[7.5] The Van-der-Waals equation of state

Consider a classical gas that is composed of N particles in volume V. The particles have hard core of radius R, and the two-body interaction is assumed to be attractive, with depth $\sim \epsilon_0$. We have formally obtained from the virial expansion the following equation of state:

$$P \approx \frac{NT}{\mathsf{V}}\left[1 + \left(\bar{b} - \frac{\bar{a}}{T}\right)\frac{N}{\mathsf{V}}\right] \tag{7.33}$$

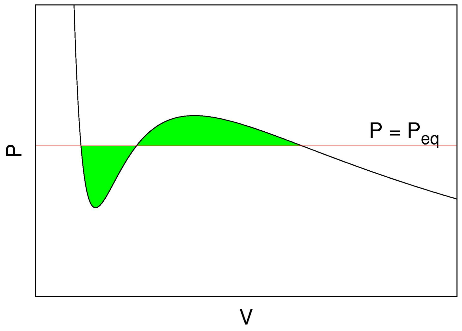
where $\bar{b} \sim R^3$ and $\bar{a} \sim \epsilon_0 R^3$. The effect of hard-core repulsion is under-estimated in this leading order perturbative expansion. The add-hock correction is to re-write the equation of state as follows:

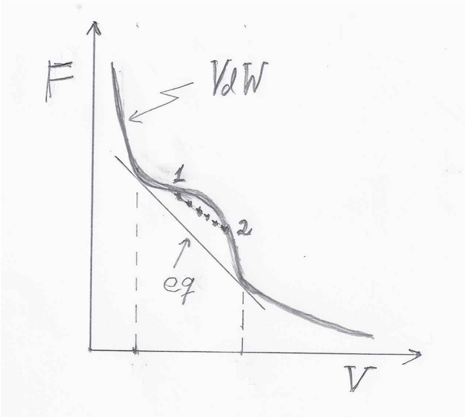
$$P = \frac{NT}{\mathsf{V} - N\bar{b}} - \left(\frac{N}{\mathsf{V}}\right)^2 \bar{a} \tag{7.34}$$

Roughly this equation can be derived by assuming that the partition function is like that of an ideal gas, where each particle experiences volume $\mathsf{V}_{\text{eff}} = (\mathsf{V} - N\bar{b})$, and mean potential $\langle U \rangle = -N\bar{a}/\mathsf{V}$. Optionally the a term could have been deduced from the virial theorem, using the estimate $\langle r \cdot (\partial U/\partial r)\rangle \sim N^2\,(\epsilon_0 R^3/\mathsf{V})$. If we plot P versus V we find that it becomes non-monotonic if the temperature is lower than a critical value. For a detailed analysis see [**Huang, section 2.3**]. The critical value of the temperature is

$$T_c = \frac{8\bar{a}}{27\bar{b}} \sim \epsilon_0 \tag{7.35}$$

The P dependence for $T < T_c$ is illustrated in the figure below [**taken from Wikipedia**]. From the relation $P = -dF/d\mathsf{V}$ one can deduce the free energy $F(\mathsf{V})$. One can argue that there is a V range of instability where the free energy can be lowered via phase separation. This is known as Maxwell construction (details below). A similar reasoning can be applied to the ferromagntic phase transition where the role of V is played by the magnetization.





Maxwell construction.– Assume that we divide the volume such that $V = \tilde{V}_1 + \tilde{V}_2$, and the particles are partitioned such that $N = \tilde{N}_1 + \tilde{N}_2$. Using the extensive property of $F(\mathsf{V}; N)$ we deduce that the free energy of the mixed phase is

$$F_{\text{mix}} \;=\; \frac{\tilde{N}_1}{N}F\left(\frac{N}{\tilde{N}_1}\tilde{V}_1\right)+\frac{\tilde{N}_2}{N}F\left(\frac{N}{\tilde{N}_2}\tilde{V}_2\right) \;\equiv\; xF(V_1)+(1-x)F(V_2) \tag{7.36}$$

where $x \in [0,1]$ is the fraction of particles in phase1, while V_1 and V_2 are the volumes that would be occupied if all the particles were in phase1 or in phase2 respectively. Observing that the mixture occupies a volume $V = xV_1 + (1-x)V_2$ we deuce that the mixture is represented by a point that is located on a chord that connects point1 and point2 of the $F(V)$ plot above (right panel). It follows that any concave segment of $F(V)$ is unstable: the free energy can be lowered via phase separation. Observing that $P(V)$ is the derivative of $F(V)$, the concave segment can be optionally determined by the "equal area" law. In reality we expect, as the volume is increased, to go along the constant pressure equilibrium line, until all the particles evaporate from the "liquid" phase to the "gas" phase.

A possibly simpler perspective on Maxwell construction is to regard the applied P as the free variable, and see how V depends on it. The grand Hamiltonian is $\mathcal{H}_G = \mathcal{H} + PV$, and the grand partition function is related by Laplace transform:

$$Z_G(P) \;=\; \int dV\; \mathrm{e}^{-A(V;P)} \qquad\qquad A(V;P) \equiv \frac{1}{T}\left(F(V)+PV\right) \tag{7.37}$$

Note that a plot of $A(V)$ versus V is related trivially to the plot of $F(V)$. The integral is dominated by the minimum of $A(V)$, which provide the most probable value of V. This leads to the standard Legendre prescription for the determination of the Gibbs function. But here the situation is somewhat subtle. As P is increased we get at some point two minima that represent stable and meta-stable solutions. As P is further increased, at some stage the two minima will swap, implying a jump at V. This swap corresponds to the Maxwell construction. We note that the volume (V) as a function of the pressure (P) is analogous to the magnetization (M) as a function of the field (h), which we discuss in more detail later on.

[7.6] From gas with interaction to Ising problem

Consider classical gas with interactions $U\left(\vec{r_1},...,\vec{r_N}\right)$. The N particle partition function is

$$Z_N \;=\; \frac{1}{N!}\left(\frac{1}{\lambda_T}\right)^{3N}\int d^{3N}r\; \mathrm{e}^{-\beta U(r_1,...,r_N)} \tag{7.38}$$

We see that the kinetic part factors out, hence the whole physics of the interactions is in the configuration integral. Therefore, without loss of generality we can consider "static gas". To further simplify the treatment we consider a "lattice gas" version:

$$\mathcal{H} \;=\; U\left(\vec{r_1},...,\vec{r_N}\right) \;=\; \sum_{\langle x,x'\rangle} u\left(x,x'\right)n(x)n\left(x'\right) \tag{7.39}$$

We can represent graphically the interaction between two sites x and x' by "bonds". The notation $\langle x,x'\rangle$ means summation over all the bonds without double counting. In the simplest case there are interactions only between near-neighbor sites. The grand partition function is

$$\mathcal{Z} \;=\; \sum_{n(\cdot)}\exp\left[-\beta\left(\sum_{\langle x,x'\rangle} u\left(x,x'\right)n(x)n\left(x'\right) - \mu\sum_x n(x)\right)\right] \tag{7.40}$$

where $n(x) = 0, 1$. We define

$$n(x) = \frac{1+\sigma(x)}{2}, \qquad\qquad \sigma(x) = \pm 1 \tag{7.41}$$

Then we get

$$\mathcal{Z}=\sum_{\sigma(x)} \exp \left[-\beta\left(-\sum_{\left\langle x, x^{\prime}\right\rangle} \varepsilon\left(x, x^{\prime}\right) \sigma(x) \sigma\left(x^{\prime}\right)-h \sum_{x} \sigma(x)+\text{const}\right)\right] \tag{7.42}$$

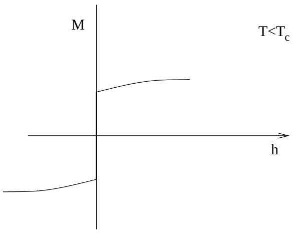
where $h=[\mu-\bar{u}]/2$. Here $\bar{u}$ is the interaction energy per site for full occupation. Note that $h=0$ implies that a fully occupied lattice has the same energy as an empty lattice. We also have changed notation $u(x,x')=-4\varepsilon(x.x')$, with $\varepsilon>0$ corresponding to attractive interaction.

We see that the calculation of $\mathcal{Z}$ for static lattice gas is formally the same as calculation of Z for an Ising model. The following analogies should be kept in mind

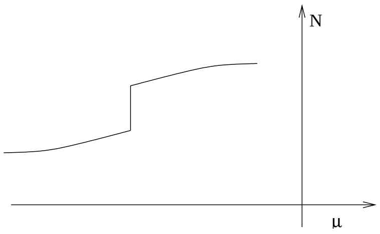
$$\begin{aligned}
\text{occupation } N & \longleftrightarrow \text{ magnetization } M=2N-\mathcal{N} && (7.43)\\
\text{chemical potential } \mu & \longleftrightarrow \text{ magnetic field } 2h && (7.44)\\
\text{fugacity } z=\mathrm{e}^{\beta\mu} & \longleftrightarrow \text{ define } z=\mathrm{e}^{2\beta h} && (7.45)\\
\text{grand canonical } \mathcal{Z}(\beta,\mu) & \longleftrightarrow \text{ canonical } Z(\beta,h) && (7.46)
\end{aligned}$$

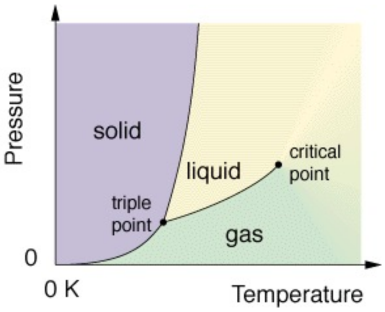
From now on we refer to Ising model, but for the formulation of some theorems in the next section it is more convenient to use the lattice gas language for heuristic reasons. Note also that N is more convenient than M because it does not skip in steps of 2.

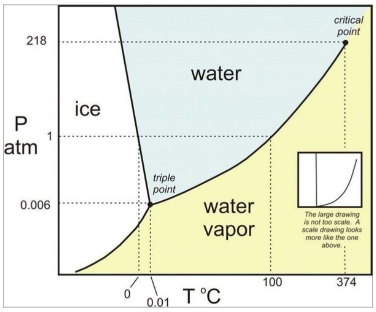
M vs h

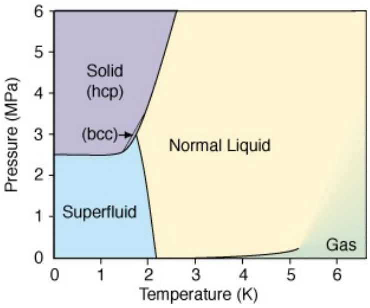


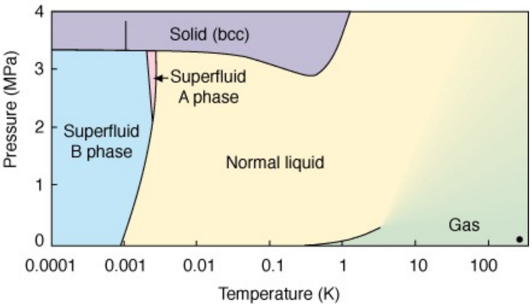
N vs μ











We shall clarify that in the thermodynamic limit (large $\mathcal{N}$) the magnetization density $M/\mathcal{N}$, when plotted as a function of h, might exhibits a jump at $h = 0$. This is called 1st order phase transition. Similarly, in the lattice gas model, the density $N/\mathcal{N}$, when plotted as a function of μ, might exhibits a jump at $\mu = \bar{u}$. This can be regarded a gas-to-liquid phase transition. In the canonical perspective we fix N and solve for μ. It is best to illustrate the procedure graphically. Having a plot of N vs μ, we get a "gas" or a "liquid" state provided the horizontal N line does not intersect the discontinuity. Otherwise there is a phase separation, where the gas and the liquid phases coexist with the same chemical potential $\mu = \bar{u}$.

In the phase diagram (T, h) of the Ising model it is customary to indicate the discontinuity of the first order transition by a solid line that stretches from $(0, 0)$ to $(T_c, 0)$. Similarly, in the phase diagram (T, μ) of the lattice gas the discontinuity is indicated by a solid line that stretches from $(0, \bar{u})$ to $(T_c, \bar{u})$. However in practice it is customary to use a (T, P) phase diagram. Here we bring the phase diagrams for conventional gas-liquid-solid transition, for water, for Helium-II and for Helium-III [taken from the web]:

[7.7] Yang and Lee theorems

Consider the lattice gas or the equivalent Ising model. We can use $n(x)$ or $\sigma(x)$ in order to specify whether a cell is filled (spin "up") or empty (spin "down"). The probability of a given configuration is determined by the grand-canonical energy $E_\sigma - \mu N_\sigma$, namely

$$p_\sigma \quad \propto \quad e^{-\beta(E_\sigma - \mu N_\sigma)} \tag{7.47}$$

Here E_σ is the Ising energy due to the interactions, and $N_\sigma = \sum_x n(x)$ is the number of "up" spins, which we call below "total magnetization". In fact the total magnetization is $2N_\sigma - \mathcal{N}$, hence μ in the lattice-gas model is like $2h$ in the Ising model. Either way we use the fugacity as the free variable and write the probability of a given configuration as follows:

$$p_\sigma \quad = \quad \frac{1}{\mathcal{Z}} \left[e^{-\beta E_\sigma}\right] \; z^{N_\sigma}, \qquad\qquad z \equiv e^{\beta\mu} \equiv e^{2\beta h} \tag{7.48}$$

Note that $z = 1$ means zero field. The partition function is

$$\mathcal{Z}(z;\beta) \quad = \quad \sum_{N=0}^{\mathcal{N}} Z_N(\beta) z^N \tag{7.49}$$

where Z_N sums over all the configurations that have N spins up, and $\mathcal{Z}$ sums over all the possible values of the "total magnetization". The Helmholtz function is

$$F(z;\beta) \quad = \quad -\frac{1}{\beta} \ln \mathcal{Z}(z;\beta) \tag{7.50}$$

The expectation value of the "total magnetization" is

$$\langle N \rangle \quad = \quad -\beta z \frac{\partial}{\partial z} F(z;\beta) \tag{7.51}$$

As we increase z we expect the magnetization $\langle N \rangle$ to grow, and $\langle N \rangle / \mathcal{N}$ to reach a well defined value in the limit $\mathcal{N} \to \infty$. Moreover, below some critical temperature we expect to find a phase transition. In the latter case we expect $\langle N \rangle$ to have a jump at zero field ($z = 1$). The Yang and Lee theorems formulate these expectations in a mathematically strict way. Given $\mathcal{N}$ it is clear that we can write the polynomial $\mathcal{Z}$ as a product over its roots:

$$\mathcal{Z}(z) \quad = \quad \text{const} \times \prod_{r=1}^{\mathcal{N}} (z - z_r) \tag{7.52}$$

Consequently

$$F(z) = -\frac{1}{\beta}\sum_{r=1}^{\mathcal{N}} \ln(z-z_r) + \text{const} \tag{7.53}$$

$$\langle N\rangle = z\sum_{r=1}^{\mathcal{N}} \frac{1}{z-z_r} \tag{7.54}$$

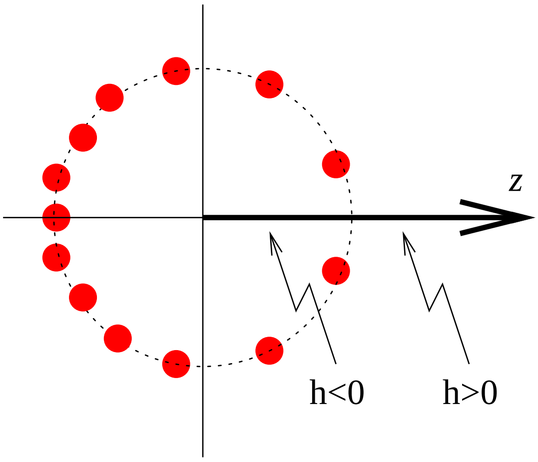
There is a strict analogy here with the calculation of an electrostatic field in a 2D geometry. In the absence of interactions (infinite temperature) we get that all the roots are at $z=-1$. Namely,

$$\mathcal{Z}(z;\beta) = \sum_{N=0}^{\mathcal{N}} C_{\mathcal{N}}^{N}\, z^N = (1+z)^{\mathcal{N}} \qquad \text{[non-interacting sites]} \tag{7.55}$$

So we do not have phase transition since the physical axis is $0<z<1$, where this function is analytic. The questions are what happens to the distribution of the roots as we increase the interaction (lower the temperature), and what is the limiting distribution in the thermodynamics limit ($\mathcal{N}\to\infty$). There are three statements that give answers to these questions due to Yang and Lee. The first statement is regarding the existence of the thermodynamics limit:

$$\lim_{\mathcal{N}\to\infty} \frac{F(z)}{\mathcal{N}} = \text{exists} \tag{7.56}$$

The second statement relates specifically to the standard Ising model, saying that all the roots are lying on the circle $|z_r|=1$. In general other distributions are possible. The third statement is that below the critical temperature the density of roots at $z=1$ becomes non-zero, and hence by Gauss law $\langle N\rangle/\mathcal{N}$ has a jump at zero field. This jump is discontinuous in the thermodynamic limit.



[8] The Ising model

[8.1] Model definition

The energy of a given Ising model configuration state is

$$E[\sigma(\cdot)] \;=\; -\sum_{\langle x,x'\rangle} \varepsilon(x,x')\,\sigma(x)\sigma(x') - \sum_x h(x)\sigma(x) \tag{8.1}$$

The canonical state is

$$p[\sigma(\cdot)] \;=\; \frac{1}{Z}\mathrm{e}^{-\beta E[\sigma(\cdot)]} \tag{8.2}$$

where the partition function is

$$Z[h(\cdot),\beta] \;=\; \sum_{\sigma(\cdot)} \exp\left[\beta\left(\sum_{\langle x,x'\rangle} \varepsilon(x,x')\,\sigma(x)\sigma(x') + \sum_x h(x)\sigma(x)\right)\right] \tag{8.3}$$

We expand $\ln[Z]$ in Taylor with respect to the field. The first order coefficients are zero due to $h \mapsto -h$ symmetry. Consequently we get for the Helmholtz function

$$F[h(\cdot),T] \;=\; F_0(T) - \frac{1}{2T}\sum_{x,x'} G(x,x')h(x)h(x') + \mathcal{O}\left(h^4\right) \tag{8.4}$$

In the absence of external field $F(T) = F_0(T)$ and we have the usual relations

$$E(T) \;=\; F(T) + TS(T) \tag{8.5}$$

$$S(T) \;=\; -\frac{\partial F(T)}{\partial T} \tag{8.6}$$

$$C(T) \;=\; T\frac{\partial S}{\partial T} = \frac{dE}{dT} \tag{8.7}$$

Next we assume weak field, leading to a linear response relation between $\langle\sigma(x)\rangle$ and $h(x)$. Namely,

$$\langle\sigma(x)\rangle \;=\; -\frac{\partial F}{\partial h(x)} \;=\; \frac{1}{T}\sum_{x'} G(x,x')h(x') \tag{8.8}$$

$$\langle\sigma(x)\sigma(x')\rangle_0 \;=\; -T\left.\frac{\partial F}{\partial h(x)\partial h(x')}\right|_0 \;=\; G(x,x') \tag{8.9}$$

For an homogeneous field we get $\langle\sigma(x)\rangle = \chi h$, and $F(T,h) = F_0(T) + (1/2)\mathcal{N}\chi h^2$, where

$$\chi \;=\; \frac{1}{T}\sum_r G(r), \qquad \text{[fluctuation-response relation]} \tag{8.10}$$

For the total magnetization we get

$$\langle\tilde{M}\rangle \;=\; \sum_x \langle\sigma(x)\rangle \;=\; \mathcal{N}\chi h \tag{8.11}$$

Optionally we could get the same result by replacing $h(x) \mapsto h$, and using $\tilde{M} = -\partial F/\partial h$. For the fluctuations of the total magnetization we get

$$\langle \tilde{M}^2 \rangle \ = \ \sum_{x,x'} \langle \sigma(x)\sigma(x') \rangle \ = \ \mathcal{N} \sum_{r} G(r) \tag{8.12}$$

Form here we deduce that

$$\chi \ = \ \frac{1}{T} \frac{\langle \tilde{M}^2 \rangle}{\mathcal{N}} \qquad \text{[fluctuation-response relation]} \tag{8.13}$$

This is merely another version of the same "fluctuation-response relation".

[8.2] The spatial correlation function

It is possible to measure $G(r)$ via a scattering experiment. Given a configuration $\sigma(x)$ the intensity of the scattering in the Born approximation is

$$I\,(q) \ \propto \ \left| \int \sigma(x) \mathrm{e}^{-i\vec{q}\cdot\vec{x}} d\vec{x} \right|^2 \tag{8.14}$$

If we average over configurations we get

$$I\,(q) \ \propto \ \int dx dx' \ \langle \sigma(x) \sigma\,(x') \rangle \ \mathrm{e}^{-iq\cdot\left(\vec{x}-\vec{x}'\right)} \ \propto \ \tilde{G}(q) \tag{8.15}$$

Here $\tilde{G}(q)$ is the FT of the correlation function $G(r) = \langle \sigma(x)\sigma(x') \rangle$, where $r = (x - x')$. For an isotropic model the result does not depend on the direction.

We would like to discuss what happens to $G(r)$ as the temperature is lowered. Specifically we would like to illuminate what is the fingerprints of approaching a critical temperature of a phase transition, below which the system is "ordered". We note that all the discussion below can be repeated if we apply an infinitesimal field $h = +0$ and approach the critical temperature from below. In the latter scenario the correlation function should be redefined by subtracting the constant $\langle \sigma \rangle^2$.

We shall see in the next section that Landau's approach in the Gaussian approximation leads to the Ornstein-Zernike expression for the FT of the correlation function:

$$\tilde{G}(q) \ = \ \left(\frac{(1/\xi)}{q^2 + (1/\xi)^2} \right) \tag{8.16}$$

This leads to

$$G(r) \sim \ \exp(-r/\xi) \qquad \text{if } \xi < \infty \tag{8.17}$$

$$G(r) \sim \ \ 1/r^{d-2} \qquad \text{for } d{>}2 \text{ if } \xi = \infty \tag{8.18}$$

Using the scaled variable $\mathsf{r} = r/\xi$ the exact FT can be expressed in terms of the modified Bessel function of the second kind:

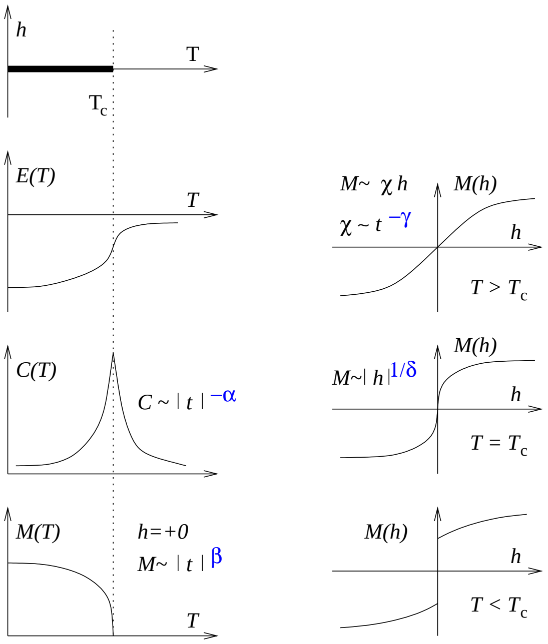
$$G(\mathsf{r}) \ = \ \frac{1}{(2\pi)^{d/2}} \left(\frac{1}{\mathsf{r}} \right)^{(d/2)-1} \boldsymbol{K}_{(d/2)-1}(\mathsf{r}) \tag{8.19}$$

In 1D it is $G(\mathsf{r}) = [1/2]e^{-\mathsf{r}}$, and in 3D it is $G(\mathsf{r}) = [1/(4\pi\mathsf{r})]e^{-\mathsf{r}}$.

The information about order-disorder transition is in $G(r)$. If $\xi < \infty$ there is no long range order, and we get $\chi < \infty$. As $\xi \to \infty$ the susceptibility diverges, which implies a phase transition. Note that for finite ξ the total magnetization $\tilde{M}$ can be regarded as a sum of random variables, its variance scales like $\mathcal{N}$, and consequently χ comes out finite, as implied by the "fluctuation-response relation". At the critical temperature the fluctuations are strongly correlated over arbitrarily large distances, and χ diverges.

[8.3] Critical behavior and the scaling hypothesis

Below we display the phases diagram in (T, h) space, and qualitative plots of the state equations. For the $2D$ Ising model with near neighbor interactions $T_c \approx 2.27\epsilon$.



The state equations in the critical region are characterized by the exponents $\alpha, \beta.\gamma, \delta$ (see below). Two other exponents ν and η are defined via the critical behavior of the correlation function, which is assumed to be a variation on the Ornstein-Zernike expression. Namely, one conjectures that the divergence of the correlation length as $T \to T_c$ is described by

$$\xi \quad \sim \quad |T - T_c|^{-\nu} \tag{8.20}$$

and that the correlation function is

$$G(r) \quad \sim \quad \frac{1}{r^{d-2+\eta}} \exp(-r/\xi) \tag{8.21}$$

Here we combined the $T = T_c$ and the $T > T_c$ into one expression. This expression describes the long range behavior. Note that the "microscopic" short range behavior is not too interesting because it is bounded by $G(0) = 1$. The divergence of χ is due to the slow power-law tails. Below T_c the behavior is similar to $T > T_c$ provided the correlation function is properly defined. Going on with the same phenomenology the conjecture is that away from T_c the correlation distance ξ is the only relevant length scale in the thermodynamic limit. This means that each "correlated block" of the system has the same contribution to the Free energy irrespective of the temperature, hence

$$F_0(T) \quad \sim \quad \frac{\mathsf{V}}{\xi^d} \quad \propto \quad |T - T_c|^{\nu d} \tag{8.22}$$

where d is the dimensionality. It is customary to define the scaled temperature as $t = |T - T_c|/T_c$, and to summarize the above conjectures as a *scaling hypothesis* that involves the critical exponents:

$$G(sr, s^{-1/\nu}t) = s^{-(d-2+\eta)}G(r,t) \tag{8.23}$$
$$F_0(s^{-1/\nu}t) = s^{-d}F_0(t) \tag{8.24}$$

From here it follows that

$$\chi(s^{-1/\nu}t) = s^{2-\eta}\chi(t) \tag{8.25}$$
$$C(s^{-1/\nu}t) = s^{(2/\nu)-d}C(t) \tag{8.26}$$

From the combined scaling relation

$$F\left(s^{-1/\nu}t, s^{-(d+2-\eta)/2}h\right) = s^{-d}F(t,h) \tag{8.27}$$

we can deduce similar relations for the magnetization. These scaling relations allow to deduce the critical exponents $\alpha, \beta.\gamma, \delta$ from d, ν, η, leading to

$$C \sim |t|^{-\alpha}, \quad \alpha = 2 - \nu d \tag{8.28}$$
$$M \sim |t|^{\beta}, \quad \beta = (d-2+\eta)\nu/2 \tag{8.29}$$
$$\chi \sim t^{-\gamma}, \quad \gamma = (2-\eta)\nu \tag{8.30}$$
$$M \sim |h|^{1/\delta}, \quad \delta = (d+2+\eta)/(d-2+\eta) \tag{8.31}$$

The so called "classical" mean-field exponents that we derive later are

$$\nu = 1/2, \qquad \eta = 0, \qquad \alpha = 0, \qquad \beta = 1/2, \qquad \gamma = 1, \qquad \delta = 3 \tag{8.32}$$

In order to get a non-trivial result for α we have to take into account Gaussian fluctuations around the mean field leading to $\alpha = [2 - (d/2)]$, in consistency with the scaling relations. However, one observes that the classical mean-field exponents satisfy the other scaling relations with $d = 4$, and not with $d = 3$. This implies that we have to go beyond mean field theory in order to establish the experimentally observed scaling behavior.

[8.4] Digression regarding scaling

A function of one variable has a scaling property if

$$F(sx) = s^{D_F}F(x) \tag{8.33}$$

where D_F is the scaling exponent. It follows that $F(x) = \text{const}\ x^{D_F}$. For example $F(x) = x^2$ has the scaling exponent $D_F = 2$. If we have say two variables then the more general definition is

$$F(s^{D_x}x, s^{D_y}y) = s^{D_F}F(x,y) \tag{8.34}$$

Note that the scaling exponents can be multiplied by the same number, and still we have the same scaling relation. It follows that there is a scaling function such that

$$F(x,y) = y^{D_F/D_y}f\left(\frac{x}{y^{D_x/D_y}}\right) \tag{8.35}$$

For example $F(x,y) = x^2 + y^3$ has the scaling exponents $D_x = 1/2, D_y = 1/3, D_F = 1$. More generally any "physical" function has an "engineering" scaling property that follows trivially from dimensional analysis.

[8.5] Solution of the 1D Ising Model

Assuming only near neighbor interactions

$$E\left[\sigma\right] \quad = \quad -\varepsilon\sum_{\langle ij\rangle}\sigma_i\sigma_j-\sum_i h_i\sigma_i \tag{8.36}$$

The partition function is

$$Z[h,\beta] \quad = \quad \sum_{\sigma(\cdot)}\mathrm{e}^{-\beta E[\sigma]} \tag{8.37}$$

For $\varepsilon = 0$ we get

$$Z[h,\beta] \quad = \quad \prod_{i=1}^{N}2\cosh\left(\beta h_i\right) \tag{8.38}$$

and hence

$$F[h,T] \quad = \quad -T\sum_{i=1}^{N}\ln\left(2\cosh\left(\frac{h_i}{T}\right)\right) \quad \approx \quad -NT\ln\left(2\right)-\frac{1}{2T}\sum_{i=1}^{N}h_i^2 \tag{8.39}$$

The correlation function is

$$G(r) \quad = \quad -T\frac{\partial F}{\partial h_i\partial h_j} \quad = \quad \delta_{ij} \quad = \quad \delta_{r,0} \tag{8.40}$$

and hence the susceptibility is

$$\chi \quad = \quad \frac{1}{T}\sum_r G(r) \quad = \quad \frac{1}{T} \tag{8.41}$$

The magnetization is

$$\tilde{M} \quad = \quad -\frac{\partial F}{\partial h} \quad = \quad N\tanh\left(\frac{h}{T}\right) \quad \approx \quad N\chi h+\mathcal{O}\left(h^3\right) \tag{8.42}$$

We turn now to the case $\varepsilon \neq 0$. Without an external field the calculation is very easy. We can define $s_{\langle ij\rangle} = \sigma_i\sigma_j$. Then the interaction can be written as $-\varepsilon\sum_b s_b$. Instead of summing over spins, we can sum over the bonds s_b. Assuming a chain of N spins the sum factorizes and we get $Z = 2[2\cosh(\beta\varepsilon)]^{\mathcal{N}-1}$. Next we would like to assume that there is non zero homogeneous field h. The calculation becomes somewhat more complicated, and requires the so called "transfer matrix" method. Let us define the matrix

$$T_{\sigma'\sigma''} \quad \equiv \quad \exp\left[\tilde{\varepsilon}\sigma'\sigma''+\frac{1}{2}\tilde{h}\left(\sigma'+\sigma''\right)\right] \quad = \quad \begin{pmatrix} \mathrm{e}^{\tilde{\varepsilon}+\tilde{h}} & \mathrm{e}^{-\tilde{\varepsilon}} \\ \mathrm{e}^{-\tilde{\varepsilon}} & \mathrm{e}^{\tilde{\varepsilon}-\tilde{h}} \end{pmatrix}, \qquad \tilde{\varepsilon}\equiv\beta\varepsilon,\ \tilde{h}\equiv\beta h \tag{8.43}$$

The eigenvalues of this matrix are

$$\lambda_{\pm} \quad = \quad \mathrm{e}^{\tilde{\varepsilon}}\cosh\left(\tilde{h}\right)\pm\mathrm{e}^{-\tilde{\varepsilon}}\sqrt{1+\mathrm{e}^{4\tilde{\varepsilon}}\sinh^2\left(\tilde{h}\right)} \tag{8.44}$$

The partition function of $\mathcal{N}$ site Ising model on a ring can be calculated as

$$Z(\beta,h) \;=\; \sum_{\sigma(\cdot)} T_{\sigma_0,\sigma_1} T_{\sigma_1,\sigma_2} ... T_{\sigma_{\mathcal{N}-1},\sigma_0} \;=\; \mathsf{trace}\left(T^{\mathcal{N}}\right) \;=\; \lambda_+^{\mathcal{N}} + \lambda_-^{\mathcal{N}} \tag{8.45}$$

and hence for very large $\mathcal{N}$ we get

$$F(T,h) \;=\; -\mathcal{N} T \ln(\lambda_+) \tag{8.46}$$

Expanding we get

$$F(T,h) \;\approx\; -\mathcal{N} T \ln\left(2\cosh\left(\frac{\varepsilon}{T}\right)\right) - \frac{1}{2}\mathcal{N}\frac{\exp\left(2\frac{\varepsilon}{T}\right)}{T}h^2 \tag{8.47}$$

Hence

$$\chi = \frac{1}{T}\exp\left(2\frac{\varepsilon}{T}\right) \tag{8.48}$$

Now we would like to calculate the correlation function at zero field.

$$G(r) \;\equiv\; \langle \sigma_0 \sigma_r \rangle \;=\; \frac{1}{Z}\sum_{\sigma_0 \sigma_r} \sigma_0 T^r_{\sigma_0 \sigma_r} \sigma_r T^{\mathcal{N}-r}_{\sigma_r \sigma_0} \tag{8.49}$$

We have

$$T_{\sigma',\sigma''} = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \tag{8.50}$$

with

$$\lambda_+ \;=\; 2\cosh(\tilde{\varepsilon}) \tag{8.51}$$
$$\lambda_- \;=\; 2\sinh(\tilde{\varepsilon}) \tag{8.52}$$

Using standard Pauli matrix notations and denoting the digonalized matrix T as Λ we get

$$G(r) = \frac{1}{Z}\mathsf{trace}\left[\sigma_z T^r \sigma_z T^{\mathcal{N}-r}\right] = \frac{1}{Z}\mathsf{trace}\left[\sigma_x \Lambda^r \sigma_x \Lambda^{\mathcal{N}-r}\right] = \frac{\lambda_+^r \lambda_-^{\mathcal{N}-r} + \lambda_-^r \lambda_+^{\mathcal{N}-r}}{\lambda_+^{\mathcal{N}} + \lambda_-^{\mathcal{N}}} \tag{8.53}$$

For very large $\mathcal{N}$ we get

$$G(r) \;=\; \left(\frac{\lambda_-}{\lambda_+}\right)^r \;=\; \mathrm{e}^{-r/\xi} \tag{8.54}$$

where

$$\xi \;=\; \left[\ln\left(\coth\left(\frac{\varepsilon}{T}\right)\right)\right]^{-1} \;\approx\; \frac{1}{2}\mathrm{e}^{2\varepsilon/T} \tag{8.55}$$

The calculation of $\sum G(r)$ involves a geometric summation, and it can be verified that it agree with the result for χ. The same result as the exact one is obtained from the approximated exponential expression if the summation is replaced by an integral.

[8.6] Solution of the 2D Ising model

The full details of the Onsager solution for this problem is in Huang. Also here the transfer matrix approach is used. Recall that the zero field solution of the 1D model is

$$\frac{1}{\mathcal{N}}\ln Z \;=\; \ln(2) \;+\; \ln(\cosh(\tilde{\varepsilon})) \tag{8.56}$$

The 2D solution is

$$\frac{1}{\mathcal{N}}\ln Z \;=\; \ln(2) \;+\; \frac{1}{2}\int\!\!\int \frac{d\theta d\theta'}{(2\pi)^2}\ln\left[(\cosh(2\tilde{\varepsilon}))^2+\sinh(2\tilde{\varepsilon})(\cos\theta+\cos\theta')\right] \tag{8.57}$$

$$\;=\; \ln(2) \;+\; \ln(\cosh(\tilde{\varepsilon})) \;+\; \frac{1}{2}\int\!\!\int \frac{d\theta d\theta'}{(2\pi)^2}\ln\left[1+\frac{\kappa}{2}(\cos\theta+\cos\theta')\right] \tag{8.58}$$

The integral is determined by the dimensionless parameter

$$\kappa \;\equiv\; \frac{2\sinh(2\tilde{\varepsilon})}{(\cosh(2\tilde{\varepsilon}))^2} \;\leq\; 1 \tag{8.59}$$

The value $\kappa = 1$, for which $\ln Z$ exhibits discontinuity in its derivative, is attained for $\sinh(\widetilde{2\varepsilon}) = 1$, from which it follows that the critical value of the interaction is $\tilde{\varepsilon} = 0.44$, leading to $T_c = 2.27\varepsilon$. This is almost half compared with the heuristic "mean field" value $T_c \approx 4\varepsilon$ that will be derived in the next lecture.

[9] Phase transitions - heuristic approach

[9.1] The ferromagnetic phase transition

The standard Ising Hamiltonian is

$$\mathcal{H} \;=\; -\varepsilon\sum_{\langle ij\rangle}\sigma_i\sigma_j \;-h\sum_i\sigma_i \tag{9.1}$$

Let us assume that in equilibrium we can regard the spins as quasi-independent, each experiencing an effective field $\bar{h}$, such that the effective Hamiltonian for the spin at site i is $\mathcal{H}^{(i)} = -\bar{h}\sigma_i$. This means that the equilibrium state is

$$p_{\sigma_1\ldots\sigma_N} \;\propto\; \exp\left[\beta\bar{h}\sum_i\sigma_i\right] \tag{9.2}$$

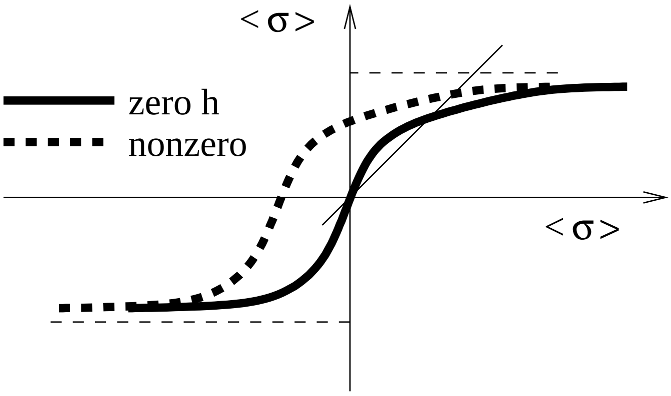
We have to find what is $\bar{h}$. The formal way is to use a variational scheme. We shall introduce this procedure later. In this section we guess the result using a self-consistent picture. By inspection of the Hamiltonian if the mean magnetization of each spin is $\langle\sigma\rangle$, then it is reasonable to postulate that

$$\bar{h} \;=\; h+\varepsilon\sum_{\text{neighbors}}\langle\sigma_j\rangle \;=\; h+c\varepsilon\langle\sigma\rangle \tag{9.3}$$

where c is the coordination number. Form $\mathcal{H}^{(i)}$ we get the self-consistent requirement

$$\langle\sigma\rangle \;=\; \tanh\left(\frac{1}{T}\left(h+c\varepsilon\langle\sigma\rangle\right)\right) \tag{9.4}$$

This equation should be solved for $\langle\sigma\rangle$, and then we get $\bar{h}$ as well.



By inspection of the plot we observe that for $h = 0$ the condition for getting a non trivial solution is $c\varepsilon/T > 1$. Therefore $T_c = c\varepsilon$. If we want to explore the behavior in the critical region it is convenient to re-write the equation in the following way:

$$h \;=\; T\tanh^{-1}\langle\sigma\rangle \;-\; T_c\langle\sigma\rangle \tag{9.5}$$

and to approximate it as

$$h \;=\; (T-T_c)\,\langle\sigma\rangle \;+\; \frac{1}{3}T_c\langle\sigma\rangle^3 \tag{9.6}$$

For $T > T_c$ we get the Curie-Weiss law, which implies a critical exponent $\gamma = 1$. Namely,

$$\langle\sigma\rangle = \frac{1}{T - T_c} h \tag{9.7}$$

For $T = T_c$ the dependence of h is characterized by the critical exponent $\delta = 3$. Namely,

$$\langle\sigma\rangle = \left(\frac{3}{T_c} h\right)^{\frac{1}{3}} \tag{9.8}$$

For zero field ($h = +0$), below T_c, the temperature dependence is characterized by $\beta = 1/2$. Namely,

$$\langle\sigma\rangle = \left(3 \frac{T_c - T}{T}\right)^{\frac{1}{2}} \tag{9.9}$$

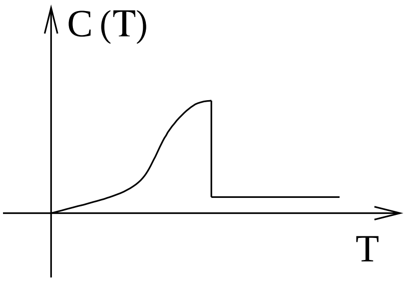
In the mean field approximation the spins are independent of each other, and therefore $\langle\sigma_i\sigma_j\rangle = \langle\sigma_i\rangle\langle\sigma_j\rangle$. It follow that the energy is

$$E = \langle H\rangle = -\frac{1}{2} c\mathcal{N}\, \varepsilon\, \langle\sigma\rangle^2 \tag{9.10}$$

For the heat capacity we get

$$C(T) = \left.\frac{dE}{dT}\right|_{h=0} = -c\epsilon\mathcal{N}\ \langle\sigma\rangle \left.\frac{\partial\langle\sigma\rangle}{\partial T}\right|_{h=0} \tag{9.11}$$

For $T > T_c$ we get $C(T) = 0$, and from below we approach a constant value. The implied critical exponent is $\alpha = 0$. To get the non-trivial mean-field result $\alpha = [2 - (d/2)]$ we have to take into account Gaussian fluctuations.



[9.2] The anti-ferromagnetic phase transition

Let us consider a less trivial example for the use of the heuristic approach. An anti-ferromagnet is described by the Ising Hamiltonian with $\varepsilon \mapsto -\varepsilon$. Specifically we consider a 2D square lattice that consists of to sub-lattices (for other lattices we might have frustrations). We mark the magnetization of the two sub lattices by M_a and M_b. We define

$$M = \frac{1}{2}(M_a + M_b) \tag{9.12}$$

$$M_s = \frac{1}{2}(M_a - M_b) \tag{9.13}$$

Without the magnetic field, the problem is the same as the ferromagnetic one with M_s as the order parameter. With magnetic field h the heuristic mean field equations become

$$M_a = \tanh\left(\frac{1}{T}(h - T_c M_b)\right) \qquad M_b = \tanh\left(\frac{1}{T}(h - T_c M_a)\right) \tag{9.14}$$

Following the same algebraic simplification procedure as in the ferromagnetic case, we get after addition and subtraction of the two resulting equations,

$$(T-T_c)\,M_s+\frac{1}{3}T_c\left(3M^2M_s+M_s^3\right) \;=\; 0 \tag{9.15}$$

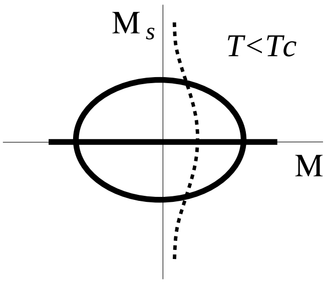
$$(T+T_c)\,M+\frac{1}{3}T_c\left(3M_s^2M+M^3\right) \;=\; h \tag{9.16}$$

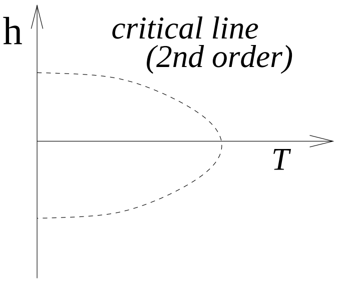
From here it follows that (see graphical illustration):

$$M_s=0 \quad \text{or} \quad 3M^2+M_s^2 \;=\; 3\left(\frac{T_c-T}{T}\right) \tag{9.17}$$

$$(2+M_s^2)M+\frac{1}{3}M^3 \;=\; \frac{h}{T_c} \tag{9.18}$$

As expected from the second equation we get $M=0$ in the absence of an external field, and from the first equation we get the order parameter $M_s(T)$, which satisfies the same equation as in the ferromagnetic problem. If we switch on the magnetic field T_c is shifted to a lower temperature.





If the magnetic field h is strong enough, it destroys the anti-ferromagnetic order and causes $M_s=0$. This is implied by the identification of the ground state:

$$E\left(\uparrow\downarrow\uparrow\downarrow\right) \;=\; \mathcal{N}\cdot\left(-\frac{1}{2}c\epsilon\right), \text{[for weak field]} \tag{9.19}$$

$$E\left(\uparrow\uparrow\uparrow\uparrow\right) \;=\; \mathcal{N}\cdot\left(\frac{1}{2}c\epsilon-h\right), \text{[for strong field]} \tag{9.20}$$

In the region where $T\sim T_c$ and $h\sim 0$ we get for the magnetization

$$M \;=\; \left(\frac{1}{T_c+T\left(1+\frac{1}{6}M_s\left(T\right)^2\right)}\right)h \;\equiv\; \chi h \tag{9.21}$$

We can get a better general expression for all of the temperature range by differentiation of the heuristic equations

$$\chi=\frac{1}{T_c+T\cosh^2\left(\frac{T_c}{T}M_s\left(T\right)\right)} \tag{9.22}$$

In the region $T\sim T_c$ substitution of $M_s\left(T\right)$ gives

$$\chi=\begin{cases}\frac{1}{T_c+T} & T_c<T\\ \frac{1}{4T_c-2T} & T<T_c\end{cases} \tag{9.23}$$

[9.3] Beyond the Ising model

We now make a slight generalization of the Ising model. We consider coupled non-inertial oscillators, meaning that the kinetic term in the Hamiltonian is neglected:

$$\mathcal{H} \ = \ \sum_j [U(s_j) - hs_j] \ - \varepsilon \sum_{\langle ij \rangle} s_i s_j \tag{9.24}$$

For the Ising model $U(s) = 0$ for $s = \pm 1$ and $U(s) = \infty$ otherwise. But more generally we assume, say, $U(s) = (\alpha/2)s^2 + (u/4)s^4$. In the absence of interaction

$$M \ \equiv \ \langle s \rangle \ = \ \text{TANH}(\chi h) \tag{9.25}$$

where TANH is a function that has by definition slope unity at the origin ($\text{TANH}'(0) = 1$), and χ is a constant that has the meaning of zero-field susceptibility. For zero non-linearity ($u = 0$) we get $\text{TANH}(x) = x$ with slope $\chi = 1/\alpha$. Otherwise the TANH becomes a concave function with temperature dependent $\chi(T)$. For the Ising model $\chi(T) = 1/T$. The heuristic mean field equation is

$$M \ = \ \text{TANH}\left[\chi\left(h + c\epsilon M\right)\right] \tag{9.26}$$

In the absence of an external field it possesses a non-trivial solution provided $c\epsilon\chi(T) > 1$, leading to a finite T_c. But if we consider dynamical degrees of freedom (see discussion of coupled rotors below), the susceptibility might be finite also at zero temperature due to quantum fluctuations. Thus, if $c\epsilon\chi(0) < 1$, phase transition does not take place. Then, by tuning the model parameters at $T = 0$, we can witness a *quantum phase transition* once we cross to a regime where $c\epsilon\chi(0) > 1$.

Note: Considering again zero non-linearity ($u = 0$), the heuristic approach implies that the system becomes unstable for $\alpha < c\epsilon$. This condition becomes more illuminating if we wrote the interaction between to oscillators as $(\epsilon/2)[s_i - s_j]^2$. The price for that is to write $U(s) = (a/2)s^2$ instead of $U(s) = (\alpha/2)s^2$ with $a = \alpha - c\epsilon$. The condition for instability becomes simply $a < 0$.

[9.4] The mean-field Hamiltonian

Assuming that M is known, we set in the Hamiltonian $s_j = M + \delta s_j$, expand the interaction term, and get

$$\mathcal{H} \ \approx \ \sum_j H^{(j)} \ - \varepsilon \sum_{\langle ij \rangle} \delta s_i \delta s_j \tag{9.27}$$

were the first sum is the mean field Hamiltonian with

$$H^{(j)} \ = \ U(s_j) \ - (h + c\varepsilon M)s_j \ + \frac{1}{2} c\varepsilon M^2 \tag{9.28}$$

Assuming that the fluctuation are uncorrelated we deduce

$$E \ = \ \langle \mathcal{H} \rangle \ \approx \ \mathcal{N} \left[\langle U(s) \rangle - \frac{1}{2} c\varepsilon M^2 - hM \right] \tag{9.29}$$

where $\langle U(s) \rangle$ should be calculated from the mean field Hamiltonian. Note that it is zero for the Ising model, while here we consider a more general class of systems. If the non-linear term and the fluctuation are neglected $\langle U(s) \rangle = (\alpha/2)M^2$.

Up to this point M has not been fixed. We have assumed that it is known from the heuristic mean field equation. Our purpose below is to get this *heuristic* equation as the *formal* outcome of a *self-consistent* mean-field approximation for the system Hamiltonian. For $\varepsilon = 0$ the "spins" are non-interacting and we get the free energy $F(h)$, from which we can derive the state equation $M = -F'(h) =\equiv f(h)$. For $\varepsilon \neq 0$, and given M, the free energy that is derived from the mean field Hamiltonian is (per spin)

$$F(h;M) \ = \ F(h+c\varepsilon M) \ + \frac{1}{2}c\varepsilon M^2 \tag{9.30}$$

From this free energy we can derive the equation of state $M = -(d/dh)F(h;M)$, which is precisely the heuristic equation. But this is a short-cut that is not always available: In more complicated models the order parameter (here it is M) is not necessarily conjugate to the control parameter (here it is h). For example, in the analysis of the superfluidity, the order parameter $\psi = \langle a \rangle$ is not conjugate to the chemical potential μ. So we need a more general procedure for the derivation of the mean-field equation. The way to go it to claim that M has to minimize $F(h;M)$. Indeed one can verify easily that $(d/dM)F(h;M) = 0$ leads to the mean-field equation.

There are two ways to justify the minimization procedure. One way is to claim that M is a variational parameter. In a later section we explain that rigorously $F(h;M)$ is the function that has to be minimized (at zero temperature it equals the energy of the ground state). The second way is to further develop the idea of "order parameter", saying that the partition function can be approximated by

$$Z \ = \ \sum_M e^{-\beta F(h;M)} \ \ \sim \ \ e^{-\beta \ \text{minimum}_M\{F(h;M)\}} \tag{9.31}$$

By inspection symmetry breaking in the evaluation of the minimum is implied if $a = (\alpha - c\epsilon) < 0$. We shall further explore this approach in later sections.

[9.5] Coupled rotors

We now consider coupled rotors. The rotors are dynamical entities, they have finite mass. We define u as the inverse moment of inertia. Note that if we started with $[\varphi, p] = i\hbar$, then with $n = p/\hbar$ we get that $u \propto \hbar^2$. Accordingly infinite mass is like taking the classical limit. The Hamiltonian is

$$\mathcal{H} \ = \ \sum_j \left[\frac{u}{2}n_j^2 - h\cos(\varphi_j)\right] - \varepsilon \sum_{\langle ij \rangle} \cos(\varphi_j - \varphi_i) \tag{9.32}$$

If we ignore the kinetic term it is formally like coupled non-inertial oscillators with $s_j = \cos(\varphi_j)$. In a classical context if we take the kinetic term into account it has no effect because it factorizes out of the partition function. The mean field Hamiltonian is

$$H^{(j)} \ = \ \frac{u}{2}n_j^2 \ - (h+c\varepsilon M)\cos(\varphi_j) \ + \frac{1}{2}c\varepsilon M^2 \tag{9.33}$$

In the quantum treatment the energy shift of the ground-sate is not $-(1/2)c\varepsilon M^2$ because of *quantum fluctuations*: the price of small φ is large uncertainty in the conjugate momentum n. The implications is that quantum fluctuations are able to diminish M at zero-temperature.

Quantum phase transition.– Let us find the condition for diminished "order" at zero-temperature. The simplest perspective is the heuristic approach. At zero temperature standard quantum-mechanical calculation using second order perturbation theory shows that the zero temperature susceptibility of a rotor is $\chi = 2/u$. It follows that symmetry-breaking is avoided if

$$2c\varepsilon \ < \ u \qquad\qquad [\text{Mott phase}] \tag{9.34}$$

We see that zero-temperature "order" is diminished either by having T or u that are larger than $\sim \varepsilon$, reflecting strong quantum or thermal fluctuations respectively. An equivalent way to deduce the above condition is to consider the ground state energy of $E_0(h)$ of $H_0 = (u/2)n^2 - h\cos(\varphi)$. For large h using harmonic-oscillator approximation $E_0 = -h + (1/2)\sqrt{uh}$, but for small h using 2nd order perturbation $E_0 = -h^2/u$. Using the latter result we get at the vicinity of $M = 0$ that the mean-field energy per rotor is

$$E = \left\langle H^{(j)} \right\rangle = \frac{a}{2}M^2, \qquad \text{with } \ a = -2\frac{(c\varepsilon)^2}{u} + c\varepsilon \tag{9.35}$$

Symmetry-breaking is avoided if $a > 0$.

[9.6] The variational approach

A different way to derive the heuristic mean-field equations is to use the variational approach. The canonical state minimizes the free energy functional. Accordingly we look for a solution to the variation problem

$$F[\rho] \ \equiv \ \langle H \rangle - TS[\rho] \ = \ \text{minimum} \tag{9.36}$$

with implicit constraint on the normalization. In the mean-field approach the canonical state is assumed to be well approximated by $\rho = \{p_\sigma\}$, where

$$p_{\sigma_1 \dots \sigma_N} \ = \ \frac{1}{\left(2\cosh\left(\beta\bar{h}\right)\right)^{\mathcal{N}}} \exp\left[-\beta\bar{h}\sum_k \sigma_k\right] \tag{9.37}$$

Here the variational parameter $\bar{h}$ is the effective mean field. We would like to determine the optimal value of $\bar{h}$ for which $F[\rho]$ is minimal. For the calculation we use the identity $F[\rho] = F_0[\rho] + \langle H - H_0 \rangle$, where $H_0 = -\bar{h}\sum_i \sigma_i$, leading to

$$F[\rho] = \mathcal{N}\left[f(\bar{h}) - \frac{1}{2}c\epsilon\, m(\bar{h})^2 - \left(h - \bar{h}\right) m(\bar{h})\right] \tag{9.38}$$

where $f(\bar{h}) = -T\ln\left(2\cosh\left(\bar{h}/T\right)\right)$ and $m(\bar{h}) = -f'(\bar{h})$ is the mean-field magnetization. The variational equation for $\bar{h}$ is as expected

$$\bar{h} \ = \ h + c\epsilon\tanh\left(\frac{\bar{h}}{T}\right) \tag{9.39}$$

Hence, we get the variational free energy

$$F(T,h) \ = \ \mathcal{N}\left[-T\ln\left(2\cosh\left(\frac{\bar{h}}{T}\right)\right) + \frac{1}{2}c\epsilon\left(\tanh\left(\frac{\bar{h}}{T}\right)\right)^2\right] \tag{9.40}$$

This is not a pleasant expression because the dependence on h is implicit in $\bar{h}$. We can differentiate this equation to find $\tilde{M}$, which involves $\partial\bar{h}/\partial h$. The calculation is lengthy, but we can skip it because the result is obvious

$$\tilde{M} \ = \ -\frac{\partial F(T,h)}{\partial h} \ = \ \mathcal{N}\tanh\left(\frac{\bar{h}}{T}\right) \tag{9.41}$$

To make calculations of the state equations more convenient we notice that $F(T,h)$ depends in a very simple way on $\tilde{M}$, hence it is useful to make the Legendre transformation

$$A(T,\tilde{M}) \ \equiv \ F(T,h) + h\tilde{M} \tag{9.42}$$

such that $dA = -SdT + hd\tilde{M}$. Note that the mean field equation for $\bar{h}$ implies that

$$h \;=\; T\tanh^{-1}(M) - c\epsilon M \qquad\qquad \text{where } \; M \equiv \frac{\tilde{M}}{\mathcal{N}} = \langle\sigma\rangle \tag{9.43}$$

Using the identity $\tanh^{-1}(x) = (1/2)\ln((1+x)/(1-x))$ one obtains

$$\begin{aligned} A\,(T,M) \;&=\; \mathcal{N}\left[-T\ln 2 + \frac{1}{2}T\ln\left(1-M^2\right) + \frac{1}{2}TM\ln\left(\frac{1+M}{1-M}\right) - \frac{1}{2}c\epsilon M^2\right] && (9.44)\\ &=\; \mathcal{N}T\left[\frac{1+M}{2}\ln\frac{1+M}{2} + \frac{1-M}{2}\ln\frac{1-M}{2}\right] - \mathcal{N}\frac{1}{2}c\epsilon M^2 && (9.45)\end{aligned}$$

From this expression it is convenient to derive explicit results for the state equations. In particular $S = -\partial A/\partial T$ and one can recover the result for the heat capacity.

[9.7] The Bragg Williams formulation

Consider an Ising model with $\mathcal{N}$ sites, at any dimension, and with any coordination number. Given a spin configuration define

$$\begin{aligned} \mathcal{N} \;&=\; \text{total number of spins} && (9.46)\\ m \;&=\; \text{total magnetization} && (9.47)\\ M \;&=\; m/\mathcal{N} && (9.48)\\ N_+ \;&=\; \text{number of up spins} = \frac{1}{2}(\mathcal{N}+m) = \frac{1}{2}\mathcal{N}(1+M) && (9.49)\\ N_- \;&=\; \text{number of down spins} = \frac{1}{2}(\mathcal{N}-m) = \frac{1}{2}\mathcal{N}(1-M) && (9.50)\\ N_{+-} \;&=\; \text{number of bonds connecting spins with opposite direction} && (9.51)\end{aligned}$$

The total number of bonds is $(1/2)c\mathcal{N}$, where c is the coordination number. It follows that

$$\begin{aligned} \sum\sigma_i \;&=\; m && (9.52)\\ \sum_{\langle ij\rangle}\sigma_i\sigma_j \;&=\; \frac{1}{2}c\mathcal{N} - 2N_{+-} && (9.53)\end{aligned}$$

If we look on two connected spins, there is a probability $(N_+/\mathcal{N})$ to have the first up, and a probability $(N_-/\mathcal{N})$ to have the the second down. Or we can have the first down and the second up. This motivates the Bragg Williams approximation:

$$N_{+-} \;\approx\; 2\left(\frac{N_+}{\mathcal{N}}\right)\left(\frac{N_-}{\mathcal{N}}\right)\frac{\mathcal{N}c}{2} \;=\; \frac{\mathcal{N}c}{4}(1-M^2) \tag{9.54}$$

Assuming that it holds for typical configurations we approximate the energy functional as

$$E[\sigma] \;\approx\; -\mathcal{N}\times\left(\frac{1}{2}c\varepsilon M^2 + hM\right) \tag{9.55}$$

We note that this expression with $c = \mathcal{N}$ if formally exact for a fully connected cluster of spins. The number of configuration with total magnetization m is

$$g_m \;=\; \frac{\mathcal{N}!}{(N_+)!\,(N_-)!} \;\approx\; \text{const}\;\exp\left[-\mathcal{N}\left(\frac{1}{2}M^2 + \frac{1}{12}M^4 + ...\right)\right] \tag{9.56}$$

In order to derive the latter approximation note that

$$-\frac{\partial}{\partial m}\ln g_m \;=\; \frac{1}{2}\left(\ln(1+M)-\ln(1-M)\right) \;\approx\; M+\frac{1}{3}M^3+\frac{1}{5}M^5+... \tag{9.57}$$

With this approximation we get

$$Z \;=\; \sum_m\sum_{\sigma\in m}\mathrm{e}^{-\beta E[\sigma]} \;\approx\; \sum_m g_m\mathrm{e}^{-\beta E(m)} \;=\; \sum_M \mathrm{e}^{-A(M)} \tag{9.58}$$

$$A(M) \;=\; \mathcal{N}\times\left[\frac{1}{2}\left(1-\beta c\varepsilon\right)M^2+\frac{1}{12}M^4-\beta hM\right] \tag{9.59}$$

In the next section we are going to clarify the following points: **(1)** The sum can be evaluated via Gaussian integration. **(2)** This Gaussian approximation can be justified if $\mathcal{N}$ is large. **(3)** Phase transition is implied. **(4)** But nevertheless the result is false for $d=1$. In the next lecture we shall further explain that the Bragg-Williams formulation fails in providing the correct description of the symmetry-breaking if the critical temperature is approached.

[9.8] The Gaussian approximation

The expression that we have obtained for Z using the Bragg Williams formulation is a typical approximation that can obtain for various models. We rewrite it as follows:

$$Z \;=\; \int d\varphi\;\mathrm{e}^{-A(\varphi)} \qquad\qquad A(\varphi) \;=\; \mathcal{N}\times\left[\frac{a}{2}\varphi^2+\frac{u}{4}\varphi^4-h\varphi\right] \tag{9.60}$$

This sum can be evaluated via Gaussian integration. The dominant contribution comes from the φ for which $A(\varphi)$ is minimal. One can easily verify that $A'(\varphi)=0$ coincides with the heuristic mean field equation that has been discussed in a previous lecture. Non trivial solutions appear for $a<0$ which implies $T_c=c\varepsilon$. Note that $a\approx(T-T_c)/T_c$.

Above the critical temperature there is a single minimum at $\bar{\varphi}=(1/a)h$ and one obtains

$$Z \;\approx\; \left(\frac{2\pi}{\mathcal{N}a}\right)^{1/2}\;\exp\left[\frac{\mathcal{N}}{2a}h^2\right] \tag{9.61}$$

In the absence of an external field, as a becomes negative, the trivial minimum $\bar{\varphi}=0$ bifurcates into two minima, namely $\bar{\varphi}=\pm(|a|/u)^{1/2}$. For these values

$$A(\bar{\varphi}) \;=\; -\frac{a^2}{4u}\;\mp\;\left(\frac{|a|}{u}\right)^{1/2}h \tag{9.62}$$

Approximating Z as the sum of two Gaussian integrals, one realizes, after expanding $A(\bar{\varphi}+\tilde{\varphi})$, that the coefficient of the $\tilde{\varphi}^2$ term is the same as above T_c, with a replaced by $2|a|$ (positive). We get that the partition function is like that of a spin:

$$Z \;\approx\; \left(\frac{\pi}{\mathcal{N}|a|}\right)^{1/2}\;\exp\left[\mathcal{N}\frac{a^2}{4u}+\frac{\mathcal{N}}{4|a|}h^2\right]\;2\cosh\left[\mathcal{N}\left(\frac{|a|}{u}\right)^{1/2}h\right] \tag{9.63}$$

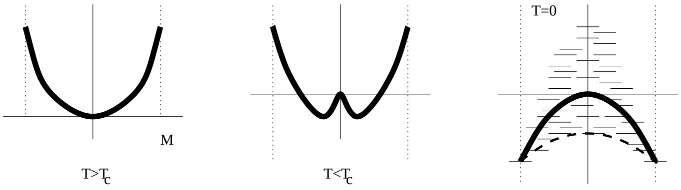
From here one deduces that for $T<T_c$ the susceptibility becomes $\chi=[1/(2|a|)]+\mathcal{N}|a|/u$ instead of $\chi=1/a$.

At this point one can ask whether it was allowed to ignore the quartic term in $A(\varphi)$. This should be checked self consistently. For $a>0$ the dispersion of φ in the Gaussian approximation is $(\mathcal{N}a)^{-1/2}$. The quartic term can be neglected if $u|\varphi|^4 \ll a|\varphi|^2$ leading to the condition $a\gg(u/\mathcal{N})^{1/2}$. This condition is always satisfied if $\mathcal{N}$ is large enough. The same condition also guarantees that for $a < 0$ the dispersion is much smaller compared with the non-zero mean field $\bar{\varphi}$. Generalization of this condition in the field-theory treatment will be discussed later and lead to the Ginzburg criterion.

It is now appropriate to point out that the above treatment implies a phase-transition in the thermodynamic limit. We first note that the existence of the thermodynamic limit for $A(\varphi)/\mathcal{N}$ could have been anticipated from general considerations. From Z we can get the free energy $F(h)/\mathcal{N}$ that will have a thermodynamic limit too. The question is whether the subsequent limits $h \to +0$ and $h \to -0$ lead to the same magnetization, or optionally whether the susceptibility χ beomes infinite below T_c. Indeed this is what we found.

[9.9] The importance of fluctuations

The above analysis is misleading. The Bragg Williams approximation underestimates the effect of fluctuations. We already know from the exact solution of the Ising model that in 1D there is no phase transition at finite temperature. We would like to explain in detail why the fluctuations in 1D smear away the phase transition. Later we shall see that also for $d = 2, 3$ the fluctuations are important: they do not smear away the phase transition, but they modify the state equations in the critical region, which explains the failure of mean field theory there, and the observed *anomalous* values of the scaling exponents.



The problem with the Bragg Williams approximation is implied by the figure above. The action $A(\varphi)$ is plotted. It is determined by the energy term $E[\varphi]$, and by the entropy term $S[\varphi]$. Recall that

$$p(\varphi) \;=\; \frac{1}{Z}\mathrm{e}^{-A(\varphi)} \;\propto\; \exp\left[-\frac{1}{T}E[\varphi] + S[\varphi]\right] \tag{9.64}$$

In the $T = 0$ panel the energy of the states is indicted by bars. By taking the "typical" value of the energy (thick solid line) we ignore a dominant fraction of less typical states that have a very low energy. These states corresponds to configurations where the spins a bunched in "zones". The simplest arrangement in 1D has two zones and its energy is $E_b = E_0 + 2\epsilon$, where $E_0 = -\mathcal{N}\epsilon$ is the ground state energy. Consequently the effective barrier between the "all up" and "all down" states is very low (thick dashed line), and the symmetry breaking is avoided at any finite temperature. The formal argument is outlined below. In contrast to that, in 2D the effective barrier is $E_b = E_0 + \mathcal{N}^{1/2}\epsilon$ and therefore symmetry breaking is realized in the thermodynamic limit.

Domain walls.– It is possible to argue that in 1D there is no phase transition at finite temperature. The argument goes as follows: consider a mixture of states with one domain wall. For such state $E[\rho] = E_0 + 2\epsilon$, where ϵ is the cost of the domain wall. But the entropic contribution is $S[\rho] = \ln[\mathcal{N}]$ where $\mathcal{N}$ is the length of the chain. It follows that for any finite T the ground state, or any (exclusive) mixture of ground-like states, do not minimize $F[\rho]$ at the thermodynamic limit. We can lower $E[\rho]$ by adding states that have with equal probability any magnetization. Consequently we get huge fluctuations whose relative amplitude does not diminish, in contrast with the $(\mathcal{N})^{-1/2}$ prediction of the mean-field Gaussian estimate. Therefore spontaneous magnetization at finite temperature is impossible.

The above argument fails in 2D because the energy cost of a domain $E[\rho] = E_0 + \mathcal{N}^{1/2}\epsilon$ domeiniate over the entropic contribution. In fact it is possible to refine the domain wall approach and deduce that for the $d = 2$ Ising model there exists spontaneous magnetization at finite temperature [see Huang p.349], in consistency with the exact solution. *However*, the possibility to witness phase transition at $d = 2$ is limited to systems with discrete symmetries. The Mermin-Wagner theorem states that a continuous symmetry cannot be spontaneously broken at finite temperature in $d \leq 2$ systems with short-range interactions. See discussion of the Heisenberg model.

[10] Phase transitions - field theory

[10.1] The Landau model

We would like to take into account the spatial fluctuations of the magnetization $\varphi(x)$ in the calculation of the partition function. We therefore use a refined version of the Bragg-Williams approach. Namely, first we sum over all microscopic configuration that corresponds to a magnetization $\varphi(x)$, and then we are left with a so-called functional integral:

$$Z[h, \text{parameters}; \Lambda, L] \; = \; \sum_{\varphi(\cdot)} \mathrm{e}^{-A[\varphi(\cdot)]} \; = \; \int D\varphi \; \mathrm{e}^{-A[\varphi(\cdot)]} \tag{10.1}$$

where the sum over configurations becomes an integral with the measure

$$D\varphi \; = \; \prod_{x \in L^d} d\varphi_x \; = \; \text{const} \prod_{|k|<\Lambda} d\tilde{\varphi}_k \; , \qquad\qquad \tilde{\varphi}_k \equiv \frac{1}{L^d} \int \varphi(x) \; \mathrm{e}^{-ikx} dx \tag{10.2}$$

In this definition $\tilde{\varphi}_k$ are the Fourier components of $\varphi(x)$, normalized such that $\varphi(x) = \sum_k \tilde{\varphi}_k e^{ikx}$. It is implicit that one assumes a finite volume L^d, and a finite momentum cutoff Λ, otherwise the functional-integral that gives Z is ill defined. To have a momentum cutoff is like to assume that space is discretized with lattice spacing $2\pi/\Lambda$. Accordingly the number of freedoms of the model is $\mathcal{N} = (L\Lambda/2\pi)^d$. Technical remark: for presentation purpose it is more convenient to work with the complex "exp" Fourier basis, but from mathematical point of view the meaning of the $D\varphi$ integration is more obvious if we work with real "sin" and "cos" Fourier basis, corresponding to the real and imaginary parts of $\tilde{\varphi}_k$. Either way the φ field is represented by $\mathcal{N}$ independent real amplitudes.

In the Landau model the assumed action is

$$A[\varphi(\cdot)] \;\; = \;\; \int d\boldsymbol{x} \left(\frac{c}{2} \left(\nabla\varphi\right)^2 + \frac{a}{2}\varphi^2 + \frac{u}{4}\varphi^4 - h\varphi \right) \;\; = \;\; L^d \sum_k \left(\frac{1}{2}(ck^2 + a)|\tilde{\varphi}(k)|^2 + ... \right) \tag{10.3}$$

The summation over the k components of the field is conventionally written as an integral with the measure $[L/(2\pi)]^d dk$. The convention $c = 1$ with regard to the prefactor of the first term fixes the dimensions of φ, and hence of all the other model parameters. We write these dimensions as L^d, accordingly

$$d_\varphi = -\frac{d-2}{2}, \qquad d_h = -\frac{d+2}{2}, \qquad d_a = -2, \qquad d_u = -(4-d), \tag{10.4}$$

The model has a thermodynamic limit, hence L is not significant, and we can calculate the Helmholtz free energy F per unit volume. In contrast to that Λ is significant. In particular we note that the model contains *two* significant dimensionless parameters that are related to the underlying microscopic Hamiltonian:

$$\tilde{a} \;=\; a/\Lambda^2 \qquad\qquad \text{Note: later we see that } \xi = a^{-1/2} \text{ is the correlation length} \tag{10.5}$$

$$\tilde{u} \;=\; u/\Lambda^{4-d} \qquad\qquad \text{Note: later we see that } a/u^{2/(4-d)} \text{ is the Ginzburg parameter} \tag{10.6}$$

Relating to the Bragg-Williams approximation we identify $a \propto (T - T_c^{(0)})$, where $T_c^{(0)}$ is the mean field critical temperature. In fact we shall see that the field theory analysis implies that for $2 \le d < 4$ the actual critical temperature is pushed down due to the fluctuations ($a_c < 0$). In the $d = 1$ case there is no phase transition.

Coarse graining.– The Landau model can be regarded as the outcome of coarse graining on scale Λ. Therefore its parameters $a(\Lambda)$ and $u(\Lambda)$ are "running coupling constants". The cutoff Λ is in the range $[\Lambda_0, \Lambda_\infty]$, where Λ_∞ reflects a limiting microscopic scale, while Λ_0 reflects the maximal spatial range over which coarse-graining is meaningful. Clearly it is the correlation distance, hence $\Lambda_0 \sim 1/\xi$. We shall see that as Λ is decreased, as the result of successive course-graining operations, we get $\tilde{u}(\Lambda) \to \tilde{u}_c$, where $\tilde{u}_c = 1/9$ for 3D. So in some sense there is only one relevant parameter (a) in this model, and results for different values of a are related by scaling.

[10.2] Related models

The Landau model stands by itself as a prototype model. It might have different physical interpretations. Possibly the simplest is to regard it as the continuum model of "coupled oscillators". If $a = u = 0$ it is formally like the Debye model. Having $a > 0$ means that the oscillators have a positive spring constant that stabilizes them at $\varphi = 0$. For $a < 0$ each oscillator is pushed away from $\varphi = 0$ and its new equilibrium position is determined by the nonliterary u of the spring. Thanks to the non-linearity of the springs the φ cannot diverge to infinity.

Above we have regarded the Landau model as a coarse grained version of the Ising model, using the Bragg-Williams approximation for each coarse-grained cell. There is an optional possibility to motivate the Landau model as an approximation for the Ising model using a somewhat more direct procedure. For this purpose one replaces the discrete summation over $\sigma = \pm 1$ by an integration over φ with a weight function:

$$\sum_{\sigma(\cdot)} \quad \rightarrow \quad \int \prod_x d\varphi_x \ \mathrm{e}^{-\frac{1}{4}u\left(\varphi_x^2-1\right)^2} \tag{10.7}$$

One should realize that the ferromagnetic interaction $-\sigma(x)\sigma(x')$ corresponds to differences $(\varphi(x) - \varphi(x'))^2$, and hence translates to the gradient term in the Landau model.

The field theory that corresponds to the Ising model contains a real field. It reflects the discrete mirror (up/down) symmetry of the system. More generally we can consider a system that has a continuous rotational symmetry. In such case the Action is $A[S]$ with vector field $S = (S_1, S_2, S_3)$. Of particular interest is to have a gauge-invariant Action $A[\Psi]$ with a complex field $\Psi = (\psi_1, \psi_2) \equiv \sqrt{n}\exp(i\varphi)$. Note that in two dimensions gauge-invariance can be regarded as a rotational-invariance.

[10.3] The Gaussian approximation

Let us start with the simplest possibility of having $u = 0$. Regarded as an approximation it is meaningful only if $a > 0$. If we had $c = 0$ the result would be the same as that of the Bragg-Williams model. If c is non-zero (equal to unity by convention) the summation still factorizes, but in k space. Assuming for simplicity $h = 0$, and not caring about a global prefactor we get the following:

$$Z \quad = \quad \prod_k \int d\tilde{\varphi}_k \ \exp\left[-\frac{L^d}{2}\left(k^2+a\right)\tilde{\varphi}_k^2\right] \quad = \quad \mathrm{const} \prod_k \left(\frac{1}{k^2+a}\right)^{1/2} \tag{10.8}$$

The free energy in the mean-field approximation was $F = TA(0) = 0$, corresponding to the mean field $\bar{\varphi} = 0$. Now we have taken the Gaussian fluctuations into account. Consequently we get a non-trivial result for the free energy:

$$F(T) \quad = \quad TA(\bar{\varphi}) \ + \ \frac{T}{2}\sum_k \ln\left(k^2+a\right) \tag{10.9}$$

In particular we can derive from this expression the Gaussian prediction for the heat capacity. Contrary to the mean field approximation, it is no longer zero. The singular contribution at the vicinity of T_c originates from the second derivative with respect to a. Accordingly

$$C(T) \quad = \quad -T\frac{d^2F}{dT^2} \quad \approx \quad \frac{T_c^2}{2}\left(\frac{L}{2\pi}\right)^d \int_0^\Lambda \frac{\Omega_d\, k^{d-1}dk}{(k^2+a)^2} \quad \propto \quad |T-T_c|^{-(4-d)/2}, \qquad \text{for } d<4 \tag{10.10}$$

where Ω_d=4π for d=3 etc. We conclude that the mean field prediction $\alpha = 0$ is replaced by $\alpha = [2-(d/2)]$ due to the $k \neq 0$ fluctuations. Below T_c we can perform a Gaussian approximation around the mean-field $\bar{\varphi}$ that will be discussed in the next section. The calculation is essentially the same, with an offset $A[\bar{\varphi}]$ that is added to the action, hence $F(T) \mapsto F(T) + TA[\bar{\varphi}]$. The non-singular contribution of this additional "mean field" term implies a discontinuity of $C(T)$ at $T = T_c$ as discussed in past lecture, and has no effect on the Gaussian value of α.

[10.4] Digression - Gaussian integrals

The partition function can be calculated exactly whenever the action is a quadratic form. The so-called Gaussian integral reduces to the product of $\mathcal{N}$ one dimensional integrals if we transform it to a basis in which the quadratic form is diagonal. For a system that has translation symmetry it is momentum space.

$$\begin{aligned}
\int D\varphi\ \mathrm{e}^{-\frac{1}{2}\sum_{i,j}A_{ij}\varphi_i\varphi_j+\sum_i h_i\varphi_i} &= \prod_k \int d\tilde{\varphi}_k\ \mathrm{e}^{-\frac{1}{2}a_k\tilde{\varphi}_k^2+\tilde{h}_k\tilde{\varphi}_k} &(10.11)\\
&= \prod_k \left(\frac{2\pi}{a_k}\right)^{1/2} \mathrm{e}^{\frac{1}{2}\left(\frac{1}{a_k}\right)\tilde{h}_k^2} \ = \ \sqrt{\det(2\pi G)}\ \exp\left[\frac{1}{2}\sum_{i,j}G_{ij}h_ih_j\right] &(10.12)
\end{aligned}$$

here $G = A^{-1}$, and note that $\det(G) = 1/\det(A)$. Note also that going back to the original basis, in the case of position-to-momentum transformation implies that $G(r)$ is the Fourier transform of $1/a(k)$.

From the above result, it follows that $G(r)$ is the correlation function $\langle\varphi(r)\varphi(0)\rangle$ for $h=0$. Otherwise $\langle\varphi\rangle$ is non-zero, and it equals to field $\bar{\varphi}$ that minimizes that action. It satisfies the equation $A\varphi = h$, whose solution is $\bar{\varphi} = Gh$. Hence G can be regarded as the "Green function".

[10.5] The mean field equation

We define the mean field $\bar{\varphi}$ via the equation $A(\varphi) =$ minimum. This gives the equation

$$\left(-\nabla^2 + a\right)\varphi + u\varphi^3 \ = \ h(x) \qquad (10.13)$$

The mean field for an homogeneous $h(x) = h$ is obtained from $a\varphi + u\varphi^3 = h$. In particular for $h = \pm 0$ we get

$$\bar{\varphi}_0 \ = \ \begin{cases} 0, & \text{for } a>0 \\ \pm\left(\frac{-a}{u}\right)^{\frac{1}{2}}, & \text{for } a<0 \end{cases} \qquad\qquad A[\bar{\varphi}_0] \ = \ \begin{cases} 0, & \text{for } a>0 \\ -\frac{a^2}{4u}, & \text{for } a<0 \end{cases} \qquad (10.14)$$

For $a > 0$ we neglect the non linear term in the action, define $\xi = a^{-1/2}$, and write the mean field equation as $\left(-\nabla^2 + (1/\xi)^2\right)\varphi(x) = h(x)$. For $a < 0$ we make the substitution $\varphi \mapsto \bar{\varphi}_0 + \varphi$, expand the action around the new minimum, and then neglect the non-linear term. The mean-field equations takes the same form as for $a > 0$, with $\xi = (2|a|)^{-1/2}$. Accordingly the first-order solution in $h(x)$ is

$$\bar{\varphi}(x) \ = \ \bar{\varphi}_0 + \int G(x-x')h(x')\,dx' + \mathcal{O}(h^2) \qquad (10.15)$$

$$\text{where} \qquad G(x-x') = \int \frac{dq}{(2\pi)^d}\,\frac{\mathrm{e}^{iq(x-x')}}{q^2+(1/\xi)^2} \qquad\qquad \xi \ = \ \begin{cases} a^{-\frac{1}{2}}, & \text{for } a>0 \\ (-2a)^{-\frac{1}{2}}, & \text{for } a<0 \end{cases} \qquad (10.16)$$

We recall that $G(r)$ is both the Green function and the correlation function in the Gaussian approximation. Hence the Gaussian critical exponents are $\nu = 1/2$ and $\eta = 0$. This ν value is consistent with what we have obtained for the heat capacity exponent α. In 3D we get $\alpha = 1/2$.

[10.6] Symmetry breaking

Let us first assume that $a > 0$ and ask whether we can trust the Gaussian approximation. Higher non-Gaussian terms in the expansion of $A[\varphi]$ around $\bar{\varphi}$ were neglected in the above treatment. The condition for this neglect is found in the same way as in the Bragg-Williams analysis. Namely, the neglect of the non-Gaussian term is justified if $u\varphi^4 \ll a\varphi^2$. This leads to the condition $\mathrm{Var}(\varphi) \ll (a/u)$. As in the Bragg-Williams analysis the same condition is deduced if we approach $a = 0$ from below, from the condition $\sqrt{\mathrm{Var}(\varphi)} \ll |\bar{\varphi}|$. So we would like to estimate the fluctuations and see if this condition is satisfied. Within the framework of the Gaussian approximation the variance of each Fourier component of the field is

$$\mathrm{Var}(\tilde{\varphi}_k) \quad = \quad \frac{1}{L^d}\left(\frac{1}{k^2+(1/\xi)^2}\right) \tag{10.17}$$

The field amplitude $\varphi(x)$ at a given point in space is the sum of $\mathcal{N}$ independent Fourier components, and accordingly

$$\mathrm{Var}(\varphi) \quad = \quad \sum_k \mathrm{Var}(\tilde{\varphi}_k) \quad = \quad G(0) \tag{10.18}$$

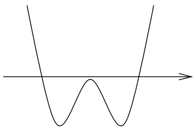
If we kept only the $k=0$ contribution, as in the Bragg-Williams analysis, we would get $\mathrm{Var}(\varphi) \sim \xi^2/L^d$, which would imply that the Gaussian approximation is always OK in the thermodynamic limit. If on the other hand we keep all the terms in the above sum, we get for $d>2$ a huge result that depends on Λ. This *bare* estimate of the variance has no significance because it reflects the renormalization of a by the large k fluctuations as discussed by [Amit 1974]. Consequently, as suggested by Ginzburg the effective cutoff for the purpose of estimating the Gaussian fluctuations is $\Lambda_0 \sim 1/\xi$, hence

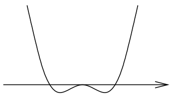
$$\mathrm{Var}(\varphi) \quad \sim \quad \int_0^{1/\xi} \frac{k^{d-1}dk}{k^2+(1/\xi)^2} \quad \sim \quad \frac{1}{\xi^{d-2}} \quad \sim \quad G(\xi) \tag{10.19}$$

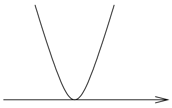
This value is determined by $(L/\xi)^d$ effective modes that each contribute to the variance ξ^2/L^d, hence it is Λ independent unlike the bare value $G(0)$. Substitution into the condition $\mathrm{Var}(\varphi) \ll (a/u)$ leads to the Ginzburg Criterion

$$|T-T_c^{(0)}| \quad \gg \quad C\ u^{2/(4-d)} \tag{10.20}$$

where C is a constant. This condition defines the border of the critical region. Within the critical region the Gaussian approximation breaks down because of non-Gaussian fluctuations.







We now turn to the question whether there is a *phase transition* within the critical region. The other possibility is that the fluctuations smear away the the phase transition leading to a smooth r rather than abrupt crossover. Namely, for $T \ll T_c^{(0)}$ there is a symmetry breaking, such that the mean field $\bar{\varphi}$ jumps from positive finite value to negative finite value as h is varied across $h=0$. Obviously, in order to observe a phase transition we have to require that this abrupt jump is not smeared by the (non-Gaussian) fluctuations within the critical region. We shall discuss below two cases in which fluctuations completely destroy the possibility to observe a phase transition.

Goldstone excitations. – First we refer to the case where the order parameter has a continuous rather than a discrete symmetry. To be specific let us assume a complex order parameter $\Psi = (\psi_1, \psi_2)$. In such case the potential $V(\Psi) = (1/2)a|\Psi|^2 + (1/4)|\Psi|^4$ looks like a Mexican hat for $r<0$. It means that instead of having two minima we have a continuous set of minima. This implies that the low frequency excitations of the system are phonon-like, called magnons in the ferromagnetic context. In general the excitations that appear if a continuous symmetry is broken are known as Goldstone excitations. They have some dispersion $\omega = c|k|$. Coming back to the partition sum, we see that we have to include the Goldstone excitations in the $\mathrm{Var}(\Psi)$ calculation, leading formally to an integral over $1/k^2$ instead of $1/(k^2+(1/\xi)^2)$. The integral is "infrared divergent" unless $d>2$. We conclude that the fluctuations destroy the possibility to observe a phase transition at $d=2$. This is know as the Mermin-Wagner theorem.

Non-Gaussian fluctuations. – Going back to the real field case, there are no Goldstone excitations, still we might have non-Gaussian excitations that smear the phase-transition. For $d>1$ the implication of such fluctuation is not too dramatic: the critical point is shifted down ($a_c < 0$) but remains finite (see discussion of the RG analysis). For $d = 1$ we already have discussed the absence of a finite temperature phase-transition using a "domain walls" perspective. Let us re-phase the explanation using a field-theory perspective. It is clear that if we have a phase transition, then *formally* $\text{Var}(\varphi) \sim \bar{\varphi}^2$ on the critical line. The question is whether it becomes $\text{Var}(\varphi) \ll \bar{\varphi}^2$ for any finite h away from the critical line. This depends on the height of the "barrier" between the two minima, and therefore cannot be deduced from the Ginzburg criterion: the latter is based on a local Gaussian approximation that does not know anything about the height of the "barrier". We shall see in the next section that in the $d = 1$ case the crossover has a finite width: there is no abrupt change in $\langle\varphi\rangle$ as $h = 0$ is crossed.

Quantum phase transition. – The Landau model is "classical" in the sense that its Hamiltonian commutes with the order parameter. This is not the case e.g. for coupled rotors (see previous lecture). In a field theory treatment the partition function $Z = \mathsf{trace}[\mathrm{e}^{-\beta H}]$ can be written as a Feynman path integral over the field $\varphi(x, \tau)$, where $\tau \in [0, \beta]$ is the so-called imaginary time. The integral is over all field configurations in $([0, \beta] \times [0, L]^d)$. Accordingly the analysis of the ground state in the thermodynamic limit ($\beta, L \to \infty$) maps formally to a classical field theory with $d_{cl} = d + 1$ dimensions. This implies that is is feasible to observe a zero temperature "quantum phase transitions", as a control parameter is varied, even for $d = 1$ and notably at $d = 2$.

[10.7] The one dimensional model

The one-dimensional field model can be solved exactly. This is merely a variation on the "transfer matrix" method. The $D\varphi$ integral is sliced and written as a trace over the product of $\mathcal{N}$ matrices. Each matrix can be written as $\exp(-dxH)$ where H is the "Hamiltonian". One realize that this is nothing else but the Feynman path integral in "imaginary time". Let us define

$$H \quad = \quad -\frac{1}{2}\frac{\partial^2}{\partial\varphi^2} + V(\varphi) \quad = \quad -\frac{1}{2}\frac{\partial^2}{\partial\varphi^2} + \left[\frac{1}{2}a\varphi^2 + \frac{1}{4}\varphi^4\right] \tag{10.21}$$

using the notation $\dot{\varphi} = d\varphi/dx$ and $x = \tau$ with periodic boundary conditions over $[0, L]$, the calculation of the partition function goes as follow:

$$Z \quad = \quad \int D\varphi \; \mathrm{e}^{-\int_0^L \frac{1}{2}\dot{\varphi}^2 + V(\varphi) d\tau} \quad = \quad \mathsf{trace}(\mathrm{e}^{-LH}) \quad = \quad \sum_n \mathrm{e}^{-L\mu_n} \tag{10.22}$$

where μ_n are the eigenvalues of H. In the thermodynamic limit $F(T, h) = LT\mu_0$ where μ_0 is the ground state energy of H. Similarly $\langle\varphi\rangle$ is just the ground state expectation value. For the correlation function we get

$$G(r) \quad \propto \quad \mathsf{trace}\left[\mathrm{e}^{-(L-r)H}\varphi\mathrm{e}^{-rH}\varphi\right] \quad \propto \quad \sum_n |\langle n|\varphi|0\rangle|^2 \mathrm{e}^{-r(\mu_n - \mu_0)} \tag{10.23}$$

where in the last equality we already dropped the terms that vanish in the thermodynamic limit. We see that the long tails are characterized the correlation length $\xi = 1/(\mu_1 - \mu_0)$. This correlation length does not diverge, reflecting that the variation of $\langle\varphi\rangle$ is smooth. The crossover at $h = 0$ has a width that equals the tunnel splitting $(\mu_1 - \mu_0)$.

[10.8] Coarse graining and scaling

The free energy $F(a,u,c;\Lambda,L)$ of an homogeneous system that is described by the Landau model, and the associated correlation function $G(r,a,u,c;\Lambda,L)$ depend on the following parameters:

$$L = \text{linear size of the model} \tag{10.24}$$
$$\Lambda = \text{largest momentum scale} \tag{10.25}$$
$$(c{=}1,a,u) = \text{microscopic related parameters} \tag{10.26}$$
$$r = \text{distance between two test points} \tag{10.27}$$

Schematically we write the free energy as $F(g;\Lambda,L)$, where g stands for any of the action parameters. The $c=1$ convention fixes the units of the field φ, as well as the engineering dimension d_g of any of the action parameters. The microscopic-related parameters have been determined, as in the Bragg-Williams approximation, by summation over all the microscopic configurations that correspond to the same coarse-grained $\varphi(x)$. Accordingly these parameters depend on the value of Λ. To emphasize this aspect one may use the notation $g(\Lambda)$.

Assume that we have used a coarse-graining cutoff Λ to construct the action. But later we might prefer to work with an action that corresponds to a somewhat lower cutoff Λ'. Obviously the result of the calculation should be the same. Accordingly we write

$$F(g;\Lambda,L) \;=\; F(g';\Lambda',L) \;=\; F(s^{d_g}g';\Lambda,sL) \;=\; s^dF(s^{d_g}g';\Lambda,L) \tag{10.28}$$

In the second equality we scaled the units by factor $s=\Lambda'/\Lambda$ in order to restore the original Λ cutoff, and in the last equality we have used the thermodynamic limit in order to restore the original L cutoff. Using a compact notation we have deduced the scaling relation

$$F(g) \;=\; s^d\; F(g_s), \qquad\qquad g_s \equiv s^{d_g}\; g(s\Lambda) \tag{10.29}$$

With regard to the correlation function we note that G, unlike F, does not depend on L, but the units of the field have been modified, hence s^d should be replaced by a different scaling factor that we discuss in the next section.

It should be clear that the units of length are arbitrary, hence F should be a well defined function of the dimensionless model parameters. It follows that we can write the scaling relation for the microscopic related parameters without giving explicit reference to Λ. Namely,

$$\tilde{g}_s \;=\; R(s)\;\tilde{g}, \qquad\qquad \tilde{g}_s \equiv \Lambda^{d_g}\; g_s \tag{10.30}$$

where $R(s)$ is a non-linear transformation that depends on s. This transformation relates values of F along a trajectory in parameter space, and by definition has the semi-group property $R(s_2)R(s_1)=R(s_2s_1)$. Using the parametrization $s=\mathrm{e}^{-\tau}$ we can write the transformation as $\tilde{g}_\tau = R(\tau)\tilde{g}_0$ and the semi-group property as $R(\tau_2)R(\tau_1)=R(\tau_2+\tau_1)$. Clearly we can generate $R(\tau)$ from infinitesimal steps, so we define a β function via the expansion $R(\tau)\tilde{g} = \tilde{g}+\tau\beta(\tilde{g})+\mathcal{O}(\tau^2)$, and write the so called renormalization group (RG) equation as

$$\frac{d\tilde{g}}{d\tau} \;=\; \beta(\tilde{g}), \qquad\qquad [\text{opposite sign convention if }\; d\tau\mapsto d\ln\Lambda] \tag{10.31}$$

Increasing the course graining parameter τ, we get a flow in g space. A fixed point of this flow represents a critical point of the model, where the system look-alike on any scale. If we start the RG trajectory at a point close to the fixed point it will flow away, meaning that on coarse-grained scale the system looks like having larger $|T-T_c|$. For the Landau model in 3D we shall see below that the RG equation for a becomes

$$\frac{d\tilde{a}}{d\tau} \;=\; \frac{1}{\nu}(\tilde{a}-\tilde{a}_c), \qquad \tilde{a}_c = -\frac{1}{5},\;\; \nu=\frac{3}{5} \tag{10.32}$$

Defining $t = (a - a_c)$ we get the solution $t_s = s^{-1/\nu}t$, leading to the scaling relation $F(t) = s^d F(s^{-1/\nu}t)$. Hence for the heat capacity exponent we get $\alpha = 2 - \nu d = 1/5$, and not the mean-filed value $\alpha = 0$, neither the Gaussain value $\alpha = 1/2$.

[10.9] Renormalization Group (RG) analysis

We outline the RG procedure that is used in order to find the $\beta(g)$ function, where g stands for the parameters (a, u, c) of the Landau model with the convention $c = 1$. For extra technical details see Section 18.7 of Huang.

Step1 of RG.– Perturbation theory allows to integrate the high Fourier components within a shell $\Lambda' < k < \Lambda$. where $\Lambda' = \Lambda - \delta\Lambda$. Namely any field configuration can be written as a sum of smooth and erratic components:

$$\varphi(x) \ = \ \sum_{|k|<\Lambda'} \varphi_k e^{ikx} + \sum_{\Lambda'<|k|<\Lambda} \varphi_k e^{ikx} \ \equiv \ \bar{\varphi}(x) \ + \ \tilde{\varphi}(x) \tag{10.33}$$

The action can be expanded with respect to $\tilde{\varphi}$ up to quadratic order. This is allowed because $\delta\Lambda$ is chosen as arbitrarily small. Using abstract notation with regard to field indexes we write the expansion as

$$A[\varphi(\cdot)] \ = \ A[\bar{\varphi}(\cdot)] \ + \ h_{\text{induced}}[\bar{\varphi}]\,\tilde{\varphi} + a_{\text{induced}}[\bar{\varphi}]\,\tilde{\varphi}^2 \tag{10.34}$$

Now it is possible to use Gaussian integration over $\tilde{\varphi}$ to get an effective expression for $A[\varphi(\cdot)]$ that involves new values for the model parameters. Accordingly

$$F(a, u, c; \Lambda, L) \ = \ F(a', u', c'; \Lambda', L) \tag{10.35}$$

Doing the algebra the result is

$$a' \ = \ a + \delta\Lambda\Big[3\Omega_d\left(\Lambda^{d-3}u - \Lambda^{d-5}au\right)\Big] \tag{10.36}$$

$$u' \ = \ u - \delta\Lambda\Big[9\Omega_d\Lambda^{d-5}u^2\Big] \tag{10.37}$$

$$c' \ = \ c \tag{10.38}$$

Note that the u of Huang should be identified with our $u/4$, and r of Huang is identified with our a. Though not the case here, one should be aware that in general the elimination of the high Fourier components might spoils the $c = 1$ convention.

Step2 of RG.– In "step2" of the RG procedure the original value of Λ is restored vis engineering scaling, and then the thermodynamic limit is assumed to restore L as well. Accordingly

$$F(a, u, c; \Lambda, L) \ = \ s^d \ F(s^{d_a}a', s^{d_u}u', c'; \Lambda, L), \qquad s \equiv e^{-\tau}, \quad \tau = \delta\Lambda/\Lambda \ll 1 \tag{10.39}$$

Note that according to the common convention $d_c = 0$.

Step3 of RG.– In "step3" of the RG procedure the field φ is re-scaled such that the convention $c = 1$ is restored. Using the notation $c' = s^{-\eta}$, and dropping reference to the restored parameters, we get

$$F(a, u) \ = \ s^d \ F(a_s, u_s) \tag{10.40}$$

$$G(r, a, u) \ = \ s^{-2d_\varphi+\eta} \ G(sr, a_s, u_s) \tag{10.41}$$

Here we suppressed c, because it has been restored to unity. In the Landau model $c' = c$ and therefore $\eta = 0$. For the two other parameters we get

$$a_s \ = \ s^{-2}a' \ = \ a \ + \ \tau\Big[2a + 3\Omega_d\left(\Lambda^{d-2}u - \Lambda^{d-4}au\right)\Big] \tag{10.42}$$

$$u_s \ = \ s^{-(4-d)}u' \ = \ u \ + \ \tau\Big[(4-d)u - 9\Omega_d\Lambda^{d-4}u^2\Big] \tag{10.43}$$

where $s = 1 - \tau$ applies for an infinitesimal step. Without the high frequency contribution the above RG relation is just a complicated way to write how the parameters are affected by engineering scaling.

RG equation.– We can illustrate the RG flow in the (a, u) space. Increasing τ means lower resolution description of the system, with effective parameters (a_s, u_s). It is convenient to use dimensionless parameters $\tilde{g} = \Lambda^{d_g} g$, such that the transformation $R(s)$ becomes free of Λ. Considering an infinitesimal τ one finds that the RG-equations of the Landau model are

$$\frac{d\tilde{a}}{d\tau} = 2\tilde{a} + 3\tilde{u} - 3\tilde{a}\tilde{u} \tag{10.44}$$

$$\frac{d\tilde{u}}{d\tau} = (4-d)\tilde{u} - 9\tilde{u}^2 \tag{10.45}$$

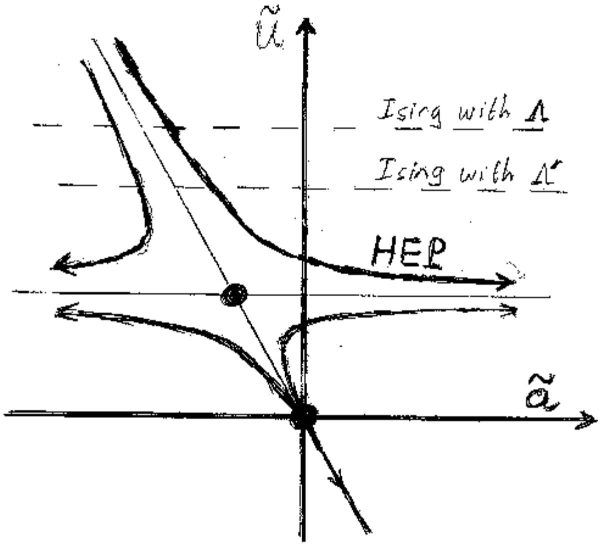
where $\tilde{a} = a/\Lambda^2$ and $\tilde{u} = \Omega_d u/\Lambda^{4-d}$.

RG flow.– The RG equation defines flow in (a, u) space. This flow is illustrated in the figure below. In the Landau model we have two fixed points. The Gaussian fixed point is for $\tilde{u}_0 = 0$ at $\tilde{a}_0 = 0$. The nontrivial fixed point is

$$\tilde{u}_c = \frac{(4-d)}{9} \tag{10.46}$$

$$\tilde{a}_c = -\left[1 - \frac{(4-d)}{6}\right]^{-1} \frac{(4-d)}{6} \tag{10.47}$$

For $d < 4$ the Gaussian fixed point is unstable and the flow is dominated by the nontrivial fixed point. One observes that the critical temperature (a_c) is shifted below the mean field Gaussian value.



[10.10] Implications of the RG results

The results of the RG analysis are used slightly differently in Statistical Mechanics ("Ising") and in high energy physics ("HEP"). We first would like to explain the subtle difference, and then to focus on the the "Ising" context.

HEP.– In the HEP context $\sqrt{a} = \mathsf{m}$ is the so-called "bare mass", and u is the "bare interaction". They are associated with the momentum exchange $q \sim \Lambda$ in, say, electron-electron scattering calculation. The low energy scale Λ_0 is the Compton wavelength that corresponds to the electron mass. For larger Λ the scattering involves "loop" corrections reflecting the virtual appearance of electron-positron pairs. Consequently the mass and the interaction become "running coupling constants". With different choices of Λ one associates different $a(\Lambda)$ and $u(\Lambda)$. The physical mass and the physical interaction for q-scattering are defined through the measured dispersion-relation and through the cross-section respectively. Both are functions of $(q; a, u)$, and are calculated from the bare parameters. With different choices of Λ we can associate different points in $(\tilde{a}, \tilde{u})$ space. It follows that the relevant physics is along a *specific* HEP line of the RG flow (see figure). Accordingly what we get from the RG analysis is how $a(\Lambda)$ and $u(\Lambda)$ depend on Λ. It turns out that the $d = 4$ Landau model has essentially the same beta function as in QED. Namely, the beta function for the QED coupling $g = e^2/(4\pi)$ is $\beta(g) = Cg^2$ with $C = 2/(3\pi)$ instead of $C = 1/9$. One obtains

$$g(\Lambda) \;=\; \frac{g_0}{1 - Cg_0 \ln(\Lambda/\Lambda_0)} \;\equiv\; \frac{1}{C \ln(\Lambda_\infty/\Lambda)} \tag{10.48}$$

where Λ_0 corresponds to the Compton length of the electron and $g_0 \approx 1/137$ is the asymptotic QED coupling. At large distances $(q < \Lambda_0)$ the interaction strength is renormalized to a universal value that is independent of the bare parameters. For short distances the interaction becomes stronger, and diverges at the Landau pole Λ_∞. Note that this divergence is possibly not physical because the derivation of the RG equation assumes that g is small.

Ising.– In the Ising context the reasoning is different. After Λ coarse-graining we get an action with a and u, which we represent as a point in $(\tilde{a}, \tilde{u})$ space. If we vary the temperature it is like going along a horizontal line. If we use a lower cutoff Λ' it would takes us to a lower horizontal line (see figure). Assuming that we have done enough coarse-graining, the value of u would become $u \approx u_c$. We therefore say that u is "irrelevant". Without loss of generality we can set $u = u_c$ in our calculations. We end up with a single RG equation for the variable $t = (a - a_c)$, namely

$$\frac{dt}{d\tau} \;=\; (2 - 3u_c)\, t \qquad\qquad \text{generic notation: } \frac{dg}{d\tau} = \lambda\, g \tag{10.49}$$

The solution of this equation is $t_\tau = \mathrm{e}^{\lambda\tau} t_0$ hence we deduce the scaling relation $F(t) = s^d F(s^{-\lambda} t)$. We therefore conclude that $F(t) \propto |t|^{d/\lambda}$, from which the dependence of the heat capacity on the temperature can be derived.

The critical exponents.– We want to understand how the RG flow explains the scaling hypothesis. In the vicinity of the fixed point we can linearize the RG equation. After linear transformation and shift we get an equation of the type $dg/d\tau = \lambda g$, whose solution is $g_\tau = \mathrm{e}^{\lambda\tau} g$. Parameters with negative eigenvalues $\lambda < 0$ vanish from the model due to the coarse graining and therefore are called "irrelevant". We keep only the relevant parameters and deduce that

$$F(g) \;=\; s^d\, F(s^{D_g} g), \qquad D_g \equiv -\lambda \tag{10.50}$$

The anomalous dimension D_g of Huang is defined with opposite sign (he is using inverse length units). In general "g" stands for a collection of (relevant) parameters, each having its own "dimension". In the Landau model the relevant parameter is related to the temperature, namely $t = (a - a_c) \propto (T - T_c)$. From the RG equation we deduce

$$D_t \;=\; -\left[2 - 3u_c\right] \;=\; -\left[2 - \frac{(4-d)}{3}\right] \;\equiv\; -\frac{1}{\nu} \tag{10.51}$$

Hence the scaling relations take the familiar form

$$F(t) \;=\; s^d\, F(s^{-1/\nu} t) \tag{10.52}$$

$$G(r,t) \;=\; s^{d-2+\eta}\, G(sr, s^{-1/\nu} t) \tag{10.53}$$

This means that the coarse grained system looks less and less critical as τ is increased. Having determined ν and $\eta = 0$ using the RG procedure, we can deduce all the other critical exponents from the scaling relations.

[10.11] The Heisenberg model

The Heisenberg model relates to a three component vector field $\mathbf{S}$. It is described by the Hamiltonian

$$\mathcal{H} \;=\; -J\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j \tag{10.54}$$

The field theory version of the Heisenberg model is the nonlinear sigma model (NLSM), where $S(\boldsymbol{r})$ is a vector field that obeys the constraint $|S(\boldsymbol{r})|=1$. The NLSM energy functional is commonly written as

$$E[S] \;=\; \frac{1}{2g}\int|\nabla S|^2 d\boldsymbol{r} \tag{10.55}$$

The Mermin-Wagner theorem:– In the Heisenberg and Landau-Ginzburg models the order parameter has a continuous symmetry with respect to spin rotations. This is different from the Ising and Landau models where the symmetry is discrete (up/down). The Mermin-Wagner theorem states that continuous symmetries cannot be spontaneously broken at finite temperature in $d\leq 2$ systems with short-range interactions. This is due to long-range fluctuations, corresponding to massless "Goldstone modes". These fluctuations cost little energy, while contribute large entropy. Hence at finite temperatures the $T=0$ broken symmetry is washed away.

Let us outline the argument that explains the dimensionality issue. Assume that there is a long range order. Use the Gaussian approximation to calculate the correlation function around the selected minimum. The Goldstone modes are massless (which is like $r=0$ in the Landau model). Hence $g(r)=\mathrm{FT}[1/k^2]$. The area under $g(r)$ diverges due to the low wavelength fluctuations if $d\leq 2$, indicating that the minimum is washed away.

[10.12] The XY model

The XY model relates to a two component vector field $\mathbf{S}$. It can be regarded as describing coupled rotors. The orientation of the ith spin in the XY plane is φ_i. Accordingly we can write

$$\mathcal{H} \;=\; -J\sum_{\langle i,j\rangle}\cos(\varphi_i-\varphi_j) \tag{10.56}$$

The associated continuous field version is defined by the energy functional

$$E[\varphi] \;=\; \frac{K}{2\pi}\int(\nabla\varphi)^2 d\boldsymbol{r} \;=\; \frac{K}{2\pi}\int|\Psi'(\boldsymbol{r})|^2 d\boldsymbol{r} \tag{10.57}$$

where $d\boldsymbol{r}$ integrates over space, and $\Psi(\boldsymbol{r})=\mathrm{e}^{i\varphi(\boldsymbol{r})}$. Note that the Landau-Ginzburg model has an order-parameter $\Psi(r)=\sqrt{n(\boldsymbol{r})}\mathrm{e}^{i\varphi(r)}$, and can be regarded as a variation of the XY model, where $n(\boldsymbol{r})$ is not constrained to unity. The low lying excitations of the XY model in 2D are vortexes. For example, a single vortex at the origin is represented by

$$\varphi(\boldsymbol{r}) \;=\; q\ \arg(x,y) \;=\; q\tan^{-1}(y/x) \tag{10.58}$$

$$|\nabla\varphi| \;=\; (q/r)\ \ \text{[tangential]} \tag{10.59}$$

$$E[\varphi] \;=\; Kq^2\ln(L/a) \tag{10.60}$$

where L is the radius of the system, and a is the lattice spacing, and q is an integer, say $q=\pm1$. One realizes that $\vec{F}=\nabla\varphi$ is like a 90deg rotated version of a field dues to a charge q in a 2D electrostatic problem, while $E[\varphi]$ corresponds to the electroststic energy. Accordingly if we have several vortexes we get

$$E[\varphi] \;=\; \text{const}-K\sum_{\langle i,j\rangle}q_iq_j\ln|\boldsymbol{r}_i-\boldsymbol{r}_j| \tag{10.61}$$

which is formally the expression for the energy of a Coulomb gas in 2D.

Note about complex representation.– Consider a field $\vec{F} = (F_x, F_y)$ in 2D that has no sources ($\nabla \cdot F = 0$) and no circulations ($\nabla \times F = 0$). These two conditions are the Cauchy-Riemann equations that allow to represent the field by a complex differentiable function $f(z) = F_x - iF_y$, where $z = x + iy$. Note that in sloppy notations $\vec{F} = f(z)^*$. Note that such functions are called holomorphic and hence they are analytic, i.e. have a convergent Taylor expansion at any point. Note also that a holomorphic function can be regarded as a conformal map $w = f(z)$ that induces a local transformation $df = Cdz$, where the local derivative C can be regarded as a rotation (due to its phase) combined with dilation (due to its modulo). From the Cauchy-Riemann no-circulation condition it follows that the field can be derived from a scalar potential ($\vec{F} = -\nabla V$). Optionally from the Cauchy-Riemann no source condition it follows that the field can be derived from a vector potential ($\vec{F} = \nabla \times (0, 0, A)$). We can summarize these two options by defining a complex potential $\Psi(z) = V(z) + iA(z)$ such that $f(z) = -\Psi'(z)$. The lines of constant $A(z)$ are called "stream lines", while the lines of constant $V(z)$ are called "propagation fronts". Differences of A have the meaning of "flux", while differences of V have the meaning of "work". For a point charge in a 2D electrostatic problem the Coulomb field is $f(z) = q/z$ and $\Psi(z) = -q\ln(z)$ corresponding to $V(x, y) = -q\ln(r)$. The vortex in the XY model is just a rotated version of a Coulomb field with $f(z) = -iq/z$ and $\Psi(z) = -iq\ln(z)$.

The Kosterlitz-Thouless transition.– Considering the XY model in 2D space, let us see what happens if we have a collection of vortexes. The entropy which is associated with the number of possibility to position the vortex in the lattice is $S = \ln[(L/a)^2]$. Accordingly the introduction of a vortex into the system implies

$$F[\rho] \quad = \quad E[\rho] - TS[\rho] \quad = \quad (K - 2T)\ln[(L/a)] \tag{10.62}$$

Hence for $T > (K/2)$ the creation of a vortex is favoured, so we expect to have a gas of quasi-independent vortexes. For $T < (K/2)$ these vortexes have to pair, which is like not having vortexes. The above argumentation implies an "infinite order phase transition", known as the Kosterlitz-Thouless transition. In consistency with the Mermin-Wagner theorem it does not lead to "long range order". Rather it describes a transition from "conventional disordered phase" at high temperature, to "quasi-long-range ordered phase" at low-temperature. The correlation function goes from exponential above the critical temperature, to powerlaw at the critical temperature and below. At the critical temperature $g(r) = 1/r^{\eta}$, with $\eta = 1/4$. Below the critical temperature a Gaussian estimate gives $\eta = T/(2K)$.

Fluctuations and Response

[11] Fluctuations

In order to know the expectation value of an operator we need only spectral information which is present in $\mathsf{g}(E, X)$ or in $Z(\beta, X)$. Note that these functions contains only spectral information about the system (no information on the dynamics). Still it is enough for the calculation of the conservative force. For example, in case of a canonical preparation

$$\langle \mathcal{F} \rangle_0 \;=\; \left\langle -\frac{\partial \mathcal{H}}{\partial X} \right\rangle \;=\; \sum_n p_n \left(-\frac{\partial E_n}{\partial X} \right) \;=\; \frac{1}{\beta} \frac{\partial \ln(Z)}{\partial X} \tag{11.1}$$

In contrast to that, the fluctuations of $\mathcal{F}(t) - \langle \mathcal{F} \rangle_0$ require knowledge of the dynamics, and cannot be calculated from the partition function. For simplicity of presentation we assume below that the fluctuating quantity of interest is re-defined such that $\langle \mathcal{F} \rangle_0 = 0$.

[11.1] The classical power spectrum

Consider a stationary stochastic classical variable $F(t)$, and define its correlation function as

$$C(t_2 - t_1) \;=\; \langle F(t_2) F(t_1) \rangle \tag{11.2}$$

The power spectrum $\tilde{C}(\omega)$ is the Fourier transform of $C(\tau)$, where $\tau = t_2 - t_1$ is the time difference. In practice a realization of F within time interval $0 < t' < t$ can be Fourier analyzed as follows:

$$F_\omega \;=\; \int_0^t F(t') \mathrm{e}^{i\omega t'} dt' \tag{11.3}$$

and we get the "Wiener-Khinchin theorem"

$$\langle |F_\omega|^2 \rangle \;=\; \tilde{C}(\omega) \times t \tag{11.4}$$

where we assume that t is much larger compared with the correlation time.

A related perspective concerns the intensity of the power spectrum:

$$\nu \;=\; \int_{-\infty}^{\infty} C(\tau) d\tau \;=\; \tilde{C}(\omega{=}0) \tag{11.5}$$

If we regard $F(t)$ as the velocity ("steps") in a random-walk process, then the zeroth Fourier component is

$$r(t) \;=\; \int_0^t F(t')\, dt' \;=\; \text{total displacement} \tag{11.6}$$

On the average $\langle r \rangle = 0$ but the variance is linear in time:

$$\mathrm{Var}(r) \;=\; \int_0^t \int_0^t \langle F(t') F(t'') \rangle \, dt'' dt' \;=\; \nu\, t \;\equiv\; 2D\, t \tag{11.7}$$

Accordingly the intensity ν is trivially related to the coefficient D of a diffusion process that is generated by the noisy signal $F(t)$.

[11.2] The quantum power spectrum

We consider a system whose dynamics is generated by Hamiltonian $\mathcal{H}$. We assume that it is prepared in a stationary state, possibly but not necessarily a thermal states. Our interest is in the fluctuations of an observable $\mathcal{F}$. We use the common interaction picture notation $\mathcal{F}(t) = \mathrm{e}^{i\mathcal{H}t}\mathcal{F}\mathrm{e}^{-i\mathcal{H}t}$. The non-symmetrized correlation function of $\mathcal{F}$ is defined as

$$S(t) \ = \ \langle \mathcal{F}(t)\mathcal{F}(0)\rangle \tag{11.8}$$

This function is complex, but its Fourier transform is real and can be calculated as follows:

$$\tilde{S}(\omega) \ = \ \int_{-\infty}^{\infty} S(t)\mathrm{e}^{i\omega t}dt \ = \ \sum_n p_n \sum_m |\mathcal{F}_{mn}|^2 \ 2\pi\delta\left(\omega - \frac{E_m - E_n}{\hbar}\right) \tag{11.9}$$

In the case of a *microcanonical* preparation at some energy E, this is the same object that appears in the Fermi-Golden-rule (FGR) for rate of decay due to transitions to other levels, namely

$$\Gamma_{\mathrm{FGR}} \ = \ \tilde{S}_E(\Omega) \times f_0^2, \qquad \text{for } \mathcal{H} - f(t)\mathcal{F}, \ \ \text{with } f(t) = f_0\mathrm{e}^{-i\Omega t} \tag{11.10}$$

See further discussion of the FGR in the Kubo formula section. In the above formula $\omega > 0$ corresponds to absorption of energy (upward transitions), while $\omega < 0$ corresponds to emission (downward transitions).

[11.3] The detailed balance relation

It is a straightforward algebra to show that for a *canonical* preparations at temperature T, where $p_n \propto \exp(-E_n/T)$, there is a detailed balance relation:

$$\tilde{S}_T(-\omega) \ = \ \exp\left(-\frac{\hbar\omega}{T}\right) \ \tilde{S}_T(\omega) \tag{11.11}$$

This implies that if we couple to the system another test system (e.g. a two level "thermometer") it would be driven by the fluctuations into a canonical state with the same temperature.

The disadvantage of $\tilde{S}_T(\omega)$ is that it has meaning only in the quantum mechanical context. We want a formulation that treat the quantum and the classical on equal footing. We therefore define spectral functions that have well defined classical limit:

$$\tilde{C}(\omega) \ \equiv \ \mathrm{FT}\ \frac{1}{2}\Big\langle \mathcal{F}(t)\mathcal{F}(0) + \mathcal{F}(0)\mathcal{F}(t)\Big\rangle \ = \ \frac{1}{2}\Big(\tilde{S}(\omega) + \tilde{S}(-\omega)\Big) \tag{11.12}$$

$$\tilde{K}(\omega) \ \equiv \ \mathrm{FT}\ \frac{i}{\hbar}\Big\langle [\mathcal{F}(t), \mathcal{F}(0)]\Big\rangle \ = \ \frac{i}{\hbar}\Big(\tilde{S}(\omega) - \tilde{S}(-\omega)\Big) \tag{11.13}$$

and deduce that at thermal equilibrium they are related as follows:

$$\tilde{K}(\omega) \ = \ i\frac{2}{\hbar}\tanh\left(\frac{\hbar\omega}{2T}\right) \ \tilde{C}(\omega) \tag{11.14}$$

We shall see later that $\tilde{K}(\omega)$ determines the absorption coefficient of the system, hence the above relation is going to be the basis for a "fluctuation-dissipation relation".

It is interesting to look on the classical limit of the detailed balance relation. The classical canonical version can be regarded as the low frequency limit of the quantum relation:

$$\tilde{K}_T(\omega) \ = \ i\omega \times \frac{1}{T}\ \tilde{C}_T(\omega) \qquad\qquad [\text{classical canonical version}] \tag{11.15}$$

It looks very nice in time domain:

$$K_T(t) \;=\; -\frac{1}{T}\,\dot{C}_T(t) \tag{11.16}$$

We shall use the latter version in order to derive what we call later the "DC version" of the a generalized fluctuation-dissipation relation.

[11.4] The classical version of "detailed balance"

The purpose of the present section is to show how a general relation between $K(t)$ and $C(t)$ can be derived within the framework of classical mechanics, assuming that the system is prepared in some arbitrary stationary state $\rho(x,p) = f(H(x,p))$. The classical canonical version that we have deduced in the previous version by taking the $\hbar\omega \to 0$ limit can be regarded as a special case with $f(H) \propto \exp(-\beta H)$. We first define $K(t)$ and $C(t)$ in a more general way:

$$C(t) \;=\; \mathsf{trace}\,\{f(H)\;A_t B\} \tag{11.17}$$

$$K(t) \;=\; \mathsf{trace}\,\{f(H)\;[A_t, B]\} \tag{11.18}$$

The trace means $dxdp$ phase-space integration, with obvious generalization to more than one freedom. We define $z = (x,p)$ and $\partial = (\partial_x, \partial_p)$. The Poisson brackets of two functions are:

$$[A,B]_{\text{PB}} \;=\; (\partial_x A)(\partial_p B) - (\partial_p A)(\partial_x B) \;\equiv\; \sum_{i,j}(\partial_i A)J_{i,j}(\partial_j B) \tag{11.19}$$

where $J_{i,j} = \text{matrix}\{0,1;-1,0\}$. One easily proves that $\mathsf{trace}\{[A,B]C\} = \mathsf{trace}\{A[B,C]\}$. Note also the chain rule $[f(H),A] = f'(H)[H,A]$. It is now possible to derive the following identity:

$$\mathsf{trace}\,\{f(H)[A_t,B]\} \;=\; \mathsf{trace}\,\{[f(H),A_t]B\} \;=\; \mathsf{trace}\,\{f'(H)[H,A_t]B\} \;=\; -\frac{d}{dt}\mathsf{trace}\,\{f'(H)A_t B\} \tag{11.20}$$

where the time evolved function A_t obeys the Hamilton equation of motion $(d/dt)A_t = -[H,A]_t$, and we use the canonical invariance $[H,A]_t = [H_t, A_t]$. For a microcanonical distribution $f(H) = \mathsf{g}(E)^{-1}\delta(H-E)$ we get

$$K_E(t) \;=\; -\frac{1}{\mathsf{g}(E)}\frac{d}{dE}\Big[\mathsf{g}(E)\;\dot{C}_E(t)\Big] \qquad\qquad \text{[classical microcanonical version]} \tag{11.21}$$

For a canonical distribution $f(H) = Z(\beta)^{-1}\exp(-\beta H)$ the weighted energy derivative is replaced by $1/T$ as anticipated from the quantum version. Optionally the canonical version can be obtained from the microcanonical version by averaging over the energy with the canonical weight $\propto \mathsf{g}(E)\exp(-E/T)$, and integration by parts. A physically appealing deduction of the connection between K and C will be implied by the derivation of the classical fluctuation-dissipation relation.

[11.5] Fluctuations of a many body system

A single particle dynamics at energy ϵ can be characterized by the single particle microcanonical fluctuation spectrum $C_\epsilon(\omega)$, and by the associated response function

$$\tilde{K}_\epsilon(\omega) \;=\; i\omega \times \frac{1}{\mathsf{g}(\epsilon)}\frac{d}{d\epsilon}\Big[\mathsf{g}(\epsilon)\;\tilde{C}_\epsilon(\omega)\Big] \tag{11.22}$$

Let us assume that we have a many body occupation that is described by an occupation function $f(\epsilon_n)$. If we consider a one-body operator $\hat{\mathbf{A}} = \sum_{mn} A_{mn} a_m^\dagger a_n$, the expectation function an additive property that relates it to the single particle expectation values:

$$\langle \hat{\mathbf{A}} \rangle \;=\; \sum_n f(E_n)\ \langle A \rangle_n \tag{11.23}$$

If C is the two-body operator such property does not in general exist: the total "interaction" is greater than the sum of the interactions within subsets. But if the two-body operator $C = [A, B]$ is defined as the commutator of two one-body operators, it is easy to show that the additive property is re-gained. According we deduce that for an N body system

$$\tilde{K}^{[N]}(\omega) \;=\; \int d\epsilon\ \mathsf{g}(\epsilon) f(\epsilon)\ \tilde{K}_\epsilon(\omega) \tag{11.24}$$

Expression $\tilde{K}_\epsilon(\omega)$ using $\tilde{C}_\epsilon(\omega)$ we get

$$\tilde{K}^{[N]}(\omega) \;=\; i\omega \times \begin{cases} \mathsf{g}(\epsilon_F)\ \tilde{C}_F(\omega) & \text{degenerate Fermi occupation } (T \ll \epsilon_F) \\ (N/T)\ \tilde{C}_T(\omega) & \text{dilute Boltzman occupation } (T \gg \epsilon_F) \end{cases} \tag{11.25}$$

where the subscripts F and T implies that $C_\epsilon(\omega)$ is evaluated at the Fermi energy, or averaged according to the thermal occupation, respectively. Note that in practice $\mathsf{g}(\epsilon_F) \sim N/\epsilon_F$, so we have a smooth crossover at $T \sim \epsilon_F$. The fluctuations of the many-body current are deduced from the detailed balance relation:

$$\tilde{C}^{[N]}(\omega) \;=\; \frac{\hbar}{2} \coth\left(\frac{\hbar\omega}{2T}\right)\ \mathrm{Im}\left[\tilde{K}^{[N]}(\omega)\right] \tag{11.26}$$

Considering a system of Fermions we get

$$\tilde{C}^{[N]}(\omega) \;=\; \begin{cases} \frac{\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2T}\right)\ \mathsf{g}(\epsilon_F)\ \tilde{C}_F(\omega) & \text{degenerate Fermi occupation} \\ N\ \tilde{C}_T(\omega) & \text{dilute Boltzmann occupation} \end{cases} \tag{11.27}$$

Contrary to the classical reasoning the zero temperature Fermi sea is not noisy $\nu_N = \tilde{C}^{[N]}(0) = 0$. The intensity ν_N of the current-fluctuations is not simply the sum over the one-particle fluctuations. The classical result is $\nu_N = N\nu_T$ where ν_T is the thermally averaged one-particle fluctuation-intensity. In contrast, the quantum result is $\nu_N = N_T\nu_F$, where ν_F is evaluated at the Fermi energy, and $N_T = T\mathsf{g}(\epsilon_F) \equiv T/\Delta$ is the effective number of particles that contribute to the noise. Strangely enough (see next lecture) the classical and the quantum calculations give the same result within the framework of the Drude model: the temperature dependence merely shifts from the "ν" to the "N".

Many body calculation.– It is interesting to see how the relation between many-body fluctuations and single particle fluctuations is deduced for a low temperature system of Fermions using a direct calculation. We consider the fluctuations of a general observable A. If we treat the many body system as a whole then we have to employ second quantization to write $\hat{\mathbf{A}} = \sum_{mn} A_{mn} a_m^\dagger a_n$. Excluding the irrelevant diagonal $n{=}m$ terms we get for a non-interacting system in a thermal state

$$\begin{aligned} \tilde{S}^{[N]}(\omega) \;&=\; \mathrm{FT}\left\langle \hat{\mathbf{A}}(t)\hat{\mathbf{A}}(0) \right\rangle \\ &=\; \sum_{nm} |A_{mn}|^2 \left\langle a_n^\dagger a_m a_m^\dagger a_n \right\rangle\ 2\pi\delta(\omega{-}(\epsilon_m{-}\epsilon_n)) \\ &=\; \sum_{nm} (1{-}f(\epsilon_m)) f(\epsilon_n) |A_{mn}|^2\, 2\pi\delta(\omega{-}(\epsilon_m{-}\epsilon_n)) \\ &=\; \int \frac{d\epsilon}{\Delta} (1{-}f(\epsilon{+}\omega)) f(\epsilon)\ \tilde{C}_\epsilon(\omega) \end{aligned} \tag{11.28}$$

If we had bosons the last expression would be $(1+f)f$ instead of $(1-f)f$. In the dilute Boltzmann limit ($f \ll 1$) we recover additivity, as expected from classical considerations with regard to uncorrelated motions of independent particles. But for non-dilute occupations the results depends of the "many body statistics". For bosons there are enhanced fluctuations due to the "bunching" of particles in the same orbital. For fermions it is the opposite effect. In the latter case let us assume that the single particle power spectrum has a well-defined mean level spacing Δ at the energy range of interest, namely at the thermal vicinity of the Fermi energy. At the limit of zero temperature the result of the integral is clearly zero for $\omega < 0$ reflecting that a zero-temperature the system can only absorb energy. For positive frequencies the zero temperature result $(\omega/\Delta)\tilde{C}_F(\omega)$ is proportional to the number levels (ω/Δ) from which transitions to empty orbitals can take place. For finite temperature we get:

$$\begin{aligned} \tilde{S}^{[N]}(\omega) &= \frac{\omega/\Delta}{1-\mathrm{e}^{-\omega/T}}\,\tilde{C}_F(\omega) && (11.29)\\ \tilde{C}^{[N]}(\omega) &= \frac{\omega}{2\Delta}\coth\left(\frac{\omega}{2T}\right)\,\tilde{C}_F(\omega) && (11.30)\\ \tilde{K}^{[N]}(\omega) &= i\frac{\omega}{\Delta}\,\tilde{C}_F(\omega) && (11.31) \end{aligned}$$

Needless to say that these results, that have been deduced here from a direct many-body calculation, are consistent with the former deduction that has been based on detailed-balance considerations.

[11.6] Fluctuations of several observables

Give several observables $\mathcal{F}^j$, and assuming that the system is prepared in a stationary state, the fluctuations can be characterized by the correlation function

$$S^{kj}(t) = \langle \mathcal{F}^k(t)\mathcal{F}^j(0)\rangle \qquad (11.32)$$

The associated spectral function $\tilde{S}^{kj}(\omega)$ is defined by a Fourier transform. For simplicity we use the notations $\mathcal{F}^1 = A$ and $\mathcal{F}^2 = B$, and write the spectral decomposition

$$\tilde{S}^{AB}(\omega) = \sum_n p_n \sum_{m(\neq n)} A_{nm}B_{mn}\,2\pi\delta\left(\omega - \frac{E_m - E_n}{\hbar}\right) \qquad (11.33)$$

It is convenient to write $S^{AB}(t)$ as the sum of two *real* spectral functions that have a good classical limit:

$$\begin{aligned} S^{AB}(t) &= C^{AB}(t) - i\frac{\hbar}{2}K^{AB}(t) && (11.34)\\ C^{AB}(t) &\equiv \frac{1}{2}\Big\langle A(t)B(0) + B(0)A(t)\Big\rangle && (11.35)\\ K^{AB}(t) &\equiv \frac{i}{\hbar}\Big\langle [A(t), B(0)]\Big\rangle && (11.36) \end{aligned}$$

We use the notations $\tilde{S}^{AB}(\omega)$, and $\tilde{C}^{AB}(\omega)$, and $\tilde{K}^{AB}(\omega)$ for their Fourier transforms. With regard to the spectral decomposition of $\tilde{C}^{AB}(\omega)$ and $\tilde{K}^{AB}(\omega)$ we note that it is convenient to write $p_n = f(E_n)$. We can simplify these expressions by interchanging the dummy indexes n,m in the second term. Thus we get

$$\begin{aligned} \tilde{C}^{AB}(\omega) &= \frac{1}{2}\sum_{n,m}(f(E_n) + f(E_m))\,A_{nm}B_{mn}\,2\pi\delta\left(\omega - \frac{E_m - E_n}{\hbar}\right) && (11.37)\\ \tilde{K}^{AB}(\omega) &= i\omega\sum_{n,m}\frac{f(E_n) - f(E_m)}{E_m - E_n}\,A_{nm}B_{mn}\,2\pi\delta\left(\omega - \frac{E_m - E_n}{\hbar}\right) && (11.38) \end{aligned}$$

Note that for a canonical state $f(E_n) - f(E_m) = \tanh((E_n - E_m)/(2T)) \times (f(E_n) + f(E_m))$. Note also that in the expression for $\tilde{K}^{AB}(\omega)$, the ω cancels the $E_m - E_n$ denominator. The reason for pulling ω out of the sum is to emphasize the low frequency dependence.

[11.7] Reciprocity relations and detailed balance

There are some reciprocity relations that should be noticed. First we note that by definition $S^{AB}(t) = \left[S^{BA}(-t)\right]^*$. In practice it is more illuminating to write the FTed version of this reciprocity relation, which can be directly deduced by inspection of the spectral decomposition. Namely,

$$\tilde{S}^{AB}(\omega) \ = \ \left[\tilde{S}^{BA}(\omega)\right]^* \tag{11.39}$$

It follows that $\tilde{C}^{AB}(\omega) = \left[\tilde{C}^{BA}(\omega)\right]^*$, while $\tilde{K}^{AB}(\omega) = -\left[\tilde{K}^{BA}(\omega)\right]^*$. There is a second reciprocity relation that follows from time reversal invariace. Also here it is simpler to look on the spectral decomposition and to remember that $[A_{n,m}]^* = A_{n^*,m^*}$, where n^* and m^* are the eigenstates of the time reversed Hamiltonian. In practical terms it means that one has to reverse the sign of the magnetic field h. Consequently $\left[\tilde{S}^{BA}(\omega;h)\right]^* = [\pm]\tilde{S}^{BA}(\omega;-h)$, where the plus (minus) applies if the signs of A and B transform (not) in the same way under time reversal. Combining with the trivial reciprocity relation we get the Onsager reciprocity relation

$$\tilde{S}^{AB}(\omega;h) \ = \ [\pm] \ \tilde{S}^{BA}(\omega;-h) \tag{11.40}$$

The Kubo formula that we discuss in the next section implies that the same reciprocity relations hold for the response kernel α^{kj}, to the susceptibility χ^{kj} and to the DC conductance $\boldsymbol{G}^{kj}$. These are called Onsager reciprocity relations

Finally, we can also generalize what we called the "detailed balance relation". In the quantum context this is a relation between "positive" and "negative" frequencies. Assuming that the system is prepared in a canonical state we have

$$\tilde{S}_T^{AB}(-\omega) \ = \ \exp\left(-\frac{\hbar\omega}{T}\right) \ \tilde{S}_T^{BA}(\omega) \tag{11.41}$$

From here it follows that

$$\tilde{K}_T^{AB}(\omega) \ = \ i\,\frac{2}{\hbar}\tanh\left(\frac{\hbar\omega}{2T}\right) \ \tilde{C}_T^{AB}(\omega) \qquad \text{[quantum canonical version]} \tag{11.42}$$

In the classical limit this relation takes the form

$$K_T^{AB}(t) \ = \ -\frac{1}{T}\,\dot{C}_T^{AB}(t) \qquad \text{[classical canonical version]} \tag{11.43}$$

where the dot indicates time derivative.

The Kubo formula that we discuss in the next section is expressed using $\tilde{K}^{AB}(t)$. But it is more convenient to use $\tilde{C}^{AB}(t)$. The canonical relation between the two is the basis for the Fluctuation-Dissipation relation.

[12] Linear response theory

[12.1] The notion of linear response

Let us assume that $X(t)$ is an input signal, while $F(t)$ is the output signal of some black box. Linear response means that the two are related by

$$F(t) \quad = \quad \int_{-\infty}^{\infty} \alpha(t-t')\; X(t')\; dt' \tag{12.1}$$

The response kernel $\alpha(t-t_0)$ can be interpreted as the output signal that follows a $\delta(t-t_0)$ input signal. We assume a causal relationship, meaning that $\alpha(\tau)=0$ for $\tau<0$. The linear relation above can be written in terms of Fourier components as:

$$F_\omega \quad = \quad \chi(\omega)\; X_\omega \tag{12.2}$$

where $\chi(\omega)$ is called the generalized susceptibility. Because of causality $\chi(\omega)$ is analytic in the upper complex plane. Consequently its real and imaginary parts are inter-related by the Hilbert transform:

$$\mathrm{Re}[\chi(\omega)] \quad = \quad \int_{-\infty}^{\infty} \frac{\mathrm{Im}[\chi(\omega')]}{\omega'-\omega}\;\frac{d\omega'}{\pi} \tag{12.3}$$

(the reverse Hilbert transform goes with an opposite sign). The imaginary part of $\chi(\omega)$ is the sine transforms of $\alpha(\tau)$, and therefore it is proportional to ω for small frequencies. Consequently it is useful to define

$$\chi_0(\omega) \quad \equiv \quad \mathrm{Re}[\chi(\omega)] \quad = \quad \int_0^{\infty} \alpha(\tau)\cos(\omega\tau)d\tau \quad \sim \quad \int_0^{\infty} \alpha(\tau)d\tau \tag{12.4}$$

$$\eta(\omega) \quad \equiv \quad \frac{\mathrm{Im}[\chi(\omega)]}{\omega} \quad = \quad \int_0^{\infty} \alpha(\tau)\frac{\sin(\omega\tau)}{\omega}d\tau \quad \sim \quad \int_0^{\infty} \alpha(\tau)\;\tau d\tau \tag{12.5}$$

The asymptotic expressions apply for small frequencies: in this "DC driving" limit one can regard χ_0 and $\eta=\eta_0$ as constants. Accordingly for small frequencies we write

$$F_\omega \quad = \quad [\chi_0(\omega)+i\omega\eta(\omega)]\;X_\omega \quad \approx \quad \chi_0\;X_\omega\;-\eta_0\;\dot{X}_\omega \tag{12.6}$$

which implies in time domain $F(t) \quad = \quad \chi_0 X - \eta_0\dot{X}$.

[12.2] Rate of energy absorption

Back to Physics, what we called above X is the deviation of a control parameter from a reference value, namely $X-X_{\mathrm{eq}}$, and what we called F is the deviation from the corresponding equilibrium value, namely, $F(t)=\langle\mathcal{F}\rangle_t-\langle\mathcal{F}\rangle_{\mathrm{eq}}$. In the "DC regime" of small frequencies we regard χ_0 and η_0 as constants, and deduce that

$$\langle\mathcal{F}\rangle_t \quad = \quad \langle\mathcal{F}\rangle_{\mathrm{eq}}\;+\chi_0\;(X-X_{\mathrm{eq}})\;-\eta_0\dot{X} \quad = \quad \langle\mathcal{F}\rangle_X\;-\eta_0\dot{X} \tag{12.7}$$

where $\langle\mathcal{F}\rangle_X$ is the canonical X-dependent expectation value. Thus, the in-phase response gives the conservative effect, while the out-of-phase response gives the dissipative term. The latter is responsible to the irreversible work as discussed in the "Work" section. The rate of dissipation is $\dot{\mathcal{W}}=\eta_0\dot{X}^2$.

The above considerations regarding dissipation can be generalized to a source that has a wide power spectrum ("AC driving"). The irreversible work equals the time integral over $F(t)\dot{X}$, and hence to the integral over $F_\omega\dot{X}_\omega$.

Assuming linear response we get an integral over $\eta(\omega)\dot{X}_\omega^2$. Note that in the context of electrical engineering $X(t)$ might represent magnetic flux, hence $\dot{X}_\omega$ are the Fourier components of the voltage. For a stationary driving source $\dot{X}_\omega^2$ is proportional to the measurement time and is characterized by a power spectrum $\tilde{S}_{\dot{X}}(\omega)$. Consequently the rate of energy absorption is

$$\dot{\mathcal{W}} \ = \ \int_{-\infty}^{\infty} \eta(\omega)\ \tilde{S}_{\dot{X}}(\omega)\ \frac{d\omega}{2\pi} \ \equiv \ \bar{\eta}_{AC}\ \mathrm{RMS}[\dot{X}]^2 \tag{12.8}$$

Possibly it is more transparent to consider a pure AC source that has a definite frequency Ω. In such a case we write

$$X(t) \ = \ \mathrm{Re}\Big[A\mathrm{e}^{-i\Omega t}\Big] \tag{12.9}$$

$$F(t) \ = \ \mathrm{Re}\Big[\chi(\Omega)\ A\mathrm{e}^{-i\Omega t}\Big] \ = \ \chi_0(\Omega)X - \eta(\Omega)\dot{X} \tag{12.10}$$

$$\dot{\mathcal{W}} \ = \ \langle -\dot{X}\mathcal{F}\rangle_t \ = \ \eta(\Omega) \times (1/2)[A\Omega]^2, \qquad \text{[averaged over cycle]} \tag{12.11}$$

Note again that only the out-of-phase response gives dissipation, and that $A\Omega/\sqrt{2}$ is the RMS value of sinusoidal driving.

[12.3] LRT with several variables

Commonly the Hamiltonian $\mathcal{H}(\boldsymbol{r},\boldsymbol{p};\ X_1, X_2, X_3)$ depends on several control parameters. Then we can define generalized forces in the usual way:

$$\mathcal{F}^k \ = \ -\frac{\partial \mathcal{H}}{\partial X_k} \tag{12.12}$$

Below X_j represent a small deviation from some reference value $X = X_{\mathrm{eq}} \equiv 0$. The postulated linear-response relation due to small $X(t)$ variation is written as

$$\langle \mathcal{F}^k \rangle_t \ = \ \sum_j \int_{-\infty}^{\infty} \alpha^{kj}(t-t')\ X_j(t')dt' \tag{12.13}$$

The low frequency limit of the linear relation between the generalized forces and the *rate* of the driving can be regarded as a generalized Ohm law that includes an additional "geometric" term. Disregarding the conservative contribution and changing notation for the dissipation coefficient the one parameter version $\langle \mathcal{F} \rangle = -G\dot{X}$ is generalized as follows:

$$\langle \mathcal{F}^k \rangle \ = \ -\sum_j \boldsymbol{G}^{kj}\ \dot{X}_j \ = \ -\sum_j \boldsymbol{\eta}^{kj}\ \dot{X}_j - \sum_j \boldsymbol{B}^{kj}\ \dot{X}_j \tag{12.14}$$

where $\boldsymbol{\eta}^{kj}$ and $\boldsymbol{B}^{kj}$ are the symmetric and anti-symmetric parts of $\boldsymbol{G}^{kj}$. In an abstract notation this formula can be written as follows:

$$\langle \mathcal{F} \rangle \ = \ -\boldsymbol{\eta}\dot{\boldsymbol{X}} - \boldsymbol{B} \wedge \dot{\boldsymbol{X}} \tag{12.15}$$

Note that second term is analogous to a magnetic Lorentz force. Later we shall see that it can be derived form the theory of adiabatic processes, where it can be expressed as a "rotor" of the Berry connection $\boldsymbol{A}$. The derivation of the first term requires the larger perspective of the Kubo formula which we discuss in the next section. It is the first term that is responsible for dissipation. Namely, the rate of dissipation is given by

$$\dot{\mathcal{W}} \ = \ -\sum_k \langle \mathcal{F}^k \rangle \dot{X}_k \ = \ \sum_{k,j} \boldsymbol{\eta}_{kj} \dot{X}_k \dot{X}_j \tag{12.16}$$

[12.4] The Kubo formula

The Kubo formula is an expression for the response kernel that relates the expectation value $\langle A\rangle_t = \mathsf{trace}(A\rho(t))$ of some observable A to driving field $f(t)$, where the driving term in the Hamiltonian $-f(t)B$ involves the operator B.

$$\alpha^{AB}(t) \;=\; \Theta(t)\,\left\langle \frac{i}{\hbar}\Big[A(t),B\Big]\right\rangle \;\equiv\; \Theta(t)\;K^{AB}(t) \qquad \text{[Kubo formula]} \tag{12.17}$$

The formula has a good classical limit, and has various derivations. See "Lecture notes in quantum mechanics". One option is to deduce $\langle A\rangle_t$ from the time evolution of the probability matrix $\rho(t)$. Another way is to regard the Kubo formula as the interaction picture version of the "rate of change formula". Namely, the rate of change of the expectation value of A is determined by the expectation value of the commutator $[\mathcal{H},A]$, hence in the interaction picture it is related to $[B,A]$.

Yet there is a very simple way to derive the Kubo formula in "one line". Assume that the system is prepared in a stationary state of $\mathcal{H}_0$, and that we provide a pulse $f(t)=\lambda\delta(t)$ at $t=0$. Accordingly the evolution operator after time t is is $U(t)=\exp(-i\mathcal{H}_0 t)\exp(i\lambda B)$. Below we use the notation $A(t)=\mathrm{e}^{i\mathcal{H}_0 t}A\mathrm{e}^{-i\mathcal{H}_0 t}$. By definition $\alpha(t)$ is the first-order approximation for the response to this pulse, accordingly we get

$$\langle A\rangle_t \;=\; \langle U(t)^{\dagger}AU(t)\rangle_{t=0} \;=\; \langle \mathrm{e}^{-i\lambda B}A(t)\mathrm{e}^{+i\lambda B}\rangle_{t=0} \;=\; \langle A\rangle_{t=0} \;+ i\lambda\langle[A(t),B]\rangle_{t=0} \tag{12.18}$$

From here the Kubo formula follows. Note that t=0 refers here to the moment that precedes the delta perturbation, at which the state of system is assumed to be *stationary*, possibly a canonical equilibrium. By default the subscript is omitted in the final result.

[12.5] Memory and Sensitivity

The so called out-of-time-order correlator (OTOC) of operators A and B is defined as follows:

$$K^{ABAB}(t) \;=\; \Big\langle [A(t),B]^{\dagger}[A(t),B]\Big\rangle \tag{12.19}$$

In order to understand its significance let us write the this correlator and the Kubo correlator for a classical particle, with the substitutions $A=x$ and $B=p$.

$$K^{AB}(t) \;=\; -\Big\langle [x(t),p]_{\mathrm{PB}}\Big\rangle \tag{12.20}$$

$$K^{ABAB}(t) \;=\; \Big\langle \Big|[x(t),p]_{\mathrm{PB}}\Big|^2\Big\rangle \tag{12.21}$$

An infinitesimal perturbation at $t=0$ shifts the initial position of the particle a distance $\lambda=\delta x$, and consequently $x(t)=x(0)-\lambda[x(t),p]_{\mathrm{PB}}$. By definition the Kubo response kernel reflects the memory for the perturbation of the initial conditions, namely $K^{AB}(t)=(1/\lambda)\,\langle\delta x(t)\rangle$. In contrast to that, the the OTOC reflects the sensitivity for the perturbation of the initial conditions. For chaotic system we have $|\delta x(t)|\sim\delta x(0)e^{\gamma t}$, where γ is known as the Lyapunov exponent. Accordingly $K^{ABAB}(t)=(1/\lambda^2)\,\big\langle|\delta x(t)|^2\big\rangle$ reflect the exponential sensitivity of the system to any small perturbation of the initial conditions. The quantum mechanical version of the OTOC in general suppresses this sensitivity.

[12.6] The Onsager regression formula

A related deduction of the Kubo formula is based on the analysis of a "quench process". We assume that a system is described by the Hamiltonian $\mathcal{H}_\lambda=\mathcal{H}_0-\lambda B$. For example B might be the volume of the gas, and then the conjugate field λ is the applied pressure. At $t=0$ the field λ is instantly turned off, such that the dynamics for $t>0$ is described by the unperturbed Hamiltonian $\mathcal{H}_0$. In the lecture regrading generalized forces it has been shown that the compressibility equals $\mathrm{Var}(B)/T$. This means that the expectation value $\langle B\rangle_t$ should decay from $\langle B\rangle_\lambda$ to $\langle B\rangle_0$, where

$$\langle B\rangle_\lambda \ = \ \langle B\rangle_0 \ + \lambda\frac{1}{T}\mathrm{Var}(B) \tag{12.22}$$

Here we repeat essentially the same calculation, but in the context of a time dependent scenario, considering an arbitrary observable A. Not caring about commutation relations ("classical limit") we get

$$\langle A\rangle_t \ = \ \mathsf{trace}\left[A\rho(t)\right] \ = \ \mathsf{trace}\left[A\ \mathrm{e}^{-i\mathcal{H}_0 t}\rho(0)\mathrm{e}^{i\mathcal{H}_0 t}\right] \ = \ \mathsf{trace}\left[A(t)\ \rho(t{=}0)\right] \tag{12.23}$$

$$= \ \frac{\mathsf{trace}\left[A(t)\exp\left(-\beta\mathcal{H}_\lambda\right)\right]}{\mathsf{trace}\left[\exp\left(-\beta\mathcal{H}_\lambda\right)\right]} \ = \ \langle A(t)\rangle_0 + \beta\lambda\Big[\langle A(t)B\rangle_0 - \langle A(t)\rangle_0\langle B\rangle_0\Big] \ + \ \text{higher orders} \tag{12.24}$$

Note that here the subscript "0" does not mean t=0, but λ=0. Initially we have $\langle A\rangle_{t=0} = \langle A\rangle_\lambda$, while after a long time the unperturbed equilibrium value is restored, namely, $\langle A\rangle_{t=\infty} = \langle A(t)\rangle_0 = \langle A\rangle_0$. Neglecting the higher orders terms the linear-response result is

$$\langle A\rangle_t \ = \ \langle A\rangle_0 \ + \lambda\frac{1}{T}C^{AB}(t) \qquad [f(t) \text{ is a step function}] \tag{12.25}$$

We see that the re-equilibration mimics the decay of the pertinent correlation function. This can be regarded as a formal way to justify the "Onsager regression hypothesis" (see later). From here we can derive the classical version of the Kubo formula. We simply have to notice that the response for a "delta pulse" is simply the derivative of the response for a "step function". Accordingly

$$\langle A\rangle_t \ = \ \langle A\rangle_0 \ - \lambda\frac{1}{T}\dot{C}^{AB}(t) \qquad [f(t) \text{ is a delta pulse}] \tag{12.26}$$

Using the relation $K(\tau) = -(1/T)\dot{C}(\tau)$, that has been derived in the lecture regarding fluctuations, we deduce the Kubo formula.

[12.7] The Onsager regression hypothesis

The Onsager regression hypothesis states that "the average regression of fluctuations should obey the same laws as the corresponding irreversible process". The regression scenario is defined as follows. We allow the system to equilibrate in the presence of an applied field. Then we turn off the field, and watch the time dependence of some observable. We already demonstrated that the Onsager regression hypothesis can be deduced in the classical limit via first order-perturbation theory treatment of the response. The quantum generalization of the Onsager regression formula is known as the fluctuation-dissipation relation, to be discussed in the next lecture.

The "regression formula" describes the relaxation of the system back to equilibrium. Consider the case of having one fluctuating variable A. If we assume that its relaxation obeys an exponential decay law $\dot{A} = -\gamma A$, then we can deduce that the rate of relaxation is

$$\gamma \ = \ -\left.\frac{\dot{A}}{A}\right|_{t=0} \ = \ -\frac{\dot{C}(0)}{C(0)} \tag{12.27}$$

In the next section we describe the departure from equilibrium with a scaled variable $X_A = A/C(0)$, and write the relaxation as $\dot{A} = -\gamma_{AA}X_A$ with $\gamma_{AA} = -\dot{C}(0)$. Then, for several variables, it would be possible to get a generalized formula $\gamma_{ij} = -\dot{C}_{ij}(0)$ with a reciprocal relation between γ_{ij} and γ_{ji}.

[12.8] Onsager reciprocity

Within the Hamiltonian framework the Onsager reciprocity is the statement that response coefficients obey relations of the type $G^{AB}(h) = G^{BA}(-h)$, where h is the magnetic field. This follows from the observation that they are related to cross-correlation functions that obey reciprocity as discussed in previous lecture. Below we provide a more general perspective of Onsager reciprocity, which is *not* based on Hamiltonian formulation, and hence can be applied to a wider range of problems in thermodynamics. We no longer assume the canonical Boltzmann ensemble. Instead we assume that the probability of a "configuration" is given by

$$p(\varphi_1, \varphi_2, ...) \quad \propto \quad \mathrm{e}^{-\mathcal{A}(\varphi_1,\varphi_2,...)} \tag{12.28}$$

For example the φ_j might represent a set of chemical reaction coordinates. Or it can stand for the amount of energy that is transferred from one body to another body. For an isolated system that is described by a microcanonical ensemble the function $\mathcal{A}(\varphi)$ is the Boltzmann entropy of a given configuration. For a system in contact with a heat bath that is described by a canonical ensemble $\mathcal{A}(\varphi) = \beta F(\varphi)$, where F is the Helmholtz function.

We use the convention that $\varphi = 0$ is the most probable value if there are no constraints nor additional fields. We assume that the deviations from equilibrium are small, such that $\mathcal{A}(\varphi)$ can approximate by a quadratic expression:

$$\mathcal{A}(\varphi) \quad = \quad \frac{1}{2}\sum_{ij} A_{ij}\ \varphi_i\varphi_j \tag{12.29}$$

As for the temporal aspect we assume that the fluctuations are characterized by some correlation function:

$$C_{ij}(t) \quad = \quad \langle \varphi_i(t)\varphi_j(0)\rangle \tag{12.30}$$

The A_{ij} determines the correlations $C_{ij}(0) = \langle \varphi_i\varphi_j\rangle = (A^{-1})_{i,j}$, but give no information on the temporal aspect. At this point it is convenient to define conjugate variables $X_k = -\partial_k\mathcal{A} = -\sum_i A_{kj}\varphi_j$, which are like restoring forces, and to realize that $\langle X_k\varphi_j\rangle = -\delta_{k,j}$. Next we assume that the relaxation of the system is described by a linear relation that reflects the tendency of the system to restore equilibrium

$$\dot{\varphi}_i \quad = \quad \sum_k \gamma_{ik}\ X_k \qquad\qquad \text{[which implies } \dot{\varphi} = \gamma A\varphi \text{ where both } A \text{ and } \gamma \text{ are "nice" matrices]} \tag{12.31}$$

From here it follows that $\langle \dot{\varphi}_i\varphi_j\rangle = -\gamma_{ij}$. Thus, as expected, we can derive response coefficients from correlation functions

$$\gamma_{ij} \quad = \quad -\dot{C}_{ij}(\tau = 0) \tag{12.32}$$

Note that the absence of the $1/T$ prefactor is because we defined the conjugate variables not from the Hamiltonian but from the "Action". The Onsager reciprocity relation follows automatically from the symmetry of the correlation function. In the absence of magnetic field, assuming time-reversible dynamics, we have $C_{ij}(\tau) = C_{ij}(-\tau)$, and hence $\gamma_{ij} = \gamma_{ji}$. A non-trivial example for the Onsager reciprocity relation is discussed with regard to the thermo-electric effect in the kinetic theory lecture.

[12.9] The Kubo formula for AC/DC driving

The DC value of the dissipation coefficient is obtained by integration:

$$\eta^{AB}\ \text{[DC limit]} \quad = \quad \int_0^\infty K^{AB}(\tau)\ \tau d\tau \tag{12.33}$$

More generally, an expression for the generalized susceptibility follows from the convolution theorem:

$$\chi^{AB}(\omega) \quad \equiv \quad \mathrm{FT}\Big[\alpha^{AB}(\tau)\Big] \quad = \quad \int_{-\infty}^{\infty} \frac{i\tilde{K}^{AB}(\omega')}{\omega - \omega' + i0}\ \frac{d\omega'}{2\pi} \tag{12.34}$$

Of particular interest is the case where $A = B$ is a generalized force that is conjugate to the variation of some parameter X such that $f(t) = (X(t) - X_0)$. This is the case of interest in the study of friction (where $\dot{f}$ is the displacement velocity) and in the study of electrical conductance (where $\dot{f}$ is the electromotive field). From the definition it follows that $K(-\tau) = -K(\tau)$, hence $K(\omega)$ is pure imaginary, and consequently the friction coefficient is

$$\eta(\omega) \equiv \frac{\mathrm{Im}[\chi(\omega)]}{\omega} = \frac{1}{i2\omega}\tilde{K}(\omega) \qquad \text{[Kubo formula for the dissipation coefficient]} \qquad (12.35)$$

[12.10] The Kubo formula - FGR version

So far we have used versions of the Kubo formula that are "good" both classically and quantum mechanically. In the quantum case one can write a version of this formula that involves the non-symmetrized correlation function:

$$\eta(\omega) = \frac{1}{2\hbar\omega}\left[\tilde{S}(\omega) - \tilde{S}(-\omega)\right] \qquad \text{[Quantum FGR version of the Kubo formula]} \qquad (12.36)$$

This expression can be deduced directly from the FGR picture as follows. Assume that $\mathcal{H}_{\text{driving}} = -f(t)B$ with $f(t) = f_0 \sin(\Omega t)$. From the FGR it follows that the rate of energy absorption due to upward transitions is $(f_0/2)^2\tilde{S}(\Omega)\Omega$. Similarly the rate of energy emission is $(f_0/2)^2\tilde{S}(-\Omega)\Omega$. The net rate of heating is the difference. By definition it is written as $\dot{\mathcal{W}} = \eta(\Omega)\overline{[\dot{f}^2]}$, where $\overline{[\dot{f}^2]} = (1/2)[f_0\Omega]^2$. Hence one deduce the above expression for η.

Below we discuss the non-trivial generalization of the Kubo linear response formalism for the case of Hamiltonian that depends on several parameters. We start with the dissipation-less quantum adiabatic limit, and continue with the full linear response analysis.

[12.11] Adiabatic response

For an extended presentation see "Lecture notes in quantum mechanics". Given an Hamiltonian $\mathcal{H}(\boldsymbol{r}, \boldsymbol{p};\ X_1, X_2, X_3)$ that depends on several control parameters, we find the *zero order* adiabatic basis $|n(X)\rangle$ with eigenenergies $E_n(X)$. Then, for a given level, we define in parameter space the "Christoffel symbols" that are known in this context as "Berry connection", and the associated "curvature field" as follows:

$$\boldsymbol{A}^j_{nm} = i\hbar\left\langle n(X)\left|\frac{\partial}{\partial X_j}m(X)\right.\right\rangle \qquad (12.37)$$

$$\boldsymbol{B}^{ij}_n = \partial_i\boldsymbol{A}^j_n - \partial_j\boldsymbol{A}^i_n \qquad (12.38)$$

We use the notation $\boldsymbol{A}^j_n = \boldsymbol{A}^j_{nn}$, and note the following identities:

$$\boldsymbol{A}^j_{nm} = \frac{-i\hbar\mathcal{F}^j_{mn}}{E_m - E_n} \qquad [n \neq m] \qquad (12.39)$$

$$\boldsymbol{B}^{ij}_n = \sum_{m(\neq n)} \frac{2\hbar\mathrm{Im}\left[\mathcal{F}^i_{nm}\mathcal{F}^j_{mn}\right]}{(E_m - E_n)^2} \qquad (12.40)$$

If we have 3 control variables it is convenient to use notations suggesting that we can formally regard $\boldsymbol{A}_n$ as a vector potential whose rotor $\boldsymbol{B}_n$ is formally like a magnetic field:

$$\boldsymbol{X} \longmapsto (X_1, X_2, X_3) \qquad (12.41)$$

$$\boldsymbol{A} \longmapsto (A^1_{nn}, A^2_{nn}, A^3_{nn}) \qquad (12.42)$$

$$\boldsymbol{B} \longmapsto (B^{23}, B^{31}, B^{12}) \qquad (12.43)$$

With the above definitions the Schrodinger equation can be written as follows:

$$\frac{d}{dt}|\psi\rangle \ = \ -\frac{i}{\hbar}\mathcal{H}(X(t))\ |\psi\rangle \tag{12.44}$$

We expand the state in the *zero order* adiabatic basis

$$|\psi(t)\rangle \ = \ \sum_n a_n(t)\ |n(X(t))\rangle \tag{12.45}$$

and get the equation

$$\frac{da_n}{dt} = -\frac{i}{\hbar}(E_n - \dot{X}\cdot \boldsymbol{A}_n)a_n - \frac{i}{\hbar}\sum_m \boldsymbol{W}_{nm}a_m \tag{12.46}$$

where

$$\boldsymbol{W}_{nm} \equiv -\sum_j \dot{X}_j \boldsymbol{A}^j_{nm} \qquad \text{for } n{\neq}m,\ \text{else zero} \tag{12.47}$$

It follows that the *first order* adiabatic state that is associated with the nth level is

$$|\psi(t)\rangle \ = \ |n(X(t))\rangle + \sum_{m\neq n}\frac{\boldsymbol{W}_{mn}}{E_n - E_m}|m(X(t))\rangle \tag{12.48}$$

Consequently the first order adiabatic response of a system that has been prepared in the nth adiabatic state is

$$\langle \mathcal{F}^k\rangle \ = \ -\sum_j \boldsymbol{B}^{kj}_n\ \dot{X}_j \ = \ -\boldsymbol{B}\wedge\dot{\boldsymbol{X}} \tag{12.49}$$

We shall explain in the next section that this corresponds to the geometric part of the response in the Kubo formula. The Kubo formula contains an additional non-adiabatic (dissipative) term that reflects FGR transitions between levels.

====== [12.12] Low frequency response

Here we go beyond adiabatic response and discuss both the adiabatic and dissipative terms that are implied by the Kubo formula. Recall that the Kubo expression for the response kernel is $\alpha^{kj}(\tau) = \Theta(\tau)\ K^{kj}(\tau)$, whose Fourier transform is the generalized susceptibility:

$$\chi^{kj}(\omega) \ = \ \int_{-\infty}^{\infty}\frac{i\tilde{K}^{kj}(\omega')}{\omega-\omega'+i0}\ \frac{d\omega'}{2\pi} \tag{12.50}$$

Taking into account that $\mathrm{Re}[\chi^{kj}(\omega)]$ is symmetric with respect to ω we have

$$\boldsymbol{G}^{kj} \ = \ \lim_{\omega\to 0}\frac{\mathrm{Im}[\chi^{kj}(\omega)]}{\omega} \ = \ \lim_{\omega\to 0}\frac{d}{d\omega}\chi^{kj}(\omega) \ = \ \int_0^{\infty} K^{kj}(\tau)\tau d\tau \tag{12.51}$$

The last expression (in time domain) is mentioned for completeness. In practice it is more convenient to proceed in frequency domain. After some straightforward algebra we get

$$\boldsymbol{G}^{kj} \ = \ \frac{1}{2}\lim_{\omega\to 0}\frac{\mathrm{Im}[\tilde{K}^{kj}(\omega)]}{\omega} - \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\mathrm{Re}[\tilde{K}^{kj}(\omega)]}{\omega^2} \ \equiv \ \boldsymbol{\eta}^{kj} + \boldsymbol{B}^{kj} \tag{12.52}$$

We notice that $\boldsymbol{\eta}^{kj}$ is a symmetric matrix while $\boldsymbol{B}^{kj}$ is anti-symmetric. Hence in abstract notation the linear-response relation can be written as a generalized Ohm law:

$$\langle \mathcal{F}^k \rangle \;=\; -\sum_j \boldsymbol{G}^{kj}\;\dot{X}_j \;=\; -\boldsymbol{\eta}\dot{\boldsymbol{X}} - \boldsymbol{B}\wedge\dot{\boldsymbol{X}} \tag{12.53}$$

This is a generalization of the adiabatic response formula. The additional term takes into account the FGR non-adiabatic transitions between levels. To see clearly the connection we substitute the spectral decomposition of $\tilde{K}^{kj}(\omega)$ and get the following expressions:

$$\chi^{kj}(\omega) \;=\; \int_{-\infty}^{\infty}\frac{i\tilde{K}^{kj}(\omega')}{\omega-\omega'+i0}\,\frac{d\omega'}{2\pi} \;=\; \sum_n f(E_n)\sum_m\left(\frac{-\mathcal{F}^k_{nm}\mathcal{F}^j_{mn}}{\hbar\omega{-}(E_m{-}E_n){+}i0}+\frac{\mathcal{F}^j_{nm}\mathcal{F}^k_{mn}}{\hbar\omega{+}(E_m{-}E_n){+}i0}\right) \tag{12.54}$$

and

$$\boldsymbol{\eta}^{kj} \;=\; \frac{1}{2}\lim_{\omega\to0}\frac{\mathrm{Im}[\tilde{K}^{kj}(\omega)]}{\omega} \;=\; -\pi\hbar\sum_{n,m}\frac{f(E_n)-f(E_m)}{E_n-E_m}\mathcal{F}^k_{nm}\mathcal{F}^j_{mn}\delta(E_m-E_n) \tag{12.55}$$

$$\boldsymbol{B}^{kj} \;=\; -\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\mathrm{Re}[\tilde{K}^{kj}(\omega)]}{\omega^2} \;=\; \sum_{n,m}(f(E_n)-f(E_m))\frac{-i\hbar\mathcal{F}^k_{nm}\mathcal{F}^j_{mn}}{(E_m-E_n)^2} \tag{12.56}$$

The Re[] and Im[] are not required because the doubles summation cares for that. The expression for $\boldsymbol{B}^{kj}$ can be written in a way that better emphasize the relation to the analysis of the adiabatic response:

$$\boldsymbol{B}^{kj} \;=\; \sum_n f(E_n)\sum_{m(\neq n)}\frac{2\hbar\mathrm{Im}\left[\mathcal{F}^k_{nm}\mathcal{F}^j_{mn}\right]}{(E_m{-}E_n)^2} \;=\; \sum_n f(E_n)\boldsymbol{B}^{kj}_n \tag{12.57}$$

[13] The fluctuation dissipation relation

[13.1] General formulation

The essence of the fluctuation dissipation relation (FDR) is to relate the response of a system to its fluctuations in equilibrium. In order to derive this relation we have to supply information on the preparation of the system, which is typically assumed to be canonical. In the classical context there is a useful microcanonical version from which the canonical version can be derived. The formal derivation of the FDR is based on the generalized detailed balance relation that allows to express $\tilde{K}^{kj}(\omega)$ using $\tilde{C}^{kj}(\omega)$.

We first consider what we call "the AC version" of the FDR. For simplicity we consider the one-variable version: the driving term in the Hamiltonian is $-X(t)\mathcal{F}$, and our interest is in the observable $\mathcal{F}$ that is conjugated to the driving field X. Recall that $\tilde{K}(\omega)$ is imaginary, and $\text{Im}[\chi(\omega)] = [1/(2i)]\tilde{K}(\omega)$. Assuming canonical preparation the detailed balance relation implies that

$$\text{Im}[\chi(\omega)] \ = \ \frac{1}{\hbar}\tanh\left(\frac{\hbar\omega}{2T}\right)\ \tilde{C}^{\mathcal{F}\mathcal{F}}(\omega) \qquad \text{[FDR, the AC version]} \tag{13.1}$$

What we call "the DC version" of the FDR is obtained by taking the small ω limit of the AC version, which is formally equivalent to the classical limit (small $\hbar$). One deduces that the low frequency dissipation coefficient is relate to the equilibrium intensity of the fluctuations:

$$\eta \ = \ \frac{\nu_T}{2T}, \qquad \nu_T \ \equiv \ \int_{-\infty}^{\infty} \langle \mathcal{F}(\tau)\mathcal{F}(0)\rangle_T \ d\tau \qquad \text{[FDR, the DC version]} \tag{13.2}$$

Note that in the above writing we assume that the equilibrium value of the fluctuating force is $\langle \mathcal{F}\rangle = 0$, else $\mathcal{F}$ should be re-defined so as to have a zero average.

For completeness we also point out the multi-variable version of the FDR in the DC limit. Here we change notion and use G^{AB} for the generalized conductance. In the DC case we know from Kubo that G is an integral over $\tau K(\tau)$. In the classical treatment $K(\tau)$ is the derivative of $C(\tau)$, hence after integration by parts

$$G^{AB} \ = \ \frac{1}{T}\int_0^{\infty} C^{AB}(\tau)\ d\tau \qquad \text{[generalized FDR, classical DC version]} \tag{13.3}$$

Note that the (1/2) prefactor is absent, and that the integration is over positive τ, and that the cross-correlation function $C^{AB}(\tau)$ does not have to be symmetric in time. The asymmetry is responsible for the *geometric* part of the conductance matrix.

[13.2] The diffusion-dissipation picture

We can illuminate the physics of FD for DC driving using a simple diffusion-dissipation picture. We show below that the DC energy absorption rate is related to the induced diffusion in energy space. To simplify the presentation we use a classical language. We can deduce that the driving induce diffusion in energy space from the relation

$$E(t) - E(0) \ = \ -\dot{X}\int_0^t \mathcal{F}(t')dt' \tag{13.4}$$

leading to

$$\langle (E(t)-E(0))^2\rangle \ = \ \dot{X}^2\int_0^t\int_0^t \langle \mathcal{F}(t')\mathcal{F}(t'')\rangle dt'dt'' \tag{13.5}$$

where the averaging assumes a microcanonical preparation. Thus we get

$$\delta E^2(t) \;=\; 2D_E t \tag{13.6}$$

where the leading order estimate for the diffusion is

$$D_E \;=\; \frac{1}{2}\dot{X}^2 \int_{-\infty}^{\infty} \langle \mathcal{F}(\tau)\mathcal{F}(0)\rangle_E \, d\tau \;=\; \frac{1}{2}\nu_E \dot{X}^2 \tag{13.7}$$

On long times we assume that the probability distribution in the democratic variable $n = \mathcal{N}(E)$ satisfy a standard diffusion equation. Transforming to the non-democratic variable E we get

$$\frac{\partial \rho}{\partial t} \;=\; \frac{\partial}{\partial E}\left(\mathsf{g}(E) D_E \frac{\partial}{\partial E}\left(\frac{1}{\mathsf{g}(E)}\rho\right)\right) \tag{13.8}$$

where $\mathsf{g}(E)$ reflects the ratio between the proper phase-space measure dn and the distorted measure dE. For more details see [arXiv]. The energy of the system is $\langle \mathcal{H}\rangle = \int E\rho(E)dE$. Taking the time derivative and integrating by parts, it follows that the rate of energy absorption is

$$\dot{\mathcal{W}} \;=\; \frac{d}{dt}\langle \mathcal{H}\rangle = -\int_0^{\infty} dE \; \mathsf{g}(E) \; D_E \; \frac{\partial}{\partial E}\left(\frac{\rho(E)}{\mathsf{g}(E)}\right) \tag{13.9}$$

For a microcanonical preparation $\rho(E) = \delta(E - \mathcal{E})$. Substitution and integration by parts leads to

$$\dot{\mathcal{W}} \;=\; \frac{d}{dt}\langle \mathcal{H}\rangle \;=\; \frac{1}{\mathsf{g}(E)}\frac{d}{dE}\left[\mathsf{g}(E)\; D_E\right]\Big|_{E=\mathcal{E}} \tag{13.10}$$

By definition $\dot{\mathcal{W}} = \eta \dot{X}^2$ and $D_E = (1/2)\nu \dot{X}^2$. Consequently the diffusion-dissipation relation reduces immediately to the microcanonical version of the fluctuation-dissipation relation:

$$\eta \;=\; \frac{1}{2}\frac{1}{\mathsf{g}(E)}\frac{d}{dE}\left[\mathsf{g}(E)\nu_E\right] \tag{13.11}$$

The canonical version $\eta = \nu_T/(2T)$ can be derived from the integral expression for $\dot{\mathcal{W}}$, upon the substitution $\rho(E) = (1/Z)\mathsf{g}(E)\mathrm{e}^{-\beta E}$. Optionally it can be obtained from the microcanonical version by canonically averaging over E and performing integration by parts.

[13.3] The wall formula

The first prototype application of the FD relation is to the calculation of the friction in the Brownian motion problem. Consider a gas of particles in a box. The system is driven by moving in it a "spoon", or a "piston" or a "Brownian body".

- The parameter in $\mathcal{H}(X)$ represents the position of the spoon.
- The generalized force is the Newtonian force $\langle \mathcal{F}\rangle$ on the spoon.
- The DC linear response relation $\langle \mathcal{F}\rangle = -\eta \dot{X}$ describes friction.
- The dissipation rate is $\dot{\mathcal{W}} = \eta \dot{X}^2$.

Our purpose below is to find an expression for the friction coefficient η using the FD relation. For this purpose we have to calculate the intensity ν_T of the fluctuations of $\mathcal{F}$ at equilibrium, and to use the relation $\eta = \nu_T/(2T)$.

Due to random collisions of the gas particles, the Brownian body experiences a "random force" that can be written as the sum of short impulses:

$$F(t) \quad = \quad \sum_j 2\mathsf{m}v_j \; \delta(t-t_j) \tag{13.12}$$

Here t_j is the time of the jth collision with velocity v_j at the x direction. Note that $|v_j| \sim v_T$, where $v_T = (T/\mathsf{m})^{1/2}$ is the thermal velocity. The rate of collision for N particles is

$$\frac{1}{\tau_0} \quad = \quad N \times \left(\frac{\mathsf{A}}{L^2}\right) \times \frac{v_T}{L} \tag{13.13}$$

where L^3 is the volume of the box that holds the gas particles, and A is the effective area of the moving wall. Accordingly the intensity of fluctuations is

$$\nu_T \quad = \quad \tilde{C}(\omega = 0) \quad = \quad \frac{1}{\tau_0}(\mathsf{m}v_T)^2 \quad = \quad \mathsf{m}^2 v_T^3 \, \frac{N}{L^3} \, \mathsf{A} \tag{13.14}$$

and for the friction we get

$$\eta \quad = \quad \frac{1}{2T}\tilde{C}(\omega = 0) \quad = \quad \rho v_T \times A \tag{13.15}$$

where $\rho = (N/L^3)\mathsf{m}$ is the mass density of the gas particles.

We note that if the dynamics of the Brownian body is described by a Langevin equation, then $\nu/\eta = 2T$ implies that a canonical equilibrium is reached. For more details see the Langevin section. This was in fact the historical deduction of the FD relation by Einstein in the context of Brownian motion study.

If the Brownian particle is moving in an incompressible fluid the above result does not apply. Instead the friction is given by *Stokes Law* (see "Additional topics / The Kinetic picture / Viscosity"), and we can use the FD relation "in reverse" in order to deduce the intensity of fluctuations.

[13.4] The Drude formula

The second prototype application of the FD relation is to the calculation of electrical conductance. Here we show how to derive the Drude formula for a gas of classical particles in an EMF driven ring. For an extended discussion of electrical conductance see the "additional topics" section of the lecture notes.

We consider a ring driven by an electro-motive force (EMF). The interaction term originates from the kinetic term $[p-(e/L)\Phi(t)]^2/(2\mathsf{m})$, where Φ is the flux and $I = (e/L)v$ is the conjugate current. Optionally we can say that the interaction is $-A(t)v$, where $A(t)$ is the vector potential and the velocity v is the conjugate variable. Summarizing:

- The parameter in $\mathcal{H}(\Phi)$ represents the magnetic flux.
- The generalized force is the current $\langle \mathcal{I} \rangle$ in the ring.
- The rate in which the flux is varied determines the EMF $= -\dot{\Phi}$ by Faraday law.
- The DC linear response relation $\langle \mathcal{I} \rangle = G \times \text{EMF}$ is Ohm law.
- The dissipation rate $\dot{\mathcal{W}} = G\dot{\Phi}^2$ describes Joule heating.

Our purpose below is to find an expression for the conductance G using the FD relation. For this purpose, following Drude, we postulate what is the velocity-velocity correlation function; calculate the intensity ν_T of the fluctuations of $\mathcal{I}$ at equilibrium, and use the relation $G = \nu_T/(2T)$.

Following Drude we assume an exponential velocity-velocity correlation function with a time constant τ_0, and RMS velocity v_0, such that the mean free path is $\ell = v_0\tau_0$. Hence we deduce that $\tilde{C}_{vv}(\omega)$ is a Lorentzian. The displacement of the particle $(x(t)-x(0))$ is the integral over the velocity $v(t')$, hence the variance is $\langle (x(t)-x(0))^2\rangle = 2Dt$ where

$$D \;=\; \frac{1}{2}\tilde{C}_{vv}(0) \;=\; \frac{1}{3}v_0^2\tau_0 \qquad\qquad \text{(for a 3D sample)} \tag{13.16}$$

For a single particle the current operator is $I=(e/L)v$, hence the intensity of the fluctuations of the current is $\nu = [(e/L)^2]\,2D$. For N classical particles at thermal equilibrium we get $\nu_T = N\,[(e/L)^2]\,2D_T$, where D_T is calculated with the thermal velocity that is defined via $(1/2)\mathsf{m}v_T^2 = (3/2)T$. For N Fermions at low temperatures we get $\nu_T = N_T\,(e/L)^2\,2D_F$, where $N_T = T/\Delta$ is the effective number of participating electron at the Fermi energy. This result has been derived in the lecture about fluctuations. Here Δ is the mean level spacing at the Fermi energy. Note that $N=(2/3)(\epsilon_F/\Delta)$. The diffusion coefficient D_F is calculated with the Fermi velocity which is determined via $(1/2)\mathsf{m}v_F^2 = \epsilon_F$. Either way we get

$$\nu_T \;=\; N_{\text{eff}}\left(\frac{e}{L}\right)^2 2D_{\text{eff}} \;=\; 2\left[\frac{N}{L^2}\frac{e^2}{\mathsf{m}}\tau_0\right]T \tag{13.17}$$

and for the conductance we get

$$G^{[N]} \;=\; \frac{1}{2T}\nu_T \;=\; \frac{N}{L^2}\frac{e^2}{\mathsf{m}}\tau_0 \;\equiv\; \frac{\mathsf{A}}{L}\sigma \tag{13.18}$$

where A is the cross section of the ring. As a byproduct of this derivation we see clearly why the conductivity σ is related to the diffusion coefficient D.

Optionally the Drude expression can be written in a way that allows to make an association with the Landauer formula of mesoscopic physics. Considering zero temperature Fermi occupation:

$$G^{[N]} \;=\; e^2\left(\frac{N}{\mathsf{m}v_F L}\right)\frac{\ell}{L} \;\equiv\; \frac{e^2}{2\pi}\mathcal{M}\frac{\ell}{L} \tag{13.19}$$

where $\mathcal{M}$ corresponds to the effective number of open modes. There is a very simple toy model for which the "exponential" velocity-velocity correlation can be deduced, and hence ℓ/L can be evaluated analytically. Consider a ring with a single stochastic scatterer that has a transmission g. The current-current correlation function $C(t)=\langle I(t)I\rangle$ at given energy E can be calculated as detailed in [arXiv]. The procedure is to use the identity $\langle BA\rangle = \sum_a p_a\langle B\rangle_a a$, where where A and B are any two operators, and $\langle B\rangle_a$ is the expectation value of B given that $A=a$. Applying this rule in our case we get $\langle I(t)I\rangle = \sum_r p_r\langle I(t)\rangle_r I_r$, where $r=(x,v)$ labels all the possible states of the particle in the ring, and $I=ev\delta(x)$ is the current through the measurement point $x=0$. The current $\langle I(t)\rangle_{x,v}$, given that the particle has been launched at x with velocity v, can be written as a sum of pulses $\sum_j q_j\delta(t-t_j)$. If the measurement point $x=0$ is situated right across the barrier, such that the barrier is at $x=\pm L/2$, one obtains

$$C(t) \;=\; \frac{ev_E}{L}\langle I(t)\rangle_{0,v_E} \;=\; e^2\frac{v_E}{L}\sum_{n=-\infty}^{\infty}(2g-1)^{|n|}\,\delta\left(t-\left(\frac{L}{v_E}n\right)\right) \tag{13.20}$$

which exhibits exponential decay of correlations as in the Drude model. Assuming low temperature Fermi occupation, with $N_T = T/\Delta$ thermal particles, that occupy levels whose spacing is $\Delta = \pi v_F/L$, we use the FD relation $G=\nu_T/(2T)$ and get

$$G^{[N]} \;=\; \frac{1}{\Delta}\int_0^{\infty} C(t) \;=\; \frac{e^2}{2\pi}\left(\frac{g}{1-g}\right) \tag{13.21}$$

For small g one can neglect the $1-g$ denominator, and this formula becomes identical with the Landauer formula. For larger g the two formulas differ. The reason for this difference concerns the geometry: Here we consider the conductance of a barrier that is integrated into a closed ring, while Landauer concerns the conductance of a barrier that is connected to open reservoirs. In the latter case the particle cannot circulate multiple times via the barrier.

[13.5] Conductor in electric field

A straightforward generalization of the driven ring problem applies for an extended piece of metal that in placed in a time dependent electric field. The electric field is described by a vector potential such that $\mathcal{E} = -\dot{A}$. The interaction term in the Hamiltonian is an extended version of the simplified $-A(t)v$ that we have assumed in previous discussion:

$$\mathcal{H}_{\text{int}} \quad = \quad -\int J(x) \cdot A(x) \, d^3x \tag{13.22}$$

In linear response theory the current is proportional to the rate in which the parameters are being changed in time. Regarding the values of A at different points in space as independent parameters the postulated linear response relation takes the form

$$\langle J(x) \rangle = \int \boldsymbol{\sigma}(x,x') \; \mathcal{E}(x') \; d^3x \tag{13.23}$$

where $\boldsymbol{\sigma}_{ij}(x,x')$ is called the conductivity matrix. The FD relation states that the conductivity is proportional to the temporal FT of $\langle J_i(x,t) J_j(x',t') \rangle$ with respect to the time difference $\tau = t - t'$. The proportionality constant is $1/(2T)$ in the DC limit.

[13.6] Forced oscillator

Consider a particle that is (say) bounded to a spring. Let us assume that the motion of $x(t) \equiv \langle \hat{x} \rangle_t$ obeys the equation $\mathsf{m}\ddot{x} + \eta\dot{x} + \mathsf{m}\Omega^2 x = \mathcal{E}$, where the external driving is due to an interaction term $-\mathcal{E}(t)\hat{x}$. Accordingly,

- The parameter in $\mathcal{H}(\mathcal{E})$ represents an electric field.
- The generalized force is the polarization $\langle x \rangle$ of the particle.
- The AC linear response relation is $\langle x \rangle = \chi(\omega) \; \mathcal{E}$.

The FD relation implies that x has fluctuations at equilibrium, that are related to the susceptibility:

$$\tilde{C}_{xx}(\omega) \quad = \quad \hbar \coth\left(\frac{\hbar\omega}{2T}\right) \; \text{Im}\Big[\chi(\omega)\Big], \qquad\qquad \chi(\omega) \quad = \quad \frac{1}{-\mathsf{m}\omega^2 - i\eta\omega + \mathsf{m}\Omega^2} \tag{13.24}$$

Note that the fluctuations of the velocity are $\tilde{C}_{vv}(\omega) = \omega^2 \tilde{C}_{xx}(\omega)$. Integrating over ω we get $C_{xx}(0)$ and $C_{vv}(0)$, from which can deduce the average energy of the oscillator. The results are consistent with the canonical expectation in the limit of zero damping.

[13.7] Forced particle

The limit $\Omega \to 0$ of the forced harmonic oscillator corresponds formally to a Brownian particle. In the classical limit we get for the power spectrum of the velocity:

$$\tilde{C}_{vv}(\omega) \quad = \quad (T/\mathsf{m}) \times \frac{2(\eta/\mathsf{m})}{\omega^2 + (\eta/\mathsf{m})^2} \tag{13.25}$$

The area of this Lorentzian is $C_{vv}(0) = T/\mathsf{m}$, as expected from the canonical formalism. The corresponding velocity-velocity correlation is Drude type (exponential), with damping constant $\gamma = \eta/\mathsf{m}$. The integral over the velocity-velocity correlation function determines the diffusion coefficient, namely

$$D \quad = \quad \frac{1}{2}\tilde{C}_{vv}(0) \quad = \quad \frac{T}{\eta} \quad = \quad \mu T \tag{13.26}$$

This is known as the Einstein relation between D and the mobility $\mu = 1/\eta$. There is an optional shortcut in the application of the FD relation, that leads directly to the above Einstein relation. Let us write the electric field as $\mathcal{E} = -\dot{A}$. The interaction term is $-A(t)v$. Accordingly,

- The parameter in $\mathcal{H}(A)$ represents the vector potential.
- The generalized force is the velocity $\langle v \rangle$ of the particle.
- The DC linear response relation $\langle v \rangle = \mu \, \mathcal{E}$ describes drift motion.
- The dissipation rate $\dot{\mathcal{W}} = \mu \mathcal{E}^2$ describes Joule heating (per particle).

The FD relation in this notations implies that v has fluctuations at equilibrium, that are related to the mobility μ. The "intensity" of the velocity fluctuations is $2D$. Hence the classical FD relation implies that the ratio of the diffusion (D) to the mobility (μ) equals the temperature (T).

[13.8] Duality between friction and mobility

In the "Forced particle" problem we have considered interaction of the type $-\hat{x}F(t)$, and defined the mobility μ, which is the response of $\langle \hat{x} \rangle_t$ to the control field $F(t)$. In the "wall formula" problem we have considered interaction of the type $-x(t)\hat{F}$, and defined the friction coefficient η, which is the response of $\langle F \rangle_t$ to the control parameter $x(t)$. The two points of view on the system are dual, and with the standard definitions we have the identification $\mu = 1/\eta$.

[13.9] The fluctuations of an Ohmic system

Nyquist Noise.– The FD relation in the electrical context is known as Nyquist theorem. It can be used "in reverse" in order to deduce the Nyquist noise $\nu = 2GT$, provided G is known from experiment. It should be clear that in non-equilibrium conditions we might have extra fluctuations, which in this example are known as *shot noise*.

Ohmic response.– Sometimes it is convenient to characterize the system by its response, and from this to deduce the power spectrum of the fluctuations. So we regard $\tilde{K}(\omega)$ as the input. Inspired by jargon of electrical engineering, so-called Ohmic response is characterized by a dissipation coefficient η that is independent of ω up to some implicit high frequency cutoff ω_c. It follows that the DC intensity of the fluctuations is $\nu = 2\eta T$, and the associated spectral functions are:

$$\begin{aligned}
\tilde{K}_{\text{ohmic}}(\omega) &= i2\eta\omega && (13.27)\\
\tilde{C}_{\text{ohmic}}(\omega) &= \frac{\hbar}{2}\coth\left(\frac{\hbar\omega}{2T}\right)\text{Im}\left[\tilde{K}(\omega)\right] = \eta\hbar\omega\coth\left(\frac{\hbar\omega}{2T}\right) && (13.28)\\
\tilde{S}_{\text{ohmic}}(\omega) &= \tilde{C}_{\text{ohmic}}(\omega) - i\frac{\hbar}{2}\tilde{K}_{\text{ohmic}}(\omega) = 2\eta\frac{\hbar\omega}{1-\mathrm{e}^{-\hbar\omega/T}} && (13.29)
\end{aligned}$$

[13.10] The fluctuations of the potential in metals

The dielectric constant of a metal is defined via the linear relation between the total electrostatic potential U_{total} and an external test charge density ρ_{ext}

$$U_{\text{total}} = \frac{1}{\varepsilon(q,\omega)}\left(\frac{4\pi e^2}{q^2}\right)\rho_{\text{ext}} \qquad (13.30)$$

For simplicity we relate here and below to one component q of the fields. The total electrostatic potential is the sum of the external potential $U_{\text{ext}} = (4\pi e^2/q^2)\rho_{\text{ext}}$, and the induced potential $U_{\text{elct}} = (4\pi e^2/q^2)\rho_{\text{elct}}$, where ρ_{elct} is the total density of the electrons. The dielectric constant can be deduced from the equations of motion $\partial\rho_{\text{elct}}/\partial t = -\nabla J$ with $J = -(\sigma/e^2)\nabla U_{\text{total}} - D\nabla\rho_{\text{elct}}$ that leads to the relation

$$\rho_{\text{elct}} = \frac{(\sigma/e^2)q^2}{i\omega - Dq^2}\, U_{\text{total}} \qquad (13.31)$$

and hence to $U_{\mathrm{total}} = (1/\varepsilon)U_{\mathrm{ext}}$, where

$$\varepsilon(q,\omega) = 1 - \frac{4\pi\sigma}{i\omega - Dq^2}. \tag{13.32}$$

Note that

$$\mathrm{Im}\left[\frac{-1}{\varepsilon(q,\omega)}\right] = \frac{4\pi\sigma\omega}{(Dq^2+4\pi\sigma)^2+\omega^2} \approx \frac{\omega}{4\pi\sigma} \tag{13.33}$$

The interaction between the electrons and an external electrostatic field is described by $\mathcal{H}_{\mathrm{ext}} = U_{\mathrm{ext}}\rho_{\mathrm{elct}}$ which can be also written as $\mathcal{H}_{\mathrm{ext}} = \rho_{\mathrm{ext}}U_{\mathrm{elct}}$. The fluctuation dissipation relation expresses $\tilde{S}^{[N]}(q,\omega)$ using the response function $\alpha(\boldsymbol{q},\omega)$ that relates U_{elct} to $-\rho_{\mathrm{ext}}$ which is

$$\alpha(\boldsymbol{q},\omega) = \frac{4\pi e^2}{\boldsymbol{q}^2}\left[1 - \frac{1}{\varepsilon(\boldsymbol{q},\omega)}\right] \tag{13.34}$$

Using the fluctuation dissipation relation

$$\tilde{S}^{[N]}(\boldsymbol{q},\omega) = \mathrm{Im}\Big[\alpha(\boldsymbol{q},\omega)\Big]\left(\frac{2}{1-\mathrm{e}^{-\omega/T}}\right) \tag{13.35}$$

we deduce

$$\tilde{S}^{[N]}(\boldsymbol{q},\omega) \approx \frac{e^2}{\sigma}\frac{1}{\boldsymbol{q}^2}\left(\frac{2\omega}{1-\mathrm{e}^{-\omega/T}}\right) \tag{13.36}$$

The Ohmic behavior is cut-off by $|\omega| \lesssim 1/\tau_c$ and $|\boldsymbol{q}| \lesssim 1/\ell$ where $\ell = v_{\mathrm{F}}\tau_c$ is the elastic mean free path, and v_{F} is the Fermi velocity. Recalling the Einstein relation $\sigma = e^2\nu D$, where $\nu = \Delta^{-1}/L^d$ is the density of states per unit volume, we can write this result more conveniently as follows:

$$\tilde{S}^{[N]}(\boldsymbol{q},\omega) \approx \frac{1}{\nu D\boldsymbol{q}^2}\left(\frac{2\omega}{1-\mathrm{e}^{-\omega/T}}\right) \tag{13.37}$$

Note that the electron charge e cancels out from this final result for the Nyquist noise spectrum. This well-known fact is due to the effects of screening: A larger value of the charge would be canceled by a correspondingly stronger suppression of density fluctuations.

System interacting with a bath

[14] The modeling of the environment

[14.1] The Born-Oppenheimer Hamiltonian

We first discuss system that is coupled to some other degrees of freedom that can be eliminated using an adiabatic scheme. This leads to the Born-Oppenheimer picture. It is strongly related to Linear response theory, and the presentation below is arranged accordingly. Linear response theory is the leading formalism to deal with driven systems. Such systems are described by a Hamiltonian

$$\mathcal{H} = \mathcal{H}(\boldsymbol{Q}, \boldsymbol{P}; X(t)) \tag{14.1}$$

where (Q, P) is a set of canonical coordinates (in case that the Hamiltonian is the outcome of "quantization"), and $X(t)$ is a set of time dependent classical parameters ("fields"). For example, X can be the position of a piston. In such case $\dot{X}$ is its velocity. More interesting is the case where X is the magnetic flux through a ring. In such a case $\dot{X}$ is the electro motive force. The Kubo formula allows the calculation of the response coefficients. In the mentioned examples these are the "friction coefficient" and the "conductance of the ring" respectively.

In the limit of a very slow time variation (small $\dot{X}$), linear response theory coincides with the "adiabatic picture". In this limit the response of the system can be described as a non-dissipative "geometric magnetism" effect (this term was coined by Berry and Robbins). If we increase $\dot{X}$ beyond a certain threshold, then we get Fermi-golden-rule transitions between levels, leading to absorption of energy ("dissipation"). Then linear response theory can be regarded as a generalization of "Ohm law".

The Born-Oppenheimer picture allows to deal with Hamiltonians of the type

$$\mathcal{H}_{\text{total}} \ = \ \mathcal{H}_0(x,p) \ + \ \mathcal{H}(\boldsymbol{Q}, \boldsymbol{P}; x) \tag{14.2}$$

Here we replaced the parameter $X(t)$ by a dynamical variable x. The standard textbook example is the study of diatomic molecules. In such case x is the distance between the nuclei. It is evident that the theory of driven systems is a special limit of this problem, which is obtained if we treat x as a classical variable. For presentation purpose let us consider the Hamiltonian

$$\mathcal{H}_{\text{total}} \ = \ \frac{1}{2M}\sum_j p_j^2 \ + \ \mathcal{H}(\boldsymbol{Q}, \boldsymbol{P}; x) \tag{14.3}$$

We define the basis $|x, n(x)\rangle = |x\rangle \otimes |n(x)\rangle$, and expand the state as

$$|\Psi\rangle \ = \ \sum_{n,x} \Psi_n(x) \ |x, n(x)\rangle \tag{14.4}$$

Using

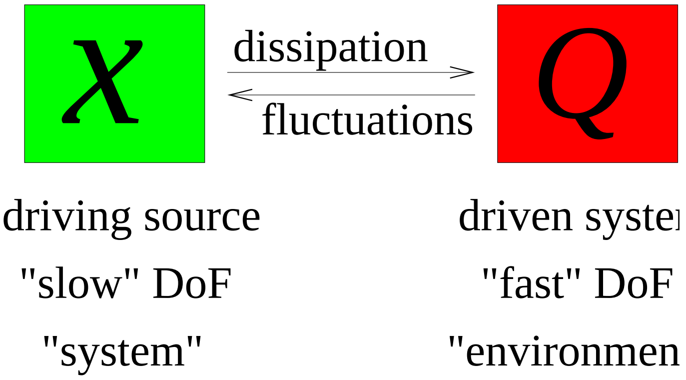
$$\langle x, n(x)|\mathcal{H}|x_0, m(x_0)\rangle \ = \ \delta(x-x_0) \times \delta_{nm} E_n(x) \tag{14.5}$$

$$\langle x, n(x)|p_j|x_0, m(x_0)\rangle \ = \ (-i\partial_j \delta(x-x_0)) \times \langle n(x)|m(x_0)\rangle \ = \ -i\partial_j \delta(x-x_0)\delta_{nm} - \delta(x-x_0)\boldsymbol{A}^j_{nm}(x) \tag{14.6}$$

we deduce that $p_j \mapsto -i\partial_j - \boldsymbol{A}^j_{nm}(x)$, and the Hamiltonian can be written as

$$\mathcal{H}_{\text{total}} \ = \ \frac{1}{2M}\sum_j (p_j - \boldsymbol{A}^j(x))^2 \ + \ \boldsymbol{E}(x) \tag{14.7}$$

The adiabatic approximation is obtained if one neglects the $n \neq m$ terms that couple the motion on different energy surfaces. These couplings are responsible to the dissipation effect.



[14.2] The bath Hamiltonian

The Hamiltonian of a system that interact with and environment is conveniently arranged as

$$\mathcal{H}_{\text{total}} \;=\; \mathcal{H}_0(x,p) \;+\; \mathcal{H}(\boldsymbol{Q},\boldsymbol{P};x) \tag{14.8}$$

For an interaction with a general (possibly chaotic) environment we write

$$\mathcal{H}_{\text{total}} \;=\; \mathcal{H}_0(x,p) \;+\; x\boldsymbol{B} \;+\; \boldsymbol{E} \tag{14.9}$$

where $\boldsymbol{E} = \{E_n\}$ is the bath Hamiltonian that can be written is some diagonal representation, while $\boldsymbol{B} = \{B_{nm}\}$ represents that interaction term with x. Above we assumed that the variation of x is small, so we can linearize the interaction term with respect to x. More generally we can write

$$\mathcal{H}_0(x,p) \;+\; \mathcal{U}(x,Q_\alpha) \;+\; \mathcal{H}_{\text{bath}}(Q_\alpha,P_\alpha) \tag{14.10}$$

It is convenient to model the environment as a huge collection of harmonic oscillators. For a particle that interacts with such bath we write

$$\mathcal{H}_0(x,p) \;=\; \frac{1}{2M}\,p^2 + V(x) \tag{14.11}$$

$$\mathcal{H}_{\text{bath}}(Q_\alpha,P_\alpha) \;=\; \sum_\alpha \left(\frac{{P_\alpha}^2}{2\mathsf{m}_\alpha} + \frac{1}{2}\mathsf{m}_\alpha\omega_\alpha^2 {Q_\alpha}^2\right) \tag{14.12}$$

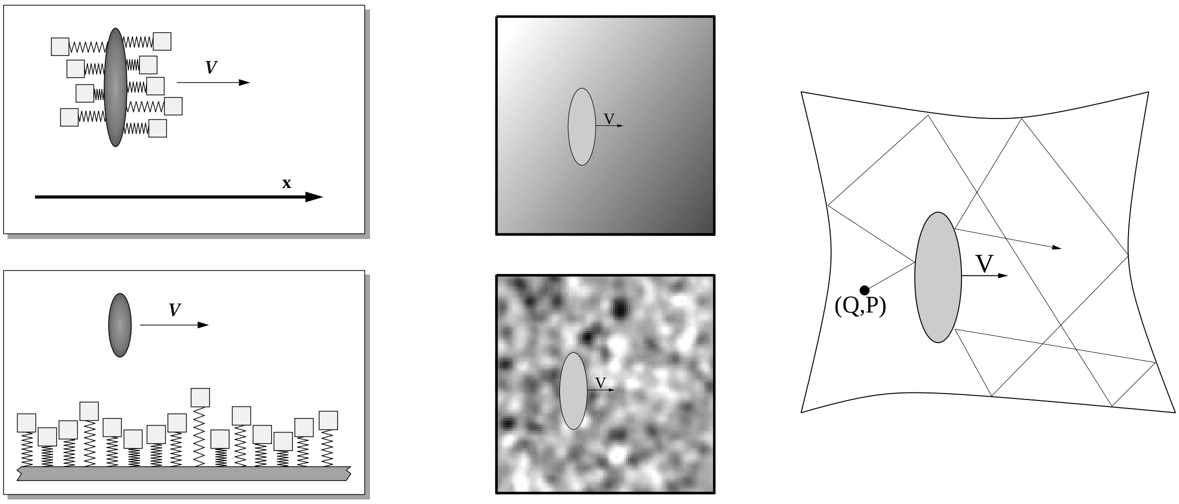
where the interaction is either ZCL-type, or more generally of DLD type:

$$\mathcal{U}_{\text{ZCL}} \;=\; -x\sum_\alpha c_\alpha Q_\alpha \tag{14.13}$$

$$\mathcal{U}_{\text{DLD}} \;=\; -\sum_\alpha c_\alpha Q_\alpha u(x{-}x_\alpha) \tag{14.14}$$

The subscripts ZCL and DLD refer to the modeling of the environment as discussed in PRE 1997. The ZCL (Zwanzig-Cladeira-Leggett) model describes an interaction with a uniform fluctuating field (see figure, upper panels), while the

DLD (diffusion-localization-dissipation) model allows the possibility of experiencing disordered fluctuations that are uncorrelated in space (see figure, lower panels). Another possibility is an interaction with chaotic degrees of freedom (see figure, right most panel).



[14.3] The bath fluctuations

It is common to model the environment as a huge collection of harmonic oscillators, and to say that the system if subject to the fluctuations of a field variable $\mathcal{F}$ which is a linear combination of the bath coordinates:

$$\mathcal{F} \;=\; \sum_{\alpha} c_{\alpha} Q_{\alpha} \;=\; \sum_{\alpha} c_{\alpha} \left(\frac{1}{2\mathsf{m}_{\alpha}\omega_{\alpha}}\right)^{1/2} (a_{\alpha} + a_{\alpha}^{\dagger}) \tag{14.15}$$

For preparation of the bath in state $\boldsymbol{n} = \{n_{\alpha}\}$ we get

$$\tilde{S}(\omega) \;=\; \sum_{\alpha}\sum_{\pm} c_{\alpha}^{2}\ |\langle n_{\alpha}{\pm}1|Q_{\alpha}|n_{\alpha}\rangle|^{2}\ 2\pi\delta(\omega \mp \omega_{\alpha}) \tag{14.16}$$

Using

$$\langle n_{\alpha}{+}1|Q_{\alpha}|n_{\alpha}\rangle \;=\; \left(\frac{1}{2\mathsf{m}_{\alpha}\omega_{\alpha}}\right)^{1/2}\ \sqrt{1+n_{\alpha}} \tag{14.17}$$

$$\langle n_{\alpha}{-}1|Q_{\alpha}|n_{\alpha}\rangle \;=\; \left(\frac{1}{2\mathsf{m}_{\alpha}\omega_{\alpha}}\right)^{1/2}\ \sqrt{n_{\alpha}} \tag{14.18}$$

we get

$$\tilde{S}(\omega) \;=\; \sum_{\alpha} \frac{1}{2\mathsf{m}_{\alpha}\omega_{\alpha}} 2\pi c_{\alpha}^{2} \Big[(1{+}n_{\alpha})\delta(\omega-\omega_{\alpha}) + n_{\alpha}\delta(\omega+\omega_{\alpha})\Big] \tag{14.19}$$

For a canonical preparation of the bath

$$\langle n_{\alpha}\rangle \;=\; f(\omega_{\alpha}) \;\equiv\; \frac{1}{\mathrm{e}^{\omega/T}-1} \tag{14.20}$$

It follows that

$$\tilde{S}(\omega) \;=\; 2J(|\omega|)\times\left\{\begin{matrix}(1+f(\omega))\\ f(|\omega|)\end{matrix}\right\} \;=\; 2J(\omega)\frac{1}{1-\mathrm{e}^{-\beta\omega}} \tag{14.21}$$

where the lower entry is for $\omega < 0$. To get the final compact expression we used the identity $f(-\omega) = -(1+f(\omega))$, and defined the spectral density of the bath as

$$J(\omega) \;=\; \frac{\pi}{2}\sum_{\alpha}\frac{c_{\alpha}^{2}}{\mathsf{m}_{\alpha}\omega_{\alpha}}\delta(\omega-\omega_{\alpha}) \qquad \text{[with anti-symmetric continuation]} \tag{14.22}$$

Ohmic response.– To get an Ohmic bath we set $J(\omega) = \eta\omega$, with some cutoff frequency ω_c. Assume that the interaction of the particle with the bath is $-xF$, as in the ZCL model. Consider a scenario of having a classical particle that is constrained to move with velocity $\dot{x}$. Then we get from the fluctuation-dissipation relation (or from a direct calculation) that the response of the bath is $\langle \mathcal{F} \rangle = -\eta\dot{x}$. This statement can be generalized for the DLD interaction, see PRE 1997 for details.

Einstein coefficient.– From the formal calculation it comes out that $\tilde{S}(\omega)$ satisfies what we call previously the detailed-balance relation, namely $[\tilde{S}(-\omega)/\tilde{S}(\omega)] = \exp(-\omega/T)$. It is the time to illuminate the historical perspective for this terminology. This is related to insights that Einstein had regarding Blackbody radiation. Planck's formula, disregarding $c/4$ factor, is an expression for $u(\omega;T)$, the electromagnetic energy density in space. Consider a two level atom that is immersed in this electromagnetic bath. It experiences fluctuations $\tilde{S}(\omega)$ that induce upward and downward transitions, namely,

$$w_{\downarrow} \;=\; A + Bu(\omega;T) \tag{14.23}$$

$$w_{\uparrow} \;=\; B'u(\omega;T) \tag{14.24}$$

Here $\omega > 0$ corresponds to the energy of the transition, and (A, B, B') are the coefficients for spontaneous emission, stimulated emission, and stimulated absorption. To get equilibrium we expect $w_{\uparrow}/w_{\downarrow} = \exp(-\omega/T)$. Considering $T = \infty$ we realize that we must have $B' = B$. Considering finite temperature we further deduce that the following relation between "Planck" and "Boltzmann" should hold

$$u(\omega;T) \;=\; \frac{A}{B}\, f(\omega;T) \tag{14.25}$$

where A and B are temperature independent by definition. The theory of electromagnetic field implies that the A/B ratio is related to the density of modes:

$$\frac{A}{B} \;=\; \omega\, g(\omega) \;=\; \frac{1}{\pi^2}\left(\frac{\omega}{c}\right)^3 \tag{14.26}$$

From a different perspective we can say that the Einstein detailed-balance argument implies that we can write for emission $\tilde{S}(\omega) = A[1 + f(\omega;T)]$, and for absorption $\tilde{S}(-\omega) = Af(\omega;T)$. This is consistent with the direct calculation of the power spectrum that we have presented previously.

[14.4] Spin bath

We consider the fluctuations of an $\mathcal{F}$ that arise from a bath of spins

$$\mathcal{F} = \sum_{\alpha} c_{\alpha} Q_{\alpha} = \sum_{\alpha} c_{\alpha}(a_{\alpha} + a_{\alpha}^{\dagger}) \tag{14.27}$$

Thus Q_α is the first Pauli matrix. Its non-trivial matrix elements are

$$\begin{aligned} \langle n_\alpha{-}1|Q_\alpha|n_\alpha\rangle &= \sqrt{n_\alpha} && (14.28)\\ \langle n_\alpha{+}1|Q_\alpha|n_\alpha\rangle &= \sqrt{1-n_\alpha} && (14.29)\end{aligned}$$

In complete analogy we get

$$\tilde{S}(\omega) = \sum_\alpha 2\pi c_\alpha^2 \Big[(1{-}n_\alpha)\delta(\omega-\omega_\alpha) + n_\alpha\delta(\omega+\omega_\alpha)\Big] \tag{14.30}$$

For canonical preparation $\langle n_\alpha\rangle = f(\omega_\alpha)$ where (from here on $\hbar = 1$)

$$\begin{aligned} f(\omega) &= \frac{1}{\mathrm{e}^{\beta\omega}+1} && (14.31)\\ f(-\omega) &= \frac{1}{1+\mathrm{e}^{-\beta\omega}} = 1-f(\omega) && (14.32)\end{aligned}$$

Thus we get

$$\tilde{S}(\omega) \;=\; 2J(|\omega|)\times\begin{cases}(1-f(\omega))\\ f(-\omega)\end{cases} \;=\; 2J(\omega)\frac{1}{1+\mathrm{e}^{-\beta\omega}} \tag{14.33}$$

and

$$\tilde{C}(\omega) = J(\omega) \tag{14.34}$$

where we define

$$J(\omega) \;=\; \pi\sum_\alpha c_\alpha^2\delta(\omega-\omega_\alpha) \qquad \text{[with symmetric continuation]} \tag{14.35}$$

For Ohmic bath $J(\omega) = \nu$, with some cutoff frequency ω_c.

[14.5] Spatially extended environment

In this section we describe fluctuations of an extended environment in space and time using the form factor $\tilde{S}(q,\omega)$. We define

$$\tilde{S}(q,\omega) \;=\; \mathrm{FT}\Big[\langle\mathcal{U}(x_2,t_2)\mathcal{U}(x_1,t_1)\rangle\Big] \tag{14.36}$$

where the expectation value assumes that the bath is in a stationary state of its unperturbed Hamiltonian. The force-force correlation function is obtained via differentiation. In particular the local power spectrum of the fluctuating force is

$$\tilde{S}(\omega) = \int\frac{dq}{2\pi}q^2 S(q,\omega) \tag{14.37}$$

and the intensity of the fluctuations at a given point in space is

$$\nu \;\equiv\; \tilde{S}(\omega{=}0) \;=\; \int\frac{dq}{2\pi}q^2 S(q,\omega{=}0) \tag{14.38}$$

For the one dimensional DLD bath we get

$$\mathcal{U} \;=\; -\sum_{\alpha} c_\alpha Q_\alpha u(x{-}x_\alpha) \tag{14.39}$$

Taking into account that the oscillators are independent of each other we get

$$\langle \mathcal{U}(x_2,t_2)\mathcal{U}(x_1,t_1)\rangle \;=\; \sum_{\alpha} c_\alpha^2 \langle Q_\alpha(t_2)Q_\alpha(t_1)\rangle u(x_2{-}x_\alpha)u(x_1{-}x_\alpha) \tag{14.40}$$

$$= \int dx \left[\sum_{\alpha} c_\alpha^2 \langle Q_\alpha(t_2)Q_\alpha(t_1)\rangle \delta(x-x_\alpha)\right] u(x_2{-}x)u(x_1{-}x) \tag{14.41}$$

$$= \left[\int u(x_2{-}x)u(x_1{-}x)\; dx\right] S(t_2-t_1) \tag{14.42}$$

$$= w(x_2-x_1)\; S(t_2-t_1) \tag{14.43}$$

Where we have assumed homogeneous distribution of the oscillators, and $S(\tau)$ is defined implicitly by the above equality. With the convention $w''(0) = -1$ it is identified as the local force-force correlation function. Consequently we get for the form factor

$$S(q,\omega) \;=\; \mathrm{FT}\Big[\langle \mathcal{U}(x_2,t_2)\mathcal{U}(x_1,t_1)\rangle\Big] \;=\; \tilde{w}(q)\; S(\omega) \tag{14.44}$$

As an example we may consider the following correlation function:

$$w(r) \;=\; \ell^2 \exp\left(-\frac{1}{2}\left(\frac{r}{\ell}\right)^2\right) \tag{14.45}$$

If the spatial correlation distance is very large we get ZCL model:

$$w(r) \;=\; \mathrm{const} - \frac{1}{2}r^2 \tag{14.46}$$

leading to

$$S(q,\omega) = \frac{2\pi}{q^2}\delta(q)\; \tilde{S}(\omega) \tag{14.47}$$

This means that the force is homogeneous in space, and fluctuates only in time, which is effectively the case if a particle or an atom interacts with long wavelength modes.

[15] Stochastic picture of the dynamics

There are various "levels" in which the dynamics of a non-isolated system can be treated. We start with the random walk problem that can describe the motion of a Brownian particle in the absence of friction. Then we discuss the Langevin equation where friction is included. The dynamics in the above problem is described by a diffusion equation and Fokker-Planck equation respectively. More generally we can talk about Master equations and in particular their simplest stochastic version which is known as rate equations.

[15.1] Random walk and diffusion

Consider a particle that can hope from site to site in a stochastic manner. Each step can be represented by a random number $f_t = \pm a$, where a is the lattice constant and t is the integer time index. The total displacement is

$$x(t) - x(0) \;=\; \sum_{t'=0}^{t} f(t') \tag{15.1}$$

Assuming a stationary stochastic process in which the correlation function is

$$\langle f(t_1) f(t_2) \rangle \;=\; C(t_1 - t_2) \tag{15.2}$$

we get that the variance is

$$\mathrm{Var}[x] \;=\; \sum_{t_1=0}^{t}\sum_{t_2=0}^{t} \langle f(t_1) f(t_2) \rangle \;=\; \sum_{t'=0}^{t}\sum_{\tau=-t'}^{+t'} C(\tau) \;\equiv\; \sum_{t'=0}^{t} 2D(t') \;\longrightarrow\; 2Dt \tag{15.3}$$

where the asymptotic value of the diffusion coefficient is

$$D \;=\; \frac{1}{2}\sum_{\tau=-\infty}^{\infty} C(\tau) \tag{15.4}$$

Most significant is to realize that there is a continuum limit of the random walk problem where the dynamics is described by the following "Langevin" equation of motion

$$\dot{x} \;=\; f(t) \qquad\qquad \rightsquigarrow \qquad\qquad x(t) - x(0) \;=\; \int f(t')\, dt' \tag{15.5}$$

and accordingly

$$D \;=\; \frac{1}{2}\int_{-\infty}^{\infty} C(\tau) d\tau \;=\; \frac{1}{2}\tilde{C}(\omega{=}0) \tag{15.6}$$

There are various generalizations of the random walk problem, where the dwell time or the size of the steps are random variables, leading in general to sub-diffusive or super diffusive behavior respectively. The latter case is known as Levi-flight.

Master Equations.– In the random walk problem the stochastic dynamics can be described by an equation for the time evolution of the probabilities p_n to find the particle in site n. This has the form of a *rate equation.* In the continuum limit it becomes a *diffusion equation* for the probability density $\rho(x)$. More generally this type of master equation is known as the *Fokker Planck equation.*

[15.2] The Langevin equation

Consider a test particle subject to a homogeneous but fluctuating field of force $\mathcal{F}$, leading to stochastic dynamics that is described by the Langeving equation $\mathsf{m}\ddot{x} = \mathcal{F}$. It is convenient to isolate the average (= "friction") term from $\mathcal{F}$, and accordingly to redefine $\mathcal{F}$ as a stochastic variable (= "noise") that has zero average. Consequently the Langevin equation is written as

$$\mathsf{m}\ddot{x} \;=\; -\eta\dot{x} + \mathcal{F}(t) \tag{15.7}$$

where $\mathcal{F}$ is a stochastic variable that satisfies $\langle \mathcal{F}(t) \rangle = 0$, and

$$\langle \mathcal{F}(t_2)\mathcal{F}(t_1) \rangle \;=\; C(t_2 - t_1) \tag{15.8}$$

It is assumed that $C(\tau)$ has a short correlation time. We are interested in the dynamics over larger time scales (we have no interest to resolve the dynamics over very short times). We also note that if $\mathcal{F}$ were a constant force, then the particle would drift with velocity $(1/\eta)\mathcal{F}$. The coefficient $\mu = 1/\eta$ is called *mobility*. The equation for the velocity $v = \dot{x}$ can be written as

$$\frac{d}{dt}\mathrm{e}^{(\eta/\mathsf{m})t}v(t) \;=\; \frac{1}{\mathsf{m}}\mathrm{e}^{(\eta/\mathsf{m})t}\mathcal{F}(t) \tag{15.9}$$

leading to the solution

$$v(t) \;=\; \frac{1}{\mathsf{m}}\int_{-\infty}^{t} dt' \mathrm{e}^{-(\eta/\mathsf{m})(t-t')}\mathcal{F}(t') \tag{15.10}$$

We see that $\tau_\eta = \mathsf{m}/\eta$ is the damping time. After time $\gg \tau_\eta$ the initial velocity is forgotten, hence the lower limit of the integration can be extended to $-\infty$. Evidently the average velocity is zero. We turn now to calculate the velocity-velocity correlation. "Squaring" and averaging over realizations we get

$$\langle v(t_2)v(t_1) \rangle = \frac{1}{\mathsf{m}^2}\int_{-\infty}^{t_1}\int_{-\infty}^{t_2} dt'dt'' \mathrm{e}^{-(\eta/\mathsf{m})(t_1+t_2-t'-t'')}C(t'-t'') \tag{15.11}$$

We treat $C(t'-t'')$ like a delta function. Then it is not difficult to find that

$$\langle v(t_2)v(t_1) \rangle \;=\; \frac{1}{2\eta\mathsf{m}}\mathrm{e}^{-(\eta/\mathsf{m})|t_2-t_1|}\int_{-\infty}^{\infty} C(\tau)d\tau \;=\; \frac{1}{\mathsf{m}}\left(\frac{\nu}{2\eta}\right)\mathrm{e}^{-|t_2-t_1|/\tau_\eta} \tag{15.12}$$

There is an optional shorter derivation of the latter result: In Fourier-space the Langevin equation is solved easily $v_\omega = [-i\mathsf{m}\omega + \eta]^{-1}\mathcal{F}_\omega$, leading to $\tilde{C}_{vv}(\omega) = [(\mathsf{m}\omega)^2 + \eta^2]^{-1}\tilde{C}(\omega)$. With $\tilde{C}(\omega) = \nu$ we get after FT the same result.

The correlation function $\langle v(t_2)v(t_1) \rangle$ for $t_1 = t_2 = t$ should be consistent with $\langle \frac{1}{2}\mathsf{m}v^2 \rangle = \frac{1}{2}T$. From this one deduces an FD relation $\nu/(2\eta) = T$ with regard to the response characteristics of the bath. The displacement $x(t) - x(0)$ of the particle is the integral over its velocity $v(t')$. On the average it is zero, but the second moment is

$$\langle (x(t) - x(0))^2 \rangle \;=\; \int_0^t\int_0^t dt'dt'' \langle v(t'')v(t') \rangle \;=\; \frac{\nu}{\eta^2} \times t \;\equiv\; 2Dt \tag{15.13}$$

Hence we have diffusion in space. From the above we deduce the Einstein relation

$$\frac{D}{\mu} \;=\; \frac{\nu}{2\eta} \;=\; \text{Temperature} \tag{15.14}$$

The two results for D/μ, and for ν/η, can be regarded as special consequences of the general FD relation, as demonstrated in a previous lecture.

[15.3] The Fokker-Planck Equation

It is natural to ask what is the "master equation" that describes the time evolution of the probability density $\rho_t(x)$ in the case of a diffusion process. We assume that the stochastic equation of motion is $\dot{x} = f(t)$ with stochastic $f(t)$ that has a zero average. A trivial generalization is to include a drift term such that the equation is $\dot{x} = u + f(t)$, where u is the so-called drift velocity. In order to derive the diffusion equation, note that for any particular realization of $f(t)$ the probability $\rho_{t+dt}(x_{t+dt})dx_{t+dt}$ must equal $\rho_t(x_t)dx_t$. Since the phase space element preserves its volume one obtains the Liouville equation $(d/dt)\rho_t(x_t) = 0$, from which one deduces the continuity equation

$$\frac{\partial}{\partial t}\rho_t(x) \quad = \quad -\frac{\partial}{\partial x}\Big[(u+f(t))\rho_t\Big] \tag{15.15}$$

From this equation it follows that ρ_{t_0+dt} can be expressed as an integral that involves $\rho_{t'}$ within $t_0 < t' < t_0 + dt$. The equation can be solved iteratively. In order to simplify notations we set without loss of generality $t_0 = 0$ and $t = t_0 + dt$. Consequently we get an expansion that involves nested terms with higher order $\partial/\partial x$ derivatives of ρ_0. For sake of clarity we drop the drift term and write

$$\rho_t \quad = \quad \rho_0 \; - \; \int_0^t dt' f(t')\frac{\partial \rho_0}{\partial x} \; + \; \int_0^t dt' f(t') \int_0^{t'} dt'' f(t'') \; \frac{\partial^2 \rho_0}{\partial x^2} \; + \; \text{higher order terms} \tag{15.16}$$

Averaging over realizations of $f()$, and neglecting the higher order terms, one obtains a diffusion equation, to which we add back the drift term:

$$\frac{\partial}{\partial t}\rho_t \quad = \quad -u\frac{\partial \rho_t}{\partial x} + D\frac{\partial^2 \rho_t}{\partial x^2} \tag{15.17}$$

The neglect of higher order terms, say $\mathcal{O}(dt^3)$ terms, is justified in the limit where the correlation time goes to zero. This is sometimes known as the Markovian approximation. It is possible to regard the diffusion equation as a continuity equation

$$\frac{\partial}{\partial t}\rho_t(x) = -\frac{\partial}{\partial x}I_t(x), \qquad\qquad I_t(x) = u\rho_t(x) - D\frac{\partial \rho_t(x)}{\partial x} \tag{15.18}$$

The expression for the current includes a drift term and a diffusion term. The diffusion term is known as Fick's law. Fick's law can be explained heuristically as reflecting a non-zero net net flow of particles across a section, due to a difference of concentrations between its two sides. Ignoring the drift, if we have a sample of length L with a steady state current then

$$I \quad = \quad -\frac{D}{L} \times \Big[\rho(L) - \rho(0)\Big] \tag{15.19}$$

This means that there is a strict analogy here to Ohm law, implying that D is formally like the conductivity of the chain, and accordingly can be obtained from a resistor network calculation. This observation is useful in analyzing diffusion is non-homogeneous networks.

The drift velocity is typically related to a the gradient of an external potential, $u = -\mu V'(x)$, with a coefficient which is called mobility. Accordingly we write

$$I(x) \quad = \quad u\rho(x) - D\frac{\partial}{\partial x}\rho(x) \quad = \quad -\mu\rho\frac{\partial V}{\partial x} - D\frac{\partial \rho}{\partial x} \tag{15.20}$$

If this expression is applied to a system in canonical equilibrium with $\rho(x) \propto \exp(-\beta V(x))$, it follows from the requirement $I(x) = 0$ that $\mu = (1/T)D$. This is called Einstein relation. It is useful in semiconductor physics. For electrons in metal it is common to define the conductivity $\sigma = \mu\rho$, and postulate that at equilibrium $\rho(x) = \int dE g(E - V(x)) f(E - E_F)$. It follows that the Einstein relation for metals is $\sigma = g(E_F)D$. Note that $g(E_F)$ is defined here as the density of one-particle states per unit volume, and it is proportional to ρ/E_F.

FPE for Langevin.– As in the case of a "random walk" one can ask what is the "master equation" that described the evolution of the probability density $\rho(x,p)$. This leads to the Fokker-Planck equation. The derivation is the same as in the case of a diffusion process. Here the diffusion is in momentum with a coefficient $\nu/2$. Including the $v(p) = p/\mathsf{m}$ drift in the position, we get the continuity equation

$$\frac{\partial}{\partial t}\rho \;=\; -\frac{\partial}{\partial x}\Big[v\rho\Big] - \frac{\partial}{\partial p}\Big[-V'(x)\rho - \eta v\rho - \frac{\nu}{2}\frac{\partial\rho}{\partial p}\Big] \tag{15.21}$$

There are quantum generalizations of the Fokker-Planck equation which we discuss in a separate section.

[15.4] The Ito-Stratonovich interpretation

Let us try generalize the derivation of the diffusion equation for a propcess that is described by the stochastic equation

$$\dot{x_j} \;=\; u_j + g_i\, f(t) \tag{15.22}$$

$$\langle f(t)f(t')\rangle \;=\; 2D\delta_\tau(t-t') \tag{15.23}$$

where the u_j and the g_j are some functions of the x_i. The "noise" has zero average, namely $\langle f(t)\rangle = 0$, and is characterized by a correlation time τ. Accordingly the $\delta_\tau(t-t')$ has a short but finite width, which is later taken to be zero. For a particular realization of the noise, the continuity equation for the Liouville distribution $\rho(x)$ reads:

$$\frac{\partial\rho}{\partial t} \;=\; -\sum_j \frac{\partial}{\partial x_j}\left[\left(u_j + g_i f(t)\right)\,\rho\right] \tag{15.24}$$

We are interested in $\rho(x)$ averaged over many-realizations of the noise. In its current form the continuity equation cannot be averaged, because ρ and f are not independent variables. To overcome this issue we write for $\rho(t+dt)-\rho(t)$ an integral expression as in the previous section. Performing the average over realizations of the noise, non-vanishing noise-related terms arise from the second-order terms and we end up with the equation

$$\frac{\partial\rho}{\partial t} = -\frac{\partial}{\partial x_j}\Big[u_j\rho - g_j D\frac{\partial}{\partial x_i}\left(g_i\rho\right)\Big] \tag{15.25}$$

Terms that originate from higher orders can be neglected in the $\tau \to 0$ limit. It is common to say that the above is the Fokker-Plank equation (FPE) that is associated with the stochastic equation according to the Stratonovich interpretation. Other "interpretations" (as we explain below) provide a similar equation with a different order of differentiation. The Stratonovich ordering is $[g_j D\partial_i(g_i\rho)]$, the Ito ordering is $[D\partial_x(g_j g_i\rho)]$, and the Hanggi ordering is $[g_j g_i D\partial_x(\rho)]$. All the interpretation are formally equivalent because the difference can be absorbed into the definition of the drift velocity u_j. So one may say that the notion of drift velocity depends on the "interpretation". To make this point physically clear let us consider again random walk on discrete lattice with rates of transitions $w_{x,x'}$. One way is to define the drift velocity at $x=3$ as $u = w_{4,3} - w_{2,3}$. Another way would be to define it at $x \in [3,4]$ as $u = w_{4,3} - w_{3,4}$. The latter definition implies that the steady state for $u=0$ would be uniform in sapce ($\rho = \text{const}$), and therefore is associated with the ordering of Hanggi. Different definitions can lead to different interpretations. As a rule of thumb the $u=0$ steady state can be used as a guide for making a self-consistent choice.

An observable X is a function of the x variables. In order to obtain an equation of motion for $\langle X\rangle$, we multiply both sides of the FPE by X, and integrate over x. Using integration by parts, and dropping the boundary terms, we get the so-called adjoint equation

$$\frac{d}{dt}\langle X\rangle \;=\; \left\langle u_j\frac{\partial X}{\partial x_j} + g_i\frac{\partial}{\partial x_i}\left[g_j D\frac{\partial X}{\partial x_j}\right]\right\rangle$$

There are cases where instead of handling FPE for the time evolution of $\rho(x)$, we can replace it by a reduced set of equations for a complete set of variables that characterize the evolving distribution. For example those variables might be moments of the distribution, say $\{\langle x\rangle, \langle y\rangle, \langle x^2\rangle, \langle xy\rangle, \langle y^2\rangle, ...\}$.

[15.5] Dynamics according to Smoluchowski and Kramers

The master equation that is associated with the Langeving equation $\mathsf{m}\ddot{x} = -V'(x) - \eta\dot{x} + \mathcal{F}(t)$ is an Kramers FPE for $\rho(x,p)$. The stochastic term induces diffusion in momentum with coefficient $\nu/2$, and the friction implies damping with rate $\gamma = \eta/\mathsf{m}$ and mobility $\mu = 1/\eta$. In the absence of external potential the interplay of noise and friction leads to diffusion in space with coefficient $D = \nu/(2\eta^2)$. For strong damping the inertial effect can be neglected and the stochastic motion can be described by a simpler equation $\dot{x} = -\mu V'(x) + \mu\mathcal{F}(t)$. The master equation that is associated with this simpler version is known as Smoluchowski diffusion equation for the density $\rho(x)$. The drift term is $-\mu V'(x)\rho(x)$, and the diffusion term has coefficient $D = (1/2)\mu^2\nu$ in consistency with Kramers FPE. The Smoluchowski diffusion equation can be formally obtained from the Kramers FPE via a leading order expansion in $1/\eta$. The details are described in Section 10 of *The Fokker-Planck Equation: Methods of Solution and Applications* by H.Risken.

A major theme in stochastic dynamics is to get the rate of crossing via barrier. This type of activation process is handled within the framework of so-called *transition state theory.* In the Smoluchowski approximation (strong damping) the current is given by

$$I(x) \quad = \quad -\mu V'(x)\rho(x) - D\frac{\partial\rho(x)}{\partial x} \quad = \quad -\frac{T}{\eta}e^{-V(x)/T}\frac{\partial}{\partial x}\left[e^{V(x)/T}\rho(x)\right] \tag{15.26}$$

We assume that $V(x) = 0$ away from the barrier, and $V(x) = V_B$ at the top of the barrier. To be specific we further assume that the curvature at the top of the barrier is ω_B (inverted harmonic potential). Assuming a steay state current $I(x) = \text{const}$, we can multiply both sides of the expression above by $e^{V(x)/T}$, and integrate over interval that contains the barrier. We get that

$$I \quad = \quad \frac{T/\eta}{\int_{x_A}^{x_C} e^{V(x)/T}dx}[\rho(x_A) - \rho(x_C)] \quad \approx \quad \frac{T}{\eta}\sqrt{\frac{\mathsf{m}\omega_B^2}{2\pi T}}\, e^{-V_B/T}\ [\rho(x_A) - \rho(x_C)] \tag{15.27}$$

Let us assume that the left region is in fact a well that has curvature ω_A around x_A, and that initially the particle is located there in a state of canonical equilibrium. The density $\rho(x_A)$ is determined by normalization, while $\rho(x_C)$ is neglected. Changing notation from I to Γ we get an expression for the rate of escape:

$$\Gamma \quad = \quad \frac{\omega_A}{2\pi} \times \left[\frac{\omega_B}{\gamma}\right] e^{-V_B/T} \quad \equiv \quad \frac{\omega_A}{2\pi} \times \text{Transmission} \tag{15.28}$$

where $\omega_A/(2\pi)$ is known as the *attempt frequency.* A more refined treatment by Kramers gives the expression

$$\Gamma \quad = \quad \frac{\omega_A}{2\pi} \times \left[\sqrt{1 + \left(\frac{\gamma}{2\omega_B}\right)^2} - \left(\frac{\gamma}{2\omega_B}\right)\right] e^{-V_B/T} \tag{15.29}$$

The square brackets in the above formula goes to unity in the formal $\gamma \to 0$ limit. But this is a fallacy. The expression is no longer valid in the weak damping regime. The reason for that is that the escape process is no longer limited by slow diffusion in space (as assumed in the derivation of the Smoluchowski diffusion equation), but rather by the slow diffusion in momentum. So it is natural to write a reduced diffusion equation in momentum, or more precisely in the action variable I. Then one deduces that in the weak damping regime the escape rate is given by

$$\Gamma \quad = \quad \frac{\omega_A}{2\pi} \times \left[\frac{\gamma I_B}{T}\right] e^{-V_B/T} \tag{15.30}$$

where I_B is the action at the escape energy, namely, the enclosed phase-space area, which is given by the *dxdp* integral over the $E < V_B$ region.

[15.6] Rate equations

A rate equation is merely a discrete version of the diffusion or Fokker-Planck equation. It can be regarded as describing a generalized "random walk" problem, where the transition rates w_{nm} are not necessarily equal in the $n \mapsto m$ and $m \mapsto n$ directions. The state of the system is described by a column vector $\boldsymbol{p}$ whose entries are the occupation probabilities p_n, such that $\sum_n p_n = 1$. The dynamics is determined by the rate equation

$$\frac{d\boldsymbol{p}}{dt} = \boldsymbol{W}\boldsymbol{p}, \qquad \boldsymbol{W} = \text{diagonal}\{-\gamma_n\} + \text{offdiagonal}\{w_{nm}\} \tag{15.31}$$

The off-diagonal elements are the rates of transitions, namely, w_{nm} is the rate of transition from m to n. The diagonal elements $-\gamma_i$ of the $\boldsymbol{W}$ matrix are determined such that each column sums to zero. Accordingly $\sum_n p_n = 1$ is conserved. Optionally the rate equation can be regarded as a continuity equation:

$$\frac{dp_n}{dt} \ = \ -\gamma_n p_n + \sum_{m(\neq n)} w_{nm} p_m \ = \ -\sum_{m(\neq n)} [w_{mn} p_n - w_{nm} p_m] \tag{15.32}$$

The steady state of the stochastic system is found from the equation $\boldsymbol{W}\boldsymbol{p}^{SS} = 0$. The relaxation modes are the eigenstates, namely $\boldsymbol{W}\psi = -\lambda\psi$, where $\{-\lambda\}$ are the eigenvalues. Note the sign convention, and note that the $\lambda = 0$ mode is the steady-state. An arbitrary initial state can be expanded in this basis, and consequently the solution of the rate equation is

$$\boldsymbol{p}(t) \ = \ e^{\boldsymbol{W}t}\boldsymbol{p}(0) \ = \ \boldsymbol{p}^{SS} + \sum_{\lambda\neq 0} C_\lambda\, e^{-\lambda t}\ \psi^{(\lambda)} \tag{15.33}$$

Detailed balance.– In the context of the "system-bath" paradigm it is common to model the system as a set of levels $\{E_n\}$ with transition rates that reflect detailed balance considerations, such that $p_n^{SS} \propto \exp[-E_n/T_B]$. Namely,

$$\frac{w_{mn}}{w_{nm}} \ \equiv \ \exp\left[\mathcal{E}_{n\rightsquigarrow m}\right] \ = \ \exp\left[\frac{E_n - E_m}{T_B}\right] \tag{15.34}$$

where $\mathcal{E}_{n\rightsquigarrow m}$ is called *stochastic field.* From a mathematical point of view detailed-balance means that any circulation of the stochastic filed is zero, i.e. $\mathcal{E}$ is a conservative field that can be derived from a potential U_n. To get equilibrium the stochastic potential has to be $U_n = E_n/T$.

A driving noise source or a work agent (see below) can be regarded as a bath that has infinite temperature. More generally one can regard the average value $(w_{nm} + w_{mn})/2$ as the *noise* which is introduced into the system by the bath, while the difference $(w_{nm} - w_{mn})$ is the *friction.* However this point of view is strictly correct only for constant density of states. If the level density grows with energy there will be a heating effect even if $T_B{=}\infty$.

Two level/site system.– The two level system is the simplest setup for illustration of equilbration process. The transition rates are $w^{\pm}$. The dynamics is generated by the matrix

$$\boldsymbol{W} \ = \ \begin{pmatrix} -w^+ & w^- \\ w^+ & -w^- \end{pmatrix} \tag{15.35}$$

Using the notation $S = p_2 - p_1$, recaling that $p_1 + p_2 = 1$, and using the noation $\gamma = w^+ + w^-$ and $u = w^+ - w^-$ we get the equation

$$\frac{dS}{dt} \ = \ -\gamma S + u \tag{15.36}$$

which implies exponential relaxation towards the equilibrium value $S_{\text{eq}} = u/\gamma$. If the transitions are induced by a bath of temperature T_B, then S_{eq} corresponds to equilibrium at temperature T_B. If we expose the system to so-called "work agent", say a sun that has infinite temperature, then the new rates are $w^{\pm} = w_B^{\pm} + w_A$, and the system will reach an equilibrium-like state that corresponds to a higher temperature. It is important to realize that the steady state solution features energy flow from the work agent via the system to the bath (and not the other way around). We say the energy is dissipated.

Three level/site system.– The three-level system is the simplest setup for illustration of non-equilibrium thermodynamics. For example, it can be regarded as a model for a 3-level laser heat engine (see figure) or a mathematically equivalent rolling marble machine (see figure). The transitions are induced by a hot bath (T_H) and by a cold bath (T_C). In the first example photons can be either emitted or absorbed by a work agent ($T_A = \infty$). The second example is further discussed below. Either way the dynamics is generated by the matrix

$$\boldsymbol{W} \;=\; \begin{pmatrix} -\gamma_1 & w_C^- & w_A \\ w_C^+ & -\gamma_2 & w_H^- \\ w_A & w_H^+ & -\gamma_3 \end{pmatrix} \tag{15.37}$$

where $\gamma_1 = w_C^+ + w_A$, and $\gamma_2 = w_C^- + w_H^+$, and $\gamma_3 = w_H^- + w_A$. The affinity of the cycle is defined as

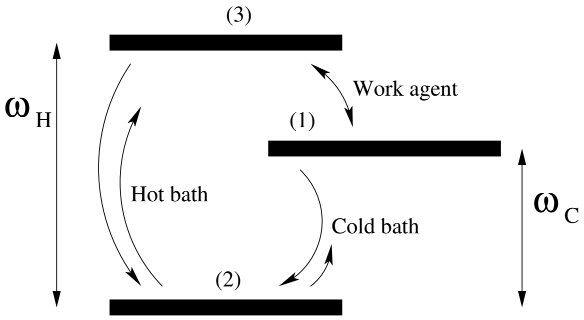
$$\Phi \;=\; \mathcal{E}_{1\rightsquigarrow 2} + \mathcal{E}_{2\rightsquigarrow 3} + \mathcal{E}_{3\rightsquigarrow 1} \;=\; \ln\left[\frac{w_{13}w_{32}w_{21}}{w_{12}w_{23}w_{31}}\right] \;=\; \frac{\omega_C}{T_C} - \frac{\omega_H}{T_H} \tag{15.38}$$

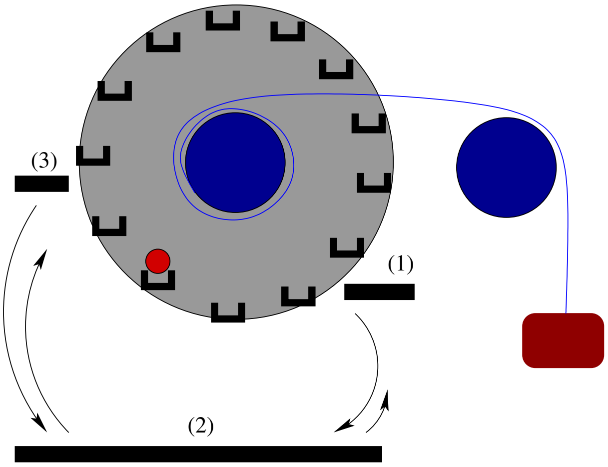
In order to have a working engine cycle we require $\Phi > 0$, which implies $(\omega_C/\omega_H) > (T_C/T_H)$. The efficiency of the engine is

$$\eta \;\equiv\; \frac{\omega_H - \omega_C}{\omega_H} \;<\; 1 - \frac{T_C}{T_H} \tag{15.39}$$

The limiting efficiency is the so-called Carnot efficiency. We can solve $\boldsymbol{W}\boldsymbol{p} = 0$ to find the probabilities (p_1, p_2, p_3) at steady state. Then we can find the probability current $I(\Phi) = (p_3 - p_1)w_A$ at steady state, and the power output of the engine $(\omega_H - \omega_C)I(\Phi)$.

Work agent.– The mechanical rolling marble machine possibly clarifies better the concept of *work agent*. Here the task of the engine is to pulls up a weight. The hot bath induce with some probability a transition of the marble form position "2" to position "3". From there, with some probability, it gets into a car of the roller coaster wheel. Then is rolls (trapped in the car) to position "1". The wheel pulls up the weight. In order to maximize efficiency it is designed such that the potential energy of the whole system (including the weight) is the same at "3" and at "1". Consequenltly there is an equal probability to make the ride from "1" to "3". However, considering the full cycle, the condition $\Phi > 0$ ensures that the net work is positive.





The N site ring.– The dynamics of a particle in an N site ring is generated by the matrix

$$\boldsymbol{W} \ = \ \begin{pmatrix} -\gamma_1 & w_2^- & 0 & ... & w_1^+ \\ w_2^+ & -\gamma_2 & w_3^- & 0 & ... \\ 0 & w_3^+ & -\gamma_3 & w_3^- & ... \\ ... & ... & ... & ... & w_N^- \\ w_1^- & 0 & ... & w_N^+ & -\gamma_N \end{pmatrix} \ = \ -\gamma\mathbf{1} + w^+\boldsymbol{D} + w^-\boldsymbol{D}^{-1} \tag{15.40}$$

In the second equality we have assumed that all the anti-clockwise rates equal w^+, and that all the clockwise rates equal w^-. Accordingly $\gamma = w^+ + w^-$. The matrices $\boldsymbol{D}$ and $\boldsymbol{D}^{-1}$ generate anti-clockwise and clockwise displacements respectively. The drift velocity is

$$\frac{d}{dt}\langle x\rangle \ = \ [w^+ - w^-]a \ \equiv \ \bar{v} \tag{15.41}$$

where a is the lattice spacing. The proof is as follows:

$$\begin{aligned}\frac{d}{dt}\langle x\rangle \ &= \ \frac{d}{dt}\sum_n p_n x_n \ = \ \sum_n x_n w_{nm} p_m \ = \ \sum_n x_n \left[w^+ p_{n-1} + w^- p_{n+1} - \gamma p_n\right] \\ &= \ \sum_n \left[w^+(x_{n+1}-x_n)p_n + w^-(x_{n-1}-x_n)p_n\right] \ = \ ... \end{aligned} \tag{15.42}$$

Irrespective of drift, we have diffusion. Say that we start a distribution at $x = 0$. For simplicity let us assume that $w^- = w^+ = w$. We get that the rate of growth of the spreading is

$$\frac{d}{dt}\left\langle x^2\right\rangle \ = \ 2wa^2 \ \equiv \ 2D \tag{15.43}$$

More generally, if the drift velocity is non-zero, we can prove that

$$\mathrm{Var}(x) \ = \ \left\langle x^2\right\rangle - \langle x\rangle^2 \ = \ 2Dt \tag{15.44}$$

where $D = (1/2)[w^+ + w^-]a^2$ is called the diffusion coefficient.

The eigenstates of $\boldsymbol{W}$ are the eigenstates of the displacement operator $\boldsymbol{D}$, namely *momentum states*. It is convenient to write the column representation ψ_n as a function, namely $\psi_n \equiv \psi(x_n)$. The momentum states are $\psi(x) = e^{ikx}$ with eigenvalues e^{-ika}. Accordingly

$$\lambda_k \ = \ \gamma - w^+e^{-ika} - w^-e^{ika} \ = \ \gamma[1-\cos(ka)] + i\bar{v}\sin(ka) \tag{15.45}$$

Diffusion.– Consider a rate equation that describes stochastic motion along chain, with transition rates $w_{nm} = w(r)$ that depend on the hopping distance $r = (n-m)$. One can deduce the drift velocity and the diffusion coefficient from the 1st and 2nd moments of the short-time spreading:

$$\bar{v} \ = \ \frac{1}{2}\sum_{r=-\infty}^{\infty} r\, w(r) \tag{15.46}$$

$$D \ = \ \frac{1}{2}\sum_{r=-\infty}^{\infty} r^2\, w(r) \tag{15.47}$$

For unbiased near-neighbor hopping with rate w we get $\bar{v} = 0$ and $D = wa^2$, where a is the lattice constant. Accordingly, if we discretize a diffusion equation by slicing the x axis into cells of width a, the effective hopping rate w should be chosen such that the diffusion coefficient is $D = wa^2$. An optionally procedure to determine $\bar{v}$ and D is via a Taylor expansion (in k) of the eigenvalue λ_k.

[15.7] Rate equations - formalism

In the remaining subsections of this lecture we discuss the formal aspects of treating rate equations. The state of the system is described by a column vector $\boldsymbol{p}$ whose entries are the occupation probabilities p_n. The dynamics is determined by the rate equation

$$\frac{d\boldsymbol{p}}{dt} = \boldsymbol{W}\boldsymbol{p}, \qquad \boldsymbol{W} = \text{diagonal}\{-\gamma_n\} + \text{offdiagonal}\{w_{nm}\} \tag{15.48}$$

Probability is conserved hence $\boldsymbol{W}$ has the left eigenvector $q^0 = \{1, 1, ...\}$ with eigenvalue $\lambda_0 = 0$. The associated right eigenvector p^0 is the steady state. The other eigenvalues $-\lambda_r$ of $\boldsymbol{W}$ might be complex, but the real part of λ_r has to be positive. This follows from the observation that for $t \to \infty$ only the steady state survives, while all the higher has to diminish. The proof is based on the Perron-Frobenius theorem with regard to $\boldsymbol{U}(t) = \exp(\boldsymbol{W}t)$. If we have detailed balance (see below) the λ_r have to be real and positive.

In general we can write the transition rates as follows:

$$w_{nm} = \exp\left[-\mathcal{B}_{nm} + \frac{\mathcal{E}_{m\rightsquigarrow n}}{2}\right] \tag{15.49}$$

where $\mathcal{B}$ is a symmetric matrix while $\mathcal{E}$ is the anti-symmetric part. The latter can be decomposed into conservative and solenoid components in a unique way:

$$\mathcal{E}_{m\rightsquigarrow n} = \ln\left(\frac{w_{nm}}{w_{mn}}\right) = (V_m - V_n) + \sum_\alpha \alpha\, \mathcal{A}^{(\alpha)}_{m\rightsquigarrow n} \tag{15.50}$$

Note that the "solenoid gauge" implies that $\mathcal{A}$ is uniform along the C_α loop. One can use a non-solenoid gauge, e.g. to have it non-zero on one bond only. Anyway we fix its gauge and normalized its circulation as follows:

$$\sum_{x\in C_\alpha} \mathcal{A}^{(\alpha)}_x = 1 \tag{15.51}$$

We can define the height of the barrier relative to the potential reference level:

$$B_{nm} = \mathcal{B}_{nm} + \frac{V_n + V_m}{2} \tag{15.52}$$

Then the expression for the transition rates takes the following form:

$$w_{nm} = \exp\left[-(B_{nm} - V_m) + \frac{1}{2}\sum_\alpha \alpha\, \mathcal{A}^{(\alpha)}_{m\rightsquigarrow n}\right] \tag{15.53}$$

The detailed balance condition of having no circulations implies that there exist a diagonal matrix $\boldsymbol{V}$ such that

$$\mathrm{e}^{\boldsymbol{V}}\boldsymbol{W}\mathrm{e}^{-\boldsymbol{V}} = \boldsymbol{W}^\dagger \tag{15.54}$$

Then we can perform a "gauge" transformation to a symmetric matrix

$$\tilde{\boldsymbol{W}} = \mathrm{e}^{\boldsymbol{V}/2}\boldsymbol{W}\mathrm{e}^{-\boldsymbol{V}/2}, \qquad \tilde{\boldsymbol{W}} = \tilde{\boldsymbol{W}}^\dagger \tag{15.55}$$

It follows that all the λ_r have non-negative real values. If we spoil the detailed-balance the matrix $\tilde{\boldsymbol{W}}$ will becomes parameterized by the affinities α, and the λ_r might become complex. Instead of the detailed balance condition we get $\mathrm{e}^{\boldsymbol{V}}\boldsymbol{W}(\alpha)\mathrm{e}^{-\boldsymbol{V}} = [\boldsymbol{W}(-\alpha)]^\dagger$ or equivalently $\tilde{\boldsymbol{W}}(\alpha) = \left[\tilde{\boldsymbol{W}}(-\alpha)\right]^\dagger$.

[15.8] Rate equations - counting statistics

We add a pointer q with conjugate variable φ such that $[q,\varphi]=i$. Now the Hilbert space is spanned by $|n,q\rangle$. The dynamics of the joint probability distribution $p_n(q)$ in the presence of affinity α is generated by the operator

$$\boldsymbol{W}(\alpha) \ = \ \sum_{n,m} |n, q+\mathcal{A}_{m\rightsquigarrow n}\rangle \ w_{nm} \ \langle m,q| \ = \ \sum_{n,m} w_{nm} \ \hat{J}^{(m\rightsquigarrow n)} \otimes \mathrm{e}^{-i\mathcal{A}_{m\rightsquigarrow n}\hat{\varphi}} \tag{15.56}$$

We change basis to $|n,\varphi\rangle$ and use the Laplace transform convention $i\varphi \mapsto \varphi$, such that

$$p_n(q) \ \equiv \ \sum_{\varphi} \tilde{p}_n(\varphi) \ \mathrm{e}^{i\varphi q} \ \equiv \ \sum_{\varphi} p_n(\varphi) \ \mathrm{e}^{\varphi q} \tag{15.57}$$

It follows that the moment generating function is

$$Z(\varphi) = \left\langle \mathrm{e}^{-\varphi q} \right\rangle = \sum_n p_n(\varphi), \qquad \text{with } p_n(\varphi) = \sum_q p_n(q)\mathrm{e}^{-\varphi q}, \tag{15.58}$$

The master equation for $p_n(\varphi)$ is block-diagonal in φ, with matrix

$$\boldsymbol{W}(\alpha;\varphi) \ = \ w_{mn}\mathrm{e}^{-\varphi\mathcal{A}_{n\rightsquigarrow m}} \ = \ \boldsymbol{W}(\alpha-2\varphi) \tag{15.59}$$

We no longer have detailed balance but $\mathrm{e}^{\boldsymbol{V}}\boldsymbol{W}(\alpha;\varphi)\mathrm{e}^{-\boldsymbol{V}} = [\boldsymbol{W}(\alpha;\alpha-\varphi)]^{\dagger}$. The comulants are determined by the lowest eigenvalue $\lambda_0(\varphi)$, leading to the NFT

$$g(\varphi) = g(\alpha-\varphi) \qquad \rightsquigarrow \qquad P(-q)/P(q) = \exp(-\alpha q) \tag{15.60}$$

[15.9] Rate equations - ergodicity

It is convenient to define a weighted distribution $q_n = p_n/p_n^0$, such that q_n =uniform once the steady state is reached. The rate equation takes the form $\dot{\boldsymbol{p}} = \boldsymbol{G}\boldsymbol{q}$, where

$$G_{nm} \ = \ W_{nm}p_m^0 \qquad \sum_n G_{nm} = \sum_m G_{nm} = 0 \tag{15.61}$$

Accordingly

$$\boldsymbol{q}^{\dagger}\boldsymbol{G}\boldsymbol{q} \ = \ -\frac{1}{2}\sum_{nm} G_{nm}(q_n-q_m)^2 \tag{15.62}$$

For an eigen-mode $\boldsymbol{G}\boldsymbol{q}^r = \lambda_r\boldsymbol{p}^r$ and it is implied that $\lambda_r\sum_n[(p_n^r)^2/p_n^0] > 0$, leading to the conclusion that $\lambda_r > 0$.

In order to characterize the approach to steady state we pick a convex function $f(x)$, for example $f(x) = x\ln(x)$ and define an ergodicity measure

$$H(t) \ = \ \sum_n p_n^0 \ f(q_n(t)) \ = \ e.g. \ = \ \sum_n p_n \ln(p_n/p_n^0) \tag{15.63}$$

Then we get

$$\frac{d}{dt}H(t) \ = \ -\sum_n G_{nm} \ \left[(f(q_n)-f(q_m)) - (q_n-q_m)f'(q_n)\right] \ < \ 0 \tag{15.64}$$

[16] Quantum master equations

[16.1] General perspective

The description of the reduced dynamics of a system that is coupled to a bath using a Master equation is commonly based on the following working hypothesis: **(i)** The bath is fully characterized by a single spectral function. **(ii)** There is a way to justify the neglect of memory effects. The latter is known as the Markovian approximation. In particular it follows that the initial preparation, whether it is factorized or not, is not an issue. If the master equation is regarded as *exact* description of the reduced dynamics it should be of the Lindblad form. Otherwise is should be regarded merely as an approximation.

There are two common approximation schemes: **(A)** In the *Microscopic regime* of atomic physics (e.g. two level atom) it is assumed that the bath induced rates are much smaller than the level spacing, and a ”secular approximation” is employed. **(B)** In the *Mesoscopic regime* of condense matter physics (e.g. Brownian motion) it is assumed that the bath is Ohmic, and accordingly its effect can be treated as a generalization of ”white noise”.

[16.2] The general Lindblad form

A master equation for the time evolution of the system probability matrix is of Lindblad form if it can be written as

$$\frac{d\rho}{dt} \ = \ -i[\boldsymbol{H},\rho] \ + \sum_r \nu_r \boldsymbol{L}_r \rho \boldsymbol{L}_r^\dagger \ - \frac{1}{2}\left[\boldsymbol{\Gamma}\rho + \rho\boldsymbol{\Gamma}\right], \qquad \boldsymbol{\Gamma} = \sum_r \nu_r \boldsymbol{L}_r^\dagger \boldsymbol{L}_r \tag{16.1}$$

where $\boldsymbol{L}_r$ are called Lindblad generators, and ν_r are positive coefficients. An optional style of writing the above master equation is

$$\frac{d\rho}{dt} \ = \ -i[\boldsymbol{H},\rho] \ + \sum_r \nu_r \left[\boldsymbol{L}_r \rho \boldsymbol{L}_r^\dagger \ - \frac{1}{2}\{\boldsymbol{L}_r^\dagger \boldsymbol{L}_r, \rho\}\right], \tag{16.2}$$

Lindblad equation is the most general form of a Markovian master equation for the probability matrix. The time dependence of an expectation values is given by the adjoint equation:

$$\frac{d}{dt}\langle \boldsymbol{Q}\rangle \ = \ \mathsf{trace}\left[\boldsymbol{Q}\frac{d}{dt}\rho\right] \ = \ \mathsf{trace}\left[\boldsymbol{Q}\mathcal{L}\rho\right] \ = \ \mathsf{trace}\left[(\mathcal{L}^\dagger \boldsymbol{Q})\rho\right] \ = \ \langle \mathcal{L}^\dagger \boldsymbol{Q}\rangle \tag{16.3}$$

If the master equation is written in the Lindblad form, the expression for $\mathcal{L}^\dagger \boldsymbol{Q}$ is the same as $\mathcal{L}\rho$ with $\boldsymbol{H} \mapsto -\boldsymbol{H}$.

[16.3] Derivation of the Lindblad form

The most general linear relation between matrices is

$$\tilde{\rho}_{\alpha\beta} \ = \ \sum_{\alpha'\beta'} \mathcal{K}(\alpha\beta|\alpha'\beta')\, \rho_{\alpha'\beta'} \tag{16.4}$$

This linear transformation can be regarded as “quantum operation” if it preserves the hermiticity and the positivity of ρ. See [arXiv (lecture 53)] for details. Changing notation to $\mathcal{K}(\alpha\beta|\alpha'\beta') = \mathcal{K}_{\alpha\alpha',\beta\beta'}$ one observes that $\mathcal{K}_{\alpha\alpha',\beta\beta'}$ should be hermitian, with non-negative eigenvalues λ_r. Accordingly we can find a spectral decomposition with a transformation matrix $T(\alpha\alpha'|r)$. Changing notation to $\boldsymbol{K}^r_{\alpha,\alpha'} = T(\alpha\alpha'|r)$ we get the Kraus representation $\tilde{\rho} = \sum_r \lambda_r [\boldsymbol{K}^r]\rho[\boldsymbol{K}^r]^\dagger$. Conservation of probability implies $\sum_r \lambda_r [\boldsymbol{K}^r]^\dagger [\boldsymbol{K}^r] = \boldsymbol{1}$. Looking on the incremental change of ρ during a small time interval dt, one obtains the Lindblad form of the Master equation.

Detailed derivation of Lindblad form from the Kraus representation can be found in [arXiv]. For completeness we present here a brief outline. We note that for zero time evolution we have as single non-zero eigenvalue $\lambda_{(0)} = N$

which is associated with the normalized identity matrix $T(\alpha\alpha'|0) = N^{-1/2}\delta_{\alpha,\alpha'} \equiv \boldsymbol{L}_0$, where N is the dimension of Hilbert space. For a small time step we substitute $\lambda_{(r\neq 0)} \equiv \nu_r dt$ and $T(\alpha\alpha'|r) \equiv \boldsymbol{L}_r$. Note that the ν_r are positive, and that the $\boldsymbol{L}_{(r\neq 0)}$ are traceless due to the orthogonality with $\boldsymbol{L}_0$. Accordingly

$$\frac{d\rho}{dt} \ = \ \sum_{r\neq 0} \nu_r \boldsymbol{L}_r \rho \boldsymbol{L}_r^{\dagger} + ... \tag{16.5}$$

The remaining terms in the Lindblad form are the $\boldsymbol{H}$-term and the $\boldsymbol{\Gamma}$-term, that are related to the $r = 0$ term, and can be straightforwardly deduced. However we prefer to point out an indirect approach. From the same argument as for quantum operations it is clear that any linear expression that preserves hermiticity can be written as $\sum_r \nu_r [\boldsymbol{L}^r]\rho[\boldsymbol{L}^r]^{\dagger}$. We transform to some general orthonormal basis where one of the operators is $\boldsymbol{F}^{(0)} = N^{-1/2}\mathbf{1}$, while by orthonormality all the other $\boldsymbol{F}^r$ are traceless. We get

$$\frac{d\rho}{dt} \ = \ \sum_{r,s} \tilde{\nu}_{r,s} [\boldsymbol{F}^r]\rho[\boldsymbol{F}^s]^{\dagger} \ = \ -i[\boldsymbol{H}, \rho] - \frac{1}{2}\{\boldsymbol{\Gamma}, \rho\} + {\sum_{r,s}}' \tilde{\nu}_{r,s} [\boldsymbol{F}^r]\rho[\boldsymbol{F}^s]^{\dagger} \tag{16.6}$$

where the last summation excludes the "0" terms. The definition of the Hamiltonian $\boldsymbol{H} \propto i\sum_r' ([\boldsymbol{F}^r] - [\boldsymbol{F}^r]^{\dagger})$ is implied. Also the $\boldsymbol{\Gamma}$-term is implied, and optionally can be deduced from the requirement of obtaining a trace-preserving map. It is now argued that the sum $\sum_{r,s}'$ should coincide, upon diagonalization, with the summation over the $\boldsymbol{L}^r$ terms. Hence the $\tilde{\nu}_{r,s}$ must have positive eigenvalues ν_r.

[16.4] The Ohmic Master Equation

Consider the the classical Langevin equation. Using canonical phase-space coordinates it reads $\dot{p} = -V'(x) - \eta v + f(t)$, where $v = \dot{x} = p/\mathsf{m}$ is the velocity, and $f(t)$ is white noise that has intensity ν. The corresponding master equation for $\rho(x, p)$ is the Fokker-Planck equation:

$$\frac{d\rho}{dt} = -\frac{\partial}{\partial x}\Big[p\rho\Big] - \frac{\partial}{\partial p}\Big[-V'(x)\rho - \eta v\rho - \frac{\nu}{2}\frac{\partial\rho}{\partial p}\Big] \tag{16.7}$$

This equation can be written with Poisson Brackets, which are replaced in the quantum context by commutators:

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] - \frac{\nu}{2}[x, [x, \rho]] - i\frac{\eta}{2}[x, \{v, \rho\}] \tag{16.8}$$

We shall discuss later the general procedure to derived this master equation from an Hamiltonian, where the interaction with the bath is via the system operator $W = x$. The same procedure can be uses for any W, leading to

$$\frac{d\rho}{dt} = -i[\mathcal{H}, \rho] - \frac{\nu}{2}[W, [W, \rho]] - i\frac{\eta}{2}[W, \{V, \rho\}] - \frac{\nu_\eta}{2}[V, [V, \rho]] \tag{16.9}$$

where v has been replaced by $V = i[\mathcal{H}, W]$, and where $\nu_\eta = 0$. This Ohmic master equation does not have the Lindblad form (see below), and hence in general complete positivity is not guaranteed. For example: if we consider the relaxation of a wavepacket in damped harmonic oscillator, then at low temperatures we end up with a sub-minimal wavepacket that violates the uncertainty relation.

The Ohmic master equation involves the bilinear form $\sum_{r,s} \tilde{\nu}_{r,s} [\boldsymbol{F}^r]\rho[\boldsymbol{F}^s]^{\dagger}$ with $\boldsymbol{F}^{(1)} = W$, and $\boldsymbol{F}^{(2)} = V$, and

$$\tilde{\nu}_{r,s} \ = \ \begin{pmatrix} \nu & -i\frac{\eta}{2} \\ i\frac{\eta}{2} & \nu_\eta \end{pmatrix} \tag{16.10}$$

In order for this equation to be Lindblad, the matrix $\tilde{\nu}_{r,s}$ should be positive. The minimal modification would be to set a non-zero $\nu_\eta = \eta^2/(4\nu)$. With this substitution, after diagonalization, one ends up with a single Lindbald term with the generator

$$\boldsymbol{L} \ = \ W + i\frac{\eta}{2\nu}V \tag{16.11}$$

Note that the pre-factors of the three terms in the modified Ohmic version are $\nu/2$ and $\nu/(2T)$ and $\nu/(32T^2)$ respectively. These terms can be regarded as arsing from an expansion in powers of (Ω/T), where Ω is the frequency of the motion. Accordingly in the high temperature regime the deviation of the standard Fokker-Planck equation from the Lindblad form is negligible.

We can also go in reverse and provide an "Ohmic interpretation" for each term in the Linblad form. Namely, consider

$$\text{Lindblad} \ = \ \boldsymbol{L}\rho\boldsymbol{L}^\dagger - \frac{1}{2}\boldsymbol{L}^\dagger\boldsymbol{L}\rho - \frac{1}{2}\rho\boldsymbol{L}^\dagger\boldsymbol{L} \tag{16.12}$$

Writing

$$\boldsymbol{L} \ = \ A + iB \tag{16.13}$$
$$C \ = \ i[A,B] \tag{16.14}$$
$$D \ = \ (1/2)\{A,B\} \tag{16.15}$$

and using the identity

$$[A,\{B,\rho\}] = \frac{1}{2}[D,\rho] - \frac{i}{2}\{C,\rho\} + A\rho B - B\rho A \tag{16.16}$$

we get the following optional expressions for the Lindblad term:

$$\text{Lindblad} \ = \ -i[D,\rho] - \frac{1}{2}\{A^2+B^2,\rho\} + A\rho A + B\rho B - i[A,\{B,\rho\}] \tag{16.17}$$
$$= \ -i[D,\rho] - \frac{1}{2}[A,[A,\rho]] - \frac{1}{2}[B,[B,\rho]] - i[A,\{B,\rho\}] \tag{16.18}$$

The first term represents "Lamb shift", the second and the third are "noise" induced diffusion terms, and the last is the "friction" term.

[16.5] System-bath interaction

In the following presentation we assume that the full Hamiltonian is

$$\mathcal{H}_{\text{total}} \ = \ \mathcal{H} - WF + \mathcal{H}_{\text{bath}} \tag{16.19}$$

where W and F are system and bath operators respectively. Neglecting the interaction, the bath is characterized by the spectral function

$$\tilde{C}(\omega) \ = \ \text{FT}\Big[\langle F(t)F(0)\rangle\Big] \tag{16.20}$$

and the convention $\langle F(t)\rangle = 0$. Whether the bath is composed of harmonic oscillators or not is regarded by the working hypothesis as not important. There is a well known discussion of this point in Feynman-Vernon paper.

The spectral function $\tilde{C}(\omega)$ is characterized by temperature T and by a cutoff frequency ω_c. The latter is assumed below to be large compared with any other temporal frequency. What we call "noise" means $\tilde{C}(-\omega) = \tilde{C}(\omega)$. What we call "finite temperature" means

$$\tilde{C}(-\omega)/\tilde{C}(\omega) \;=\; \exp(-\omega/T) \tag{16.21}$$

What we call "white noise" or "infinite temperature Ohmic bath" corresponds to $\tilde{C}(\omega) = \nu$, leading to

$$C(t) \;=\; \langle F(t)F(0)\rangle \;=\; \nu\delta(t) \tag{16.22}$$

What we call "high temperature Ohmic bath" takes into account that $\tilde{C}(\omega)$ possesses an antisymmetric component, which is implied by the Boltzmann ratio. Namely, in order to have the Boltzmann ratio to leading order in ω we have to add to ν an antisymmetric term $\nu \times [\omega/(2T)]$. Consequently

$$C(t) \;=\; \langle F(t)F(0)\rangle \;=\; \nu\delta(t) + i\eta\delta'(t) \tag{16.23}$$

where $\eta = \nu/(2T)$ is the so called friction coefficient. If we want to have from first principles an expression that holds for arbitrary ω, we can model the bath as a collection of harmonic oscillators with spectral density $J(\omega)$. Then we get (see "the modeling of the environment" lecture):

$$\tilde{S}(\omega) \;=\; 2J(\omega)\frac{1}{1-\mathrm{e}^{-\omega/T}} \tag{16.24}$$

This expression is consistent with the above definition of Ohmic bath provided we set $J(\omega) = \eta\omega$. For $W := x(t)$, meaning that the bath is driven by a particle that has a given velocity $\dot{x}$, we get from the fluctuation-dissipation relation (or from a direct calculation) that the response of the bath is $\langle F\rangle = -\eta\dot{x}$.

For a general bath, non-necessarily Ohmic, it is useful to define a bath spectral function via a Fourier-Laplace transform

$$G(\omega) \;\equiv\; \int_0^{\infty} C(t)e^{-i\omega t}dt \;\equiv\; \frac{1}{2}\tilde{C}(\omega) - i\Delta(\omega) \tag{16.25}$$

It is also useful to look on W in the interaction picture:

$$W(t) \;=\; e^{i\mathcal{H}t}We^{-i\mathcal{H}t} \;=\; \sum_{n,m}|n\rangle W_{nm}\mathrm{e}^{i(E_n-E_m)t}\langle m| \;\equiv\; \sum_{\Omega}\mathrm{e}^{-i\Omega t}W_{\Omega} \tag{16.26}$$

We can say that the unperturbed system Hamiltonian $\mathcal{H}$ induces spectral decomposition $W = \sum_{\Omega} W_{\Omega}$ of the interaction. For non-degenerated spectrum $W_0 = \sum_n |n\rangle\langle n|$ is the diagonal part of the W-matrix in the energy representation, and each $W_{\Omega}^{\dagger} = W_{-\Omega}$ with $\Omega \neq 0$ corresponds to a pair of coupled levels. Additionally it is useful to define

$$\tilde{W} \;\equiv\; \int_0^{\infty} C(t)W(-t)dt \;=\; \sum_{\Omega} G(\Omega)W_{\Omega} \tag{16.27}$$

Coming back to the Ohmic case, it is useful to define a "velocity" operator $V = i[\mathcal{H}, W]$. Accordingly, in the Ohmic case, we get

$$\tilde{W} \;\approx\; \frac{\nu}{2}\left(W + i\frac{\eta}{\nu}V\right) \tag{16.28}$$

The notations above are useful for the purpose of writing down the Master equation for the time evolution of the reduced probability matrix.

[16.6] The Redfield master equation

We first demonstrate the derivation of the Master equation in the case of white noise. The Hamiltonian is $\mathcal{H}(t) = \mathcal{H} + f(t)W$, were $f(t)$ represents white noise: that means that upon ensemble average $\langle f(t)\rangle = 0$, while $\langle f(t)f(t')\rangle = \nu\delta(t-t')$. Given $\rho(t_0) \equiv \rho$, the Liouville von-Neumann equation can be solved iteratively to determine $\rho(t_0+dt)$, where dt is a small time interval. Without loss of generality we set t_0=0 and $t = t_0+dt$ and get:

$$\rho(t) \;=\; \rho - i\int_0^t dt'\,[\mathcal{H}(t'),\rho] - \int_0^t\int_0^{t'} dt'dt''\,[\mathcal{H}(t'),[\mathcal{H}(t''),\rho]] + ... \tag{16.29}$$

Averaging over realizations of $f(t)$ all the odd orders in this expansion vanish, while the leading dt contribution comes only from the zero order term that involves $\mathcal{H}$ and from the second order term that involves W. Consequently we get the following Master equation:

$$\frac{d\rho}{dt} \;=\; -i[\mathcal{H},\rho] - \frac{1}{2}\nu[W,[W,\rho]] \;=\; -i[\mathcal{H},\rho] - \frac{1}{2}\{\Gamma,\rho\} + \nu W\rho W \tag{16.30}$$

where $\Gamma = \nu WW$. Note that the first two terms in the second expression generate so called non-Hermitian dynamics with the effective Hamiltonian $\mathcal{H}_{\text{eff}} = \mathcal{H} - (i/2)\Gamma$, while the last term represents "continuous measurement".

The generalization of the "white noise" derivation for a system that is coupled to a high temperature Ohmic bath is straightforward. It is based on the assumption that at any moment the system-bath state is "factorized", which can be justifies if ω_c^{-1} is sufficiently small. We define the interactions-representation of the probability matrix via $\rho(t) \equiv U(t)\tilde{\rho}(t)U(-t)$ where $U(t) = \mathrm{e}^{-i\mathcal{H}t}$. The iterative procedures provides for $\tilde{\rho}(t)$ the same expansion as in the previous subsection with $\mathcal{H}(t)$ replaced with $F(t)W(t)$, where $W(t) = U(-t)WU(t)$. Consequently we get the so-called Redfield equation

$$\frac{d\rho}{dt} \;=\; -i[\mathcal{H},\rho] + \tilde{W}\rho W + W\rho\tilde{W}^{\dagger} - W\tilde{W}\rho - \rho\tilde{W}^{\dagger}W \tag{16.31}$$

Note that an optional style of writing this expression is with $-[W,\,\tilde{W}\rho - \rho\tilde{W}^{\dagger}]$, which reduces to $-[W,\,[\tilde{W},\rho]]$ for an hermitian $\tilde{W}$. If instead one substitutes the non-hermitian Ohmic expression for $\tilde{W}$, one obtains the Ohmic master equation, that contains both noise and friction terms. As noted above, one can add to the Ohmic master equation a term $[V,[V,\rho]]$ that represents an extra white noise coupled via V.

[16.7] The secular approximation

We come back one step, and consider again general bath, not necessarily Ohmic. Instead of assuming small correlation time, we shall assume weak interaction. Specifically, in atomic physics applications the induced rate of transitions w becomes much smaller compared with the Rabi-Bloch frequency Ω of the coherent oscillations. Accordingly it is appropriate to write that master equation in the interaction picture:

$$\frac{d\tilde{\rho}}{dt} \;=\; \tilde{W}(t)\tilde{\rho}W(t) + W(t)\tilde{\rho}\tilde{W}(t)^{\dagger} - W(t)\tilde{W}(t)\tilde{\rho} - \tilde{\rho}\tilde{W}(t)^{\dagger}W(t) \tag{16.32}$$

Substitution of the $\mathcal{H}$-induced spectral decomposition of the W-s one observes terms that oscillate with frequencies $\Omega+\Omega'$. We keep only the terms that oscillate with ~ 0 frequency, and hence do not average to zero. For example, in $\tilde{W}\rho W$ we keep only the $G(\Omega)W_{\Omega}\rho W_{-\Omega}$ terms. Consequently we obtain the so called secular approximation

$$\frac{d\rho}{dt} \;=\; -i[\mathcal{H},\rho] + \sum_{\Omega}\left[\tilde{C}(\Omega)\; W_{\Omega}\rho W_{\Omega}^{\dagger} - G(\Omega)\; W_{\Omega}^{\dagger}W_{\Omega}\rho - G(\Omega)^{*}\; \rho W_{\Omega}^{\dagger}W_{\Omega}\right] \tag{16.33}$$

The imaginary part of $G(\Omega)$, aka Lamb shift, can be absorbed into the Hamiltonian $\mathcal{H}$, so we end up with a simple sum over Lindblad terms that are weighted by the spectral intensities $\tilde{C}(\Omega)$, namely,

$$\frac{d\rho}{dt} \ = \ -i[\mathcal{H}_{\text{eff}},\rho] + \sum_{\Omega} \tilde{C}(\Omega) \left[W_{\Omega}\rho W_{\Omega}^{\dagger} - \frac{1}{2}\{W_{\Omega}^{\dagger}W_{\Omega},\rho\} \right] \tag{16.34}$$

In particular one should distinguish the $\Omega \neq 0$ terms that induce inter-level transitions from the $\Omega = 0$ term that commutes with the Hamiltonian.

[16.8] The Pauli master equation

For a system that has no degeneracies (for example a few-level atom) it is natural to write the secular equation in the $\mathcal{H}$ basis. One realizes that the dynamics of the diagonal elements decouples from that of the off-diagonal elements. Namely, the first term in the secular approximation induces FGR transitions with rates

$$w_{nm} \ = \ \tilde{C}(-(E_n{-}E_m)) \ |W_{nm}|^2 \tag{16.35}$$

The corresponding decay constants are $\Gamma_n = \sum'_m w_{nm}$. The ratio w_{nm}/w_{mn} is not unity unless we consider white noise source (infinite temperature). For finite temperatures the FGR rates favor downwards transitions. Consequently we get the so-called Pauli rate equation for the probabilities p_n

$$\frac{d\boldsymbol{p}}{dt} \ = \ \mathcal{W}\,\boldsymbol{p}, \qquad\qquad \mathcal{W} = \begin{pmatrix} -\Gamma_1 & w_{12} & ... \\ w_{21} & -\Gamma_2 & ... \\ ... & ... & ... \end{pmatrix} \tag{16.36}$$

For the off-diagonal terms we get

$$\frac{d\rho_{nm}}{dt} \ = \ \Big[-i(E_n - E_m) - \gamma_{nm} \Big] \rho_{nm}, \qquad\qquad [\text{for } n \neq m] \tag{16.37}$$

with dephasing rates

$$\gamma_{nm} \ = \ \frac{\nu}{2}|W_{nn} - W_{mm}|^2 + \frac{1}{2}(\Gamma_n + \Gamma_m) \ \equiv \ \gamma_{\varphi} + \Gamma_{\text{rlx}} \tag{16.38}$$

where the first term originates from the $\Omega = 0$ generator, while the second term originates from the $\Omega \neq 0$ transitions. We note that the above results can by derived from heuristic consideration, without going through the heavy machinery of the master equation formalism. Taking the white noise master equation as a starting point, it is enough to realize that the elements of ρ_{nm} can be classified according to their unperturbed frequencies $(E_n - E_m)$. Elements that are oscillating with different frequencies, have a negligible cross interaction. In particular the dynamics of the p_n, that have ~ 0 frequencies, decouple from the dynamics of the off-diagonal elements, leading to FGR picture of transitions. For the off diagonal terms the reasoning is similar, and there is an additional dephasing γ_{φ} due to the noisy detuning. The finite temperature case is merely a variation on the same reasoning.

[16.9] Damped harmonic oscillator

Recall that for a damped particle with coupling $-\boldsymbol{x}F$, an Ohmic bath has the spectral function $J(\omega) = \eta\omega$, such that the power spectrum of the fluctuations is $S(\omega) = 2J(\omega)[1 + f(\omega)]$ for $\omega > 0$, and $S(\omega) = 2J(|\omega|)f(|\omega|)$ for $\omega < 0$, where $f(\omega) = 1/(e^{\omega/T} - 1)$. For a particle of mass m such bath produces friction that leads to damping rate $\gamma = \eta/\mathsf{m}$.

Consider the the case of damped Harmonic oscillator of frequency Ω and damping rate γ. Here it is customary to write the interaction as $(2\mathsf{m}\Omega)^{-1/2}[\boldsymbol{a} + \boldsymbol{a}^{\dagger}]F$. Accordingly the W_{Ω} operators are $(2\mathsf{m}\Omega)^{-1/2}\boldsymbol{a}$ and its conjugate. In the secular approximation we get the master equation

$$\frac{d\rho}{dt} \ = \ -i[\Omega\boldsymbol{a}^{\dagger}\boldsymbol{a},\rho] + \gamma(1 + f(\Omega)) \left[\boldsymbol{a}\rho\boldsymbol{a}^{\dagger} - \frac{1}{2}\{\boldsymbol{a}^{\dagger}\boldsymbol{a},\rho\} \right] + \gamma f(\Omega) \left[\boldsymbol{a}^{\dagger}\rho\boldsymbol{a} - \frac{1}{2}\{\boldsymbol{a}\boldsymbol{a}^{\dagger},\rho\} \right] \tag{16.39}$$

The adjoint equation for the expectation value of $\boldsymbol{n} = \boldsymbol{a}^\dagger \boldsymbol{a}$ implies relaxation towards equilibrium with damping rate γ, namely, $(d/dt)\langle \boldsymbol{n} \rangle = -\gamma[\langle \boldsymbol{n} \rangle - f(\Omega)]$.

[16.10] The Bloch equation

Let us consider a two level system. The probability matrix is conveniently expressed using the Bloch vector $\vec{S} = (S_x, S_y, S_z)$, were $S_j = \langle \boldsymbol{\sigma}_j \rangle$, namely,

$$\rho(t) \;=\; \frac{1}{2}\Big(1 + S_x\boldsymbol{\sigma}_x + S_y\boldsymbol{\sigma}_y + S_z\boldsymbol{\sigma}_z\Big) \tag{16.40}$$

Note that $S_z = p_+ - p_-$ is the population probability difference, while S_x and S_y are the so called "coherences". Using the adjoint equation one can easily show that the equation of motion for the Bloch vector takes the form

$$\frac{dS}{dt} \;=\; -\vec{\Omega} \times S \;-\; \gamma\,(S - S_{\text{eq}}) \tag{16.41}$$

where S is regarded as a column vector, and $\gamma = \text{diag}(\gamma_x, \gamma_y, \gamma_z)$ is a diagonal matrix. The first term is generated by the unperturbed Hamiltonian: We assume $\mathcal{H} = -(\Omega/2)\sigma_z$, hence $\vec{\Omega} = (0, 0, \Omega)$.

We consider the effect of having a coupling term $-WF(t)$, where $F(t)$ represents a bath or a noise source. Even without going through the master equation formalism it is clear that consistency with the canonical formalism implies that the equilibrium states is

$$S_{\text{eq}} \;=\; \left(0, 0, \tanh\left(\frac{\Omega}{2T}\right)\right) \tag{16.42}$$

We now refer separately to different versions of the Bloch equation. The different versions are distinguished by the assumptions regarding W, the intensity ν of the $F(t)$ fluctuations, and their spectral characteristics.

Pure dephasing.– The simplest possibility is to have a so-called pure dephasing effect due to a $W = \sigma_z$ interaction with a white noise source that has an intensity ν_φ. In the master equation it introduces a diffusion term $(\nu_\varphi/2)[W, [W, \rho]]$. The implication is to have in the Bloch equation

$$\gamma[\text{Dephasing}] \;=\; \text{diag}\,(2\nu_\varphi, 2\nu_\varphi, 0) \tag{16.43}$$

The interaction with the noise commutes with $\mathcal{H}$ therefore there is no equilibration in the S_z direction. For this reason if we replace the noise source by a finite temperature bath, it will have a similar effect.

Ohmic version.– Next in complexity is to consider a high temperature Ohmic bath coupled via $W = \sigma_x$. Using the notations of the previous sections we have here a "position" coordinate $W = \sigma_x$ and a conjugate "velocity" coordinate $V = \Omega\sigma_y$. Consequently, after some straightforward algebra we deduce that

$$\gamma[\text{Ohmic}] \;=\; \text{diag}\,(0, 2\nu, 2\nu) \tag{16.44}$$

Due to the lack of commutation we have an additional "friction" term $2\eta\Omega$ in the master equation for dS_z/dt, which implies $S_{eq} = (0, 0, \eta\Omega/\nu)$. This is consistent with the canonical expectation, upon the substitution $\nu/\eta = 2T$, provided the condition $(\Omega/T) \ll 1$ is satisfied. This is the regime where the high temperature Ohmic approximation is valid.

The dephasing in the Ohmic version of the Bloch equation is non-isotropic in the transverse XY plane. Note that the S_y transverse component satisfy the equation

$$\ddot{S}_y + 2\nu\dot{S}_y + \Omega^2 S_y = 0 \tag{16.45}$$

which leads to damped frequency $\Omega_{\text{eff}} = \sqrt{\Omega^2 - \nu^2}$. In the secular and NMR versions that we discuss in the next paragrpahs the dephasing is isotropic in the XY plane and therefore Ω is not affected.

Secular version.– We now consider what comes out, for the same coupling, within the framework of the secular approximation. Note that this approximation, unlike the high temperature Ohmic version, assumes large Ω. Using the Pauli equation prescription we realize that the FGR average transition rate is ν. Hence we get

$$\gamma[\text{Secular}] \;=\; \text{diag}\,(\nu, \nu, 2\nu) \tag{16.46}$$

One observes that due to the perturbative nature of this approximation the transverse relaxation looks isotropic. Disregarding this artifact, one should keep in mind that the secular approximation allows to consider the case of non-Ohmic bath. From the general derivation it should be realized that ν in the above equation is determined exclusively by the $\tilde{C}(\pm\Omega)$ components of the fluctuations.

NMR version.– The so called nuclear-magnetic-resonance version of the Bloch equation consider a general W. Formally it is like to add to the secular version of the previous paragraph an additional pure dephasing effect. Accordingly we write the Bloch equation as

$$\frac{dS_z}{dt} \;=\; -\frac{1}{T_1}(S_z - S_{\text{eq}}) \tag{16.47}$$

$$\frac{dS_{x,y}}{dt} \;=\; -[\Omega \times S]_{x,y} - \frac{1}{T_2}S_{x,y} \tag{16.48}$$

where the equilibrium value is

$$S_{\text{eq}} \;=\; \frac{w_{+-} - w_{-+}}{w_{+-} + w_{-+}} \tag{16.49}$$

as in the secular version. The rates for the diagonal relaxation and for the off-diagonal transverse depahsing are:

$$\frac{1}{T_1} \;=\; w_{+-} + w_{-+} \;\;\equiv\;\; \gamma_{\text{rlx}} \tag{16.50}$$

$$\frac{1}{T_2} \;=\; \frac{\gamma_{\text{rlx}}}{2} + \gamma_\varphi \;\;\equiv\;\; \frac{\gamma}{2} \tag{16.51}$$

The pure dephasing rate γ_φ originates from the diagonal elements of W_{nm} and hence is formally proportional to the intensity $\tilde{C}(0)$, while the FGR transition rates originate from the off-diagonal elements of W_{nm}, and hence are proportional to $\tilde{C}(\pm\Omega)$, were $\Omega = |E_+ - E_-|$ is the level spacing.

[16.11] Dicke super-radiance

Consider N two-level atoms that each of then interact with a local bath, namely the interaction term is $\sum_j (1/2)\boldsymbol{\sigma}_j^x F_j(t)$. The term “bath” refers here to modes of the electromagnetic field. Each of the atoms satisfies a Bloch equation. If we sum over over all the Bloch equations we get an equation for the expectation value of $\boldsymbol{S} = \sum_j (1/2)\boldsymbol{\sigma}_j$. At zero temperature we have only spontaneous emissions and the equation takes the form $(d/dt)S^z = -\gamma[S^z - S]$ where $S = (N/2)$. Note that the zero temperature equilibrium state of all spins "up" corresponds in our convention to having all the atoms in the lower level.

If the atoms are packed densely, such that all of them interact with the same bath-modes, the interaction term takes the form $\sum_j (1/2)\boldsymbol{\sigma}_j^x F(t)$, which equals $S^z F(t)$. In the secular approximations we keep only the interaction with $W = S^+ = (S^z + iS^y)$. Working out the Lindblad term we get the modified Bloch equation

$$\frac{d}{dt}S^z = -\gamma\left[(1+S^z)S^z - (1+S)S\right] \tag{16.52}$$

Note that for $N=1$ this is the regular Bloch equation. But for $N \gg 1$ it can be approximated by

$$\frac{d}{dt}S^z = -\gamma \left[S_z^2 - \left(\frac{N}{2}\right)^2\right] \tag{16.53}$$

Assuming that we start with excited atoms (all spins "down"), the rate of decay accelerates, and enhanced by factor N^2 during the time when $S^z \sim 0$. This is in contrast with normal uncorrelated decay where the enhancement factor is N. The explicit solution of this equation is

$$S^z(t) \;=\; \frac{N}{2}\tanh\left[\frac{N}{2}\,\gamma\,(t-t_0)\right] \tag{16.54}$$

where t_0 is the time when S^z crosses zero, and the emission rate attains its maximal super-raddiance value.

[16.12] The Bloch equations in Laser physics

The minimal model for a Laser consist of cavity mode that has frequency Ω, and N two-level atoms (below for simplicity $N=1$) that each of them has excitation energy $\mathcal{E}$. The cavity mode is like damped harmonic oscillator, because it can leak outside with rate κ, and the atoms can decay with rate $\gamma_{\downarrow}$, but are also pumped with rate $\gamma_{\uparrow}$. We define $\gamma = \gamma_{\uparrow} + \gamma_{\downarrow}$ and $f = \gamma_{\uparrow} - \gamma_{\downarrow}$. We also define $\gamma_{\perp} = \gamma + \gamma_{\varphi}$ which includes an optional pure dephasing effect. Without the κ and the γ-s the system is described by the Hamiltonian

$$\mathcal{H} \;=\; \Omega \boldsymbol{a}^{\dagger}\boldsymbol{a} + \frac{\mathcal{E}}{2}\boldsymbol{\sigma}^z + g(\boldsymbol{a}^{\dagger}+\boldsymbol{a})\boldsymbol{\sigma}^x \tag{16.55}$$

where g is the coupling constant, ans in the so-called Rabi model. With the dissipation terms we can derive semi-classical equations that couple the Bloch dynamics to the damped oscillator:

$$\frac{d}{dt}\boldsymbol{a} \;=\; -\left(i\Omega + \frac{\kappa}{2}\right)\boldsymbol{a} - ig\boldsymbol{\sigma}^x \tag{16.56}$$

$$\frac{d}{dt}\boldsymbol{c} \;=\; -\left(i\mathcal{E} + \frac{\gamma_{\perp}}{2}\right)\boldsymbol{c} + ig(\boldsymbol{a}^{\dagger}+\boldsymbol{a})\boldsymbol{\sigma}^z \tag{16.57}$$

$$\frac{d}{dt}\boldsymbol{\sigma}^z \;=\; -\gamma\boldsymbol{\sigma}^z + f + 2g(\boldsymbol{a}^{\dagger}+\boldsymbol{a})\boldsymbol{\sigma}^y \tag{16.58}$$

Above we defined the lowering operator $\boldsymbol{c} = (1/2)[\boldsymbol{\sigma_x} - i\boldsymbol{\sigma_y}]$, such that $\boldsymbol{\sigma}_x = \boldsymbol{c}^{\dagger} + \boldsymbol{c}$. For N atoms the equations are written with $\boldsymbol{S} = \sum_j (1/2)\boldsymbol{\sigma}_j$. For $g=0$ the equations for $\boldsymbol{S}$ are the standard Bloch equations with steady state at $S^z = (N/2)[f/\gamma]$. Below we keep N=1. In the absence of driving ($\gamma_{\uparrow}=0$) the system relaxes to the normal ground state (a=0, σ_z= − 1) provided $g < \sqrt{\Omega\mathcal{E}}/2$. Otherwise it relaxes to a so-called super-radiant ground state with $a \neq 0$. The term "super-radiant" is a bit misleading here - there are no oscillations, and therefore no radiation is emitted once the equilibrium is reached. In order to have lasing f should be large enough. Above a threshold value the steady state is a non-equilibrium limit-cycle (NELC), aka the lasing state. In order to find the NELC it is convenient to transform the equations into a "rotating frame" such that $\mathcal{E} \sim \Omega \mapsto 0$. Counter-rotating (non-resonant) terms in the Rabbi interaction term are neglected (so-called Tavis-Jaynes-Cummings approximation). Reduced equations are obtained for the variables $\boldsymbol{n} = \boldsymbol{a}^{\dagger}\boldsymbol{a}$ and $\boldsymbol{S}^z = (1/2)\boldsymbol{\sigma}^z$, namely

$$\frac{d}{dt}\boldsymbol{n} \;=\; -\left[\kappa - 2\frac{g^2}{\gamma_{\perp}}\boldsymbol{S}^z\right]\boldsymbol{n} \tag{16.59}$$

$$\frac{d}{dt}\boldsymbol{S}^z \;=\; -\left[\gamma + 2\frac{g^2}{\gamma_{\perp}}\boldsymbol{n}\right]\boldsymbol{S}^z + \frac{f}{2} \tag{16.60}$$

Note that $\boldsymbol{S}^z + \boldsymbol{n}$ is a constant of motion due to the rotating wave approximation. From $(d/dt)\boldsymbol{n} = 0$ it follows that at steady state either $\boldsymbol{n} = 0$ or $\boldsymbol{S}^z = (1/2)(\kappa\gamma_\perp/g^2)$. Then from $(d/dt)\boldsymbol{S}^z = 0$ it follows that at steady state

$$\boldsymbol{n}[\mathrm{SS}] \ = \ \frac{f}{2\kappa} - \frac{\gamma\gamma_\perp}{2g^2} \tag{16.61}$$

The threshold condition $f > \kappa\gamma\gamma_\perp/g^2$ to get lasing is implied by positivity of the RHS. Below threshold the attractor is the trivial fixed point at $\boldsymbol{n} = 0$.

[16.13] Many body rate equations

In the simplest approximation quantum master equation are approximated by Pauli master equation with Fermi-Golden-Rule rates. In the many body context it is more convenient to consider the adjoint equations, which are the equations of motion for the expectation values, and possibly for higher moments. Below we consider consider many body rate equations. By this we mean equations of motion for the expectation values of the occupation operators, namely, $n_j \equiv \langle \boldsymbol{n}_j \rangle$. For a closed system $\sum_j n_j = N$ is a constant of motion.

Recall that the dynamics of a single particle is described by a master equation $(d/dt)p_j = \sum_i [I_{i\to j} - I_{j\to i}]$ where the probability current from orbital i to orbital j is $I_{i\to j} = w_{ji}p_i$. If the transitions are induced by a heat bath we have

$$\frac{w_{ij}}{w_{ji}} \ = \ \exp[-(\varepsilon_i - \varepsilon_j)/T] \tag{16.62}$$

This implies that the system relaxes to a canonical equilibrium. The simplest many-body variation is to consider a system of classical non-interacting particles. The adjoint equation for the occupations is

$$\frac{d}{dt}n_j \ = \ \sum_i [I_{i\to j} - I_{j\to i}] \tag{16.63}$$

where the current of particles that are transported from orbital i to orbital j is $I_{i\to j} = w_{ji}n_i$. If the transitions are induced by the same heat bath as in the single particle problem, the detailed balance condition $[I_{i\to j} - I_{j\to i}] = 0$ implies $n_i/n_j = \exp[-(\varepsilon_i - \varepsilon_j)/T)]$, and therefore we get the Boltzmann distribution $n_j = f(\varepsilon_j - \mu)$, where μ is determined by N.

Bosons / Fermions.– Consider a system of Bosons or a system of Fermions. The transitions are induced by a bath that couples to operators that induce hopping, namely, $\boldsymbol{a}_j^\dagger \boldsymbol{a}_i$. The Fermi-Golden-Rule implies that the current of particles that are transported from orbital i to orbital j is

$$I_{i\to j} \ = \ w_{ji}\,(1 \pm n_j)\,n_i \tag{16.64}$$

In order to address all possibilities in a compact way we can interpret ± as "0" for classical particles, "+1" for Boson, and "-1" for Fermion. The detailed balance condition $[I_{i\to j} - I_{j\to i}] = 0$ is satisfied by the Boltzmann / Bose / Fermi distributions respectively, namely $n_j = f(\varepsilon_j - \mu)$, where μ is determined by N. To prove this statement note that the respective distribution functions satisfy the identity

$$\frac{f(\omega)}{1 \pm f(\omega)} \ = \ \exp[-\omega/T] \tag{16.65}$$

Condensation.– Here it is appropriate to recall that condensation of Bosons in the ground orbital is implied if N is large. From dynamical point of view the ground orbital, labeled by "0", is characterized by $w_{0,j} > w_{j,0}$ for any j. The Bose function is finite for any $\varepsilon_j > \mu$, and any excess amount of particles forces $\mu = \varepsilon_0$, such that $i = 0$ can accommodate an arbitrary large number of them.

Additional topics

[17] The kinetic picture

[17.1] The Boltzmann distribution function

The number of one particle states within a phase space volume is $d\mathcal{N} = d^3r d^3p/(2\pi\hbar)^3$. The occupation of this phase space volume is:

$$dN \;\equiv\; f(\boldsymbol{r},\boldsymbol{p})\frac{d\boldsymbol{r}d\boldsymbol{p}}{(2\pi\hbar)^3} \tag{17.1}$$

where $f(\boldsymbol{r},\boldsymbol{p})$ is called Boltzmann distribution function. In equilibrium we have

$$f(\boldsymbol{r},\boldsymbol{p})\Big|_{\text{eq}} \;=\; f_\beta(\epsilon_{\boldsymbol{p}} - \mu) \tag{17.2}$$

where $f_\beta(\epsilon - \mu)$ is either the Bose or the Fermi occupation function, or possibly their Boltzmann approximation. If we use $(\boldsymbol{r},\boldsymbol{v})$ with measure d^3rd^3v instead of $(\boldsymbol{r},\boldsymbol{p})$ we have

$$f(\boldsymbol{r},\boldsymbol{v}) \;=\; \left(\frac{\mathsf{m}}{2\pi}\right)^3 f(\boldsymbol{r},\boldsymbol{p}) \tag{17.3}$$

By integrating over $\boldsymbol{r}$ and over all directions we get the velocity distribution

$$F(v) = L^3 \times 4\pi v^2 \left(\frac{\mathsf{m}}{2\pi}\right)^3 f_\beta\left(\frac{1}{2}\mathsf{m}v^2 - \mu\right) \tag{17.4}$$

If we use Boltzmann approximation for the occupation function and express μ using N and T we get

$$F(v) = N\left(\frac{\mathsf{m}}{2\pi T}\right)^{3/2} \; 4\pi v^2 \; \mathrm{e}^{-\frac{1}{2}\mathsf{m}v^2/T} \tag{17.5}$$

We note that

$$N \;=\; \iint \frac{d\boldsymbol{r}d\boldsymbol{p}}{(2\pi\hbar)^3} f(\boldsymbol{r},\boldsymbol{p}) \;=\; \int d\epsilon \mathsf{g}(\epsilon) f_\beta(\epsilon-\mu) \;=\; \int F(v)dv \tag{17.6}$$

[17.2] The Boltzmann equation

The Liouville equation for $\rho(r,p)$ is merely a continuity equation in phase space. It can be written as $(d/dt)\rho = 0$ where d/dt unlike $\partial/\partial t$ is the total derivative reflecting the change in the occupation of a phase space cell. The Boltzmann equation for $f(r,p)$ is formally identical to the Liouville equation in the absence of collisions, and with collisions becomes $(d/dt)\rho = g(r,p)$, where $g(r,p)$ is the net rate in which particles are generated at (r,p) due to collisions. Accordingly the Boltzmann equation is

$$\left[\frac{\partial}{\partial t} + v(p)\cdot\frac{\partial}{\partial x} + \mathcal{F}(r)\cdot\frac{\partial}{\partial p}\right] f(r,p) \;=\; g_{[f]}(r,p) \tag{17.7}$$

where $v(p) = p/\mathsf{m}$ is the dispersion relation, and $\mathcal{F}(r) = -V'(r)$ is the force due to some external potential. The notation emphasizes that $g(r,p)$ is a functional of the f distribution. It can be written as a difference of ingoing and outgoing fluxes due to collisions. A distribution that gives zero in the left hand side of the Boltzmann equation is called "ergodic". A distribution that gives $g=0$ at any point is "locally equilibrated". If a locally equilibrated distribution is ergodic it constitutes an equilibrium solution of the Boltzmann equation. If there is no such solution, one can look for a non-equilibrium steady-state (NESS) solution. For example, assume that g is different in two regions of space reflecting the presence baths with different temperatures; In such case there exists a non-ergodic NESS solution that features a non-zero heat transport through the system.

The standard Boltzmann expression for $g(r,p)$ is based on 2body collision mechanism and "molecular chaos" assumption. See chapter 4 of **Huang** or chapter 14 of **Reif**. Assuming that collisions from (p,p_0) to (p_1,p_2) has the same rate as that of the inverse process, it takes the following form:

$$g_{[f]}(r,p) \;=\; \int \frac{dp_0}{2\pi} \int \frac{dp_1}{2\pi}\frac{dp_2}{2\pi}\; w(p,p_0|p_1,p_2)\; [f(r,p_2)f(r,p_1) - f(r,p_0)f(r,p)] \tag{17.8}$$

The gas reaches a steady state in accordance with the Boltzmann H theorem. The formal solution for the steady state implies the Maxwell-Boltzmann distribution for the velocities. A much simpler expression for $g(r,p)$ appears while discussing electronic transport. See chapters 16 and 13 of **Ashcroft & Mermin**. Here the scattering mechanics is 1body collisions of the electrons with the lattice, leading to

$$g_{[f]}(r,p) \;=\; \int \frac{dp'}{2\pi} \left[w_{p,p'} f(r,p') - w_{p',p} f(r,p)\right] \tag{17.9}$$

Note that the first term, that corresponds to electrons that are scattered out of the phase-space cell can be written as $-(1/\tau)f$ where $(1/\tau) \sim \mathcal{N}w$ is the decay rate to the other $\mathcal{N}$ cells to which it is connected. If we assume that f is close to an equilibrium solution f_β, it follows that we can approximate $f \approx f_\beta$ in the ingoing flux term. Hence we get the so called relaxation time approximation:

$$g_{[f]}(r,p) \;\approx\; \frac{f_\beta(\epsilon(p)-\mu) - f(r,p)}{\tau} \tag{17.10}$$

NESS is reached if $\beta(r)$ or $\mu(r)$ or the potential $V(r)$ are non-uniform in space. Using the relaxation time approximation the solution that can be written schematically as follows:

$$f(t) \;=\; \int_{-\infty}^{t} \left[\frac{1}{\tau}\exp\left(-\frac{t-t'}{\tau}\right)\right]\; f_\beta(t')\; dt' \tag{17.11}$$

where $f_\beta(t')$ stands for f_β that is evaluated at the point $(r(t'),p(t'))$, which is connected by an unscattered classical trajectory that ends at (r,p) at time t. Assuming τ to be small one can easily obtain a first order solution. For example, in the presence of a constant field of force the NESS becomes

$$f(r,p) \;\approx\; f_\beta - \tau\mathcal{F}v(p)\left(-\frac{\partial f_\beta}{\partial\epsilon}\right) \tag{17.12}$$

where $f_\beta(\epsilon(p))$ is the the equilibrium occupation function that is calculated in the absence of the field. The above NESS carries current whose density can be written as $J=\sigma\mathcal{F}$, where

$$\sigma \;=\; \int \frac{d^3p}{(2\pi)^3}\tau v^2\left(-\frac{\partial f_\beta}{\partial\epsilon}\right) \;=\; \int \frac{g(\epsilon)}{\mathsf{V}}\tau v^2\;\left[-f'_\beta(\epsilon-\epsilon_F)\right] \;=\; \frac{g(\epsilon_F)}{\mathsf{V}}v_F^2\tau \tag{17.13}$$

The last equalities assume a zero temperature Fermi occupation. If $g(\epsilon)$ corresponds to the standard dispersion relation, one obtains the Drude formula $\sigma = (N/\mathsf{V})(\tau/\mathsf{m})$.

[17.3] The calculation of incident flux

Given N gas particles that all have velocity v we can calculate the number of particles that hit a wall element per unit time (=flux), and also we can calculate the momentum transfer per unit time (=force). Using spherical coordinates, such that normal incidence is θ=0, one obtains (per unit area):

$$J \;=\; \iint_{|\theta|<\pi/2} \left[\frac{d\Omega}{4\pi}\frac{N}{\mathsf{V}}\right] v\cos(\theta) \;=\; \left[\frac{1}{2}\int_0^1 \cos(\theta)d\cos(\theta)\right]\frac{N}{\mathsf{V}}v \;=\; \frac{1}{4}\left(\frac{N}{\mathsf{V}}\right)v \tag{17.14}$$

$$P \;=\; \iint_{|\theta|<\pi/2} \left[\frac{d\Omega}{4\pi}\frac{N}{\mathsf{V}}\right] v\cos(\theta)\; 2\mathsf{m}v\cos(\theta) \;=\; \left[\int_0^1 \cos^2(\theta)d\cos(\theta)\right]\frac{N}{\mathsf{V}}\mathsf{m}v^2 \;=\; \frac{1}{3}\left(\frac{N}{\mathsf{V}}\right)\mathsf{m}v^2 \tag{17.15}$$

If we have the distribution $F(v)$ of the velocities, or optionally if we are provided with the one-particle energy distribution, the total flux is given by an integral:

$$J_{\text{incident}} \;=\; \int_0^\infty \frac{1}{4}\left(\frac{F(v)dv}{\mathsf{V}}\right)v \;=\; \int_0^\infty \frac{1}{4}\left(\frac{\mathsf{g}(\epsilon)f(\epsilon)d\epsilon}{\mathsf{V}}\right)v_\epsilon \tag{17.16}$$

Similar expression holds for the pressure P, where one can make the identification $\epsilon = (1/2)\mathsf{m}v_\epsilon^2$, and recover the familiar Grand canonical result.

[17.4] Blackbody radiation

The modes of the electromagnetic field are labeled by the wavenumber k and the polarization α. For historical reasons we use k instead of p for the momentum and ω instead of ϵ for the energy. The dispersion relation is linear $\omega = c|k|$. The density of modes is

$$\mathsf{g}(\omega)d\omega = 2\times\frac{\mathsf{V}}{(2\pi c)^3}4\pi\omega^2 d\omega \tag{17.17}$$

Recall that the canonical state of oscillators can be formally regarded as the grand canonical equilibrium of $\mu = 0$ Bose particles, with the occupation function

$$\langle n_{k\alpha}\rangle \;=\; \frac{1}{\mathrm{e}^{\beta\omega_{k\alpha}}-1} \;\equiv\; f(\omega_{k\alpha}) \tag{17.18}$$

For the total energy E we have

$$E \;=\; \int_0^\infty \omega d\omega\; \mathsf{g}(\omega)\; f(\omega) \;=\; \mathsf{V}\int_0^\infty d\omega\frac{1}{\pi^2c^3}\left(\frac{\omega^3}{\mathrm{e}^{\beta\omega}-1}\right) \tag{17.19}$$

For the total number of photons N we have a similar integral but without the ω. The calculation of the incident flux of photons is the same as in the case of non-relativistic particles with $v \mapsto c$. Accordingly we get $J = (1/4)(N/\mathsf{V})c$. For the flux of energy we just have to replace N by E, namely

$$J_{\text{incident}}[\text{energy}] \;=\; \frac{1}{4}\left(\frac{E}{\mathsf{V}}\right)c \;=\; \int_0^\infty d\omega\left[\frac{1}{4\pi^2c^2}\left(\frac{\omega^3}{\mathrm{e}^{\beta\omega}-1}\right)\right] \tag{17.20}$$

The calculation of the pressure (the rate of momentum transfer) is again the same as in the case of non-relativistic particles, with $\mathsf{m}v \mapsto (\omega/c)$. Accordingly we get for the radiation pressure $P = (1/3)(E/\mathsf{V})$. Note that $P \mapsto (1/2)P$ for an absorbing surface.

Considering the thermal equilibrium between blackbody radiation from the environment, and an object that has an absorption coefficient $a(\omega)$, detailed balance consideration implies that

$$J_{\text{emitted}}\,(\omega)\,d\omega \;=\; a(\omega)J_{\text{incident}}\,(\omega)\,d\omega \tag{17.21}$$

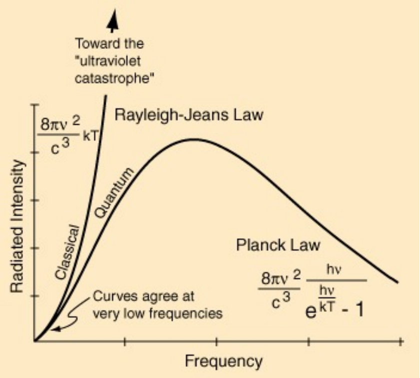
It follows that we can regard $a(\omega)$ as the emissivity of the object. From here we get the Planck formula

$$J_{\text{emitted}}(\omega) \;=\; a(\omega)\frac{1}{4\pi^2c^2}\left(\frac{\omega^3}{\mathrm{e}^{\beta\omega}-1}\right) \;=\; \frac{a(\omega)}{4\pi^2c^2}\,T^3\,\left(\frac{\nu^3}{\mathrm{e}^{\nu}-1}\right) \tag{17.22}$$

where $\nu = \omega/T$ is the scaled frequency. See Figure below taken from hyperphysics. Note that the peak of a blackbody radiation is at $\nu \approx 3$ which is known as Wein's law. Upon integration the total blackbody radiation is

$$J_{\text{emitted}} \;=\; \int_0^\infty J_{\text{emitted}}(\omega)d\omega \;=\; \frac{1}{4\pi^2c^2}\left(\frac{\pi^4}{14}\right)T^4 \tag{17.23}$$

which is know as Stephan-Boltzmann Law. Note that the units of the flux are energy per time per unit area.



[17.5] Viscosity

We have considered above the rate in which momentum is transferred to a wall due to *ballistic* collisions, leading to pressure. There is a somewhat related effect that is called "viscosity". It is simplest to explain the concept with regard to a gas whose particles have a short mean free path ℓ, such that in equilibrium each gas particle has a diffusion coefficient $D = v_T\ell$, where v_T is the mean thermal velocity.

Assume out of equilibrium steady state in which the average velocity of the gas particles $\boldsymbol{u}(x, y, z)$ is in the x direction but its magnitude varies in the y direction. Due to the transverse diffusion there will be momentum transfer across the $y = 0$ plane, which implies that the "upper" flow exerts a force on the "lower" region of the fluid (which is possibly the boundary layer of some "wall"). We shall explain below that if the area of the boundary region is A, then the force on it is given by the "stress-shear equation"

$$F_x \;=\; \mu\mathsf{A}\frac{du_x}{dy} \tag{17.24}$$

where $\mu = \rho D$ is the viscosity, and ρ is the mass density of the gas. The argument goes as follows: Divide the y axis into layers of width dy. Define w, the effective transition rate of particles between layers, such that $D = wdy^2$. Define the flow of momentum between layers as $J(y) = [(\rho dy)u_x(y)] \times w$. Hence $J(dy/2) - J(-dy/2)$ is the rate in which momentum is transferred across $y = 0$, leading to the desired result.

[17.6] The Navier-Stokes equation

The variables that describe the flow of gas or liquid are the density $\rho(x)$ and the velocity $\mathbf{u}(x)$. More generally we can add also temperature $\theta(x)$, and heat flow $\mathbf{q}(x)$. The conservation laws are for the mass, for the momentum, and for the energy. The conservation of the momentum corresponds to the second law of Newton, and formally can be written as [Huang section 5.3]:

$$\frac{d\mathbf{u}_j}{dt} \quad\equiv\quad \left(\frac{\partial}{\partial t}+\sum_i \mathbf{u}_i\frac{\partial}{\partial x_i}\right)\mathbf{u}_j \quad=\quad \frac{1}{\rho}\left[\mathbf{f}_j \;-\; \sum_i \frac{\partial}{\partial x_i}\mathbf{P}_{ij}\right] \tag{17.25}$$

Following the presentation as in **Huang** one obtains the Navier-Stokes equation [Wiki] that describes the rate of change of the velocity due to momentum transfer in a vicious fluid:

$$\rho\frac{d\mathbf{u}}{dt} \quad=\quad \mathbf{f}-\nabla\left(P-\frac{\mu}{3}\nabla\cdot\mathbf{u}\right)+\mu\nabla^2\mathbf{u} \tag{17.26}$$

This equation is valid in the hydrodynamics regime, where the mean free path is small compared with to the geometrical length scales. The left hand side contains the non-linear advection term $\rho u\partial u$. The right hand side includes a scalar-pressure term, a viscosity term, and an optional external force term (say gravitation). For incompressible flow $\nabla\cdot\mathbf{u}=0$, and Euler equation is obtained if the viscosity is completely neglected.

Sound waves.– As we see the viscosity μ plays a major role in the Navier-Stokes equation. Usually the equation is supplemented by a continuity equations for the mass, and for the energy, as well as by state equation that connects the pressure to the density. For compressible fluid with state equation $P[\rho]$ the continuity and the Euler equations for the time derivatives of $\rho(x)$ and $\mathbf{u}(x)$ lead to sound waves with velocity

$$c^2 \quad=\quad \frac{\partial P}{\partial\rho} \quad=\quad \frac{\kappa}{\rho} \tag{17.27}$$

Once the viscosity is taken into account we get damping of the sound waves.

Stokes law.– A well known result that comes from the Navier-Stokes equation is Stokes law for the friction force that is exerted on a spherical object of radius R

$$F[\text{stick}] \;=\; -6\pi\mu R\, v_{\text{sphere}}, \qquad\qquad F[\text{slip}] \;=\; -4\pi\mu R\, v_{\text{sphere}} \tag{17.28}$$

Roughly the shear is $1/R$ while the area is R^2 hence the friction is proportional to R. and not to the area of the sphere. The traditional version (with 6π) assumes no-slip boundary conditions. The way to derive it is to find the velocity field for the flow, and then to use the "stress-shear equation" of the previous section. For details see Huang p.119 and [PRA 1970]. The optional derivation via a microscopic theory is quite complicated, see [JCP 1980].

Reynolds number.– The dimensionless parameter in the Navier-Stokes equation, that characterizes the effect of the non-linear advection term, is the Reynolds number. Consider for example the Stokes problem where the relevant length scale is R, we define

$$\text{Re} \quad=\quad \frac{\rho v}{\mu}R \quad=\quad \frac{v}{D}R \tag{17.29}$$

The original geometry that has been considered by Reynolds refers to flow of fluid via a pipe, where R is the downstream distance from the injection point. A boundary layer of thickness $\delta\sim\sqrt{Dt}$ is formed near the walls of the pipe after a distance that correspond to $t=R/v$. The flow is laminar for $R<\delta$. At larger downstream distance (larger "Re") the laminar flow becomes turbulent. This turbulence arises due to loss of stability of the laminar solution. Let us consider again the motion of a spherical particle in a fluid. The derivation of Stokes law assumes small "Re". For large "Re" a turbulent region is formed downstream after the particle, and the v dependence of the friction acquire a fractional exponent. If the translation velocity v is very large the friction becomes proportional to v^2 reflecting transfer of momentum by a moving wall. This should be contrasted by Stokes law that assumes a flow that curves smoothly to the sides of the sphere, and joins at the back of the sphere.

[17.7] Heat current in an open geometry

If we have two boxes, and energy can flow from one to the other, then the heat current I_Q is simply defined as the rate I_E of energy transfer. But if we have a flow I_N of particles, this simple-minded reasoning fails. We would like to argue below the the correct expression for the heat current is

$$I_Q \quad = \quad I_E - \mu I_N \tag{17.30}$$

This expression assumes quasi-reversible flow at well-defined temperature and energy.

First of all let us recognize that if dN particles are transferred from one box to a second box, then the transferred energy dE is ill-defined. Assume for example that the particles are transferred from an energy level ϵ of the first box to an energy level with the same energy at the second box. We get $dE = \epsilon dN$, which depends on the arbitrary energy reference of the Hamiltonian, and hence has no physical significance. But the quantity $dQ = dE - \mu dN$ is well defined. The question is how to rationalize that dQ is indeed the appropriate definition of heat in this context.

Referring to a box with N particles and energy E, recall that a quasi-reversible process of taking an energy $-dE$ requires the supply of energy $dQ = dE$, such as $dS = 0$. In complete analogy, taking $-dN$ particles with energy $-dE$ requires compensation $dQ = dE - \mu dN$, such as $dS = 0$.

[17.8] Thermo-electricity

Reversible flow through a conductor, with no entropy production due to Joule heating, can be regarded as a sequence of quasi-reversible transfer operations. In each step heat is taken or given to the phonons that dwell in another segment of the conductor. The net results is the transfer of energy from one end of the wire to the other end. This reasoning leads to the Mott analysis of the Peltier effect. The expression for the electric current of charge e carriers has the form (Here $J = I/\mathsf{A}$ is the current density):

$$J_N \quad = \quad e^2\mathcal{E} \int c(\varepsilon)\,(-f'(\varepsilon-\mu))\; d\varepsilon \quad \equiv \quad \sigma\mathcal{E} \tag{17.31}$$

while the expression for the quasi-reversible heat current is

$$J_Q = e\mathcal{E} \int (\varepsilon-\mu)\; c(\varepsilon)\,(-f'(\varepsilon-\mu))\; d\varepsilon \quad \equiv \quad \sigma S T \mathcal{E} \tag{17.32}$$

Using the Sommerfeld expansion we deduce that

$$I_Q \quad = \quad \frac{\pi^2}{3e} T^2 \frac{c'(\mu)}{c(\mu)}\; I_N \quad \equiv \quad ST\, I_N \tag{17.33}$$

where $\Pi = ST$ is known as the Peltier coefficient, and S is known as the Seebeck coefficient. From the Onsager reciprocity it follows that the same coefficient appears in the linear relation between J_N and ∇T, as explained below.

A thermal current can be induced also by a temperature gradient. Namely,

$$J_Q \quad = \quad -\kappa \nabla T \tag{17.34}$$

A relation between the thermal conductivity κ and the electrical conductivity σ can be obtained using a straightforward extension of the above derivation (see Ashcroft p.253):

$$\kappa \quad = \quad \frac{\pi^2}{3e^2} T \sigma \tag{17.35}$$

This is known as the Wiedemann-Franz law. We now turn to discuss more general circumstances of having both potential and temperature gradients.

Considering again two boxes, the natural thermodynamic coordinates are $\varphi_N = (N_2 - N_1)/2$ and $\varphi_E = (E_2 - E_1)/2$. Note that $J_N = \dot{\varphi}_N$ and $J_E = \dot{\varphi}_E$. In the continuum limit J is re-defined as the current density. The entropy function is $S(X_N, X_E)$, and the conjugate variables are $X_N = \nabla(\mu/T)$ and $X_E = -\nabla(1/T)$. Here ∇ is the difference, while in the continuum limit it becomes the gradient. The linear relation between the Js and the Xs involves coefficients γ_{ij}. The Onsager relation is invariant under the change of reference energy, but the coefficients depend on the choice of reference. It is customary to set $\mu = 0$ as the reference. Accordingly the linear relations take the following form:

$$\begin{aligned} J_N &= \gamma_\sigma \frac{\mathcal{E}}{T} + \gamma_\perp \nabla\left(\frac{1}{T}\right) \equiv \sigma\left(\mathcal{E} - S\nabla T\right) && (17.36) \\ J_Q &= \gamma_\perp \frac{\mathcal{E}}{T} + \gamma_\kappa \nabla\left(\frac{1}{T}\right) \equiv \sigma S T\, \mathcal{E} - \kappa \nabla T && (17.37) \end{aligned}$$

From the J_N equation it follows that in an open circuit a temperature gradient would be balanced by an induced electric field $\mathcal{E} = S\nabla T$. This is called Seebeck effect.

[18] Scattering approach to mesoscopic transport

The most popular approach to transport in mesoscopic devices takes the scattering formalism rather than the Kubo formalism as a starting point, leading to the Landauer and the BPT formulas. We first cite these formulas and then summarize their common derivation. This should be compared with the Kubo-based derivation of the previous section.

[18.1] The Buttiker-Pretre-Thomas-Landauer formula

We assume without loss of generality that there are three parameters (x_1, x_2, x_3) over which we have external control, where $x_3 = \Phi$ is the AB flux. The expression for the current $\mathcal{I}_\mathrm{A}$ that goes *out* of lead A, assuming DC linear response, can be written as

$$I_\mathrm{A} = -\sum_j \boldsymbol{G}^{3j}\dot{x}_j \tag{18.1}$$

where $-\dot{x}_3 = -\dot{\Phi}$ is the EMF, and therefore G^{33} is the conductance in the usual sense. The Büttiker-Prétre-Thomas-Landauer formula for the generalized conductance matrix is

$$\boldsymbol{G}^{3j} \ = \ \frac{e}{2\pi i}\mathsf{trace}\left(P_\mathrm{A}\frac{\partial S}{\partial x_j}S^\dagger\right) \tag{18.2}$$

In particular for the Ohmic conductance we get the Landauer formula:

$$\boldsymbol{G}^{33} \ = \ \frac{e^2}{2\pi\hbar}\mathsf{trace}(\boldsymbol{t}\boldsymbol{t}^\dagger) \tag{18.3}$$

In order to explain the notations in the above formulas we consider a two lead system. The S matrix in block form is written as follows:

$$S = \begin{pmatrix} \boldsymbol{r}_\mathrm{B} & \boldsymbol{t}_\mathrm{AB}\mathrm{e}^{-i\phi} \\ \boldsymbol{t}_\mathrm{BA}\mathrm{e}^{i\phi} & \boldsymbol{r}_\mathrm{A} \end{pmatrix} \tag{18.4}$$

where $\boldsymbol{r}$ and $\boldsymbol{t}$ are the so called reflection and transmission (sub) matrices respectively. We use the notation $\phi = e\Phi/\hbar$. In the same representation, we define the left lead and the right lead projectors:

$$P_\mathrm{A} = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{pmatrix}, \qquad P_\mathrm{B} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} \end{pmatrix} \tag{18.5}$$

The following identity is important in order to obtain the Landauer formula from the BPT formula:

$$\frac{dS}{d\Phi} \ = \ i\frac{e}{\hbar}(P_\mathrm{A}SP_\mathrm{B} - iP_\mathrm{B}SP_\mathrm{A}) \ = \ i\frac{e}{\hbar}(P_\mathrm{A}S - SP_\mathrm{A}) \ = \ -i\frac{e}{\hbar}(P_\mathrm{B}S - SP_\mathrm{B}) \tag{18.6}$$

Another important identity is

$$\mathsf{trace}(P_\mathrm{A}SP_\mathrm{B}S^\dagger) \ = \ \mathsf{trace}(\boldsymbol{t}\boldsymbol{t}^\dagger) \ = \ \sum_{a\in A}\sum_{b\in B}|\boldsymbol{t}_{ab}|^2 \tag{18.7}$$

The $\mathsf{trace}()$ operataion is over the channel indexes.

[18.2] Floquet theory for periodically driven systems

The solution of the Schrodinger equation

$$i\frac{d\psi}{dt} = \mathcal{H}\psi \tag{18.8}$$

with time independent $\mathcal{H}$ is

$$|\psi(t)\rangle = \sum_{\mathcal{E}} \mathrm{e}^{-i\mathcal{E}t}|\psi^{(\mathcal{E})}\rangle \tag{18.9}$$

where the stationary states are found from

$$\mathcal{H}|\psi^{(\mathcal{E})}\rangle = \mathcal{E}|\psi^{(\mathcal{E})}\rangle \tag{18.10}$$

Consider now the more complicated case where $\mathcal{H}$ depends periodically on time. Given that the basic frequency is ω we can write

$$\mathcal{H}(t) = \sum \mathcal{H}^{(n)}\mathrm{e}^{-in\omega t} \tag{18.11}$$

The solution of the Schrodinger equation is

$$|\psi(t)\rangle = \sum_{\mathcal{E}} \sum_{n=-\infty}^{\infty} \mathrm{e}^{-i(\mathcal{E}+n\omega)t}|\psi^{(\mathcal{E},n)}\rangle \tag{18.12}$$

where the Floquet states are found from

$$\sum_{n'} \mathcal{H}^{(n-n')}|\psi^{(\mathcal{E},n')}\rangle = (\mathcal{E}+n\omega)|\psi^{(\mathcal{E},n)}\rangle \tag{18.13}$$

and $\mathcal{E}$ is defined modulo ω.

[18.3] The Floquet scattering matrix

In scattering theory we can define a Floquet energy shell $\mathcal{E}$. The solution outside of the scattering region is written as

$$|\psi(t)\rangle = \sum_{n=n_{\text{floor}}}^{\infty} \mathrm{e}^{-i(\mathcal{E}+n\omega)t} \sum_{a} \left[A_{an}\frac{1}{\sqrt{v_{an}}}\mathrm{e}^{-ik_{an}r} - B_{an}\frac{1}{\sqrt{v_{an}}}\mathrm{e}^{+ik_{an}r}\right] \otimes |a\rangle \tag{18.14}$$

where v_{an} and k_{an} are determined by the available energy $\mathcal{E}+n\omega$. The current in a given channel is time dependent, but its DC component is simply $\sum_n(|B_{an}|^2 - |A_{an}|^2)$. Therefore the continuity of the probability flow implies that we can define an on-shell scattering matrix

$$B_{bn_b} \ = \sum_{an_a} \boldsymbol{S}_{bn_b,an_a} \ A_{an_a} \tag{18.15}$$

We can write this matrix using the following notation

$$\boldsymbol{S}_{bn_b,an_a} \ \equiv \ \boldsymbol{S}_{b,a}^{n_b-n_a}(\mathcal{E}+n_a\omega) \tag{18.16}$$

Unitarity implies that

$$\sum_{bn_b} |\boldsymbol{S}_{bn_b,an_a}|^2 \;=\; \sum_{bn} |\boldsymbol{S}^n_{b,a}(\mathcal{E})|^2 = 1 \tag{18.17}$$

$$\sum_{an_a} |\boldsymbol{S}_{bn_b,an_a}|^2 \;=\; \sum_{an} |\boldsymbol{S}^n_{b,a}(\mathcal{E}+n\omega)|^2 = 1 \tag{18.18}$$

If the driving is very slow we can use the adiabatic relation between the incoming and outgoing amplitudes

$$B_b(t) \;=\; \sum_a \boldsymbol{S}_{ba}(X(t))\; A_a(t) \tag{18.19}$$

where $\boldsymbol{S}_{ba}(X)$ is the conventional on-shell scattering matrix of the time independent problem. This relation implies that

$$\boldsymbol{S}^n_{b,a}(\mathcal{E}) = \frac{\omega}{2\pi}\int_0^{\omega/2\pi} \boldsymbol{S}_{ba}(X(t))\; \mathrm{e}^{in\omega t} dt \tag{18.20}$$

For sake of later use we note the following identity

$$\sum_n n|\boldsymbol{S}^n_{b,a}|^2 = \frac{i}{2\pi}\int_0^{2\pi/\omega} dt \frac{\boldsymbol{S}_{ba}(X(t))}{\partial t}\boldsymbol{S}_{ba}(X(t)) \tag{18.21}$$

[18.4] Current within a channel

Consider a one dimensional channel labeled as a. Let us take a segment of length L. For simplicity assume periodic boundary condition (ring geometry). If one state n is occupied the current is

$$I_{a,n} \;=\; \frac{e}{L}v_{a,n} \tag{18.22}$$

If several states are occupied we should integrate over the energy

$$I_a \;=\; \sum_n f_a(E_n) I_{a,n} \;=\; \int f_a(E)\frac{LdE}{2\pi v_a}\left(\frac{e}{L}v_a\right) \;=\; \frac{e}{2\pi}\int f_a(E)dE \tag{18.23}$$

For fully occupied states withing some energy range we get

$$I_a \;=\; \frac{e}{2\pi}(E_2-E_1) \;=\; \frac{e^2}{2\pi}(V_2-V_1) \tag{18.24}$$

If we have a multi channel lead, then we have to multiply by the number of open channels.

[18.5] The Landauer formula

Consider a multi channel system which. All the channels are connected to a scattering region which is described by an $\boldsymbol{S}$ matrix. We use the notation

$$g_{ba} = |\boldsymbol{S}_{ba}|^2 \tag{18.25}$$

Assuming that we occupy a set of scattering states, such that $f_a(E)$ is the occupation of those scattering states that incident in the ath channel, we get that the outgoing current at channel b is

$$I_b = \frac{e}{2\pi}\int dE \left[\left(\sum_a g_{ba} f_a(E)\right) - f_b(E)\right] \tag{18.26}$$

Inserting $1 = \sum_a g_{ba}$ in the second term we get

$$I_b = \frac{e}{2\pi}\int dE \left[\sum_a g_{ba}(f_a(E) - f_b(E))\right] \tag{18.27}$$

Assuming low temperature occupation with

$$f_a(E) = f(E - eV_a) \approx f(E) - f'(E)eV_a \tag{18.28}$$

we get

$$I_b = -\frac{e^2}{2\pi}\sum_a g_{ba}\ (V_b - V_a) \tag{18.29}$$

which is the multi channel version of the Landauer formula. If we have two leads A and B we can write

$$I_{\mathrm{B}} = -\frac{e^2}{2\pi}\left[\sum_{b\in B}\sum_{a\in A} g_{ba}\right]\ (V_{\mathrm{B}} - V_{\mathrm{A}}) \tag{18.30}$$

Form here it follows that the conductance is

$$G = \frac{e^2}{2\pi}\sum_{b\in B}\sum_{a\in A} g_{ba} = \frac{e^2}{2\pi}\mathsf{trace}(P_{\mathrm{B}}\boldsymbol{S}P_{\mathrm{A}}\boldsymbol{S}^{\dagger}) \tag{18.31}$$

where P_{A} and P_{B} are the projectors that define the two leads.

[18.6] The BPT formula

Assuming that the scattering region is periodically driven we can use the Floquet scattering formalism. The derivation of the expression for the DC component I_b of the current in channel b is very similar to the Landauer case, leading to

$$\begin{aligned}
I_b &= \frac{e}{2\pi}\int dE \left[\left(\sum_{a,n} |\boldsymbol{S}^n_{ba}(E-n\omega)|^2 f_a(E+n\omega)\right) - f_b(E)\right] && (18.32)\\
&= \frac{e}{2\pi}\int dE \left[\sum_{a,n} |\boldsymbol{S}^n_{ba}(E-n\omega)|^2 (f_a(E-n\omega) - f_b(E))\right] && (18.33)\\
&= \frac{e}{2\pi}\int dE \left[\sum_{a,n} |\boldsymbol{S}^n_{ba}(E)|^2 (f_a(E) - f_b(E+n\omega))\right] && (18.34)\\
&\approx \frac{e}{2\pi}\int dE \left[\sum_{a,n} n\omega|\boldsymbol{S}^n_{ba}(E)|^2 (-f'_a(E))\right] = \frac{e}{2\pi}\left[\sum_{a,n} n\omega|\boldsymbol{S}^n_{ba}(E)|^2\right] && (18.35)
\end{aligned}$$

In the last two steps we have assumed very small ω and zero temperature Fermi occupation. Next we use an identity that has been mentioned previously in order to get an expression that involves the time independent scattering matrix:

$$I_b = i\frac{e}{2\pi}\sum_a \frac{\omega}{2\pi}\int_0^{2\pi/\omega} dt \frac{\boldsymbol{S}_{ba}(X(t))}{\partial t}\boldsymbol{S}_{ba}(X(t)) \tag{18.36}$$

which implies that the pumped charge per cycle is

$$Q = i\frac{e}{2\pi}\oint dX \sum_{b\in B}\sum_a \frac{\boldsymbol{S}_{ba}(X)}{\partial X}\boldsymbol{S}_{ba}(X) \equiv -\oint G(X)dX \tag{18.37}$$

with

$$G(X) = -i\frac{e}{2\pi}\sum_{b\in B}\sum_a \frac{\boldsymbol{S}_{ba}(X)}{\partial X}\boldsymbol{S}_{ba}(X) = -i\frac{e}{2\pi}\mathsf{trace}\left(P_{\mathrm{B}}\frac{\partial \boldsymbol{S}}{\partial X}\boldsymbol{S}^{\dagger}\right) \tag{18.38}$$

Note: since $\boldsymbol{S}(X)$ is unitary it follows that the following generator is Hermitian

$$\boldsymbol{H}(X) = i\frac{\partial \boldsymbol{S}}{\partial X}\boldsymbol{S}^{\dagger} \tag{18.39}$$

The trace of a product of two hermitian operators is always a real quantity.

[18.7] BPT and the Friedel sum rule

If only one lead is involved the BPT formula becomes

$$dN = -i\frac{1}{2\pi}\mathsf{trace}\left(\frac{\partial \boldsymbol{S}}{\partial X}\boldsymbol{S}^{\dagger}\right)\, dX \tag{18.40}$$

where dN is the number of particles that are absorbed (rather than emitted) by the scattering region due to change dX in some control parameter. A similar formula known as the Friedel sum rule states that

$$d\mathcal{N} = -i\frac{1}{2\pi}\mathsf{trace}\left(\frac{\partial \boldsymbol{S}}{\partial E}\boldsymbol{S}^{\dagger}\right)\, dE \tag{18.41}$$

where $\mathcal{N}(E)$ counts the number of states inside the scattering region up to energy E. Both formulas have a very simple derivation, since they merely involve counting of states. For the purpose of this derivation we close the lead at $r = 0$ with Dirichlet boundary conditions. The eigen-energies are found via the equation

$$\det(\boldsymbol{S}(E,X) - \mathbf{1}) \;=\; 0 \tag{18.42}$$

Let us denote the eigenphases of $\boldsymbol{S}$ as θ_r. We have the identity

$$i\sum_r \delta\theta_r = \delta[\ln\det\boldsymbol{S}] = \mathsf{trace}[\delta\ln\boldsymbol{S}] = \mathsf{trace}[\delta\boldsymbol{S}\boldsymbol{S}^{\dagger}] \tag{18.43}$$

Observing that a new eigenvalue is found each time that one of the eigenphases goes via $\theta = 0$ we get the desired result.

[19] The theory of electrical conductance

[19.1] The Hall conductance

The calculation of the Hall conductance is possibly the simplest non-trivial example for adiabatic non-dissipative response. The standard geometry is a 2D "hall bar" of dimension $L_x \times L_y$. In "Lecture notes in quantum mechanics" we have considered what happens if the electrons are confined in the transverse direction by a potential $V(y)$. Adopting the Landauer approach it is assumed that the edges are connected to leads that maintain a chemical potential difference. Consequently there is a net current in the x direction. From the "Landau level" picture it is clear that the Hall conductance G_{xy} is quantized in units $e^2/(2\pi\hbar)$. The problem with this approach is that the more complicated case of disorder $V(x,y)$ is difficult for handling. We therefore turn to describe a formal Kubo approach. From now on we use units such that $e = \hbar = 1$.

We still consider a Hall bar $L_x \times L_y$, but now we impose periodic boundary condition such that $\psi(L_x, y) = \mathrm{e}^{i\phi_x}\psi(0, y)$ and $\psi(x, L_y) = \mathrm{e}^{i\phi_y}\psi(x, 0)$. Accordingly the Hamiltonian depends on the parameters (ϕ_x, ϕ_y, Φ_B), where Φ_B is the uniform magnetic flux through the Hall bar in the z direction. The currents $I_x = (e/L_x)v_x$ and $I_y = (e/L_y)v_y$ are conjugate to ϕ_x and ϕ_y. We consider the linear response relation $I_y = -G_{yx}\dot{\phi}_x$. This relation can be written as $dQ_y = -G_{yx}d\phi_x$. The Hall conductance quantization means that a 2π variation of ϕ_x leads to one particle transported in the y direction. The physical picture is very clear in the standard $V(y)$ geometry: the net effect is to displace all the filled Landau level "one step" in the y direction.

We now proceed with a formal analysis to show that the Hall conductance is quantized for general $V(x,y)$ potential. We can define a "vector potential" A_n on the (ϕ_x, ϕ_y) manifold. If we performed an adiabatic cycle the Berry phase would be a line integral over A_n. By Stokes theorem this can be converted into a $d\phi_x d\phi_y$ integral over B_n. However there are two complementary domains over which the surface integral can be done. Consistency requires that the result for the Berry phase would come out the same modulo 2π. It follows that

$$\frac{1}{2\pi}\int_0^{2\pi}\int_0^{2\pi} B_n d\phi_x d\phi_y \quad = \quad \text{integer} \quad \text{[Chern number]} \tag{19.1}$$

This means that the ϕ averaged B_n is quantized in units of $1/(2\pi)$. If we fill several levels the Hall conductance is the sum $\sum_n B_n$ over the occupied levels, namely

$$G_{yx} \quad = \quad \sum_{n\in\text{band}}\sum_m \frac{2\mathrm{Im}[I^y_{nm}I^x_{mn}]}{(E_m - E_n)^2} \tag{19.2}$$

If we have a quasi-continuum it is allowed to average this expression over (ϕ_x, ϕ_y). Then we deduce that the Hall conductance of a filled band is quantized. The result is of physical relevance if non-adiabatic transitions over the gap can be neglected.

[19.2] The Drude formula

The traditional derivation of the Drude formula is based on the Boltzmann picture. Optionally one can adopt a Langevine-like picture. The effect of the scattering of an electron in a metal is to randomize its velocity. This randomization leads to a statistical "damping" of the average velocity with rate $1/t_\ell$. On the other hand the electric field accelerates the particle with rate $e\mathcal{E}/\mathsf{m}$. In steady state the drift velocity is $v_{drift} = (e\mathcal{E}/\mathsf{m})t_\ell$, and the current density is $J = (N/\mathsf{V})ev_{drift}$ leading to the Drude conductivity $\boldsymbol{\sigma} = (N/\mathsf{V})(e^2/\mathsf{m})t_\ell$. Consequently the conductance of a ring that has a length L and a cross-section A is

$$G \;=\; \frac{\mathsf{A}}{L}\boldsymbol{\sigma} \;=\; \frac{N}{L^2}\left(\frac{e^2}{\mathsf{m}}\right)t_\ell \;=\; e^2\left(\frac{N}{\mathsf{m}v_F L}\right)\frac{\ell}{L} \;\equiv\; \frac{e^2}{2\pi\hbar}\mathcal{M}\frac{\ell}{L} \tag{19.3}$$

where $\ell = v_F t_\ell$ is the mean free path at the Fermi energy, and $\mathcal{M}$ is the effective number of open modes. Below we would like to derive this result formally from the FD relation.

The canonical version of the FD relation takes the form $G = [1/(2T)]\nu_T$, where ν is the intensity of the current fluctuations and G is the conductance. This is known as Nyquist version of the FD relation. One way to go is to calculate ν_T for a many body electronic system, see how this is done in a previous lecture. But if the electrons are non-interacting it is possible to do a shortcut, relating the conductance of the non-interacting many body electronic system to its single particle fluctuations. This can be regarded as a generalizations of the canonical Nyquist formula. The generalization is obtained by re-interpretation of $f(E)$ as the Fermi occupation function (with total occupation N), rather than probability distribution. Assuming a Boltzmann occupation one obtains $G^{[N]} = [N/(2T)]\nu_T$. A similar generalization holds for a microcanonical occupation, from which one can deduce results for other occupations. In particular for low temperature Fermi occupation of non-interacting particles one obtains:

$$G^{[N]} \;=\; \frac{1}{2}\mathsf{g}(E_F)\,\nu_{E_F} \;=\; \frac{1}{2}\mathsf{g}(E_F)\left(\frac{e}{L}\right)^2\int\langle v_\parallel(t)v_\parallel(0)\rangle dt \;=\; \left(\frac{e}{L}\right)^2\mathsf{g}(E_F)\mathcal{D}_0 \tag{19.4}$$

The crossover from the high temperature "Boltzmann" to the low temperature "Fermi" behavior happens at $T \sim E_F$. Assuming exponential velocity-velocity correlation function with time constant τ_0, such that the mean free path is $\ell = v_F\tau_0$, we get $D_0 = v_F\ell$. disregarding numerical prefactors the density of states can be written as $\mathsf{g}(E_F) = (L/v_F)\mathcal{M}$, where $\mathcal{M}$ is the number of open modes. From here we get the Drude formula

$$G^{[N]} \;=\; \left(\frac{e}{L}\right)^2\mathsf{g}(E_F)\mathcal{D}_0 \;=\; \frac{e^2}{2\pi\hbar}\,\mathcal{M}\frac{\ell}{L} \tag{19.5}$$

Relating to electrons that are moving in a lattice with static disorder, the mean free path can be deduced from the Fermi Golden Rule (FGR) picture as follows: Assuming isotropic scattering, the velocity-velocity correlation function is proportional to the survival probability $P(t) = \mathrm{e}^{-t/t_\ell}$. Ignoring a factor that has to do with the dimensionality $d = 2, 3$ of the sample the relation is

$$\langle v(t)v(0)\rangle \;\approx\; v_{\mathrm{E}}^2\,P(t) \;=\; v_{\mathrm{E}}^2\mathrm{e}^{-|t|/t_\ell} \tag{19.6}$$

where the FGR rate of the scattering is

$$\frac{1}{t_\ell} \;=\; 2\pi\varrho_{\mathrm{E}}|U_{mn}|^2 \;=\; \frac{\pi a}{v_{\mathrm{E}}}W^2 \tag{19.7}$$

In the last equality we have used $|U_{\boldsymbol{nm}}|^2 \approx [a/(\mathcal{M}L)]W^2$, where a is the lattice spacing, and W is the strength of the disorder. Disregarding prefactors of order unity we deduce the so-called Born approximation for the mean free path:

$$\ell \;=\; v_{\mathrm{E}}t_\ell \;\approx\; \frac{1}{a}\left(\frac{v_{\mathrm{E}}}{W}\right)^2 \tag{19.8}$$

[19.3] Formal calculation of the conductance

The DC conductance G of a ring with N non-interacting electrons is related by Kubo/FD expression to the density of one-particle states $\mathsf{g}(E_F)$ at the Fermi energy, and to the $\tilde{C}_{vv}(\omega \sim 0)$ fluctuations of velocity. The latter can be deduced semi-classically from the velocity-velocity correlation function, or from the matrix elements of the velocity operator using the quantum-mechanical spectral decomposition. Optionally one can use path integral or Green function diagrammatic methods for the calculation.

Let us summarize some optional ways in which the Kubo/FD expression for the Ohmic conductance can be written. If we use the spectral decomposition with $p_n = \mathsf{g}(E_F)^{-1}\delta(E_n - E_F)$, we get

$$G \;=\; \frac{1}{2}\mathsf{g}(E_F)\left(\frac{e}{L}\right)^2\tilde{C}_{vv}(0) \;=\; \pi\sum_{nm}\left(\frac{e}{L}\right)^2|v_{nm}|^2\,\delta(E_n - E_F)\,\delta(E_m - E_n) \tag{19.9}$$

It is implicit that the delta functions are "broadened" due to the assumed non-adiabaticity of the driving, else we shall get vanishing dissipation. The calculation of G is the adiabatic regime requires a more careful treatment, and possibly goes beyond LRT. As long as the broadening is large compared to the level spacing, but small compared with other energy scales, the result is not too sensitive to the broadening parameter, and small corrections are commonly ignored, unless the ring is very small. Schematically the above expression can be written as

$$G \;=\; \pi\hbar\, \mathsf{g}(E_F)^2 \left(\frac{e}{L}\right)^2 \overline{|v_{nm}|^2} \;=\; \pi\hbar\, \mathsf{g}(E_F)^2\, \overline{|\mathcal{I}_{nm}|^2} \tag{19.10}$$

where the bar indicates that an average should be taken over the near diagonal matrix elements of the velocity operator near the Fermi energy. A somewhat more fancy way to write the same is

$$G \;=\; \pi\, \mathsf{trace}\Big[\mathcal{I}\, \delta(E_F - \mathcal{H})\, \mathcal{I}\, \delta(E_F - \mathcal{H})\Big] \;=\; \frac{1}{\pi}\, \mathsf{trace}\left[\mathcal{I}\, \mathrm{Im}[\mathsf{G}(E_F)]\, \mathcal{I}\, \mathrm{Im}[\mathsf{G}(E_F)]\right] \tag{19.11}$$

where $\mathsf{G} = 1/(E - \mathcal{H} + i0)$ is the one-particle retarded Green function. This opens the way to formal calculations that are based on path integral or diagrammatic methods.

For a chaotic ring, the dispersion $\overline{|\mathcal{I}_{nm}|^2}$ of the off-diagonal matrix elements is equal, up to a symmetry factor, to the dispersion of the diagonal matrix elements. Note that $\mathcal{I}_{nn} = -\partial E_n/\partial\Phi$. It is common to use the notation $\phi = (e/\hbar)\Phi$. Hence one obtains the Thouless relation:

$$\boldsymbol{G}^{[N]} \;=\; \text{factor} \times \frac{e^2}{\hbar} \times \frac{1}{\Delta^2}\, \overline{\left|\frac{\partial E_n}{\partial \phi}\right|^2} \tag{19.12}$$

where the numerical factor depends on symmetry considerations, and Δ is the mean level spacing at the Fermi energy. There is a more refined relation by Kohn. The Thouless relation is a useful staring point for the formulation of the scaling theory for localization.

====== [19.4] Conductivity and Conductance

Consider a ring geometry, and assume that the current is driven by the flux Φ. In order to have a better defined model we should specify what is the vector potential $\mathcal{A}(\boldsymbol{r})$ along the ring. We can regard the values of $\mathcal{A}$ at different points in space as independent parameters (think of tight binding model). Their sum (meaning $\oint \mathcal{A}(\boldsymbol{r})\cdot d\boldsymbol{r}$) should be Φ. So we have to know how Φ is "distributed" along the ring. This is not just a matter of "gauge choice" because the electric field $\mathcal{E}(\boldsymbol{r}) = -\dot{\mathcal{A}}(\boldsymbol{r})$ is a gauge invariant quantity. So we have to know how the voltage is distributed along the ring. However, as we explain below, in linear response theory this information is not really required. Any voltage distribution that results in the same electro-motive force, will create the same current.

In linear response theory the current is proportional to the rate in which the parameters are being changed in time. Regarding the values of $\mathcal{A}$ at different points in space as independent parameters, linear response theory postulates a linear relation between $\langle J(\boldsymbol{r})\rangle$ and $\mathcal{E}(\boldsymbol{r}')$ that involves the conductivity matrix $\boldsymbol{\sigma}(r, r')$ as a kernel. The current density has to satisfy the continuity equation $\nabla \cdot \langle J(r)\rangle = 0$. From here it follows that if we replace $\mathcal{A}$ by $\mathcal{A} + \nabla\Lambda(r)$, then after integration by parts we shall get the same current. This proves that within linear response theory the current should depend only on the electromotive force $-\dot{\Phi}$, and not on the way in which the voltage is distributed. Note that $\mathcal{A} \mapsto \mathcal{A} + \nabla\Lambda(\boldsymbol{r})$ is not merely a gauge change: A gauge transformation of time dependent field requires a compensating replacement of the scalar potential (which is not the case here).

In the following it is convenient to think of a device which is composed of "quantum dot" with two long leads, and to assume that the two leads are connected together as to form a ring. We shall use the notation $\boldsymbol{r} = (\mathsf{r}, s)$, where r is the coordinate along the ring, and s is a transverse coordinate. In particular we shall distinguish a left "section" $\mathsf{r} = \mathsf{r}_\mathrm{B}$ and a right section $\mathsf{r} = \mathsf{r}_\mathrm{A}$ of the two leads, and we shall assume that the dot region is described by a scattering matrix S_{ab}.

We further assume that all the voltage drop is concentrated across the section $\mathsf{r} = \mathsf{r}_\mathrm{B}$, and we measure the current $\mathcal{I}_\mathrm{A}$ through the section $\mathsf{r} = \mathsf{r}_\mathrm{A}$. With these assumptions we have two pairs of conjugate variables, which are $(\Phi_\mathrm{A}, \mathcal{I}_\mathrm{A})$

and $(\Phi_{\rm B},\mathcal{I}_{\rm B})$. Note that the explicit expression for the current operator is simply

$$\mathcal{I}_{\rm A} = e\frac{1}{2}(v\ \delta(\mathsf{r}-\mathsf{r}_{\rm A}) + \delta(\mathsf{r}-\mathsf{r}_{\rm A})v) \tag{19.13}$$

where v is the r component of the velocity operator. We are interested in calculating the conductance, as define through the linear response relation $\langle \mathcal{I}_{\rm A}\rangle = -G^{AB}\dot{\Phi}_{\rm B}$. The Kubo expression takes the form

$$G^{AB} = \frac{\hbar}{\pi}\ \mathsf{trace}\left[\mathcal{I}_{\rm A}\ \mathrm{Im}[\mathsf{G}]\ \mathcal{I}_{\rm B}\ \mathrm{Im}[\mathsf{G}]\right] \tag{19.14}$$

This is yet another version of the Kubo formula. Its advantage is that the calculation of the trace involves integration that is effectively restricted to two planes, whereas the standard version (previous section) requires a double integration over the whole "bulk".

[19.5] From the Kubo formula to the Landauer formula

Before we go on we recall that it is implicit that for finite system Im[G] should be "smeared". In the dot-leads setup which is described above, this smearing can be achieved by assuming very long leads, and then simply "cutting" them apart. The outcome of this procedure is that $\mathsf{G}^{\pm}$ is the Green function of an open system with outgoing wave (ingoing wave) boundary conditions. As customary we use a radial coordinate in order to specify locations along the lead, namely $\mathsf{r} = \mathsf{r}_a(r)$, with $0 < r < \infty$. We also define the channel basis as

$$\langle \mathsf{r}, s|a, r\rangle \ = \ \chi_a(s)\ \delta(\mathsf{r}-\mathsf{r}_a(r)) \tag{19.15}$$

The wavefunction in the lead regions can be expanded as follows:

$$|\Psi\rangle = \sum_{a,r}\left(C_{a,+}\mathrm{e}^{ik_a r} + C_{a,-}\mathrm{e}^{-ik_a r}\right)\ |a, r\rangle \tag{19.16}$$

We define projectors P^{+} and P^{-} that project out of the lead wavefunction the outgoing and the ingoing parts respectfully. It follows that $P^{+}\mathsf{G}^{+} = \mathsf{G}^{+}$, and that $P^{-}\mathsf{G}^{+} = 0$, and that $\mathsf{G}^{-}P^{-} = 0$ etc. We define the operator

$$\begin{aligned}\Gamma_{\rm A} \ &= \ \sum_{a\in A}|a, r_{\rm A}\rangle\hbar v_a\langle a, r_{\rm A}| && (19.17)\\ &= \ \delta(r-r_{\rm A})\otimes\sum_{a\in A}|a\rangle\hbar v_a\langle a| && (19.18)\end{aligned}$$

where $v_a = (\hbar k_a/\mathrm{mass})$ is the velocity in channel a. The matrix elements of the second term in Eq.(19.18) are

$$\Gamma_{\rm A}(s,s') = \sum_{a\in A}\chi_a(s)\ \hbar v_a\ \chi_a^*(s') \tag{19.19}$$

The operator $\Gamma_{\rm B}$ is similarly defined for the other lead. Note that these operators commute with the projectors $P^{\pm}$. It is not difficult to realize that the current operators can be written as

$$\begin{aligned}I_{\rm A} \ &= \ (e/\hbar)[-P^{+}\Gamma_{\rm A}P^{+} + P^{-}\Gamma_{\rm A}P^{-}] && (19.20)\\ I_{\rm B} \ &= \ (e/\hbar)[+P^{+}\Gamma_{\rm B}P^{+} - P^{-}\Gamma_{\rm B}P^{-}] && (19.21)\end{aligned}$$

Upon substitution only two (equal) terms survive leading to the following version of Kubo formula:

$$G^{BA} = \frac{e^2}{2\pi\hbar}\ \mathsf{trace}\left[\Gamma_{\rm B}\ \mathsf{G}^{+}\ \Gamma_{\rm A}\ \mathsf{G}^{-}\right] \tag{19.22}$$

There is a well known expression (Fisher-Lee) that relates the Green function between plane A and plane B to the S matrix. Namely:

$$\mathsf{G}^{+}(s_{\mathrm{B}}, s_{\mathrm{A}}) = -i \sum_{a,b} \chi_b(s_{\mathrm{B}}) \frac{1}{\sqrt{\hbar v_b}} S_{ba} \frac{1}{\sqrt{\hbar v_a}} \chi_a^{*}(s_{\mathrm{A}}) \tag{19.23}$$

Upon substitution we get

$$G^{BA} = \frac{e^2}{2\pi\hbar} \sum_{a\in A} \sum_{b\in B} |S_{ba}|^2 \tag{19.24}$$

This is the Landauer formula. Note that the sum gives the total transmission of all the open channels.

[19.6] From the Kubo formula to the BPT formula

It should be emphasized that the original derivations of the Landauer and the BPT formulas are based on a scattering formalism which strictly applies only in case of an open system (= system with leads which are connected to reservoirs). In contrast to that Kubo formula is derived for a closed system. However, it can be shown that by taking an appropriate limit it is possible to get the BPT formula from the Kubo formula. Namely,

$$\begin{aligned} \eta^{kj} &= \frac{\hbar}{\pi} \, \mathsf{trace}\left[F^k \, \mathrm{Im}[\mathsf{G}^{+}] \, F^j \, \mathrm{Im}[\mathsf{G}^{+}]\right] && (19.25) \\ &= \frac{\hbar}{4\pi} \mathsf{trace}\left[\frac{\partial S^{\dagger}}{\partial x_i} \frac{\partial S}{\partial x_j}\right] && (19.26) \end{aligned}$$

$$\begin{aligned} \boldsymbol{B}^{3j} &= -\frac{i\hbar}{2\pi} \, \mathsf{trace}\left[F^3 \, (\mathsf{G}^{+}{+}\mathsf{G}^{-}) \, F^j \, \mathrm{Im}[\mathsf{G}^{+}]\right] && (19.27) \\ &= \frac{e}{4\pi i} \mathsf{trace}\left[P_{\mathrm{A}} \left(\frac{\partial S}{\partial x_j} S^{\dagger} - \frac{\partial S^{\dagger}}{\partial x_j} S\right)\right] + \mathrm{intrf} && (19.28) \end{aligned}$$

So the sum is

$$\boldsymbol{G}^{3j} = \frac{e}{2\pi i} \mathsf{trace}\left(P_{\mathrm{A}} \frac{\partial S}{\partial x_j} S^{\dagger}\right) \tag{19.29}$$

For more details see Phys. Rev. B **68**, 201303(R) (2003).

[20] Irreversibility and Nonequilibrium processes

[20.1] The origin of irreversibility

Assume an isolated system with Hamiltonian $\mathcal{H}(X)$, where X is a set of control parameters that determine the "fields". For simplicity assume that at $t=0$ the system is in a stationary state. A driving process means that $X=X(t)$ is changed in time. In particular a cycle means that $X(t_{\text{final}})=X(t{=}0)$. A driving process is called *reversible* is we can undo it. In the latter case the combined process (including the "undo") is a closed cycle, such that at the end of the cycle the system is back in its initial state. Generally speaking a driving cycle becomes reversible only in the adiabatic limit. Otherwise it is irreversible.

Micro-reversibility.– One should not confuse reversibility with micro-reversibility. The latter term implies that the mechanical evolution has time reversal symmetry (TRS). This TRS implies that if we could reverse that state of the system at some moment (and also the magnetic field if exists) then ideally the system would come back to its initial state. This is called Lodschmit Echo. In general it is impossible to reverse the state of the system, and therefore in general micro-reversibility does not imply reversibility!

Sudden process.– The irreversibility of typical systems is related to *chaos*. The simplest example is free expansion. In this example X is the location of a piston. At $t=0$ the system is prepared in an ergodic state, say a microcanonical state on the energy surface $\mathcal{H}(X_A)=E$. The piston is moved outwards abruptly form X_A to X_B. After some time of ergodization the system will become ergodic on $\mathcal{H}(X_B)=E$. There is no way to reverse this process.

Slow driving.– The more interesting scenario is a slow cycle. Using the assumption of chaos it can be argued that at the end of the cycle the state will occupy a shell around $\mathcal{H}(X_A)=E$. If the system is driven periodically (many cycles), the thickness of this shell grows like $\sqrt{D_E t}$ with $D_E \propto \dot{X}^2$. This diffusion in energy space implies (with some further argumentation) monotonic increase of the average energy. Thus irreversibility implies dissipation of energy: The system is heated up on the expense of the work which is being done by the driving source.

Non equilibrium steady state.– Another reason for irreversibility is having a "frustrated" system that is connected to several baths, each in different temperature, as in the prototype problem of heat conduction. Typically, after a transient, a steady state is reached. But this steady state is not a canonical thermal equilibrium state. With such configuration one can associate a rate of "entropy production".

[20.2] The notion of Entropy

The term "entropy" is used in a diverse way. In order to avoid confusion we distinguish between the Shanon entropy, the Von-Neumann entropy, the Boltzmann entropy, and the Thermodynamic entropy. All are calculated by the same look-alike formula $S=-\sum_r p_r \log(p_r)$, but the context and the meaning of the p_r is in general not the same.

Information entropy:– If $\{p_r\}$ are the probabilities to get an output r of a measurement, then S provides a measure for the *uncertainty* which is involved in our knowledge of the statistical state. This point of view that regards S as an information measure has been promoted by Shanon. In the quantum mechanical context we define "classical state" as implying 100% certainty for *any* measurement. Such states do not exist in Nature. Rather the states of minimum uncertainty in N dimensional Hilbert space are the pure states, and they have finite information entropy. See quant-ph/0401021. They should be contrasted with the worst mixed state whose entropy is $S=\log(N)$.

Von-Neumann entropy:– Von-Neumann has used a Shanon look-alike formula in order to characterize the *purity* of a quantum state. In the Von-Neumann definition, the p_r are the weights of the pure states in the mixture, namely $S=-\mathsf{trace}[\rho \ln \rho]$, where ρ is the probability matrix. It is important to realize that the Von-Neumann entropy has nothing to do with the theory of irreversibility. If we consider for example the free expansion of a wavepacket in a big chaotic box, then we have $S=0$ at any moment. Still it is nice that the Von-Newman entropy of a canonical state coincides with the thermodynamic definition.

Boltzmann entropy:– Boltzmann has defined S is a way that allows to discuss irreversibility. The idea was to divide the phase space of a system into small cells, and to characterize the statistical state in this representation using S. Then Boltzmann has proposed that S has the tendency to increase with time if the motion is chaotic (a variation of this idea is the "H theorem" that refers to the reduced one-particle description of a gas particle). The same reasoning can be carried out in the quantum mechanical context where the division of Hilbert space into "cells" is defined by a complete set of projectors. Obviously in the latter context recurrences imply that the dynamics of a quantized closed chaotic system looks irreversible only for a limited time.

Thermodynamic entropy:– Using ideal gas thermometer we have identified the empirical temperature $\theta = 1/\beta$, a notion that is postulated by the 0th law of thermodynamics. Later we have shown that $đQ = \sum_r dp_r E_r$ has an integration factor $T = 1/\beta$ as postulated in thermodynamics (see below). Thus we can write $đQ = TdS$, where the definition of S is implied. It turns out that $S(T) = -\mathsf{trace}[\rho_{eq} \ln \rho_{eq}]$, where ρ_{eq} is a canonical state of temperature T.

[20.3] Digression - traditional thermodynamics

Let us discuss how "entropy" is defined in "traditional thermodynamics" without relaying on Statistical Mechanics. The first step is to characterize any thermal state by empirical temperature θ. This is well defined by the "zeroth law" of thermodynamics. The second step is to represent all the thermal states as points in a $\boldsymbol{X} = (X, \theta)$ space. Now we can define "adiabatic surface" as the set of states that can be reached via a reversible adiabatic process that does not involve exchange of energy with the environment. We can label each surface by an number $S(\boldsymbol{X})$, that we call "entropy" (with quotations marks). The convention would be that $S[A] < S[B]$ if we can get from A to B via an irreversible process.

If we have a reversible process that starts at point $\boldsymbol{X}$, and ends at point $\boldsymbol{X} + d\boldsymbol{X}$ the change in "entropy" is $dS = \boldsymbol{\nabla} S \cdot d\boldsymbol{X}$. At the same time we can write for the heat $đQ = \boldsymbol{F} \cdot d\boldsymbol{X}$. By definition both $dS = 0$ and $đQ = 0$ define the same adiabatic surfaces. It follows that there is an "integration factor" such that $\boldsymbol{F} = T(X, \theta)\boldsymbol{\nabla} S$, and hence one can write $đQ = TdS$. We now postulate that there is a possibility to define S such that T is a function of θ alone. This leads to the definitions of the "absolute temperature" and of the "thermodynamic entropy".

Let us rephrase the thermodynamic postulate in a more illuminating way. Consider a reversible isothermal process at temperature θ_H that connects two adiabatic surfaces. Consider a second reversible isothermal process at temperature θ_C that connects the same surfaces. To say that $đQ$ has an integration factor that depends on θ alone means that the ratio $đQ_H/đQ_C$ depends only on the temperatures θ_H and θ_C. Hence we can define "absolute temperature" using the definition of Carnot, and the definition of S is implied.

In Carnot's picture the ratio $đQ_H/đQ_C$ has to do with the efficiency of the heat transfer process. According to Carnot the maximal ratio $đQ_H/đQ_C$ depends only on the temperatures θ_H and θ_C. In "traditional thermodynamics" Carnot's statement is regarded as the consequence of either Clausius or Kelvin's statements that we derive later. If Carnot's statement were false, one would be able to combine two reversible processes that do not have the same "efficiency" in order to produce a device that can pump heat from cold to hot bath without investing work.

During a reversible quasi-static process the change of the entropy of a system a is $\int đQ_a/T_a$, while that of a second system is $\int đQ_b/T_b$. If we have $T_a = T_b = \theta$, it follows that the total entropy change has an additive property, hence entropy is an extensive quantity.

[20.4] The space of all possible states

Canonical states:– The following visualization is useful. Consider a systems that has energy levels $\epsilon_n(X)$. Any canonical state ρ of the system can be represented as a point in a (X, T) plane, and has some entropy $S(T; X)$. Note that $T = 0$ states have zero entropy and energy $E = \epsilon_0(X)$. We can use S as an optional coordinate instead of T, and define $E_{\text{eq}}(X, S)$ as the energy of the canonical state that has entropy S.

Excited states.– We now add a 3rd vertical axis for the energy. In this extended (X, S, E) representation the canonical states form a surface $E_{\text{eq}}(X, S)$. We refer to this surface as the floor. Non-canonical states with the *same* entropy as the canonical state have a higher energy and accordingly are represented by points *above* the floor.

$$E^*[\text{energy of an excited state that has entropy } S] \quad > \quad E_{\text{eq}}(X, S) \tag{20.1}$$

These excited states are represented in the extended (X, S, E) space as points that reside "above" the canonical state $E_{\text{eq}}(X, S)$. Accordingly, all states along a vertical line have the same entropy, but only the lowest state "on the floor" is canonical. The trivial example is of course the excited pure states, that by definition have zero entropy, while their energy $E^* = \epsilon_n(X)$ is larger than $E_{\text{eq}} = \epsilon_0(X)$.

General processes:– We visualize a thermodynamic process as a trajectory in the (X, S, E) space, or optinaly we can project is on the (X, T) plane. A reversible quasi-static process that connects points A and B on the floor is represented by a *solid* line in the (X, T) plane. An actual non-reversible process, that resides "above" the floor, is represented by a *dashed* line in the (X, T) plane. In a closed system Boltzmann told us that the entropy during a process always increases. Loosely speaking this means that the probability at the end of the process is scattered on more "energy levels".

Thermodynamic processes:– If the system can be attached to baths we can consider a more restricted set of processes that we call "Thermodynamic processes". Such processes start and end at the "floor". In other words, we assume that before and after the process the system is found in equilibrium with a heat bath. The process is irreversible if during the intermediate stages it is represented by a dashed line that resides "above" the floor.

[20.5] Statistical-Mechanics version of the second law

The Boltzmann entropy is defined as $S = -\sum_r p_r \ln p_r$, where p_r is the probability to be in the rth cell in phase space. The Boltzmann version of the second law states that for any process from state "A" to state "B"

$$S^{universe}[B] - S^{universe}[A] \quad > \quad 0 \tag{20.2}$$

The Boltzmann entropy is a theoretical construct and hence the statistical version of the second law has no practical value. We have to "translate" both the definition of entropy and the "second law" into a thermodynamic language. For this purpose it is essential to assume that both A and B are equilibrium states (while during the process the system may be out of equilibrium). Then we can identify the Boltzmann entropies $S(A)$ and $S(B)$ with the thermodynamic entropies of states A and B. We shall see in the next section how it helps to formulate a thermodynamic version of the second law in terms of "Heat" and "Work".

[20.6] Thermodynamic version of the second law

In order to translate this microscopic formulation of Boltzmann into the practical language of thermodynamics one assumes: **(1)** In the initial and final states the system is in equilibrium with bodies that have well defined temperatures T_A and T_B respectively; **(2)** During the process the system absorbs heat from equilibrated bodies that have well defined temperatures, while the system itself might be out of equilibrium; **(3)** The change in the entropy of an equilibrated body that has a well defined temperature T is $-đQ/T$, where $đQ$ is the heat transfer with the usual sign convention. With these assumptions we get the thermodynamic version of the second law:

$$\mathcal{S} \quad \equiv \quad \Big[S^{sys}[B] - S^{sys}[A]\Big] - \int_A^B \frac{đQ}{T_{baths}} \quad > \quad 0 \tag{20.3}$$

In particular for a closed cycle we get the Clausius inequality for the entropy production

$$\mathcal{S} \quad = \quad -\oint \frac{đQ}{T_{baths}} \quad > \quad 0 \tag{20.4}$$

Clausius statement:– The simplest application of the Clausius inequality concerns the direction of heat flow. Consider a cycle $(AB)^{\#}$ in which the system is in contact with T_A, and later in contact with T_B (work is not involved). The result of such cycle is the transfer of an amount q of energy from T_A to T_B. Assuming $T_B < T_A$ it follows from the Clausius inequality that q must be positive, which loosely speaking means that heat can flow only from the high to the low temperature. (work-free heat pumps do not exist).

Kelvin statement:– Another immediate implication of the Clausius inequality is that there exist no process whose sole result is to transfer heat into work. If such process existed one would have at the end of each cycle a single bath with $Q > 0$, and hence the total entropy of the universe would decrease. Also the inverse statement is true: if it were possible to device a work-free pump that violates Clausius statement, then it would be possible to violate Kelvin's statement. The proof is based on the possibility to combine such pump device with a Carnot engine.

Maximum work principle:– Consider an isothermal process. We use the standard assumptions: the temperature of the bath is T_0, the initial state is equilibrium, and also at the end of the process we wait until an equilibrium is reached. Using the first law of thermodynamics (energy conservation) we can extract the heat Q from the the first law, namely, $Q = (E(B) - E(A)) - \mathcal{W}$, where $\mathcal{W}$ is the work that has been done on the system. Using $F(A) = E(A) - T_0 S(A)$ and $F(B) = E(B) - T_0 S(A)$, we express $S(B) - S(A)$ in terms of of $F(B) - F(A)$, leading to what we call *Kelvin's expression* for the entropy production:

$$\mathcal{S} \ = \ \frac{\mathcal{W} - [F(B) - F(A)]}{T_0} \ \equiv \ \frac{\mathcal{W}_{\text{irvrs}}}{T_0} \tag{20.5}$$

The last equality, that defines the notion of irreversible work, is physically-meaningful for an isothermal quasistatic process (see argumentation below). Irrespective of that, in any case, the second law implies that

$$\mathcal{W} \ > \ [F(B) - F(A)] \ = \ \text{minimal work required to carry out the process} \tag{20.6}$$

The work that can be extracted from an engine is $W = -\mathcal{W}$. Obviously in order to extract positive work W we need $F(A) > F(B)$. The *maximum* work that can be extracted is equal to the free energy difference $[F(A) - F(B)]$. In particular it follows that if the universe included only one bath, with one temperature, it would not be possible to extract work from a closed cycle.

Irreversible work:– Assuming that the state of the system is canonical-like at *any* instant of time, with a well define temperature T_{sys} at any moment along the $A \mapsto B$ process. We have established that the change of energy can be written as $dE = -ydX + T_{\text{sys}} dS^{\text{sys}}$. The second term originates from transitions between levels. These transitions are induced by the coupling to the environment and/or by the non-adiabaticity of the driving. On the the other hand by definition $dE = đ\mathcal{W} + đQ$. We have identified $dW = ydX$ as the reversible work that could be done by the system. The irreversible work is the difference $đ\mathcal{W}_{\text{irvrs}} = đ\mathcal{W} - (-dW) = đ\mathcal{W} + ydX$. Optionally, we can use the first law to write $đ\mathcal{W}_{\text{irvrs}} = T_{\text{sys}} dS^{\text{sys}} - đ\mathcal{Q}$. In an actual experiment, the total irreversible work can be calculated by integrating over one of these expressions.

Quasistatic version of the second law:– The above discussed relation $T_{\text{sys}} dS^{\text{sys}} = đ\mathcal{W}_{\text{irvrs}} + đ\mathcal{Q}$ can be exploited in order to obtain a *quasi-static* version of the second law:

$$\mathcal{S} \ = \ \int_A^B \frac{đ\mathcal{W}_{\text{irvrs}}}{T_{sys}} \ + \ \int_A^B \left(\frac{1}{T_{sys}} - \frac{1}{T_{baths}}\right) đQ \ > \ 0 \tag{20.7}$$

This version reflects that the origin of reversibility in a quasi-static process is: (i) irreversible work due to e.g. frictional effects; (ii) irreversible heat flow due to finite temperature difference between the system and the bath during heat conduction.

[20.7] Mesoscopic version of the second law

Below we further discuss *non-equilibrium fluctuation theorems* (NFTs). These are mesoscopic versions of the second law, where $\mathcal{S}$ is regarded a random variable. The statement is that $\langle e^{-\mathcal{S}} \rangle = 1$. From that it follows that $\langle \mathcal{S} \rangle > 0$. The average is over many "runs" of the experiment.

We shall focus on two versions of NFT. The "heat version" is the Clausius statement for a closed cycle, while the "work version" concerns processes that do not involve baths. For the "heat version" we adopt the Clausius definition of $\mathcal{S}$ in terms of Q_b. For the "work version" we assume that the temperature of the system in the beginning of the cycle is T_0, and adopt Kelvin's expression for $\mathcal{S}$.

It is important to realize that in the "work version" the definition of $\mathcal{S}$ is ad hoc, because the final state of the system is ill-defined as far as thermodynamic entropy is concerned. It would be an error to regard $\mathcal{S}$ as entropy production: as an extreme counter-example consider a strictly adiabatic process where the Boltzmann entropy stays constant, though $\mathcal{S}$ is non-zero (it is zero only for an isothermal-adiabatic process). Nevertheless, we can add an additional step of post-equilibration, during which work is not being done, in order to provide physical meaning to the ad-hoc definition of $\mathcal{S}$. In such revised protocol $\mathcal{S}$ is contributed by non-adiabaticity of the work process, and also by irreversible flow of heat into the bath.

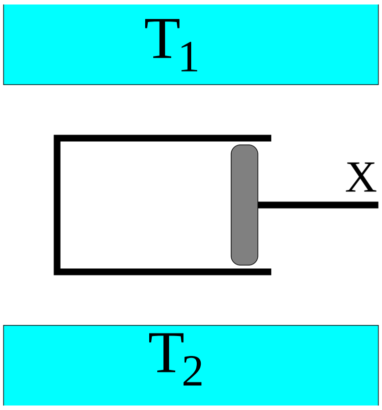
[20.8] The Carnot Cycle paradigm

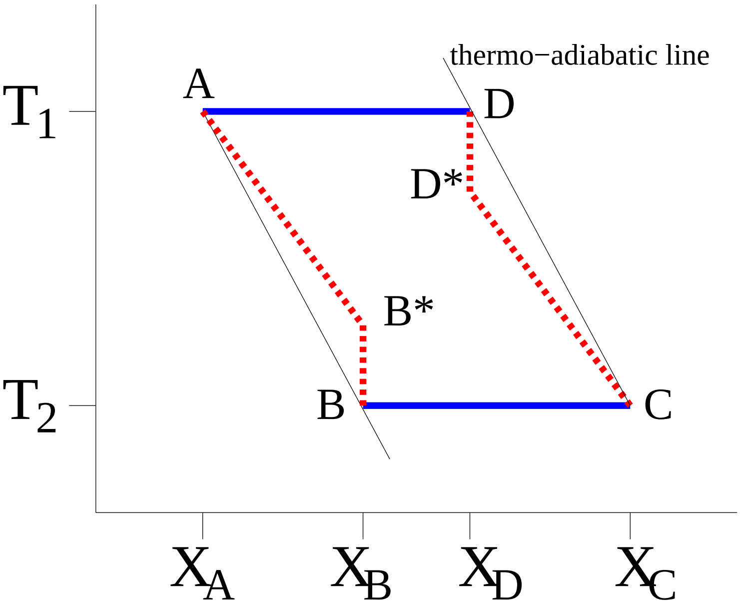
A *strict adiabatic process* is a quasi-static process during which the system is totally isolated from the environment. For such process we have the adiabatic theorem. Namely, assuming that the motion is chaotic the system that has been prepared with definite energy E will remain on the the same adiabatic surface (classical version) or in the same energy level (quantum version) if a parameter X is being changed very slowly. If the system is prepared with probability p_n in some energy shell (classical) or energy level (quantum) then this probability will not change during the process, and hence also the entropy will remain constant. In the classical version n is the phase space volume of the evolving energy surface, while in the quantum mechanical formulation it is the index that labels the energy levels. In the classical limit $n \in [0, \infty]$, and the associated energy is denoted as $E = \epsilon_n(X)$.

We can represent all the possible states of a system as points in (X, S, E) space as described in a previous section. The thermo-adiabatic lines connects canonical points that have the same entropy. Such lines are going along the "floor" of the (X, S, E) space. A *thermo-adiabatic process* is defined as a quasi-static process along a thermo-adiabatic line. We can think of such process as composed of many infinitesimal steps, where each step consists of a strict adiabatic process followed by a contact interaction with a bath that has the appropriate temperature.

To see that the quasi-static limit exists, note the following: If a system is prepared in a canonical state $E_{\text{eq}}(X_0, S)$, Then its energy after a strict adiabatic process is $E^* > E_{\text{eq}}(X, S)$ for any X away from X_0. For a small variation dX the energy difference can be expanded as $dE^* \propto dX^2$. If after such a variation the system is connected to a bath that has the *appropriate* temperature, such that $S(T; X) = S$, it would relax to a canonical state with the same entropy, but with the lower energy $E_{\text{eq}}(X, S)$. This relaxation involves an entropy production $dS^{\text{env}} = dE^*/T$ due to the release of energy to the bath. Integrating dS^{env} over the whole process we see that in the quasi-static limit the entropy production goes to zero.

A strict Carnot cycle involves only two heat baths. The cycle (ABB^*CDD^*) is illustrated in the Figure. The initial preparation is canonical at $A(T_1, X_A)$. The process from $A(T_1, X_A)$ to $B^*(X_B)$ is *strictly* adiabatic. At the end of this stage the obtained state is not canonical. The process from $B^*(X_B)$ to $B(X_B, T_2)$ is the equilibration due to contact with a bath that has the temperature T_2. It is an irreversible relaxation process in which the system goes to a lower energy with the same entropy. At the end of this process the obtained state is canonical. The process form $B(X_B, T_2)$ to $C(X_C, T_2)$ is quasi-static in *contact* with the same heat bath. The process from $C(X_C, T_2)$ to $D^*(X_D)$ is *strictly* adiabatic. The process from $D^*(X_D)$ to $D(X_D, T_1)$ and later back to $A(T_1, X_A)$ is in contact with the heat bath T_1.





[20.9] Fluctuations away from equilibrium

It is customary to say that at equilibrium the expectation value of an observable reflects the typical value of this observable, while the fluctuations are relatively small. If the central limit theorem applies the RMS/mean should scale as $1/\sqrt{N}$. However, it turns out that the *full* statistics might reveal interesting information about the underlying dynamics. In the following we shall discuss processes where the distribution function of work or entropy production does not satisfy the symmetry relation $P(-s) = P(s)$. Rather it satisfies a detailed-balance look-alike relation:

$$P(-s) \;=\; \mathrm{e}^{-\beta s}\, P(s), \qquad \text{[beta-symmetric distribution]} \tag{20.8}$$

It follows that $P(s)$ can be written as a product of a symmetric function and an exponential factor $\mathrm{e}^{\beta s/2}$. Another consequence of the β-symmetry is

$$\langle \mathrm{e}^{-\beta s} \rangle \;=\; 1, \qquad \text{[convex average]} \tag{20.9}$$

The latter equality can be re-phrased as follows: In analogy with the definition of *harmonic* average and *geometric* average that are defined as the inverse of $\langle (1/s) \rangle$ and as the exp of $\langle \log(s) \rangle$ respectively, here we can define a *convex* average that is defined as the log of the above expression. The convex average is zero for a β-symmetric distribution, while the standard algebraic average is positive

$$\langle s \rangle \;>\; 0, \qquad \text{[convex inequality]} \tag{20.10}$$

While for a symmetric distribution the average value $\langle s \rangle$ has to be zero, this is no longer true for a β-symmetric distribution. Rather the average should be related to the variance. To be specific let us assume that s has Gaussian distribution. It can be easily verified that such distribution has β-symmetry with $\beta = 2\mu/\sigma^2$, where $\mu = \langle s \rangle$ is the average value and $\sigma^2 = \mathrm{Var}(s)$ is the variance. This relation between the first and second moment can be regarded as a fluctuation dissipation relation:

$$\langle s \rangle \;=\; \frac{1}{2}\beta\ \mathrm{Var}(s), \qquad \text{["fluctuation dissipation" relation]} \tag{20.11}$$

We can formalize this relation for non-Gaussian distribution in terms of comulant generating function $g(\lambda)$ which is defined through

$$\langle \mathrm{e}^{-\lambda s} \rangle \;\equiv\; \mathrm{e}^{g(\lambda)} \tag{20.12}$$

Note that due to normalization $g(0) = 0$, while $g'(0) = -\mu$ and $g''(0) = \sigma^2$. In particular for a Gaussian $g(\lambda) = -\mu\lambda + (1/2)\sigma^2\lambda^2$. For a symmetric distribution $g(-\lambda) = g(\lambda)$. But for β-symmetry we must have

$$g(\beta - \lambda) \;=\; g(\lambda), \qquad \text{[characterization of beta-symmetric distribution]} \tag{20.13}$$

Again we see that for a Gaussian β-symmetry implies a relation between the mean and the variance.

In the following we shall consider two versions of the non-equilibrium fluctuation theorem. In one version we consider the statistics $P(\mathcal{W})$ of the work $\mathcal{W}$ that is done by an agent during a cycle that involves a thermally isolates system. In the second version we consider the statistics $P(\mathcal{S})$ of the entropy production $\mathcal{S}$ during a cycle that involves exchange of energy with several heat baths.

[20.10] The distribution function of the work

The Crooks relation and Jarzynski equality concern the probability distribution of the *work* that is done during a non-equilibrium process. For presentation purpose let us consider a gas in cylinder with a movable piston. Initially the piston is in position A, and the gas in equilibrium with temperature T_0. The canonical probabilities are

$$p_r^{(A)} = \frac{1}{Z(A)} \mathrm{e}^{-(1/T_0)E_r^{(A)}}, \qquad \text{where } Z(A) = \exp\left[-\frac{F(A)}{T_0}\right] \tag{20.14}$$

Now we displace the piston to position B doing work $\mathcal{W}$. After that we can optionally allow the system to relax to the bath temperature T_0, but this no longer affects $\mathcal{W}$. The distribution of work is defines as

$$P_{A\rightsquigarrow B}(\mathcal{W}) = \sum_r p_r^{(A)}\, \delta\Big(\mathcal{W} - (E_r^{(B)} - E_r^{(A)})\Big) \tag{20.15}$$

It is implicit here that we assume a conservative deterministic classical system with a well-defined invariant measure that allows division of phase space into "cells". The phase-space states $|r^{(B)}\rangle$ are associated with $|r^{(A)}\rangle$ through the dynamics in a one-to-one manner. In other words, the index r in the above definition labels a trajectory that starts at r. If the dynamics is non-adiabatic the order of the cells in energy space is likely to be scrambled: if the $E_r^{(A)}$ are indexed in order of of increasing energy; it is likely that $E_r^{(B)}$ will become disordered.

If the dynamics is not deterministic the above definition can be modified in an obvious way. To be specific let us consider the quantum case, where the probability to make a transition form an eigenstate $|n^{(A)}\rangle$ of the initial Hamiltonian, to an eigenstate $|m^{(A)}\rangle$ of the final Hamiltonian, is given by

$$\mathrm{P}_{A\rightsquigarrow B}(m|n) = \Big|\langle m^{(B)}|U_{A\rightsquigarrow B}|n^{(A)}\rangle\Big|^2 \tag{20.16}$$

Then we define the spectral kernel:

$$P_{A\rightsquigarrow B}(\omega) = \sum_{n,m} p_n^{(A)}\ \mathrm{P}_{A\rightsquigarrow B}(m|n)\ \delta\Big(\omega - (E_m^{(B)} - E_n^{(A)})\Big) \tag{20.17}$$

Since we consider here a closed system, we can identify the work as the energy difference $\mathcal{W} = \omega$. For further discussion of how work can be defined in the quantum context see arXiv:1202.4529

[20.11] The Crooks relation

We have defined the probability distribution $P_{A\rightsquigarrow B}(\mathcal{W})$ for a process that starts at equilibrium with the piston at position A. The probability distribution $P_{B\rightsquigarrow A}(\mathcal{W})$ is defined in the same way for a reversed process: initially the piston is in position B, and the gas in equilibrium with temperature T_0, then the piston is displaced to position A. The Crooks relation states that

$$\frac{P_{B\rightsquigarrow A}(-\mathcal{W})}{P_{A\rightsquigarrow B}(\mathcal{W})} = \exp\left[-\frac{\mathcal{W} - (F(B) - F(A))}{T_0}\right] \tag{20.18}$$

The derivation of this relation using the "quantum" language is trivial and follows exactly the same steps as in the derivation of the detailed balance relation for any spectral function $\tilde{S}(\omega)$. The only difference is that here we have an extra factor $\exp[F(B) - F(A)]$, on top of the Boltzmann factor, that arises because the $p_n^{(A)}$ in the forward process involves a normalization factor $1/Z(A)$, while the $p_m^{(B)}$ is the reversed process involves a normalization factor $1/Z(B)$.

The Crooks relation can be written as $P(-\mathcal{S})/P(\mathcal{S}) = e^{-\mathcal{S}}$, where

$$\mathcal{S} \equiv \frac{\mathcal{W} - (F(B) - F(A))}{T_0} \tag{20.19}$$

corresponds to entropy production. To see that there is a consistency with the Clausius definition of entropy production, consider a protocol with an additional stage, during which the system equilibrates with a bath that has temperature T_0. The result would be the transfer of extra heat $-\Delta\mathcal{Q} = \mathcal{W} - (F(B) - F(A))$, that corresponds to the irreversible work, hence $\mathcal{S} = -\Delta\mathcal{Q}/T_0$ is the entropy production.

[20.12] The Jarzynski equality

Multiplying both sides of the Crooks relation by $P_{B\rightsquigarrow A}(\mathcal{W})$, integrating over $\mathcal{W}$, and taking into account the normalization of $P(-\mathcal{W})$, one obtains the Jarzynski equality

$$\left\langle \exp\left[-\frac{\mathcal{W}}{T_0}\right]\right\rangle \ = \ \exp\left[-\frac{F(B)-F(A)}{T_0}\right] \tag{20.20}$$

It follows from the Jarzynski equality that $\langle\mathcal{W}\rangle > [F(B) - F(A)]$, which is consistent with Kelvins's work principle. It reduces to $\mathcal{W} = (F(B) - F(A))$ in the the case of a quasi-static adiabatic *isothermal* process. The term 'isothermal' requires clarification in the present context. For a small mesoscopic system the quasi-static adiabatic limit implies that $P(\mathcal{W})$ has a distribution over the possible values $\mathcal{W}_n = E_n(B) - E_n(A)$. But if the system consists also of a very large bath, then it is possible to prove that the quasi-static adiabatic limit, when applied to the extended system, implies $\mathcal{W} = F(B) - F(A)$ with probability one in the thermodynamic limit.

An optional one-line derivation of the Jarzynski equality in the context of deterministic classical dynamics is as follows:

$$\left\langle \exp\left[-\frac{\mathcal{W}}{T_0}\right]\right\rangle \ = \ \frac{1}{Z(A)}\sum_r \mathrm{e}^{-(1/T_0)E_r(A)} \ \exp\left[-\frac{E_r(B)-E_r(A)}{T_0}\right] \ = \ \exp\left[-\frac{F(B)-F(A)}{T_0}\right] \tag{20.21}$$

The Crooks relation could have been derived in a similar way, but we had preferred to get it using the "quantum" language, and to regard the Jarzynski equality as its implication.

[20.13] The fluctuation dissipation relation

Let us see what is the implication on the Crooks relation with regard to a simple closed cycle for which $F(B) = F(A)$. In such case $P(\mathcal{W})$ is a β-symmetric distribution. It follows that there is a "fluctuation dissipation relation"

$$\langle\mathcal{W}\rangle \ = \ \frac{1}{2T}\,\mathrm{Var}(\mathcal{W}) \tag{20.22}$$

Considering a multi-cycle process $\mathrm{Var}(\mathcal{W}) = 2D_E t$ and $\langle\mathcal{W}\rangle = \dot{\mathcal{W}}t$, leading to the dissipation-diffusion relation that we have derived in past lecture $\dot{\mathcal{W}} = (1/T)D_E$, from which follows the dissipation-fluctuation relation $\eta = \nu/(2T)$.

[20.14] The non-equilibrium fluctuation theorem

The non-equilibrium fluctuation theorem (Bochkov, Kuzovlev, Evans, Cohen, Morris, Searles, Gallavotti) regards the probability distribution of the *entropy production* during a general non-equilibrium process. The clearest formulation of this idea assumes that the dynamics is described by a rate equation. The transition rates between state n and state m satisfies

$$\frac{w(m|n)}{w(n|m)} \ = \ \exp\left[-\frac{E_m-E_n}{T_{nm}}\right] \tag{20.23}$$

Where T_{nm} is the temperature that controls the nm transition. We can regard the rate equation as describing a random walk process. Consider a trajectory $x(t)$. If the particle makes a transition from m to n the entropy production is $(E_m - E_n)/T_{nm}$. Hence we get for example

$$\frac{w(1|2)w(2|3)w(3|4)}{w(4|3)w(3|2)w(2|1)} \;=\; \exp\left[-\frac{E_1-E_2}{T_{1,2}} - \frac{E_2-E_3}{T_{2,3}} - \frac{E_3-E_4}{T_{3,4}}\right] \;\equiv\; \mathrm{e}^{-\mathcal{S}[1\rightsquigarrow 2\rightsquigarrow 3\rightsquigarrow 4]} \tag{20.24}$$

In general we write

$$\frac{P[x(-t)]}{P[x(t)]} \;=\; \exp\Big[-\mathcal{S}[x]\Big] \tag{20.25}$$

From this "microscopic" relation we deuce that the probability distribution of the energy production satisfies $P(-\mathcal{S})/P(\mathcal{S}) = e^{-\mathcal{S}}$, hence $\langle e^{-\mathcal{S}}\rangle = 1$ and $\langle \mathcal{S}\rangle > 0$.

[20.15] Fluctuations of current in a ring

A simple example for the practicality of this relation concerns the fluctuations of the current I that emerge due to the motion of a particle in a ring. Given a trajectory $q \equiv It$ is the winding number and $\mathcal{S} \equiv q\Phi$ is the entropy production. The non-equilibrium fluctuation theorem implies that $P(-q)/P(q) = \exp(-q\Phi)$. Note that in the case of an electric current $\Phi = eV/T$, where V is the electro-motive force.

[20.16] Thermodynamic Uncertainty Relations

The prototype thermodynamic uncertainty relations concerns a stochastic cyclic process (e.g. the motion of a molecular motor) that is described by a rate equation. The rate of a forward step is w^+, and the the rate of a backward step is w^-. The ratio is $w^-/w^+ = \exp(Q_0/T)$, where Q_0 is the energy of the chemical reaction. Thus the count q of cycles (the net number of "steps" of the molecular rotor) executes a biased random walk process, with $\langle q\rangle = (w^+ - w^-)t$ and $\mathrm{Var}(q) = (w^+ + w^-)t$. The associated entropy production is $S = \langle q\rangle \times (Q_0/T)$. It follows that the signal to noise ratio (SNR) is

$$\mathrm{SNR} \;=\; \frac{\langle q\rangle}{\sqrt{\mathrm{Var}(q)}} \;=\; \sqrt{S\frac{T}{Q_0}\tanh\left(\frac{Q_0}{2T}\right)} \;<\; \sqrt{\frac{S}{2}} \tag{20.26}$$

This relation expresses the observation that the the SNR of a stochastic process is bounded by the entropy production.

[20.17] Analysis of heat conduction

A prototype application of the non-equilibrium fluctuation theorem concerns the analysis of heat flow form hot bath T_H to cold bath T_C. The temperature difference is $\epsilon = T_H - T_C$. We assume that the conductor that connects the two baths can be modeled using a master equation. The transition between states of the conductor are induced by the bath and are like a random walk. With any trajectory we can associate quantities Q_H and Q_C that represent that heat flow from the baths into the conductor. From the fluctuation theorem it follows that

$$\frac{P(-Q_H,-Q_C)}{P(Q_H,Q_C)} \;=\; \exp\left[\frac{Q_C}{T_C} + \frac{Q_H}{T_H}\right] \tag{20.27}$$

Next we define the absorbed energy $\bar{Q} = Q_H + Q_C$ and the heat flow $Q = (Q_H - Q_C)/2$. We realize that in the long time limit $Q \sim t$ while the fluctuations of $\bar{Q}$ are bounded. Accordingly we get

$$\frac{P(-Q)}{P(Q)} \;=\; \exp\left[-\left(\frac{1}{T_C} - \frac{1}{T_H}\right)Q\right] \tag{20.28}$$

If we use a Gaussian approximation, we get a "fluctuation-dissipation" relation

$$\langle Q \rangle \;=\; \frac{1}{2}\left(\frac{1}{T_C}-\frac{1}{T_H}\right)\mathrm{Var}(Q) \tag{20.29}$$

The relation can be linearized with respect to $\epsilon = T_H - T_C$. The thermal conductance is defined through $\langle Q \rangle = K\epsilon \times t$, and the intensity of fluctuations through $\mathrm{Var}(Q) = \nu \times t$. Thus we deduce that

$$\langle \dot{Q} \rangle \;=\; K \times (T_H - T_C), \qquad \text{with } K = \frac{1}{2T^2}\nu \tag{20.30}$$

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