# Assemblage: Exercises in Statistical Mechanics

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===== **[A] Ensemble Theory - classical gases**

A01. Assume that the entropy S and the number of states in phase space Ω of a physical system are related through an arbitrary function, $S = f(\Omega)$. Show that the additive character of S and the multiplicative character of Ω *necessarily* require that $f(\Omega) \sim \ln \Omega$.

A02. Consider mixing of two gases with initial different temperatures, T_1, T_2, particle numbers N_1, N_2 and volumes V_1, V_2, respectively. Evaluate the mixing entropy (i.e. the change of entropy upon mixing) in two cases: (i) the gases are identical, (ii) the gases are distinct (but have equal mass). Show that the mixing entropy in case (ii) is larger and argue for the reason.

A03. Consider N particles in a two level system, n_1 particles in energy level E_1 and n_2 particles in energy level E_2. The system is in contact with a heat reservoir at temperature T. Energy can be transferred to the reservoir by a quantum emission in which $n_2 \to n_2 - 1, n_1 \to n_1 + 1$ and energy $E_2 - E_1$ is released. [Note: $n_1, n_2 \gg 1$.]

   (a) Find the entropy change of the two level system as a result of a quantum emission.
   (b) Find the entropy change of the reservoir corresponding to (a).
   (c) Derive the ratio n_2/n_1; do not assume a known temperature for the two level system. (Note: equilibrium is maintained by these type of energy transfers).

A04. Consider N particles, each fixed in position and having a magnetic moment μ , in a magnetic field H. Each particle has then two energy states, $\pm\mu H$. Treat the particles as distinguishable.

   (a) Evaluate the entropy of the system $S(n)$ where n is the number of particles in the upper energy level; assume $n >> 1$. Draw a rough plot of $S(n)$.
   (b) Find the most probable value of n and its mean square fluctuation.
   (c) Relate n to the energy E of the system and find the temperature. Show that the system can have negative temperatures. Why a negative temperature is not possible for a gas in a box?
   (d) What happens if a system of negative temperature is in contact with a heat bath of fixed temperature T_0?

A05. A rubber band is modeled as a single chain of $N \gg 1$ massless non-interacting links, each of fixed length a. Consider a one-dimensional model where the links are restricted to point parallel or anti-parallel to a given axis, and the chain is attached to end points at a distance L (see figure). Note that the chain may extend beyond the length L; only its end points are fixed.
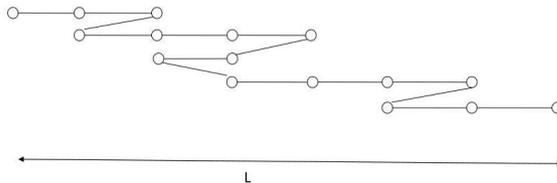
   (a) Evaluate the entropy $S(L, N)$.

(b) The rubber is now uniformly squeezed such that stretched configurations are ener- getically favored. Assume here a simplified form of this energy that favors large L, $E(L) = -\frac{1}{2}\sigma\frac{L^2}{N}$.

Calculate the free energy and the force $f(x,T)$ that the chain applies at its end points, where $x = L/Na$. Expand $f(x,T)$ at small x and plot as function of x. Interpret the sign of f: does the rubber try to expand or to contract?

(c) Below some temperature T_c and for some range of L the system is unstable. Identify T_c and the unstable range.

(d) Consider the unforced chain $f = 0$, find $x(T)$ and solve for $x \ll 1$. Plot $x(T)$, qualitatively .

A06. Consider an ensemble of N harmonic oscillators with an energy spectrum of each oscillator being $\left(n + \frac{1}{2}\right)\hbar\omega, n = 0, 1, 2, ...$

(a) Evaluate the asymptotic expression for $\Omega(E)$, the number of ways in which a given energy E can be distributed.

(a) Consider these oscillators as classical and find the volume in phase space for the energy E. Compare the result to (a) and show that the phase space volume corresponding to one state is h^N.

A07. Show that, for a statistical system in which the interparticle interaction potential $u(r) \sim r^\gamma$ the virial $\mathcal{V}$ is given by $\quad \mathcal{V} = -3PV - \gamma U \quad$ where U is the mean *potential energy* of the system. Hence, the mean kinetic energy K is

$$K = -\mathcal{V}/2 = (3PV + \gamma U)/2 = \frac{1}{\gamma + 2}(3PV + \gamma E)$$

where $E = K + U$. What happens when $\gamma = -2$?

A08. Consider a gas of noninteracting particles with kinetic energy of the form $\varepsilon(\mathbf{p}) = \alpha|\mathbf{p}|^{3(\gamma-1)}$ where α is a constant; $\mathbf{p}$ is the momentum quantized in a box of size L^3 by $p_x = hn_x/L, p_y = hn_y/L, p_z = hn_z/L$ with n_x, n_y, n_z integers. Examples are nonrelativistic particles with $\gamma = 5/3$ and extreme relativistic particles with $\gamma = 4/3$.

(a) Use the microcanonical ensemble to show that in an adiabatic process (i.e. constant S, N) PV^γ =const.

(b) Deduce from (a) that the energy is $E = Nk_BT/(\gamma - 1)$ and the entropy is $S = \frac{k_B N}{\gamma - 1}\ln(PV^\gamma) + f(N)$. What is the most general form of the function f(N)?

(c) Show that $C_p/C_v = \gamma$.

(d) Repeat (a) by using the canonical ensemble.

A09. A system is allowed to exchange energy and volume with a large reservoir. Consider the system with the reservoir in a microcanonical ensemble and derive the distribution of states of the system in terms of temperature and pressure.

(a) Define the partition function $Z_N(P,T)$ and identify the thermodynamic potential $-k_BT\ln[Z_N(P,T)]$.

(b) Solve Ex. A05(b) for $f(x,T)$ with $\sigma = 0$ by using the ensemble in (a). [A05 considers molecule chain with flexible joints.]
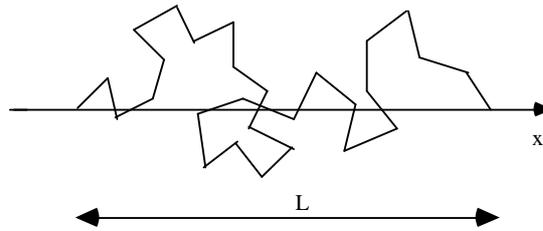
A10. As shown in the figure, a chain molecule consists of N units, each having a length a. The units are joined so as to permit free rotation about the joints. At a given temperature T, derive the relation between the tension f acting between both ends of the three-dimensional chain molecule and the distance L between the ends.

A11. An ideal gas of N molecules of mass m is enclosed in a centrifuge with radius R and height L. The centrifuge rotates at angular frequency Ω. Choosing the z axis along the axis of the centrifuge, the (classical) Hamiltonian function for each molecule is

$$\mathcal{H} = \frac{(\vec{p})^2}{2m} - \Omega(xp_y - yp_x).$$

(a) Find the canonical partition function at temperature T [Hint: integrate first over momenta].

(b) Find the radial force on the outer wall of the cylinder.

A12. N monomeric units are arranged along a straight line to form a chain molecule. Each unit can be either in a state α (with length a and energy E_α) or in a state β (with length b and energy E_β).

(a) Derive the relation between the length L of the chain molecule and the tension f applied between at the ends of the molecule.

(b) Find the compressibility $\chi_T = (\partial L/\partial f)_T$. Plot schematically $L(fa/k_BT)$ and $\chi_T(fa/k_BT)$ and interpret the shape of the plots.

A13. A perfect lattice is composed of N atoms on N sites. If M of these atoms are shifted to interstitial sites (i.e. between regular positions) we have an imperfect lattice with M defects. The number of available interstitial sites is N' and is of order N. The energy needed to create a defect is ω .

(a) Evaluate the number of defects M at a temperature T (you may assume that there is a dominant term in the partition sum). Show that to first order in $e^{-\omega/2T}$ (i.e. $\omega \gg T$)

$$M = \sqrt{NN'}exp\left(-\omega/2T\right).$$

(b) Evaluate the contribution of defects to the entropy and to the specific heat to first order in $\exp\left(-\omega/2T\right)$.

A14. N atoms of mass m of an ideal classical gas are in a cylinder with insulating walls, closed at one end by a piston. The initial volume and temperature are V_0 and T_0, respectively.

(a) If the piston is moving out rapidly the atoms cannot perform work, i.e. their energy is constant. Find the condition on the velocity of the piston that justifies this result.

(b) Find the change in temperature, pressure and entropy if the volume increases from V_0 to V_1 under the conditions found in (a).

(c) Find the change in temperature, pressure and entropy if the volume increases from V_0 to V_1 with the piston moving very slowly, i.e. an adiabatic process.

A15. Consider a solid with N non-magnetic atoms and N_i non-interacting magnetic impurities with spin s. There is a weak spin-phonon interaction which allows energy transfer between the impurities and the non-magnetic atoms.

(a) A magnetic field is applied to the system at a constant temperature T. The field is strong enough to line up the spins completely. What is the change in entropy of the system due to the applied field? (neglect here the spin-phonon interaction).

(b) Now the magnetic field is reduced to zero adiabatically. What is the qualitative effect on the temperature of the solid? Why is the spin-phonon interaction relevant?

(c) Assume that the heat capacity of the solid is $C_V = 3Nk_B$ in the relevant temperature range. What is the temperature change produced by the process (b)? (assume the process is at constant volume).

A16. Consider a system of N spins on a lattice at temperature T, each spin has a magnetic moment . In presence of an external magnetic field each spin has two energy levels, μH.

(a) Evaluate the changes in energy δE and in entropy δS as the magnetic field increases from 0 to H. Derive the magnetization $M(H)$ and show that

$$\delta E = T\delta S - \int_0^H M(H')\, dH'.$$

Interpret this result.

(b) Show that the entropy $S(E, N)$ can be written as $S(M, N)$. Deduce the temperature change when H is reduced to zero in an adiabatic process. Explain how can this operate as a cooling machine to reach $T \approx 10^{-4} K$. (Note: below $10^{-4} K$ in realistic systems spin-electron or spin-spin interactions reduce $S(T, H = 0) \to 0$ as $T \to 0$. This method is known as cooling by adiabatic demagnetization.

A17. Consider a gas of N hard spheres in a box. A single sphere occupies a volume ω, while its center of mass can explore a volume V (if the rest of the space is empty). There are no other interactions between the spheres except for the constraints of hard core exclusion.

(a) Calculate the partition function for this gas. You will need to integrate over the spatial part of phase space. Use the approximation

$$\int_{|x_i - x_j| > a} d^3x_1 d^3x_2 ... d^3x_N \approx V(V - \omega)(V - 2\omega)...(V - (N-1)\omega)$$

and explain under which physical circumstances this approximation is valid.

(b) Calculate the entropy. Use the approximation

$$(V - a\omega)(V - (N - a)\omega) \approx (V - N\omega/2)^2$$

where a is an integer. When is this approximation valid?

(c) Find the equation of state.

(d) Show that the isothermal compressibility $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is always positive.

A18. An ideal gas of classical charged particles with mass m is confined between two capacitor plates of area A, separated by distance L. The capacitors produce a force f perpendicular to the plates which pushes the particles to the lower plate. The particles can be absorbed on either plate, with an absorption potential $-\epsilon < 0$; on each plate the particles can move freely. The system is in equilibrium at temperature T. The average density of the non-adsorbed particles, i.e. those between the plates, is n_0.

(a) Evaluate the density $n(x, y, z)$, choosing z perpendicular to the plates.

(b) Evaluate the densities on the lower and upper plates.

(c) Evaluate the forces acting on the top and bottom plates. Is there a net force on the capacitor?

A19. An ideal classical gas of N particles of mass m is in a container of height L which is in a gravitational field of a constant acceleration g. The gas is in uniform temperature T.

   (a) Find the dependence $P(h)$ of the pressure on the height h.

   (b) Find the partition function and the internal energy. Examine the limits $mgL \ll k_BT$ and $mgL \gg k_BT$ and interpret the meaning of these limits.

   (c) Find $P(h)$ for an adiabatic atmosphere, i.e. the atmosphere has been formed by a constant entropy process in which T, μ, are not equilibrated, but $Pn^{-\gamma} = \text{const}$; equilibrium is maintained within a layer at height h. Find $T(h)$ and $n(h)$ in terms of the density n_0 and temperature T_0 at $h = 0$.

A20. The DNA molecule forms a double stranded helix with hydrogen bonds stabilizing the double helix. Under certain conditions the two strands get separated resulting in a sharp "phase transition" (in the thermodynamic limit). As a model for this unwinding, use the "zipper model" consisting of N parallel links which can be opened from one end (see figure). If the links $1, 2, 3, ..., p$ are all open the energy to open to $p+1$ link is ϵ and if the
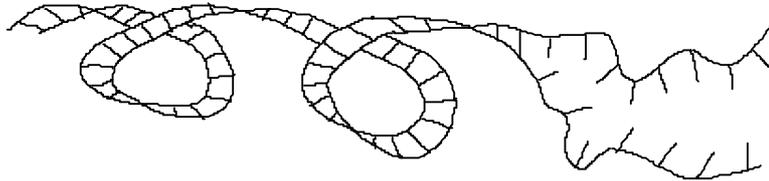
earlier links are closed the energy to open the link is infinity. The last link $p = N$ cannot be opened. Each open link can assume G orientations corresponding to the rotational freedom about the bond.

   (a) Construct the canonical partition function. Find then the average number of open links $\langle p \rangle$ as function of $x = Ge^{-\varepsilon/k_BT}$. Show that

$$\langle p \rangle = \tfrac{1}{2}N[1 + \frac{1}{6}N(x-1) + O(N^3(x-1)^3)]$$

so that the slope $d\langle p \rangle/dx \sim N^2$ at $x = 1$. Plot $\langle p \rangle/N$ schematically as function of x for large but finite N and for $N \to \infty$.

   (b) Derive the entropy S and the heat capacity C_V at $x = 1$ for large but finite N and plot $S(x)$ and $C_V(x)$ for $N \to \infty$. What is the order of the phase transition?

A21. Fluctuations in the grand canonical ensemble: A fluid in a volume V is held (by a huge reservoir) at a temperature T and chemical potential μ . Do not assume an ideal gas.

   (a) Find the relation between $\langle (E - \langle E \rangle)^3 \rangle$ and the heat capacity $C_V(T, \zeta)$ at constant fugacity ζ.

   (b) Find the relation between $\langle (N - \langle N \rangle)^3 \rangle$ and the isothermal compressibility $k_T(V, \mu) = -(\partial v/\partial \mu)_{V,T}$ where $v = V/\langle N \rangle$

   [Hint: Evaluate 3rd derivatives of the grand canonical partition function.]

   (c) Find (a) and (b) explicitly for a classical ideal gas.

A22. Consider a one-dimensional classical gas of N particles in a length L at temperature T. The particles have mass m and interact via a 2-body "hard sphere" interaction (x_i is the position of the i-th particle):

$$
\begin{aligned}
V(x_i - x_j) &= \infty \qquad && |x_i - x_j| < a \\
&= 0 && |x_i - x_j| > a
\end{aligned}
$$

(a) Evaluate the exact free energy F(T,L,N).

(b) Find the equation of state and identify the first virial coefficient; compare with its direct definition.

(c) Show that the energy is $E = Nk_BT/2$. Why is there no effect of the interactions on E ?

(d) In three dimensions $V(|\mathbf{r}_i - \mathbf{r}_j|)$ is defined as above with $\mathbf{r}$ the position vector. Explain why should the effective volume satisfy $V > V_{eff} > V - v_0 N$ where v_0 is the excluded volume for each particle (i.e. $4\pi a^3/3$, where a is the particle's diameter) and $Z = V_{eff}^N/(\lambda^{3N} N!)$. Find $E(T)$ and explain how can it be consistent with the presence of a phase transition.

A23. An equipartition type relation is obtained in the following way:

Consider N particles with coordinates $\vec{q}_i$, and conjugate momenta $\vec{p}_i$ (with $i = 1, ..., N$), and subject to a Hamiltonian $\mathcal{H}(\vec{p}_i, \vec{q}_i)$.

(a) Write down the expression for the classical canonic partition function $Z[\mathcal{H}]$ and show that it is invariant under the rescaling $\vec{q}_i \to \lambda \vec{q}_i$ and $\vec{p}_i \to \vec{p}_i/\lambda$ of a pair of conjugate variables, i.e. $Z[\mathcal{H}_\lambda]$ is independent of λ, where $\mathcal{H}_\lambda$ is the Hamiltonian obtained after the above rescaling.

(b) Now assume a Hamiltonian of the form $\mathcal{H} = \sum_i \frac{(\vec{p}_i)^2}{2m} + V(\{\vec{q}_i\})$. Use the result that $Z[\mathcal{H}_\lambda]$ is independent of λ to prove the virial relation

$$
\left\langle \frac{(\vec{p}_1)^2}{m} \right\rangle = \left\langle \frac{\partial V}{\partial \vec{q}_1} \cdot \vec{q}_1 \right\rangle
$$

where the brackets denote thermal averages.

(c) Show that classical equipartition, $\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \delta_{ij} k_B T$, also yields the result (b). Give an example of a quantum system where classical equipartition fails.

(d) Quantum mechanical version: Write down the expression for the quantum partition function. Show that it is also invariant under the rescalings $\vec{q}_i \to \lambda \vec{q}_i$ and $\vec{p}_i \to \vec{p}_i/\lambda$ where $\vec{p}_i$ and $\vec{q}_i$ are now quantum mechanical operators. (Hint: Use Schrödinger's equation and $\vec{p}_i = -i\hbar\partial/\partial\vec{q}_i$.) Show that the result in (b) is valid also in the quantum case.

A24. Ideal gases of molecules A, B undergo the reaction A$\leftrightarrow$B. Given are f_A, f_B the single molecule partition functions of A, B, respectively, and N the fixed total number of molecules. The sum of weights for a configuration N_A, N_B is the partition function

$$
Z = \sum_{N_A, N_B = N - N_A} \frac{f_A^{N_A} f_B^{N_B}}{N_A! N_B!} = \frac{(f_A + f_B)^N}{N!} . \tag{1}
$$

(a) Show that $\langle N_A \rangle = N \frac{f_A}{f_A + f_B}$ and find the analogous result for $\langle N_B \rangle$.

(b) Show that $\langle (N_A - \langle N_A \rangle)^2 \rangle = \langle N_A \rangle \langle N_B \rangle / N$.

A25. Adiabatic cooling: Consider an ideal gas whose N atoms have mass m, spin $\frac{1}{2}$ and a magnetic moment μ; the energy levels of each particle are $\frac{p^2}{2m} \pm \mu B$ in a magnetic field B where p is the momentum.

(a) Evaluate the entropy as $S_{kin} + S_{spin}$ due to kinetic and spin terms, respectively, and show that by reducing B to zero adiabatically the initial T_i and final T_f temperatures satisfy

$$
\ln \frac{T_f}{T_i} = \frac{2}{3Nk_B}[S_{spin}(T_i, B) - S_{spin}(T_f, 0)]
$$

(b) Find the lower limit for $\frac{T_f}{T_i}$ by allowing the large B limit.

(c) Extend (b) to the case of space dimensionality d and general spin S.

A26. Polymer in two dimensions: Configurations of a polymer are described by a set of vectors $\mathbf{t}_i$ of length a in two dimensions (for i = 1,...,N), or alternatively by the angles ϕ_i between successive vectors, as indicated in the figure below. The energy of a configuration $\{\phi_i\}$ is

$$\mathcal{H} = -\kappa \sum_{i=1}^{N-1} \mathbf{t}_i \cdot \mathbf{t}_{i+1} = -\kappa a^2 \sum_{i=1}^{N-1} \cos \phi_i$$

(a) Show that $\langle \mathbf{t}_n \cdot \mathbf{t}_m \rangle = a^2 e^{-|n-m|/\xi}$ and obtain an expression for the "persistence length" $a\xi$; you can leave the answer in terms of simple integrals.

Hint: Show $\mathbf{t}_n \cdot \mathbf{t}_m = a^2 \mathrm{Re}\{e^{i\sum_{j=n}^{m-1} \phi_j}\}$.

(b) Consider the end-to-end distance $\mathbf{R}$ as illustrated in the figure. Show that for $N \gg 1$, $\langle R^2 \rangle = a^2 N \coth(1/2\xi)$. [Note: $\sum_{j=1}^{n} x^j = x\frac{1-x^n}{1-x}$]
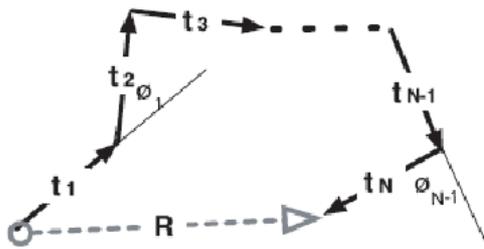
A27. This is an MCE version of A23: An equipartition type relation is obtained in the following way:

Consider N particles with coordinates $\vec{q}_i$, and conjugate momenta $\vec{p}_i$ (with $i = 1, ..., N$), and subject to a Hamiltonian $\mathcal{H}(\vec{p}_i, \vec{q}_i)$.

(a) Using the classical micro canonical ensemble (MCE) show that the entropy S is invariant under the rescaling $\vec{q}_i \to \lambda \vec{q}_i$ and $\vec{p}_i \to \vec{p}_i/\lambda$ of a pair of conjugate variables, i.e. $S[\mathcal{H}_\lambda]$ is independent of λ, where $\mathcal{H}_\lambda$ is the Hamiltonian obtained after the above rescaling.

(b) Now assume a Hamiltonian of the form $\mathcal{H} = \sum_i \frac{(\vec{p}_i)^2}{2m} + V(\{\vec{q}_i\})$. Use the result that $S[\mathcal{H}_\lambda]$ is independent of λ to prove the virial relation

$$\left\langle \frac{(\vec{p}_1)^2}{m} \right\rangle = \left\langle \frac{\partial V}{\partial \vec{q}_1} \cdot \vec{q}_1 \right\rangle$$

where the brackets denote MCE averages. Hint: S can also be expressed with the accumulated number of states $\Sigma(E)$.

(c) Show that classical equipartition, $\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \delta_{ij} k_B T$, also yields the result (b). Note that this form may fail for quantum systems.

(d) Quantum mechanical version: Write down the expression for the entropy in the quantum case. Show that it is also invariant under the rescalings $\vec{q}_i \to \lambda \vec{q}_i$ and $\vec{p}_i \to \vec{p}_i/\lambda$ where $\vec{p}_i$ and $\vec{q}_i$ are now quantum mechanical operators. (Hint: Use Schrödinger's equation and $\vec{p}_i = -i\hbar \partial/\partial \vec{q}_i$.) Show that the result in (b) is valid also in the quantum case.

A28. A cylindrical container has N particles of mass m that are an ideal classical gas; the cylinder has a cross section area A. The cylinder has a fixed bottom at height $h = 0$ and a piston of mass M at height $h > 0$ that limits the motion of the particles to $[0, h]$. The mass of the piston is M and has a potential energy αh (e.g. it is charged in an external electric field, while the particles are neutral). The Hamiltonian contains the kinetic energies of the particles and the piston, as well as the piston's potential energy. The system is kept at a constant temperature T.

(a) Find the energy of the system. [Note: $\int_0^\infty x^n e^{-x} dx = n!$]

(b) Find the average height $\langle h \rangle$ and its fluctuations $\sqrt{\langle h^2 \rangle - \langle h \rangle^2}$.

(c) A naive application of equipartition gives a wrong result for $\langle h \rangle$. Identify where does the standard proof of equipartition fail.

Adsorption

A41. Surfactant Adsorption: A dilute solution of surfactants can be regarded as an ideal three dimensional gas. As surfactant molecules can reduce their energy by contact with air, a fraction of them migrate to the surface where they can be treated as a two dimensional ideal gas. Surfactants are similarly adsorbed by other porous media such as polymers and gels with an affinity for them.

(a) Consider an ideal gas of classical particles of mass m in d dimensions, moving in a uniform potential of strength ϵ_d. Show that the chemical potential at a temperature T and particle density n_d, is given by

$$\mu_d = \epsilon_d + k_B T \ln[n_d \lambda^d] \qquad \text{where} \qquad \lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

(b) If a surfactant lowers its energy by ϵ_0 in moving from the solution to the surface, calculate the concentration of coating surfactants as a function of the solution concentration n (at $d = 3$).

(c) Gels are formed by cross-linking linear polymers. It has been suggested that the porous gel should be regarded as fractal, and the surfactants adsorbed on its surface treated as a gas in d_f dimensional space, with a non-integer d_f. Can this assertion be tested by comparing the relative adsorption of surfactants to a gel, and to the individual polymers (assuming it is one dimensional) before cross-linking, as a function of temperature?

A42. A surface having N_0 adsorption centers has N ($< N_0$) non-interacting gas molecules adsorbed on it. The partition function of a single adsorbed molecule is $a(T) = \Sigma_i e^{-\beta \epsilon_i}$ where ϵ_i are internal energy levels of each molecule.

(a) Evaluate the chemical potential of the adsorbed molecules.

(b) The adsorbed molecules are in equilibrium with those in the gas phase. The molecules in the gas phase are non-interacting and each has internal energy levels ϵ_i' with $a'(T) = \Sigma_i e^{-\beta \epsilon_i'}$ and a mass m. Evaluate the gas pressure and density.

A43. 1. Consider a 3-dimensional gas of atoms with a chemical potential μ that can adsorb on any of M sites on a surface; at each site at most one atom can be adsorbed. At the adsorption site an atom forms an electric dipole $\mathbf{d}$ that can be oriented at any direction *away* from the surface (see figure). In presence of an electric field $\mathbf{E}$ perpendicular to the surface the dipole has energy $-Ed\cos\theta$ where $|\theta| \leq \pi/2$ is the angle between $\mathbf{d}$ and $\mathbf{E}$.

(a) Evaluate the number N of adsorbed atoms. Normalize the phase space of each adsorbed atom to 1. Derive the limit $E \to 0$ and explain why is the result finite, in spite of the adsorption energy being 0 at $E = 0$.

(b) Find the average electric dipole perpendicular to the surface.
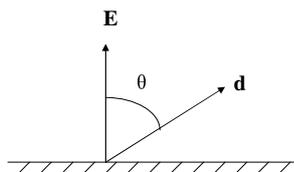
Reactions

A51. (a) Evaluate the chemical potential of a classical ideal gas in two dimensions in terms of the temperature and the density per unit area.

(b) An H_2 molecule decomposes into H atoms when it is absorbed upon a certain metallic surface with an energy gain ϵ per H atom due to binding on the surface. (This binding is not to a particular site on the surface, i.e. the H atoms are free to move parallel to the surface). Consider H_2 as an ideal gas with mass $2\mathsf{m}_H$ and derive the density adsorbed per unit area as function of ϵ, temperature and the H_2 pressure.

[Hint: Chemical equilibrium is obtained by minimizing the total free energy with respect to one of the densities.]

A52. (a) Consider ideal gases of atoms A, atoms B and atoms C undergoing the reaction $\nu C \leftrightarrow A + B$ (ν is an integer).

If n_A, n_B and n_C denote the respective densities show that in equilibrium

$$\frac{(n_C)^\nu}{n_A n_B} = V^{2-\nu}\frac{(f_C)^\nu}{f_A f_B} = K(T) \text{ (law of mass action)}.$$

Here V is the volume while the f's are the respective single particle partition functions. The quantity $K(T)$ is known as the *equilibrium constant* of the reaction.

(b) Derive the equilibrium constant of the reaction $H_2 + D_2 \leftrightarrow 2HD$ in terms of the masses m_H, m_D and ω_0 the vibrational frequency of HD. Assume temperature is high enough to allow classical approximation for the rotational motion. Show that $K(\infty) = 4$.

A53. The partition functions of a diatomic molecules AB or A_2 (within an ideal gas) has the form

$$f_{AB} = g_{AB}(T)(m_A m_B)^{3/2} \quad \text{or} \quad f_{A_2} = \tfrac{1}{2}g_{A_2}(T)m_A^3$$

where m_A, m_B are atomic masses and B is an isotope of A; g_{AB} and g_{A_2} are independent of the isotope masses.

(a) a) Explain the origin of the factor $\frac{1}{2}$.

(b) In the reaction $H_2 + Cl_2 \leftrightarrows 2HCl$ the Cl atom has two isotopes Cl^{35} and Cl^{37}. Write the relevant four reactions and their laws of mass action.

(c) Show that the relative abundance of Cl^{35} and Cl^{37} in Cl_2 is the same as in HCl, i.e. the various densities n satisfy

$$\frac{2n_{Cl_2^{37}} + n_{Cl^{35}Cl^{37}}}{2n_{Cl_2^{35}} + n_{Cl^{35}Cl^{37}}} = \frac{n_{HCl^{37}}}{n_{HCl^{35}}}$$

======= **[B]   Ensemble Theory - quantum gases**

B01. For a single quantum particle of mass m, spectra $p^2/2m$ in a volume V the partition function is $Z_1(m) = gV/\lambda^3$ with $\lambda = h/\sqrt{2\pi m k_B T}$. The particle has a spin degeneracy g ($g = 2s + 1$ for spin s).

(a) Calculate the partition function of two such particles if they are either bosons or fermions.

(b) Calculate the corrections to the energy E, and the heat capacity C, due to Bose or Fermi statistics.

(c) Find the second virial coefficient a_2, defined as $PV = NkT[1 + a_2 n\lambda^3]$ to leading order in the small parameter $n\lambda^3$.

B02. (a) Consider an ideal Bose gas and show that

$$\frac{C_P}{C_V} = \frac{5g_{1/2}(\zeta)g_{5/2}(\zeta)}{3g_{3/2}^2(\zeta)}$$

where ζ is the fugacity. Why is $C_P \to \infty$ in the condensed phase?

(b) Find γ in the adiabatic equation of state. Note that in general $\gamma \neq C_P/C_V$.

B03. Consider an ideal Bose gas in d dimensions whose single particle spectrum is given by $\epsilon = \alpha|\mathbf{p}|^s, s > 0$.

(a) Find the condition on s, d for the existence of Bose-Einstein condensation. In particular show that for nonrelativistic particles in two dimensions ($s = d = 2$) the system does not exhibit Bose-Einstein condensation.

(b) Show that

$$P = \frac{s}{d}\frac{E}{V} \quad \text{and} \quad C_V(T \to \infty) = \frac{d}{s}Nk_B$$

B04. The specific heat of He^4 at low temperatures has the form

$$C_v = AT^3 + B(T)e^{-\Delta/k_B T}$$

(a) What can you deduce about the excitations of the system? (assume the the density of states of these excitations has the form $N(\epsilon) \sim \epsilon^p$ as $\epsilon \to 0$.)

(b) What would be the form of C_v for a similiar system in a two dimensional world?

B05. Consider an ideal Bose gas of particles with mass m in a uniform gravitational field of accelaration g.

(a) Show that the critical temperature for the Bose-Einstein condensation is

$$T_c = T_c^0 \left[1 + \frac{8}{9}\frac{1}{\zeta(3/2)}\left(\frac{\pi mgL}{k_B T_c^0}\right)^{1/2}\right]$$

where L is the height of the container, $mgL \ll k_B T_c^0$ and $T_c^0 = T_c(g = 0)$.
[Hint: $g_{3/2}(\zeta) = g_{3/2}(1) - 2\sqrt{-\pi \ln \zeta} + O(\ln \zeta)$.]

(b) Show that the condensation is accompanied by a discontinuity in the specific heat at T_c,

$$\Delta C_V = -\frac{9}{8\pi}\zeta(3/2)Nk_B\left(\frac{\pi mgL}{k_B T_c^0}\right)^{1/2}.$$

[Hint: ΔC_V is due to discontinuity in $(\partial\zeta/\partial T)_{N,V}$.]

B06. Consider an ideal Bose gas with spin 1 in a magnetic field B. The Hamiltonian for each particle is $\mathcal{H} = \frac{\mathbf{p}^2}{2m} - \gamma B S_z$ where $S_z = 1, 0, -1$ and γ is the gyromagnetic ratio. The average density is n and particle mass is m.

(a) Particles of which S_z can condense? Find an equation for the condensation temperature T_c. Solve this equation explicitly for (i) $B = 0$, and (ii) large B, $\gamma B \gg k_B T_c$; keep the lowest order correction.

(b) Plot, qualitatively, $T_c(B)/T_c(\infty)$ as function of B. If T is below but close to the value of $T_c(B \to \infty)$ describe what happens as B is increased from $B = 0$. Find the critical B for condensation in the limit of (a-ii).

(c) Evaluate the specific heat in the limit of (a-ii).

(d) Evaluate the condensate fraction $\langle n_0 \rangle / n$ as function of T in the case of (a-ii).

B07. A cylindrical container of length L and base area A is divided in two by a freely moving partition of mass M. To the left of the partition there are N_a identical bosons of mass m_a, and to the right there are N_b bosons of mass m_b.

Assume that (i) The state of the gas on the left may be described by a Boltzman approximation, and (ii) the gas on the right is a Bose condensate. Under these assumptions:

(a) Find the location of the partition when the system is in equilibrium at temperature T.

(b) Find the conditions that assumptions (i) and (ii) are valid in equilibrium.

(c) Find the frequency of small oscillations of the partition around equilibrium.

B08. Consider a two dimensional bose gas in a harmonic potential with energy eigenvalues $\hbar\omega(n_1 + n_2 + 1)$ where n_1, n_2 are integers. [This is how the recent cold atom experiments realize condensation].

(a) Show that the average particle number is

$$N = \left(\frac{k_B T}{\hbar\omega}\right)^2 g_2(\zeta) + N_0$$

where N_0 is the the ground state occupation and $g_2(\zeta)$ as defined in class. Assume $k_B T \gg \hbar\omega$ so that summations on n_1, n_2 can be replaced by integrals.

(b) Use $g_2(1) = \pi^2/6$ to infer the Bose Einstein condensation temperature T_c. [Note that N here is not taken to its thermodynamic limit; the transition is still fairly sharp if $N \gg 1$.]

(c) Show that for $T < T_c$: $N_0 = N[1 - (T/T_0)^2]$.

B09. The universe is pervaded by a black body radiation corresponding to a temperature of $3K$. In a simple view, this radiation was produced from the adiabatic expansion of a much hotter photon cloud which was produced during the big bang.

(a) Why is the recent expansion adiabatic rather than, for example, isothermal? It is also known that the expansion velocity is sufficiently small. Smallness compared with what is needed? explain.

(b) If in the next 10^{10} years the volume of the universe increases by a factor of two, what then will be the temperature of the black body radiation?

(c) By what factor does the energy change in the process (b)? Explain the process by which the energy changes and show that this specific process indeed reproduces the change in energy.

B10. Given an optical fiber of length L and cross section is A. Assume that the fiber is a one-dimensional medium for the electromagnetic radiation which is in equilibrium at temperature T.

(a) Find the energy per unit length.

(b) Find the radiation pressure on the ends of the fiber.

(c) If the radiation is allowed to escape from the end of the fiber, find the energy flux.

(d) Suggest a condition on T so that the one dimensional approximation is valid.

B11. The current experimental realizations of Bose Einstein condensation rely on trapping cold atoms in a potential. Close to its minimum, the potential can be expanded to second order, and has the form

$$U(\vec{r}) = \tfrac{1}{2} m \sum_\alpha \omega_\alpha^2 x_\alpha^2$$

where $\alpha = 1, ..., d$, d is the space dimensionality and the trapping potential may have different frequencies ω_α in different directions.

(a) We are interested in the limit of wide traps such that $\hbar\omega_\alpha \ll k_B T$, and the discreteness of the allowed energies can be largely ignored. Show that in this limit, the number of states $N(E)$ with energy less than or equal to E, and the density of states $\rho(E) = dN(E)/dE$ are given by

$$N(E) = \frac{1}{d!} \prod_{\alpha=1}^{d} \left(\frac{E}{\hbar\omega_\alpha} \right) \qquad \Rightarrow \qquad \rho(E) = \frac{1}{(d-1)!} \frac{E^{d-1}}{\prod_{\alpha=1}^{d} \hbar\omega_\alpha}$$

[Hint: The volume of the hyper-pyramid defined by $\sum_{i=1}^{d} x_i \leq R$ and $x_i \geq 0$, in d dimensions is $R^d/d!$.]

(b) Show that in a grand canonical ensemble, the number of particles in the trap is

$$\langle N \rangle = g_d(\zeta) \prod_{\alpha=1}^{d} \left(\frac{k_B T}{\hbar\omega_\alpha} \right)$$

where $g_n(\zeta)$ is the usual Bose function.

(c) Find the chemical potential in the high temperature limit.

(d) Find the temperature T_c for BE condensation (no need to evaluate the g_d integrals). At which dimensions there is no solution with finite T_c?

[Note that the condensate is confined by the trap to a finite size so that the system does not have a proper thermodynamic ($N \to \infty$) limit. Nonetheless, there is a reasonable sharp crossover temperature T_c, at which a macroscopic fraction of particles condenses to the ground state.]

B12. Consider fermions of mass m and spin $\frac{1}{2}$ in a gravitational field with constant acceleration g and at uniform temperature T.

(a) Assume first that the fermions behave as classical particles and find their density $n(h)$ as function of the height $h \geq 0$ and the density $n(0)$.

(b) Near the bottom $h = 0$ the fermions are degenerate, i.e. their Fermi energy $\epsilon_F^0 \equiv \epsilon_F(h = 0)$ is $\epsilon_F^0 \gg k_B T$. Assume here $T = 0$ and find the local fermi momentum $p_F(h)$ and the density $n(h)$ in terms of $n(0)$.

(c) Consider now $T \neq 0$ (but still $\epsilon_F^0 \gg k_B T$) and estimate the height h_c where at $h > h_c$ the fermions are non-degenerate. Find n(h) at $h \gg h_c$ in terms of $n(0)$.

B13. Adiabatic Bose gas: Consider an ideal Bose gas with particles of mass m in a gravitational field of a constant acceleration g. An adiabatic situation is formed by a constant entropy process in which T, μ, are not equilibrated between layers at different heights h, though within each layer equilibrium is maintained [see the classical analog, Ex. A19].

The gas at $h = 0$ is in its condensed phase, i.e. $n_0 \lambda^3(T_0) \equiv \alpha_0 > 2.612$. Find $P(h)$, $T(h)$ and $n(h)$ in terms $T_0 = T(h = 0)$ and $n_0 = n(h = 0)$. Show that the gas is condensed at all $h > 0$ and find $T(h)$, $n(h)$ and the condensed density $\langle N_0(h) \rangle / V$. Show that $\frac{\langle N_0(h) \rangle}{n(h)}$ is h independent and explain why is this expected.

B21. (a) The following reaction occurs inside a star

$$\gamma + \gamma \leftrightarrow e^+ + e^-$$
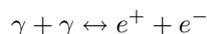
where γ is a photon and $e^\pm$ are the positron and electron, respectively. Assume overall charge neutrality and that the system is in equilibrium at temperature T. Find an expression for the densities of $e^\pm$. (In general $e^\pm$ with mass m are relativistic). Find an explicit result for these densities in the limit $k_B T << mc^2$. (Hint: no conservation law for photons).

(b) Repeat (a) for the reaction

$$\gamma + \gamma \leftrightarrow \pi^+ + \pi^-$$
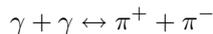
where $\pi^\pm$ are bosons with mass m_π. Can these bosons become Bose-condensed if the temperature is sufficiently lowered? What are the densities at $T = 0$?

(c) The photons in (b) are now eliminated from the system, but the density of the bosons is maintained. If these bosons are cooled, is there a temperature at which Bose condensation is possible? [Assume that the initial temperature satisfies $k_B T << m_\pi c^2$]. What are the densities at $T = 0$?

(d) Consider initial equal densities $\bar{n}$ for e^+ and for e^-. The $e^\pm$ are allowed to equilibrate with $\pi^\pm$ via the reaction

$$e^+ + e^- \leftrightarrow \pi^+ + \pi^-$$
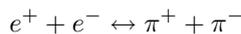
Write equations that determine the chemical potentials at $T \neq 0$. Consider now $T = 0$ and determine if Bose Einstein condensation is possible and if so what is the condition for that. Consider both $m_e > m_\pi$ and $m_e < m_\pi$ situations.

B22. Consider the reaction

$$\gamma + \gamma \leftrightarrow e^+ + e^-$$
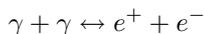
where the net charge of the system is fixed by the density difference $n_0 = n_+ - n_-$; γ is a photon and $e^\pm$ are the positron and electron, respectively.

(a) Derive equations from which the densities n_+ and n_- can be determined in terms of n_0, temperature T, and the mass m of either e^+ or e^-.

(b) Find the Fermi momentum p_F at $T = 0$ for non-relativistic e^+, e^- and the condition on n_0 that allows a non-relativistic limit.

(c) Solve (a) for $p_F^2/2m << k_B T << mc^2$. (Hint: Find first an expression for the product $n_+ n_-$).

B23. Consider a neutron star as non-relativistic gas of non-interacting neutrons of mass m in a spherical symmetric equilibrium configuration. The neutrons are held together by a gravitational potential $-mMG/r$ of a heavy object of mass M and radius r_0 at the center of the star (G is the gravity constant and r is the distance from the center).

(a) Assume that the neutrons are classical particles at temperature T and find their density $n(r)$ at $r > r_0$ for a given $n(r_0)$. Is the potential confining, i.e. is there a solution with $n(r) \to 0$ at $r \to \infty$?

(b) Consider the neutrons as fermions at $T = 0$ and find $n(r)$. Is the potential confining? [Hint: classify solutions according to their chemical potential μ.]

(c) Is the potential confining for fermions at $T \neq 0$? when is the result (a) valid?

B24. A collection of free nucleons is enclosed in a box of volume V. The energy of a single nucleon of momentum $\mathbf{p}$ is $\epsilon_{\mathbf{p}} = p^2/2m + mc^2$ where $mc^2 = 1000 MeV$.

(a) Pretending that there is no conservation law for the number of nucleons, calculate the partition function at temperature T. (Nucleons are fermions).

(b) Calculate the average energy density and average particle density.

(c) In view of (a) and (b), discuss the necessety for a consevation law for the number of nucleons.

B25. Given N fermions (with spin $\frac{1}{2}$) in a volume V of type F which can decay into a boson B (of spin 0) and a fermion of type A in the reaction $F \to A + B$. The reaction has an energy gain of ϵ_0 (i.e. $A + B$ have lower energy than F) and the masses are m_F, m_A, m_B respectively.

(a) Assuming ideal gases at temperature T, write the equations which determine the densities n_F, n_A, n_B in equilibrium.

(b) Write the equations of (a) at $T = 0$ and plot (qualitatively) the densities as functions of ϵ_0. Find ϵ_c such that for $\epsilon_0 > \epsilon_c$ the number of F fermions vanishes.

(c) Assume that the condensation of bosons B occurs at T_c such that $k_B T_c \ll \frac{p_F^2}{2m_A}$ where p_F is the Fermi momentum of fermions A. Evaluate T_c and rewrite the condition $k_B T_c \ll \frac{p_F^2}{2m_A}$ in terms of the given parameters.

B26. Determine the velocity of sound in a degenerate ($T = 0$) Fermi gas in terms of the Fermi velocity.

B27. If liquid ^{3}He is pressurized adiabatically, it becomes a solid and the temperature drops. This is a method of cooling by pressurization. Develop the theory of this process in the following steps:

(a) Assume that the liquid state is an ideal Fermi liquid with a low temperature entropy $S = \frac{1}{2}\pi^2 N k_B T / T_F$ where N is the number of particles and $T_F \approx 5\,^\circ$K is the Fermi temperature. Find the temperature-pressure relation in an adiabatic process for $T \ll T_F$.

(b) At low temperatures the entropy of solid ^{3}He comes almost entirely from the spins while below $10^{-3}\,^\circ$K the spins become antiferromagnetically ordered; assume that at $T \gtrsim 10^{-3}\,^\circ$K the spins are independent. Draw schematically the entropy of both solid and liquid ^{3}He as function of temperature and draw the adiabatic trajectory for increasing pressure. Below which temperature T^* must the initial temperature be for the method to work?

(c) Of what order is the liquid-solid transition? Evaluate the jump in the specific heat.

(d) Use Clapeyron's relation to deduce the shape of the $P(T)$ coexistence solid-liquid curve near T^*. Assume that the difference Δv of the specific volumes is temperature independent and that the solid is denser.

(e) Consider an initial pressure that is below the $P(T)$ coexistence line. Draw schematically the adiabatic trajectory on the P-T plane, using the result (a). What is now the condition on the initial temperature for the cooling method to work, in terms of the initial (P, T) and the coexistence line $P(T)$?

B28. The neutrino is a massless fermion with spin $\frac{1}{2}$.

(a) Assuming neutrinos in thermal equilibrium, write the density in terms of the fugacity ζ and the temperature T (take in account the quantum nature of the neutrinos). Evaluate the integral in the limit of high T and at $T = 0$. What is the condition for high T?

(b) b. Given an initial density n_0 of neutrons. Some of these neutrons β decay to protons, electrons and antineutrinos via the reaction

$$n \to p + e^- + \bar{\nu}.$$
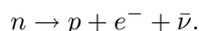
All the particles are fermions with spin $\frac{1}{2}$. The masses m_n, m_p, m_e are given and the antineutrino is massless. Assuming quantum ideal gases with p, n, e^- nonrelativistic, write the equilibrium equations for the proton density n_p. Consider only the following two cases (i) a high temperature limit, and (ii) $T = 0$. In both cases solve explicitly in the limit $n_p \ll n_0$.

B29. A d dimensional container ($d = 1, 2, 3$) contains fermions of density n, temperature $T = 0$, mass m and spin $\frac{1}{2}$, having a magnetic moment $\bar{m}$. The container is placed in a magnetic field $H/\bar{m}$ so that the fermion spectra is $\epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m} \pm H$ where $\mathbf{p}$ is the momentum. (Note that orbital effects are neglected, possible e.g. at d=2 with the field parallel to the layer).

(a) Evaluate the chemical potential $\mu(H)$, for small H: Consider first an expansion to lowest order in H and then evaluate $d\mu/dH$ to note the change at finite H.

(b) Beyond which H_c does the consideration in (a) fail? Find $\mu(H)$ at $H > H_c$ and plot qualitatively $\mu(H)/\mu_0$ as function of H/μ_0 (where $\mu_0 = \mu(H = 0)$) for $d = 1, 2, 3$, indicating the values of $\mu(H)/\mu_0$ at H_c.

(c) Of what order is the phase transition at H_c, at either $d = 1, 2, 3$? Does the phase transition survive at finite T? (no need for finite T calculations – just note analytic properties of thermodynamic functions).

(d) The container above, called A, with $H \neq 0$ is now attached to an identical container B (same fermions at density n, $T = 0$), but with $H = 0$. In which direction will the fermions flow initially? Specify your answer for $d = 1, 2, 3$ at relevant ranges of H.

B30. Consider 3 types of Fermions A,B,C with the reaction A+A$\leftrightarrows$B+C. The energies as function of momentum $\mathbf{p}$ are

$$\epsilon_A(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}, \qquad \epsilon_B(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} + \Delta, \qquad \epsilon_C(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} - \Delta.$$

The system has initially only fermions A with density $2n_0$. All fermions have spin $\frac{1}{2}$.

(a) Find the chemical potentials of B and C fermions in terms of μ, the chemical potential of the A fermions. Write an equation that determines μ at any temperature T for dimensionality $d = 3$. Show that $n_C = 2n_0/3$.

(b) Allow now an additional reaction B$\leftrightarrows$C. Consider $T = 0$ and dimensionalities $d = 1, 2, 3$. Define μ_0 as the chemical potential of n_0 fermions of type A, and show that

$$2\mu_0^{d/2} = \mu^{d/2} + (\mu + \Delta)^{d/2} + (\mu - \Delta)^{d/2}.$$

Identify the range of Δ/μ_0 for which this equation is valid.

(c) Show that in addition to the range in (b) there are 2 more distinct ranges of Δ/μ_0 and find the corresponding equations for μ. Evaluate $\frac{d\mu}{d\Delta}$, determine the sign of this derivative in each regime and plot $\mu(\Delta)$ qualitatively for $d = 1, 2, 3$.

(d) Of which order are the 2 phase transitions for $d = 1, 2, 3$?

B31. Consider 3 types of bosons A,B,C with the reaction A+A$\leftrightarrows$B+C. The energies as function of momentum $\mathbf{p}$ are

$$\epsilon_A(\mathbf{p}) = \frac{\mathbf{p}^2}{2m}, \qquad \epsilon_B(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} + \Delta, \qquad \epsilon_C(\mathbf{p}) = \frac{\mathbf{p}^2}{2m} - \Delta.$$

The system has initially only bosons A with density $2n_0$. All bosons are spinless.

(a) Find the chemical potentials of B and C bosons in terms of μ, the chemical potential of the A bosons. Show that the density of C bosons is $n_C = 2n_0/3$.

(b) Find the critical temperature T_c for Bose condensation. Which bosons condense first?

(c) Allow now an additional reaction B$\leftrightarrows$C. Write an equation for μ and find T_c. Which bosons condense first?

(d) Find the condensed fraction at $T < T_c$. Find the densities n_A, n_B, n_C at $T = 0$.

$=\!=\!=\!=\!=\!=$ **[C]   Phase Transitions**

C01. The boiling point of a certain liquid is $95\,^{\circ}C$ at the top of a mountain and $105\,^{\circ}C$ at the bottom. Its latent heat is 1000 cal/mole. Calculate the height of the mountain. (Assume that the gas phase is an ideal gas with density much lower than that of the liquid; use the average mass of 30 gr/mole.) The air is at uniform temperature of 27C.

C02. Apply the mean field approximation to the classical spin-vector model

$$\mathcal{H} = -J\sum_{\langle i,j\rangle}\mathbf{s}_i\cdot\mathbf{s}_j - \mathbf{h}\cdot\sum_i\mathbf{s}_i$$

where $\mathbf{s}_i$ is a unit vector and i,j are neighboring sites on a lattice; each pair is counted once. The lattice has N sites and each site has γ neighbors.

  (a) Define a mean field $\mathbf{h}^{eff}$ and evaluate the partition function Z in terms of $\mathbf{h}^{eff}$.

  (b) Find an equation for the magnetization $M(T) = \langle\cos\theta_i\rangle$ at $\mathbf{h} = 0$ where θ_i is the angle relative to the orientation of $\mathbf{M}$. Find the transition temperature T_c.

  (c) The mean field hamiltonian (at $\mathbf{h} = 0$) is $\mathcal{H}^{MF} = -J\gamma M\sum_i s_i + \frac{1}{2}J\gamma M^2 N$. Explain this form, derive the free energy F, and re-derive the equation for $M(T)$ in (b) by a minimum condition.

  (d) Identify exponents γ, β as $T \to T_c$ for the susceptibility $\chi \sim (T - T_c)^{-\gamma}$ above T_c and for $M \sim (T_c - T)^{\beta}$ below T_c.

  (e) Show that there is a jump in C_V at T_c.

C03. (a) Antiferromagnetism is a phenomenon akin to ferromagnetism. The simplest kind of an antiferromagnet consists of two equivalent antiparallel sublattices A and B such that members of A have only nearest neighbors in B and vice versa. Show that the mean field theory of this type of (Ising) antiferromagnetism yields a formula like the Curie-Weiss law for the susceptibility $\chi \sim (T - T_c)^{-1}$, except that $T - T_c$ is replaced by $T + T_c$; T_c is the transition temperature into antiferromagnetism (Neel's temperature).

  (b) Below T_c the susceptibility χ of an antiferromagnet drops again. Show that in the mean field theory of (a) the rate of increase of immediately below T_c is twice the rate of decrease immediately above. (Assume that the applied field is parallel to the antiferromagnetic orientation.)

C04. Model of ferroelectricity: Consider electric dipoles $\mathbf{p}$ on sites of a simple cubic lattice which point along one of the crystal axes, $\pm\langle 100\rangle$. The interaction between dipoles is

$$U = \frac{\mathbf{p}_1\cdot\mathbf{p}_2 - 3(\mathbf{p}_1\cdot\mathbf{r})(\mathbf{p}_2\cdot\mathbf{r})/r^2}{4\pi\epsilon_0 r^3}$$

where $\mathbf{r}$ is the distance between the dipoles, $r = |\mathbf{r}|$ and ϵ_0 is the dielectric constant.

  (a) Assume nearest neighbor interactions and find the ground state configuration. Consider either ferroelectric (parallel dipoles) or anti-ferroelectric alignment (anti-parallel) between neighbors in various directions.

  (b) Develop a mean field theory for the ordering in (a) for the average polarization P at a given site at temperature T: Write a mean field equation for $P(T)$ and find the critical temperature T_c.

  (c) Find the susceptibility $\chi = \left(\frac{\partial P}{\partial E}\right)_{E=0}$ at $T > T_c$ for an electric field $E||\langle 100\rangle$, using the mean field theory.

C05. The following mechanical model illustrates the symmetry breaking aspect of second order phase transitions. An airtight piston of mass M is inside a tube of cross sectional area a (see figure). The tube is bent into a semicircular shape of radius R. On each side of the piston there is an ideal gas of N atoms at a temperature T. The volume to the right of the piston is $aR\left(\frac{\pi}{2} - \phi\right)$ while to the left is $aR\left(\frac{\pi}{2} + \phi\right)$. The free energy of the system has the form

$$F = MgR\cos\phi - Nk_BT\left[\ln\frac{aR\left(\frac{\pi}{2} - \phi\right)}{N\lambda^3} + \ln\frac{aR(\frac{\pi}{2} + \phi)}{N\lambda^3} + 2\right]$$
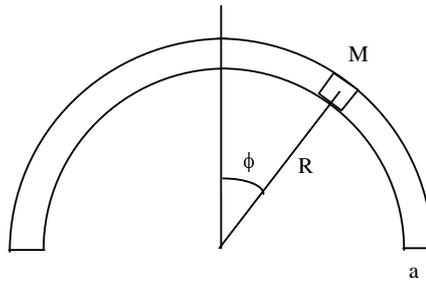
(a) Explain the terms in F. Interpret the minimum condition for $F(\phi)$ in terms of the pressures in the two chambers.

(b) Expand F to 4th order in ϕ, show that there is a symmetry breaking transition and find the critical temperature T_c.

(c) Describe what happens to the phase transition if the number of atoms on the left and right of the piston is $N(1+\delta)$ and $N(1-\delta)$, respectively. (It is sufficient to consider $|\delta| << 1$ and include a term $\sim \phi\delta$ in the expansion (b)).

(d) At a certain temperature the left chamber (containing $N(1+\delta)$ atoms) is found to contain a droplet of liquid coexisting with its vapor. Which of the following statements may be true at equilibrium:

   (i) The right chamber contains a liquid coexisting with its vapor.
   (ii) The right chamber contains only vapor.
   (iii) The right chamber contains only liquid.

C06. A cubic crystal which exhibits ferromagnetism at low temperature, can be described near the critical temperature T_c by an expansion of a Gibbs free energy

$$G(\mathbf{H}, T) = G_0 + \tfrac{1}{2}r\mathbf{M}^2 + u\mathbf{M}^4 + v\sum_{i=1}^{3} M_i^4 - \mathbf{H} \cdot \mathbf{M}$$

where $\mathbf{H} = (H_1, H_2, H_3)$ is the external field and $\mathbf{M} = (M_1, M_2, M_3)$ is the total magnetization; $r = a(T - Tc)$ and G_0, a, u and v are independent of $\mathbf{H}$ and T, $a > 0, u > 0$. The constant v is called the cubic anisotropy and can be either positive or negative.

(a) At $\mathbf{H} = 0$, find the possible solutions of $\mathbf{M}$ which minimize G and the corresponding values of $G(0, T)$ (these solutions are characterized by the magnitude and direction of $\mathbf{M}$. Show that the region of stability of G is $u + v > 0$ and determine the stable equilibrium phases when $T < T_c$ for the cases (i) $v > 0$, (ii) $-u < v < 0$.

(b) Show that there is a second order phase transition at $T = T_c$, and determine the critical indices α, β and γ for this transition, i.e. $C_{V,H=0} \sim |T - T_c|^{-\alpha}$ for both $T > T_c$ and $T < T_c$, $|\mathbf{M}|_{H=0} \sim (Tc - T)^{\beta}$ for $T < T_c$ and $\chi_{ij} = \partial M_i/\partial H_j \sim \delta_{ij}|T - T_c|^{-\gamma}$ for $T > T_c$.

C07. Consider a ferromagnet with magnetic moments $m(\mathbf{r})$ on a simple cubic lattice interacting with their nearest neighbors. [The symmetry is an Ising type, i.e. $m(\mathbf{r})$ is the moment's amplitude in a preferred direction]. The ferromagnetic coupling is J and the lattice constant is a. Extend the mean field theory to the situation that the magnetization is not uniform but is slowly varying:

(a) Find the mean field equation in terms of $m(\mathbf{r})$, its gradients (to lowest order) and an external magnetic $H(\mathbf{r})$, which in general can be a function of $\mathbf{r}$.

(b) Consider $T > T_c$ where T_c is the critical temperature so that only lowest order in $m(\mathbf{r})$ is needed. For a small $H(\mathbf{r})$ find the response $m(\mathbf{r})$ and evaluate it explicitly in two limits: (i) uniform H, i.e. find the

susceptibility, and (ii) $H(\mathbf{r}) \sim \delta^3(\mathbf{r})$. Explain why in case (ii) the response is the correlation function and identify the correlation length.

C08. Lattice gas model: Consider N classical particles of mass m where each particle is located on a unit cell of a simple cubic lattice with a lattice constant a. Each unit cell can contain either 0 or 1 particles, providing an "excluded volume" type interaction. The number of unit cells is M, i.e. the volume is $V = Ma^3$. Therefore $0 < N < M$ and the density is $0 < n < 1/a^3$. There is no constraint on the momentum of each particle.

(a) Evaluate the grand partition function and the density $n(\mu, T)$ where μ is the chemical potential and T is the temperature.

(b) Find the pressure P in terms of T and n. Identify the limit $n \to 0$ and explain what happens in the limit $n \to 1/a^3$.

(c) This model does not show a first order transition as in a full lattice gas model. What ingredient is missing here?

C09. Mean field theory of the Potts model. Consider a cubic lattice in 3 dimensions with N sites. Each lattice site i has a variable σ_i that can take q discrete values, $\sigma_i = 0, 1, 2, ..., q-1$. (E.g. an Ising model has $q = 2$).

(a) Consider first an external field h that couples only to $\sigma_i = 0$, i.e. the Hamiltonian is just

$$\mathcal{H}_0 = -h \sum_i \delta_{\sigma_i,0}$$

where $\delta_{\sigma_i,0}$ is a Kronecker delta function (i.e. =1 when its arguments are equal, and =0 otherwise). Find the free energy at a temperature T. Find also the probability P_0 that $\sigma_i = 0$, i.e. $P_0 = \langle \delta_{\sigma_i,0} \rangle$.

(b) The Potts model is defined by the hamiltonian

$$\mathcal{H} = -J \sum_{i,j} {}' \delta_{\sigma_i,\sigma_j}$$

where the sum is on the 6 nearest neighbors and $\sum'$ means that each bond is counted once. The order parameter is defined by $m = \langle \delta_{\sigma_i,0} \rangle - \frac{1}{q}$. Justify this choice and explain what symmetry has been broken. The mean-field Hamiltonian is

$$\mathcal{H}^{MF} = -6Jm \sum_i \delta_{\sigma_i,0} + NA(m)$$

where $A(m)$ is σ_i independent. Justify this form and identify $A(m)$ by comparing $\langle \mathcal{H} \rangle = \langle \mathcal{H}^{MF} \rangle$ keeping only mean field $\sim m$ terms.

(c) Identify an effective h_{eff} to be used in the results of (a) and find an equation for $m(T)$. Sketch a graphic solution. Assuming a 2nd order transition (i.e. $m(T)$ is continuous) find the critical temperature T_c.

(d) Find the mean field free energy $\mathcal{F}^{MF}(m)$. From a minimum on m rederive the equation for $m(T)$.

C20. Stoner ferromagnetism: The conduction electrons in a metal can be treated as a gas of fermions of spin $\frac{1}{2}$ (with up/down degeneracy), and density $n = N/V$. The Coulomb repulsion favors wave functions which are antisymmetric in position coordinates, thus keeping the electrons apart. Because of the full (position and spin) antisymmetry of fermionic wave functions, this interaction may be approximated by an effective spin-spin coupling which favors states with parallel spins. In this simple approximation, the net effect is described by an interaction energy

$$U = \alpha \frac{N_+ N_-}{V}$$

where N_+ and $N_- = N - N_+$ are the numbers of electrons with up and down spins, and V is the volume.

(a) Define $n_\pm = N_\pm/V = n/2 \pm \delta$ and assume $\delta \ll n$. Expand the total energy at temperature $T = 0$ (kinetic and interaction) to 4th order in δ and find the critical value α_c such that for $\alpha > \alpha_c$ the electron gas can lower its total energy by spontaneously developing a magnetization. (This is known as the Stoner instability.)

(b) Explain the instability qualitatively, and sketch the behavior of the spontaneous magnetization as a function of α.

(c) Reconsider (a) at finite but low temperatures T, and find $\alpha_c(T)$ (consider the effect to the lowest nonzero order of T). You can use the known $F(T)$ for fermions at low T.

C21. Consider the Ising model of magnetism with long range interaction: the energy of a spin configuration $\{s_i\}$ with $s_i = \pm 1$ on an arbitrary lattice is given by,

$$E = -(J/2N)\sum_{i,j} s_i s_j - h\sum_i s_i$$

where $J > 0$ and the sum is on all i and j (in the usual Ising model the sum is restricted to nearest neighbors) and $h = \mu_B H$, H is the magnetic field.

(a) Write E in terms of $m = \sum_i s_i/N$ i.e. $E(m,h) = -(1/2)JNm^2 - hNm$; why is N included in the definition of the coupling J/N?

(b) Evaluate the free energy $F_0(m; T, h)$ assuming that it is dominated by a single m which is then a variational parameter. From the minima of F_0 find $m(h, T)$ and a ciritical temperature T_c. Plot qualitatively $m(h)$ above and below the transition.

(c) Plot qualitatively $F_0(m)$ for $T > T_c$ and $T < T_c$ with both $h = 0$ and $h \neq 0$. Explain the meanings of the various extrema.

(d) Expand $F_0(m; T, h = 0)$ up to order m^4. What is the meaning of the m^2 coefficient?

C22. Consider the Ising model in one dimension with periodic boundary condition and with zero external field.

(a) Consider an Ising spin σ_i ($\sigma_i = \pm 1$) at site i and explain why do you expect $\langle \sigma_i \rangle = 0$ at any temperature $T \neq 0$. Evaluate $\langle \sigma_i \rangle$ by using the transfer matrix method. What is $\langle \sigma_i \rangle$ at $T = 0$?

(b) Find the correlation function $G(r) = \langle \sigma_1 \sigma_{r+1} \rangle$ and show that when $N \to \infty$ (N is the number of spins) $G(r)$ has the form $G(r) \sim e^{-r/\xi}$. At what temperature ξ diverges and what is its significance?

C23. (a) Consider the Ising spin model on a bipartite lattice, i.e. it has two sublattices A,B such that each site on lattice A has its nearest neighbors on sublattice B, and vice versa. The Hamiltonian is

$$\mathcal{H} = -J\sum_{\mathbf{n}, \boldsymbol{\delta}} \sigma(\mathbf{n})\sigma(\mathbf{n} + \boldsymbol{\delta}) - h\sum_{\mathbf{n}} \sigma(\mathbf{n}) \tag{2}$$

where $\mathbf{n}$ are the lattice sites, $\boldsymbol{\delta}$ labels the nearest neighbors, h is proportional to a magnetic field and $\sigma(\mathbf{n}) = \pm$. For $h = 0$ show that the free energy satisfies $F(J, T) = F(-J, T)$, hence the critical temperatures satisfy $T_c^F = T_c^{AF}$ for the ferromagnetic ($J > 0$) and anti-ferromagnetic ($J < 0$) transitions. Define the order parameters at $T < T_c$ and the magnetic susceptibilities to h at $T > T_c$ and find their relationship, if any.

(b) Consider the one dimensional Ising model with the Hamiltonian $\mathcal{H} = -\sum_{n,n'} J(n - n')\sigma(n)\sigma(n')$ with $\sigma(n) = \pm 1$ at each site n and $J(n) = b/n^\gamma$ is a long range interaction and $b > 0$. Find the energy of a domain wall (i.e. $n < 0$ spins are $-$ and $n \geq 0$ are $+$) and show that the argument for the absence of spontaneous magnetization at finite temperatures fails when $\gamma < 2$.

C24. Consider a one dimensional Ising model of spins $\sigma_i = \pm 1$, $i = 1, 2, 3, ..., N$ and $\sigma_{N+1} = \sigma_1$. Between each two spins there is a site for an additional atom, which if present changes the coupling J to $J(1 - \lambda)$. The Hamiltonian is then

$$H = -J\sum_{i=1}^{N} \sigma_i \sigma_{i+1}(1 - \lambda n_i)$$

where $n_i = 0$ or 1 and there are $N' = \sum_{i=1}^{N} n_i$ atoms ($N' < N$), i.e. on average $\langle n_i \rangle = N'/N$.

(a) Evaluate the partition sum by allowing all configurations of spins and of atoms.

(b) If the atoms are stationary impurities one needs to evaluate the free energy F for some random configuration of the atoms and then average F over all configurations. (The reasons for this average are given in Ex. C25). Evaluate the average F. Find the entropy difference of (a) and (b) and explain its origin.

C25. Consider a system with random impurities. An experiment measures one realization of the impurity distribution and many experiments yield an average denoted by $\langle ... \rangle$. Consider the free energy as being a sum over N independent subsystems, i.e. parts of the original system, with average value $F = (1/N) \sum_{i=1}^{N} F_i$; the subsystems are identical in average, i.e. $\langle F_i \rangle = \langle F \rangle$.

(a) The subsystems are independent, i.e. $\langle F_i F_j \rangle = \langle F_i \rangle \langle F_j \rangle$ for $i \neq j$, although they may interact through their surface. Explain this.

(b) Show that $\langle (F - \langle F \rangle)^2 \rangle \sim 1/N$ so that even if the variance $\langle (F_i - \langle F \rangle)^2 \rangle$ may not be small any measurement of F is typically near its average.

(c) Would the conclusion (b) apply to the average of the partition function Z, i.e. replacing F_i by Z_i ?

C26. N ions of positive charge q and N with negative charge $-q$ are constrained to move in a two dimensional square of side L. The interaction energy of charge q_i at position $\mathbf{r}_i$ with another charge q_j at $\mathbf{r}_j$ is $-q_i q_j \ln |\mathbf{r}_i - \mathbf{r}_j|$ where $q_i, q_j = \pm q$. The Hamiltonian is then (m is the mass of each ion and $\mathbf{p}_i$ are momenta)

$$H = \sum_{i=1}^{2N} \mathbf{p}_i^2/2m - \sum_{i<j}^{2N} q_i q_j \ln |\mathbf{r}_i - \mathbf{r}_j|$$

(a) By rescaling space variables to $\mathbf{r}_i' = C\mathbf{r}_i$, where C is an arbitrary constant, show that the partition function $Z(L)$ satisfies: $Z(L) = C^{N(\beta q^2 - 4)} Z(CL)$. Deduce that $Z(L) = A^{N(2 - \beta q^2/2)} Z(1)$ where $A = L^2$ is the area. [Hint: $\sum_{i<j}^{2N} q_i q_j = -q^2 N$].

(b) Calculate the pressure and show that at low T the system is unstable. Comment on the reason for this instability and on how the model should be modified.

(c) Assume that $Z(1)$ has N dependent factors only from the momentum integrals and from the Gibbs factors (this neglects a short range part of the interaction). Find the chemical potential $\mu(T, N, A)$ and solve for $N(\mu, T, A)$. Find the limit of N for a fixed μ when $A \to \infty$ for both $T > T_c = q^2/4$ and $T < T_c$. Interpret these results.

C27. Given a free energy with the homogenous form

$$F = t^{2-\alpha} f(t/h^{1/\phi})$$

where h is the magnetic field and $t = (T - T_c)/T_c$.

(a) Show that α is the conventional critical exponent of the specific heat.

(b) Express the conventional β, δ exponents in terms of α, ϕ and show that $2 - \alpha = \beta(\delta + 1)$.

C28. Potts model in 1-dimension (1d) . A set of N atoms, each with p states is arranged on a 1d chain with periodic boundary conditions. The atom at the n-th site is in a state i_n that is chosen from the set $\{1, 2, ..., p\}$. Two neighboring atoms at sites n and $n+1$, respectively, have an interaction energy $-J$ $(J > 0)$ if they are in the same state, i.e. $i_n = i_{n+1}$, and 0 interaction otherwise. The Hamiltonian is therefore

$$H = -J \sum_{i=1}^{N} \delta_{i_n, i_{n+1}}$$

where $\delta_{i_n, i_{n+1}}$ is the Kronecker symbol, and the boundary conditions are $i_{N+1} = i_1$.

(a) Derive the free energy for $p = 2$. (Consider here and below the limit $N \to \infty$.)

(b) Derive the free energy for a general p. Hint: Show that the eigenvector of the transfer matrix whose all entries are equal has the largest eigenvalue.

(c) Find the internal energy E at the low and high temperature limits and interpret the results.

C29. (a) Consider the Ising model in 1-dimension with $\sigma_k = \pm$ at site k and energy

$$\mathcal{H} = -J \sum_{k=1}^{N-1} \sigma_k \sigma_{k+1}$$

Consider an open chain, i.e. $k = 1$ and $k = N$ are connected only to one neighbor. Find an expression for the free energy F and show that it is identical to the case with periodic boundary conditions. (no need to evaluate F explicitly.)

(b) Consider spin 1 in 1-dimension with $S_k = 1, 0, -1$ at site k and energy

$$\mathcal{H} = -J \sum_{k=1}^{N} S_k S_{k+1} - \mu B \sum_{k=1}^{N} S_k$$

and with periodic boundary conditions $S_N + 1 = S_N$. Write the transfer matrix and explain how to obtain the free energy (no need for explicit derivation).

===== [D]   Non-equilibrium – classical and quantum

D01. Consider an ideal gas in an external potential $\phi(\mathbf{r})$.

(a) Let $H = \int d^3v \int d^3r f(\mathbf{r}, \mathbf{v}, t) \ln f(\mathbf{r}, \mathbf{v}, t)$
where $f(\mathbf{r}, \mathbf{v}, t)$ is arbitrary except for the conditions on density n and energy E

$$\int d^3r \int d^3v f(\mathbf{r}, \mathbf{v}, t) = n \ , \ \int d^3r \int d^3v \left[\tfrac{1}{2}mv^2 + \phi(\mathbf{r})\right] f(\mathbf{r}, \mathbf{v}, t) = E \,.$$

Find $f(\mathbf{r}, \mathbf{v})$ (i.e. t independent) which maximizes H. (Note: do not assume binary collisions, i.e. the Boltzmann equation).

(b) Use Boltzmann's equation to show that the general form of the equilibrium distribution of the ideal gas (i.e. no collision term) is $f[\tfrac{1}{2}mv^2 + \phi(\mathbf{r})]$ where the local force is $\nabla \phi$. Determine this solution by allowing for collisions and requiring that the collision term vanishes. Find also the average density $n(r)$.

D02. Consider the derivation of Liouville's theorem for the ensemble density $\rho(p, q, t)$ in phase space (p, q) corresponding to the motion of a particle of mass m with friction γ

$$\frac{dq}{dt} = \frac{p}{m}, \ \ \frac{dp}{dt} = -\gamma p \,.$$

(a) Show that Liouville's theorem is replaced by $d\rho/dt = \gamma\rho$.

(b) Assume that the initial $\rho(p, q, t = 0)$ is uniform in a volume ω_0 in phase space and zero outside of this volume. Find $\rho(p, q, t)$ if ω_0 is a rectangle $-\bar{p} < p < \bar{p}, \ -\bar{q} < q < \bar{q}$. Find implicitly $\rho(p, q, t)$ for a general ω_0.

(c) what happens to the occupied volume ω_0 as time evolves? (assume a general shape of ω_0). Explain at what t this description breaks down due to quantization.

(d) Find the Boltzmann entropy as function of time for case (b). Discuss the meaning of the result.

D03. Electrons in a metal can be described by a spectrum $\epsilon(\mathbf{k})$, where $\mathbf{k}$ is the crystal momentum, and a Fermi distribution $f_0(\mathbf{k})$ at temperature T.

(a) Find the correction to the Fermi distribution due to a weak electric field $\mathbf{E}$ using the Boltzmann equation and assuming that the collision term can be replaced by $-[f(\mathbf{k}) - f_0(\mathbf{k})]/\tau$ where τ is the relaxation time. Note that $d\mathbf{k}/dt = e\mathbf{E}/\hbar$ and the velocity is $\mathbf{v_k} = \nabla_{\mathbf{k}}\epsilon(\mathbf{k})/\hbar$, i.e. in general $d\mathbf{v}_k/dt$ is $\mathbf{k}$ dependent.

(b) Find the conductivity tensor σ , where $\mathbf{J} = \sigma\mathbf{E}$. In what situation would σ be non-diagonal? Show that σ is non-diagonal if the mass tensor $(\frac{1}{m*})_{i,j} = \frac{1}{\hbar^2}\frac{\partial^2\epsilon(\mathbf{k})}{\partial k_i \partial k_j}$ is not diagonal.

(c) Find σ explicitly for $\epsilon = \hbar^2 k^2/2m*$ in terms of the electron density n. ($m*$ is an effective mass).

D04. Coarse grained entropy. The usual $\rho(p, q, t)$, i.e. the normalized state density in the 6N dimensional phase space (p, q), satisfies Liouville's theorem $d\rho/dt = 0$. We wish to redefine $\rho(p, q, t)$ so that the corresponding entropy increases with time.

Divide phase space to small sub-volumes Ω_ℓ and define a coarse grained density

$$\bar{\rho}(p, q, t) = \bar{\rho}_\ell = \frac{1}{\Omega_\ell}\int_{\Omega_\ell}\rho(p, q, t)dpdq \qquad (p, q) \in \Omega_\ell$$

so that $\bar{\rho}(p, q, t)$ is constant within each cell Ω_ℓ. Define the entropy as

$$\eta(t) = -\int\bar{\rho}(p, q, t)\ln\bar{\rho}(p, q, t)dpdq = -\sum_\ell\Omega_\ell\bar{\rho}_\ell\ln\bar{\rho}_\ell .$$

Assume that at $t = 0$ $\rho(p, q, 0)$ is uniform so that $\rho(p, q, 0) = \bar{\rho}(p, q, 0)$.

(a) Show that $\eta(0) = -\int\rho(p, q, t)\ln\rho(p, q, t)dpdq$.

(b) Show that $\eta(t)$ increases with time, i.e.

$$\eta(t) - \eta(0) = -\int\rho\left[\ln\frac{\bar{\rho}}{\rho} + 1 - \frac{\bar{\rho}}{\rho}\right]dpdq \geq 0 .$$

Hint: Show that $\ln x + 1 - x \leq 0$ for all $x > 0$.

D05. Equilibrium and kinetics of light and matter:

(a) Consider atoms with fixed positions that can be either in their ground state a_0, or in an excited state a_1, which has a higher energy ϵ. If n_0 and n_1 are the densities of atoms in the the two levels, find the ratio n_1/n_0 at temperature T.

(b) Consider photons γ of frequency $\omega = \epsilon/\hbar$ and momentum $|\mathbf{p}| = \hbar\omega/c$, which can interact with the atoms through the following processes:
(i) *Spontaneous emission*: $a_1 \rightarrow a_0 + \gamma$
(ii) *Absorption*: $a_0 + \gamma \rightarrow a_1$
(iii) *Stimulated emission*: $a_1 + \gamma \rightarrow a_0 + \gamma + \gamma$.
Assume that spontaneous emission occurs with a probability σ_1 (per unit time and per unit (momentum)^3) and that absorption and stimulated emission have constant (angle independent) differential cross-sections of σ_2 and $\sigma_3/4\pi$, respectively.
Show that the Boltzmann equation for the density $f(\mathbf{r}, p, t)$ of the photon gas, treating the atoms as fixed scatterers of densities n_0 and n_1 is

$$\frac{\partial f(\mathbf{r}, p, t)}{\partial t} + \frac{\mathbf{p}c}{|\mathbf{p}|}\cdot\frac{\partial f(\mathbf{r}, p, t)}{\partial \mathbf{r}} = -\sigma_2 n_0 cf(\mathbf{r}, p, t) + \sigma_3 n_1 cf(\mathbf{r}, p, t) + \sigma_1 n_1$$

(c) Find the equilibrium solution f_{eq}. Equate the result, using (a), to that the expected value per state $f_{eq} = \frac{1}{h^3}\frac{1}{e^{\hbar\omega/k_B T}-1}$ and deduce relations between the cross sections.

(d) Consider a situation in which light shines along the x axis on a collection of atoms whose boundary is at $x = 0$ (see figure). The incoming flux is uniform and has photons of momentum $\mathbf{p} = \hbar\omega\hat{x}/c$ where $\hat{x}$ is a unit vector in the x direction. Show that the solution has the form

$$Ae^{-x/a} + f_{eq}$$

and find the penetration length a.
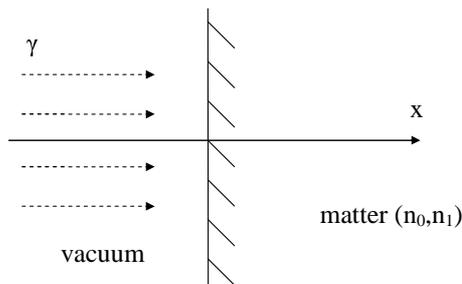
D06. A thermalized gas particle at temperature T is suddenly confined to positions q in a one dimensional trap. The corresponding state is described by an initial density function $\rho(q, p, t = 0) = \delta(q)f(p)$ where $\delta(q)$ is Dirac's delta function and

$$f(p) = \frac{e^{-p^2/2mk_BT}}{\sqrt{2\pi mk_BT}}.$$ (3)

(a) Starting from Liouville's equation with the Hamiltonian $\mathcal{H} = p^2/2m$ derive $\rho(q, p, t)$. For a given time t draw the points in the (p, q) plane where $\rho(q, p, t)$ is finite and emphasize the segment where $f(p)$ is large, $p < \sqrt{mk_BT} \equiv p_0$.

(b) Derive the expressions for the averages $\langle q^2 \rangle$ and $\langle p^2 \rangle$ at $t > 0$.

(c) Suppose that hard walls are placed at $q = \pm Q$. Repeat the plot of (a) and again emphasize the range $p < p_0$. What happens in this plot at long times $t > 2Qm/p_0 \equiv \tau_0$? What is the meaning of the time τ_0?

(d) A "coarse grained" density $\tilde{\rho}$ is obtained by ignoring variations of ρ below some small resolution in the (q, p) plane; e.g., by averaging ρ over cells of the resolution area. Find $\tilde{\rho}(q, p)$ for the situation in part (c) at long time $t \gg \tau_0$, and show that it is stationary.

D07. Consider a classical gas of particles with mass m between two plates separated by a distance W. One plate at $y = 0$ is maintained at a temperature T_1, while the other plate at $y = W$ is at a different temperature T_2. A zeroth order approximation to the particle density is,

$$f_0(\mathbf{p}, x, y, z) = \frac{n(y)}{[2\pi mk_BT(y)]^{3/2}} e^{-\frac{p^2}{2mk_BT(y)}}$$

(a) The steady state solution has a uniform pressure; it does not have a uniform chemical potential. Explain this statement and find the relation between $n(y)$ and $T(y)$.

(b) Show that f_0 does not solve Boltzmann's equation.

Consider a relaxation approximation, where the collision term of Boltzmann's equation is replaced by a term that drives a solution f_1 towards f_0, i.e.

$$[\frac{\partial}{\partial t} + \frac{p_y}{m}\frac{\partial}{\partial y}]f_0(\mathbf{p}, y) = -\frac{f_1(\mathbf{p}, y) - f_0(\mathbf{p}, y)}{\tau}$$

and solve for f_1.

(c) The rate of heat transfer is $Q = n\langle p_y p^2 \rangle_1/(2m^2)$; $\langle ... \rangle_1$ is an average with respect to f_1. Justify this form and evaluate Q using the integrals $\langle p_y^2 p^4 \rangle_0 = 35(mk_bT)^3$ and $\langle p_y^2 p^2 \rangle_0 = 5(mk_bT)^2$. Identify the coefficient of thermal conductivity κ, where $Q = -\kappa\frac{\partial T}{\partial y}$.

(d) Find the profile $T(y)$.

(e) Show that the current is $\langle J_y \rangle = 0$. Explain why this result is to be expected.

(f) For particles with charge e add an external field E_y and extend Boltzmann's equation from (b). Evaluate, for uniform temperature, J_y and the conductivity σ, where $J_y = \sigma E_y$. Check the Wiedemann-Franz law, $\kappa/\sigma T =$const.

D20. Fluctuation Dissipation Theorem (FDT) for velocities: Consider an external $F(t) = \frac{1}{2}f_0 e^{-i\omega t} + \frac{1}{2}f_0^* e^{i\omega t}$ coupled to the momentum as

$$H = \frac{p^2}{2M} + V(x; \text{env}) - \frac{1}{M}F(t)p$$

where "env" stands for the environment's coordinates and momenta.

(a) Define the velocity response function by $\langle v(\omega)\rangle = \alpha_v(\omega)F(\omega)$ and show that the average dissipation rate is

$$\overline{\frac{dE}{dt}} = \tfrac{1}{2}\omega|f_0|^2 \text{Im}\,\alpha_v(\omega)\,.$$

(b) Construct a Langevin's equation with $F(t)$ and identify $\alpha_v(\omega)$. [Identify also $\alpha_{p/M}(\omega)$ and show that $\text{Im}\,\alpha_v(\omega) = \text{Im}\,\alpha_{p/M}(\omega)$.] Using the known velocity correlations $\phi_v(\omega)$ (for $F = 0$) show the FDT

$$\phi_v(\omega) = \frac{2k_B T}{\omega}\text{Im}\,\alpha_v(\omega)\,.$$

D21. Consider the Langevin equation for a particle with mass M and veloscity $\mathbf{v}(t)$ in a medium with viscosity γ and a random force $\mathbf{A}(t)$.

(a) Show that in equilibrium $\langle \mathbf{v}(t)\mathbf{A}(t)\rangle = 3k_B T\gamma/M$.

(b) Given $\langle \mathbf{v}(t)\mathbf{v}(0)\rangle \sim e^{-\gamma|t|}$ and $\langle \mathbf{v}\rangle = 0$, use $\mathbf{v}(t) = \dot{\mathbf{x}}(t)$ to evaluate $\langle \mathbf{x}^2(t)\rangle$ [do not use Langevin's equation] .

D22. A balance for measuring weight consists of a sensitive spring which hangs from a fixed point. The spring constant is is K, i.e. the force opposing a length change x is $-Kx$. The balance is at a temperature T and gravity acceleration is g. A small mass m hangs at the end of the spring.

(a) Write the partition function and evaluate the average $\langle x\rangle$ and the fluctuation $\langle (x - \langle x\rangle)^2\rangle$. What is the minimal m which can be meaningfully measured?

(b) Write a Langevin equation for $x(t)$ with friction γ and a random force $A(t)$. Assuming $\langle A(t)A(0)\rangle = C\delta(t)$ evaluate the spectrum $|\tilde{x}(\omega)|^2$ where $\tilde{x}(\omega)$ is the Fourier transform of $\tilde{x} = x - \langle x\rangle$. Evaluate $\langle \tilde{x}^2(t)\rangle$ and from (a) find the coefficient C. [You may use $\int d\omega/[(\omega^2 - K/m)^2 + \gamma^2\omega^2] = m\pi/\gamma K$.]

(c) Consider response to a force that couples to the velocity, i.e. the Langevin equation acquires a term $-\partial F/\partial t$. Evaluate the dissipation function $\text{Im}\,\alpha_v(\omega)$, the power spectrum of the velocity $\phi_v(\omega)$ and show that the fluctuation dissipation theorem holds.

D23. An electrical circuit has in series components with capacitance C, inductance L, resistance R and a voltage source $V_0 \cos\omega t$ with frequency ω.

(a) Write a Langevin equation for this circuit and identify the response function $\alpha_Q(\omega) = \langle Q(\omega)\rangle/(\frac{1}{2}V_0)$. Use this to write the energy dissipation rate.

(b) Use the fluctuation dissipation relation to identify the Fourier transform $\Phi_Q(\omega)$ of the charge correlation function. Evaluate $\langle Q^2(t)\rangle$ and compare with the result from equipartition.

(c) Consider the special case of $1/C = 0$ and find the long time behavior of $\langle [Q(t) - Q(0)]^2\rangle$ (hint: approximate the t dependence by a cutoff $\omega = 1/t$). Interpret the result.

(d) Evaluate the current fluctuations for the general case (finite C) $\langle I^2(t)\rangle$ and compare with the result from equipartition. Under what conditions does one get Nyquist's result $\langle I^2\rangle_{\omega_1 \leftrightarrow \omega_2} = \frac{2k_B T}{\pi R}(\omega_2 - \omega_1)$?

Hint: $\int_{-\infty}^{\infty} \frac{d\omega/2\pi}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} = \frac{1}{2\gamma\omega_0^2}$, $\qquad \int_{-\infty}^{\infty} \frac{\omega^2 d\omega/2\pi}{(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2} = \frac{1}{2\gamma}$.

D24. Consider a Millikan type experiment to measure the charge e of a particle with mass m. The particle is in an electric field E in the z direction, produced by a capacitor whose plates are distance d apart. The experiment is at temperature T and in a poor vacuum, i.e. τ_{col} is short. (τ_{col} is the average time between collisions of the air molecules and the charged particle). The field is opposite to the gravity force and the experiment attempts to find the exact field E^* where $eE^* = mg$ by monitoring the charge arriving at the plates.

(a) Write a Langevin equation for the velocity $\mathbf{v}$ with a friction coefficient γ describing the particle dynamics. If $E = E^*$ find the time T_D (assuming $\gamma T_D >> 1$) after which a current noise due to diffusion is observed. What is the condition on τ_{col} for the validity of this equation?

(b) When $E \neq E^*$ the equation has a steady state solution $\langle v_z \rangle = v_d$. Find the drift velocity v_d. Rewrite the equation in terms of $\tilde{v}_z = v_z - v_d$ and find the long time limit of $\langle z^2 \rangle$. From the condition that the observation time is $<< T_D$ deduce a limit on the accuracy in measuring E^*.

(d) If the vacuum is improved (i.e. air density is lowered) but T is maintained, will the accuracy be improved?

D25. A galvanometer at temperature T has a mass m, a deflection spring with an oscillation frequency ω_0 and a damping resistance R. The position x of the spring measures the current I via the equation

$$\ddot{x} + \omega_0^2 x = -\gamma \dot{x} + A(t) + \alpha I$$

where $A(t)$ is a random force, γ is the friction and α is an instrument parameter, converting current into force.

(a) What is the lower limit on a current which can be safely recorded?

(b) Evaluate the dissipation rate and identify R by equating the dissipation with $I^2 R/2$ where I is a current with frequency $\sim \omega_0$. Rewrite (a) in terms of R (instead of α).

D26. Shot noise: The discreteness of the electron charge e implies that the current is not uniform in time and is a source of noise. Consider a vacuum tube in which electrons are emitted from the negative electrode and flow to the positive electrode; the probability of emitting any one electron is independent of when other electrons are emitted. Suppose that the current meter has a response time τ. If T is the average time between the emission of two electrons, then the average current is $\langle I \rangle = e/T = \frac{e}{\tau} t$, where $t = \tau/T$ is the transmission probability, $0 \leq t \leq 1$.

(a) Show that the fluctuations in I are $\langle \delta I^2 \rangle = \frac{e^2}{\tau^2} t(1-t)$. Why would you expect the fluctuations to vanish at both $t = 0$ and $t = 1$? [Hint: For each τ interval $n_i = 0$ or $n_i = 1$ and $\langle n_i \rangle = \tau/T$; discretize time in units of τ.]

(b) Consider the meter response to be in the range $0 < |\omega| < 2\pi/\tau$. Show that for $t \ll 1$ the fluctuations in a frequency interval $d\omega$ are $d\langle \delta I^2 \rangle = e\langle I \rangle d\omega/2\pi$. At what frequencies does this noise dominate over the Johnson noise in the circuit?

(c) Show that the 3rd order commulant is $\langle ((I - \langle I \rangle))^3 \rangle = \frac{e^3}{\tau^3} t(1-t)(1-2t)$.

D27. Consider a classical system of charged particles with a Hamiltonian $H_0(p, q)$. Turning on an external field $\mathbf{E}(t)$ leads to the Hamiltonian $H = H_0(p, q) - e\Sigma_i \mathbf{q}_i \cdot \mathbf{E}(t)$.

(a) Show that the solution of Liouville's equation to first order in $\mathbf{E}(t)$ is

$$\rho(p, q, t) = e^{-\beta H_0(p,q)} \left[1 + \beta e \Sigma_i \int_{-\infty}^t \dot{\mathbf{q}}_i(t') \cdot \mathbf{E}(t')dt' \right] .$$

(b) In terms of the current density $\mathbf{j}(\mathbf{r}, t) = e\Sigma_i \dot{\mathbf{q}}_i \delta^3(\mathbf{r} - \mathbf{q}_i)$ show that for $\mathbf{E} = \mathbf{E}(\omega)e^{i\omega t}$ the linear response is $\langle j^\mu(t) \rangle = \sigma^{\mu\nu}(\omega)E^\nu(\omega)e^{i\omega t}$ where μ, ν , are vector components and

$$\sigma^{\mu\nu}(\omega) = \beta \int_0^\infty d\tau e^{-i\omega\tau} d^3 r \langle j^\mu(0,0)j^\nu(\mathbf{r}, -\tau) \rangle_0$$

where $\langle ... \rangle_0$ is an average of the $\mathbf{E} = 0$ system. This is the (classical) Kubo's formula.

c) Rewrite (b) for $\mathbf{j}(\mathbf{r}, t)$ in presence of a position dependent $\mathbf{E}(\mathbf{r}, t)$. Integrating $\mathbf{j}(\mathbf{r}, t)$ over a cross section perpendicular to $\mathbf{E}(\mathbf{r}, t)$ yields the current $I(t)$. Show that the resistance $R(\omega)$ satisfies

$$R^{-1}(\omega) = \beta \int_0^\infty d\tau e^{-i\omega\tau} \langle I(0)I(\tau) \rangle_0$$

For a real $R(\omega)$ (usually valid below some frequency) deduce Nyquist's theorem.

D28. (a) Write the Diffusion constant D in terms of the velocity-velocity correlation function. [Assume that this correlation has a finite range in time].

(b) Use Kubo's formula (Ex. D27), assuming uncorrelated particles, to derive the Einstein-Nernst formula for the mobility $\mu = eD/k_BT$. [$\mu = \sigma(\omega = 0)/ne$ and n is the particle density].

D29. Consider a damped harmonic oscillator with mass M whose coordinate $x(t)$ satisfies

$$\ddot{x} + \gamma\dot{x} + \Omega^2 x = A(t)$$

where the power spectrum of $A(t)$, in the quantum case, is

$$\phi_A(\omega) = \frac{\hbar\omega\gamma}{M} \coth\frac{\hbar\omega}{2k_BT} .$$

(a) Deduce the power spectrum of the velocity $\phi_v(\omega)$.

(b) For $\gamma \to 0$ show that $\phi_v(\omega) \to \delta(\omega - \Omega)$ and that $\langle\frac{1}{2}Mv^2\rangle = \frac{1}{4}\hbar\Omega\coth\frac{\hbar\omega}{2k_BT}$. Explain why is this the expected result.

(c) Bonus: Evaluate $\langle\frac{1}{2}Mv^2\rangle$ with $\gamma \neq 0$.

D30. Particles with charge e and velocities $\mathbf{v}_i$ couple to an external vector potential by $V_{int} = -\frac{e}{c}\sum_i \mathbf{v}_i \cdot \mathbf{A}$ and the electric field is $\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}$. The current density (per unit volume) is $\mathbf{j} = e\sum_i \mathbf{v}_i$.

(a) Identify the response function for an a component field with a given frequency, $E_a(\omega)$, in terms of the conductivity $\sigma(\omega)$ where $\mathbf{j}_a = \sigma(\omega)\mathbf{E}_a$ (assume an isotropic system so that $\sigma(\omega)$ is a scaler). Deduce the energy dissipation rate in terms of $\sigma(\omega)$ and $E_a(\omega)$. Compare with Ohm's law. What is the symmetry of $\mathrm{Re}\sigma(\omega)$ when ω changes sign?

(b) Use the fluctuation dissipation theorem to show the (classical) Kubo formula:

$$\mathrm{Re}\sigma(\omega) = \frac{1}{k_BT} \int_0^\infty \langle j_a(0) \cdot j_a(t)\rangle \cos(\omega t)dt$$

(c) Write the Diffusion constant D in terms of the velocity-velocity correlation function, assuming that this correlation has a finite range in time.

Use Kubo's formula from (b) in the DC limit of zero frequency to derive the Einstein-Nernst formula for the mobility $\mu = \frac{\sigma}{ne} = eD/k_BT$, where n is the particle density. (assume here uncorrelated particles).

(d) The quantum current noise is defined as

$$S(\omega) = \int_0^\infty dt\langle j_a(t)j_a(0) + j_a(0)j_a(t)\rangle \cos(\omega t).$$

Use the quantum FDT to relate this noise to the conductivity. When is the classical result (b) valid? What is the noise at $T = 0$?

D31. Consider the reaction A↔B for molecules A,B that evolves via a Langevin type equation

$$\frac{dN_A(t)}{dt} = k_1 N_B(t) - k_2 N_A(t) + A(t) \qquad (*)$$

where the total number of molecules $N = N_A(t) + N_B(t)$ is fixed. k_1, k_2 are reaction constants and $A(t)$ is random with averages $\langle A(t)\rangle = 0$, $\langle A(t)A(t')\rangle = C\delta(t - t')$.

(a) Solve for $\langle N_A(t)\rangle$ with the initial condition $N_A(0) = 0$ and show that its value at long time $\bar{N}_A$ yields $k_1/k_2 = f_A/f_B$, where results of question (A24) are used.

(b) Solve for $\langle[\delta N_A(t)]^2\rangle$ where $\delta N_A(t) = N_A(t) - \bar{N}_A$ and from its long time form and the results of question (A24b) show that $C = \frac{2k_1 k_2}{k_1 + k_2}N$.

(c) The chemical potential of B is now modified by a term $\delta\mu_B(t) = \delta\mu_B(\omega)e^{-i\omega t}$. The response $\alpha(\omega)$ is defined by the long time form $\langle N_A(t)\rangle = \alpha(\omega)\delta\mu_B(\omega)e^{-i\omega t} + \bar{N}_A$. Show that $\delta\mu_B(t) = -k_B T\frac{\delta k_2(t)}{k_2}$ by using the correspondence with question (A24), where $k_2 \to k_2 + \delta k_2(t)$ in Eq. (*). Solve the resulting equation for $\langle N_A(t)\rangle$ and identify $\alpha(\omega)$.

(d) Solve Eq. (*) for the equilibrium fluctuation in the absence of external forces ($\delta\mu_B(t) = 0$)

$$\phi_{N_A}(\omega) = \int \langle \delta N_A(t)\delta N_A(t+\tau)\rangle e^{i\omega\tau} d\tau \tag{4}$$

and check the (classical) fluctuation dissipation theorem. [Use the $t \to \infty$ form for the equilibrium correlation].

D32. An electrical circuit has in series components with capacitance C, resistance R and a voltage source $V_0 \cos\omega t$ with frequency ω.

(a) Write a Langevin equation for this circuit and identify the response function $\alpha_Q(\omega) = \langle Q(\omega)\rangle/(\frac{1}{2}V_0)$. Use this to write the energy dissipation rate.

(b) Use the (classical) fluctuation dissipation relation to identify the Fourier transform $\Phi_Q(\omega)$ of the charge correlation function. Evaluate $\langle Q^2(t)\rangle$ and compare with the result from equipartition. [Note: $\int_0^\infty \frac{dx}{1+x^2} = \frac{\pi}{2}$]

(c) Consider the fluctuations of the random potential $\langle V(t)V(t')\rangle = A\delta(t-t')$ and identify A.

(d) The capacitance energy is $E = \frac{Q^2}{2C}$. Evaluate The fluctuations in E, i.e. $\sqrt{\langle E^2\rangle - \langle E\rangle^2}$ where the average is on the random voltage. Compare with the energy fluctuations of a canonical ensemble. (Here $V_0 = 0$).

D51. Consider a fluid in two compartments connected with a small hole. Although particles can pass easily through the hole, it is small enough so that within each compartment the fluid is in thermodynamic equilibrium. The compartments have pressure, temperature, volume and particle number P_1, T_1, V_1, N_1 and P_2, T_2, V_2, N_2, respectively. There is an energy transfer rate dE/dt and particle transfer rate dN/dt through the hole.

(a) Identify the kinetic coefficients for dE/dt and dN/dt driven by temperature and chemical potential differences. Rewrite the equations in terms of $\Delta T = T_1 - T_2$ and $\Delta P = P_1 - P_2$ to first order in ΔT and ΔP.

(b) If $\Delta T = 0$ one measures $\epsilon_1 = (dE/dt)/(dN/dt)$. One can also adjust the ratio $\epsilon_2 = \Delta P/\Delta T$ so that $dN/dt = 0$. Show the relation

$$\epsilon_2 = \frac{1}{T}[\frac{E}{V} + P - \frac{N}{V}\epsilon_1]$$

(E/V or P for either compartment).

(c) Assume that the work done during the transfer by the pressure is via reducing the effective volume to zero within the hole. Evaluate ϵ_1 and show that $\epsilon_2 = 0$.

D52. Consider the coefficients γ_{ij} in Onsager's relations for heat and current transport (see lecture notes pages 70-71). Consider also Boltzmann's equation as in Ex. D07.

(a) Show that γ_{22} is related to the conductivity $\sigma = ne^2\tau/m$.

(b) Show that $\langle J_y\rangle = 0$ and identify γ_{21}. [Note that $eV_i = \mu_i$ the local chemical potential.]

(c) Identify the thermal conductivity κ in terms of γ_{ij}. Use $\kappa = \frac{5}{2m}k_B^2 n\tau T$ (result of D07c) to find γ_{11}.