Ex3009: Entropy and heat capacity of quantum ideal gases

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The problem: Consider an N particle ideal gas confined in volume V at temperature T. Find (a) the entropy S and (b) the heat capacity C, highlighting its dependence on the temperature.
(1) Consider classical gas.
(2) Consider Fermi gas at low temperatures, using leading order Sommerfeld expansion.
(3) Consider Bose gas below the condensation temperature.
(4) Consider Bose gas above the condensation temperature.
(5) What is $C_{Bose}/C_{classical}$ at the condensation temperature?
(6) For temperatures that are above but very close to the condensation temperature, find an approximation for C_V in terms of elementary functions.

Hints: In (4) use the Grand-Canonical formalism to express N and E as a function of the temperature T and the fugacity z. Use the equation for N in order to deduce an expression for $\left(\frac{\partial z}{\partial T}\right)_N$ Note that the derivative of the polylogarithmic function $L_\alpha(z)$ is $(1/z)L_{\alpha-1}(z)$. Final results should be expressed in terms of (N, V, T), but it is allowed to define and use the notations λ_T and ϵ_F and T_c. In item (4) the final result can include ratios of polylogarithmic functions, with the fugacity z as an implicit variable. Note that such ratios are all of order unity throughout the whole temperature range provided $\alpha > 1$, while functions with $\alpha < 1$ are singular at $z = 1$.

The solution:

(1) Classical Gas:

Defining the thermal wavelength:

$$\lambda_T = \left(\frac{2\pi}{mT}\right)^{\frac{1}{2}} \tag{1}$$

The partition function:

$$Z_N = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N \tag{2}$$

The free energy is:

$$F = -T\ln\left(\frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N\right) \approx -NT\ln\left(\frac{V}{\lambda_T^3}\right) + T\left(N\ln(N) - N\right) \tag{3}$$

We have used the Stirling approximation:

$$\ln(N!) \approx N\ln(N) - N \tag{4}$$

(a) **The entropy is given by:**

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = N\left[\ln\left(\frac{V}{N\lambda_T^3}\right) + \frac{5}{2}\right] \tag{5}$$

(b) **The heat capacity:**

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \frac{3}{2}N \tag{6}$$

(2) Fermi gas at low temperature $T \ll \epsilon_F$**.**

In order to calculate the grand free energy, lets start by recalling the Sommerfeld expansion of the number of particles and the energy:

$$N = V\frac{1}{6\pi^2}(2m)^{\frac{3}{2}}\mu^{\frac{3}{2}}\left(1+\frac{\pi^2}{8}\left(\frac{T}{\mu}\right)^2+...\right) \tag{7}$$

$$E = V\frac{3}{5}\frac{1}{6\pi^2}(2m)^{\frac{3}{2}}\mu^{\frac{5}{2}}\left(1+\frac{5\pi^2}{8}\left(\frac{T}{\mu}\right)^2+...\right) \tag{8}$$

The pressure is related to the energy by:

$$P = \frac{2}{3}\frac{E}{V} \tag{9}$$

By extensiveness, the grand free energy is:

$$F_G = -PV = -V\frac{2}{5}\frac{1}{6\pi^2}(2m)^{\frac{3}{2}}\mu^{\frac{5}{2}}\left(1+\frac{5\pi^2}{8}\left(\frac{T}{\mu}\right)^2+...\right) \tag{10}$$

(a) The entropy is: (to the first order)

$$S = -\left(\frac{\partial F_G}{\partial T}\right)_{\mu,V} = \frac{\pi^2}{2}V\frac{1}{6\pi^2}(2m)^{\frac{3}{2}}\mu^{\frac{1}{2}}T \tag{11}$$

We would like to express the entropy using the number of particles because we are interested in a closed system, where the number of particles is fixed. It is convenient to express the result in terms of the Fermi energy:

$$\mu = \epsilon_F\left(1-\frac{\pi^2}{12}\left(\frac{T}{\epsilon_F}\right)^2+...\right) \tag{12}$$

In leading order the $O(T^2)$ correction to $\mu(T)$ can be ignored and we get the leading linear approximation

$$S = \frac{\pi^2}{2}N\frac{T}{\epsilon_F} \tag{13}$$

(b) The heat capacity (to the first order)

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \frac{\pi^2}{2}N\frac{T}{\epsilon_F} \tag{14}$$

(3) Bose gas $T_C > T$:

In order to find the grand free energy, we need the pressure, which is:

$$P = \frac{T}{\lambda_T^3}\zeta\left(\frac{5}{2}\right) \tag{15}$$

By extensiveness:

$$F_G = -PV = -V\frac{T}{\lambda_T^3}\zeta\left(\frac{5}{2}\right) \tag{16}$$

(a) The entropy:

$$S = -\left(\frac{\partial F_G}{\partial T}\right)_{\mu,V} = \frac{5}{2}V\left(\frac{m}{2\pi}\right)^{\frac{3}{2}}T^{\frac{3}{2}}\zeta\left(\frac{5}{2}\right) \tag{17}$$

Formally one can regard the entropy S of a Bose gas, as the sum over entropies S_r of harmonic oscillators that have frequencies $\omega_r = \epsilon_r - \mu$. Below the condensation temperature the zero-frequency mode $\omega_0 = 0$ contributes an infinite offset S_0 to the total entropy. This offset should be excluded if the system is closed, because then the occupation of the lower orbital is not an independent variable but is dictated by the occupations of the excited orbitals. Differently phrased, one may say that in the regime $T < Tc$ the Bose gas is formally equivalent to a cavity with photons/phonons.

(b) The heat capacity:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{15}{4}V\left(\frac{m}{2\pi}\right)^{\frac{3}{2}}T^{\frac{3}{2}}\zeta\left(\frac{5}{2}\right) \tag{18}$$

(4) Bose gas $T > T_C$.

The system is closed, so in order to find the grand free energy, we use the expressions for the number of particles and the energy of Bose gas $T > T_C$.

$$N = V\left(\frac{m}{2\pi}\right)^{\frac{3}{2}} T^{\frac{3}{2}} L_{\frac{3}{2}}(z) = \text{constant} \tag{19}$$

The energy is:

$$E = \frac{3}{2}V\left(\frac{m}{2\pi}\right)^{\frac{3}{2}} T^{\frac{5}{2}} L_{\frac{5}{2}}(z) \tag{20}$$

The grand free energy, as before:

$$F_G = -PV = -\frac{2}{3}E \tag{21}$$

Therefore:

$$F_G = -V\left(\frac{m}{2\pi}\right)^{\frac{3}{2}} T^{\frac{5}{2}} L_{\frac{5}{2}}(z) \tag{22}$$

(a) The entropy is:

$$S = -\left(\frac{\partial F_G}{\partial T}\right)_{\mu,V} = \left(\frac{m}{2\pi}\right)^{\frac{3}{2}} V\left[\frac{5}{2}T^{\frac{3}{2}} L_{\frac{5}{2}}(z) + T^{\frac{5}{2}}\frac{\partial L_{\frac{5}{2}}(z)}{\partial T}\right] \tag{23}$$

In order to calculate $\frac{\partial}{\partial T}L_{\frac{5}{2}}(z)$ We use:

$$L'_{\frac{5}{2}}(z) = \frac{1}{z}L_{\frac{3}{2}}(z) \tag{24}$$

and

$$\left(\frac{\partial z}{\partial T}\right)_{\mu} = -\frac{1}{T}z\ln(z) \tag{25}$$

And get:

$$\frac{\partial}{\partial T}L_{\frac{5}{2}}(z) = -\frac{1}{T}L_{\frac{3}{2}}(z)\ln(z) \tag{26}$$

Substituting to the entropy expression:

$$S = \left(\frac{mT}{2\pi}\right)^{\frac{3}{2}} VL_{\frac{3}{2}}(z)\left[\frac{5}{2}\frac{L_{\frac{5}{2}}(z)}{L_{\frac{3}{2}}(z)} - \ln(z)\right] \tag{27}$$

This equation is true also for $T < T_C$ since $\mu = 0$ and hence $z = 1$. Identifying the prefactor in the last equation as the number of particles,

$$S = N\left[\frac{5}{2}\frac{L_{\frac{5}{2}}(z)}{L_{\frac{3}{2}}(z)} - \ln(z)\right] \tag{28}$$

In the Boltzmann regime ($z \ll 1$) this agree with the classical gas result Eq(5).

(b) Heat capacity:
Our system is closed, so the number of particles should stay constant. We calculate the heat capacity using the energy. (Alternatively we could have done it using the entropy).

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = \frac{15}{4}V\left(\frac{m}{2\pi}\right)^{\frac{3}{2}}T^{\frac{3}{2}}L_{\frac{5}{2}}(z) + V\frac{3}{2}\left(\frac{m}{2\pi}\right)^{\frac{3}{2}}T^{\frac{5}{2}}\frac{\partial}{\partial T}L_{\frac{5}{2}}(z) \tag{29}$$

Regarding in (19) as an implicit equation for z as a function of the free variables N and T we get by differentiation:

$$\frac{3}{2}T^{\frac{1}{2}}L_{\frac{3}{2}}(z) + T^{\frac{3}{2}}L'_{\frac{3}{2}}(z)\frac{\partial z}{\partial T} = 0 \tag{30}$$

Now, we know that

$$L'_{\frac{3}{2}}(z) = \frac{1}{z}L_{\frac{1}{2}}(z) \tag{31}$$

Hence.

$$\frac{1}{z}\left(\frac{\partial z}{\partial T}\right)_N = -\frac{3}{2T}\frac{L_{\frac{3}{2}}(z)}{L_{\frac{1}{2}}(z)} \tag{32}$$

[1]Lets substitute at Eq(29):

$$C_V = \frac{15}{4}V\left(\frac{m}{2\pi}\right)^{\frac{3}{2}}T^{\frac{3}{2}}L_{\frac{5}{2}}(z) + \frac{3}{2}V\left(\frac{m}{2\pi}\right)^{\frac{3}{2}}T^{\frac{5}{2}}L_{\frac{3}{2}}(z)\left(-\frac{3}{2T}\frac{L_{\frac{3}{2}(z)}}{L_{\frac{1}{2}(z)}}\right) \tag{33}$$

$$C_V = \left(\frac{mT}{2\pi}\right)^{\frac{3}{2}}VL_{\frac{3}{2}}(z)\left[\frac{15}{4}\frac{L_{\frac{5}{2}}(z)}{L_{\frac{3}{2}}(z)} - \frac{9}{4}\frac{L_{\frac{3}{2}}(z)}{L_{\frac{1}{2}}(z)}\right] \tag{34}$$

Expressing the heat capacity using the number of particles, We finally get:

$$C_V = N\left[\frac{15}{4}\frac{L_{\frac{5}{2}}(z)}{L_{\frac{3}{2}}(z)} - \frac{9}{4}\frac{L_{\frac{3}{2}}(z)}{L_{\frac{1}{2}}(z)}\right] \tag{35}$$

In the Boltzman approximation $z \ll 1$ and $L_\alpha(z) \approx z$, and by substitution one can see: $C_V = \frac{3}{2}N$ - in agreement with the classical heat capacity.

[1]Note that this derivative in constant number is different from the same derivative in constant chemical potential.

(5) In the critical temperature:

$$C_V = N\frac{15\zeta(\frac{5}{2})}{4\zeta(\frac{3}{2})} \approx 1.92N \tag{36}$$

This result can be deduced using Eq(18) or alternatively Eq(35). In the latter equation, the right term in the right-hand-side vanish since $L_{\frac{1}{2}}(z)$ diverges at $z \to 1$. Thus,

$$\frac{C_{Bose}}{C_{Classical}} \approx 1.28 \tag{37}$$

So it is easier to heat a classical gas by 28% than Bose quantum gas.

(6) We basically need to approximate polylogarithmic raios: $L_{\frac{3}{2}}(z)/L_{\frac{1}{2}}(z), L_{\frac{5}{2}}(z)/L_{\frac{3}{2}}(z)$ near $z = 1$ (look at Eq. (35)).
For $z \to 1^+, T \to T_C, \mu \to 0^-$ we shall use the formula:

$$F_{\alpha<1}(e^{\beta\mu}) = \int_0^\infty dx \frac{x^{\alpha-1}}{\frac{e^x}{z} - 1} = \Gamma(\alpha)L_\alpha(z) \approx \frac{1}{1-\alpha}(-\beta\mu)^{-(1-\alpha)} \tag{38}$$

Setting $\alpha = \frac{1}{2}$ we get that for $T \to T_C$:

$$L_{\frac{1}{2}}(z) \approx \frac{2}{\sqrt{\pi}}\frac{1}{\sqrt{-\beta\mu}} \tag{39}$$

To get an approximation for $L_{\frac{3}{2}}(z)$, we remember Eq.(31) and integrate:

$$L_{\frac{3}{2}}(z) \approx \zeta\left(\frac{3}{2}\right) - \frac{4}{\sqrt{\pi}}\sqrt{-\frac{\mu}{T_C}} \tag{40}$$

So:

$$\frac{L_{\frac{3}{2}}(z)}{L_{\frac{1}{2}}(z)} \approx \zeta\left(\frac{3}{2}\right)\frac{\sqrt{\pi}}{2}\sqrt{\frac{-\mu}{T_C}} \tag{41}$$

On top of that we need:

$$\frac{L_{\frac{5}{2}}(z)}{L_{\frac{3}{2}}(z)} \approx \frac{\zeta(\frac{5}{2})}{\zeta\left(\frac{3}{2}\right) - \frac{4}{\sqrt{\pi}}\sqrt{-\frac{\mu}{T_C}}} \approx \frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2})}\left[1 + \frac{4}{\sqrt{\pi}\zeta(\frac{3}{2})}\sqrt{\frac{-\mu}{T_C}}\right] \tag{42}$$

But the latter expressions depend on μ, which we would like to relate to the small parameter:

$$t = \frac{T - T_C}{T_C} \tag{43}$$

So we approximate the number of particles $N \propto T^{\frac{3}{2}}L_{\frac{3}{2}}(z)$ near the condensation temperature:

$$T^{\frac{3}{2}} = \left(T_C(1 + \frac{T - T_C}{T_C})\right)^{\frac{3}{2}} \approx T_C^{\frac{3}{2}}\left(1 + \frac{3}{2}t\right) \tag{44}$$

Putting this together with Eq. (40) in the expresion for N:

$$N = V\left(\frac{mT_C}{2\pi}\right)^{\frac{3}{2}}(1 + \frac{3}{2}t)\left[\zeta\left(\frac{3}{2}\right) - \frac{4}{\sqrt{\pi}}\sqrt{-\frac{\mu}{T_C}}\right] \tag{45}$$

After a little algebra,

$$\sqrt{-\frac{\mu}{T_C}} \approx \frac{3\sqrt{\pi}\zeta\left(\frac{3}{2}\right)}{8}t \tag{46}$$

Now we are ready to get the heat capacity:

$$C_V = N\left(\frac{15}{4}\frac{\zeta(\frac{5}{2})}{\zeta(\frac{3}{2}} + \left(\frac{3\zeta(\frac{5}{2})}{2\zeta(\frac{3}{2})} - \frac{27\pi\zeta(\frac{3}{2})^2}{64}\right)t\right) \approx N(1.92 - 8.27t) \tag{47}$$

Comparing with item (3) - the heat capacity is continuous.