

TSP-2022/23 — Thermal and Statistical Physics (Part II)

Problem sheet II: questions 1-10

1. Point defect

A point defect in a solid may be occupied by 0, 1 (spin up or down) or 2 electrons, and the solid provides a reservoir of electrons at chemical potential μ . The energy for occupation by a single electron is ϵ , and that for 2 electrons is $2\epsilon + U$, where U is the Coulomb repulsion energy between the electrons. Obtain an expression for the average electron occupancy of the defect and sketch $\langle n \rangle(\mu - \epsilon)$ for low temperatures $T \ll U/k_B$.

Solution: A table of states, occupancies, and energies may be constructed as follows.

i	N_i	E_i
1	0	0
2	1 \uparrow	ϵ
3	1 \downarrow	ϵ
4	2	$2\epsilon + U$

The grand partition function is

$$\Xi = \sum_i e^{-\beta(E_i - N_i\mu)} = 1 + 2e^{-\beta(\epsilon - \mu)} + e^{-\beta(2\epsilon + U - 2\mu)},$$

and the grand potential is $\Phi = -k_B T \ln \Xi$. The average electron occupancy of the defect is

$$N = -\frac{\partial \Phi}{\partial \mu} = k_B T \frac{1}{\Xi} \frac{\partial \Xi}{\partial \mu}.$$

$$\frac{\partial \Xi}{\partial \mu} = 2\beta e^{-\beta(\epsilon - \mu)} + 2\beta e^{-\beta(2\epsilon + U - 2\mu)},$$

and therefore

$$N = \frac{2e^{-\beta(\epsilon - \mu)} + 2e^{-\beta(2\epsilon + U - 2\mu)}}{1 + 2e^{-\beta(\epsilon - \mu)} + e^{-\beta(2\epsilon + U - 2\mu)}}.$$

Alternatively we can write the average directly from the discrete probability

$$N = \frac{\sum_i N_i e^{-\beta(E_i - N_i\mu)}}{\sum_i e^{-\beta(E_i - N_i\mu)}} = \frac{2e^{-\beta(\epsilon - \mu)} + 2e^{-\beta(2\epsilon + U - 2\mu)}}{1 + 2e^{-\beta(\epsilon - \mu)} + e^{-\beta(2\epsilon + U - 2\mu)}}.$$

Note that if we set $U = 0$, we obtain the familiar Fermi-Dirac distribution:

$$N = \frac{2}{e^{-\beta(\epsilon - \mu)} + 1}.$$

The sketch of N vs. $\mu - \epsilon$ should show two steps, one when the chemical potential exceeds ϵ , where the occupancy rises from 0 to 1, then a second one when the chemical potential exceeds $\epsilon + U$, where the occupancy rises to 2 (Fig. 1). This can be obtained by considering the limits of N for $U\beta \rightarrow \infty$ for various choices of $\mu - \epsilon$ such as $\mu - \epsilon < 0$, $\mu - \epsilon = 0$, $\mu - \epsilon > U$, and so on. Note that the wide plateau for which $N = 1$ would correspond physically to a magnetic moment bound to the defect.

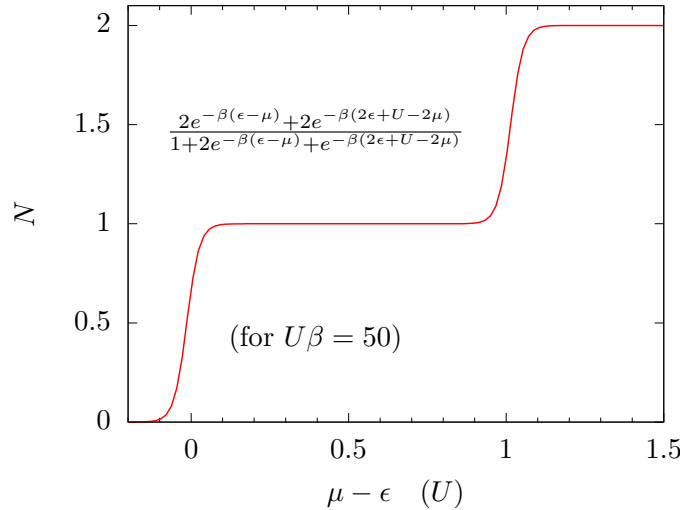


Figure 1: Use computers to help with tricky questions! Here, gnuplot: `'plot [-0.2:1.5] 2*(exp(beta*x)+exp(-beta*(-2*x+U)))/(1+2*exp(beta*x)+exp(-beta*(-2*x+U)))'`

2. Plasma

Show that the equilibrium constant K_N for the ionisation reaction $\text{He} \rightleftharpoons \text{He}^+ + \text{e}^-$ is to a good approximation

$$K_N = \frac{1}{4V} \left(\frac{2\pi\hbar^2}{m_e k_B T} \right)^{3/2} e^{e\phi/k_B T}$$

where ϕ is the first ionisation potential of He, which is 24.6 V.

Find the proportion of He that is ionised at 10^4 K (i) at atmospheric pressure, and (ii) at 10^{-2} Nm $^{-2}$. What is the cause of the change in the equilibrium constant? This effect is important for spectral lines from interstellar gases, one finds a surprisingly large intensity corresponding to spectral lines of ionised atoms.

Solution: For $\text{He} \rightleftharpoons \text{He}^+ + \text{e}^-$ the equilibrium constant is $K_N = N_{\text{He}}/(N_{\text{He}^+}N_{\text{e}^-}) = Z_1^{\text{He}}/(Z_1^{\text{He}^+}Z_1^{\text{e}^-})$, where we have used results from the handout. Remembering that the He^+ and e^- each have two spin states, the single-particle partition functions are

$$\begin{aligned} Z_1^{\text{He}} &= (V/\lambda_{\text{He}}^3(T)) e^{\beta e\phi} \\ Z_1^{\text{He}^+} &= 2(V/\lambda_{\text{He}^+}^3(T)) \\ Z_1^{\text{e}^-} &= 2(V/\lambda_{\text{e}^-}^3(T)) \\ \Rightarrow \frac{N_{\text{He}}}{N_{\text{He}^+}N_{\text{e}^-}} &= \frac{\lambda_{\text{He}^+}^3 \lambda_{\text{e}^-}^3}{\lambda_{\text{He}}^3} \frac{1}{4V} e^{e\phi/k_B T}. \end{aligned}$$

Ignoring the mass difference between He and He^+ , so that $\lambda_{\text{He}^+} = \lambda_{\text{He}}$, we get

$$K_N = \frac{1}{4V} \left(\frac{2\pi\hbar^2}{m_e k_B T} \right)^{3/2} e^{e\phi/k_B T}. \quad (1)$$

Now $N_{\text{He}^+} = N_{\text{e}^-}$, so

$$\begin{aligned} N_{\text{e}^-}^2 &= N_{\text{He}} 4V \left(\frac{m_e k_B T}{2\pi\hbar^2} \right)^{3/2} e^{-e\phi/k_B T} \\ n_{\text{e}^-}^2 &= n_{\text{He}} 4(n_{\text{He}} + 2n_{\text{e}^-}) \frac{k_B T}{p} \left(\frac{m_e k_B T}{2\pi\hbar^2} \right)^{3/2} e^{-e\phi/k_B T}. \end{aligned}$$

To get the last equation we have first used the ideal gas law in the form $V = (N_{\text{He}} + 2N_{\text{e}^-})k_B T/p$, and then divided through by V^2 . Next, dividing through by n_{He}^2 gives a quadratic equation for the ratio of the electron and Helium densities. Solving and substituting the numbers gives ratios of 7.4×10^{-5} at 1 atmosphere, and 0.33 at 10^{-2} Pa.

The ratio is pressure dependent because the probability of dissociation only depends on the temperature, while the probability of recombination also depends on the probability of two dissociation products running into each other, so it depends on p . At low pressure recombination becomes much less likely.

3. Trap

Atoms can be held in a spherical trap with the potential energy potential $V(r) = ar$. Calculate the partition function Z_N of a gas of N indistinguishable non-interacting atoms in this trap at temperature T in the classical limit. Sketch the temperature dependence of the entropy of the classical gas in this trap for two different values of a and demonstrate that by decreasing a adiabatically, the gas can be cooled reversibly.

Find the chemical potential of the system. Estimate the number of atoms required for quantum statistics to become important.

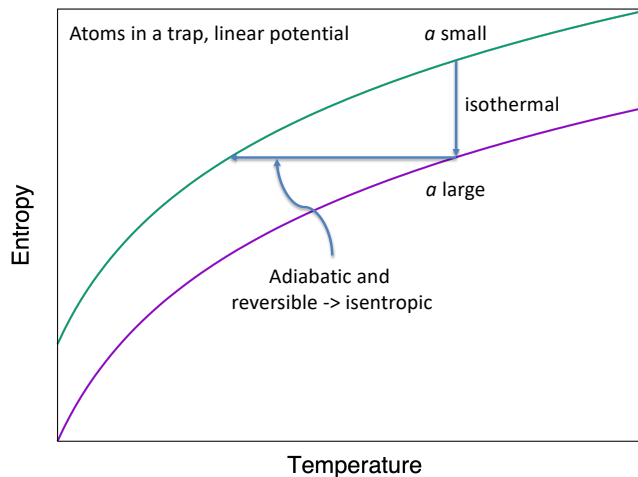
Solution: The single-particle partition function Z_1 contains the same momentum integral as for a classical ideal gas, which contributes λ^{-3} , but instead of the total volume, we now have a space integral:

$$Z_1 = \frac{1}{\lambda^3} \int_0^\infty 4\pi r^2 dr e^{-ar} = \frac{8\pi(k_B T)^3}{a^3 \lambda^3}$$

This gives the N -particle partition function $Z_N = Z_1^N/N!$ and the free energy $F = -k_B T \ln Z_N$, from which we obtain an entropy

$$S = -\frac{\partial F}{\partial T} = k_B N \left(\ln \frac{8\pi(k_B T)^3}{N(a\lambda)^3} + 11/2 \right)$$

This has the form $S = S_0 + 4.5 \ln T - 3 \ln a$, so with decreasing a , we slide from one constant- a curve to another, thereby lowering the temperature:



The chemical potential is obtained as $\mu = \frac{\partial F}{\partial N} = k_B T \ln \left(\frac{Na^3 \lambda^3}{8\pi k_B^3 T^3} \right)$. Quantum statistics become relevant, when this approaches 0 from below, which leads to the inequality $Na^3 \lambda(T)^3 > 8\pi k_B^3 T^3$ (but keep in mind $\lambda \propto T^{-1/2}$) to get into the quantum regime. Check: the volume explored by the classical gas is of order $(k_B T/a)^3$, so this inequality is similar to that for the standard gas, $N\lambda^3/V > 1$.

4. Degenerate or non-degenerate

The temperature at the centre of the sun is $T = 1.6 \times 10^7$ K, and plasma at the centre of the sun consists of hydrogen at a density of $\rho_H = 6 \times 10^4$ kg m⁻³ and helium at a density of $\rho_{He} = 1 \times 10^5$ kg m⁻³.

- Calculate the thermal wavelengths of the electrons, protons and He nuclei.
- Determine whether the electrons, protons and He nuclei are degenerate or non-degenerate under these conditions.
- Estimate the pressure at the centre of the sun due to these particles and that due to the radiation pressure.
- Is it the pressure due to the particles or the radiation which prevents gravitational collapse of the sun?

Solution: (a) The thermal wavelengths are, as usual

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}.$$

Therefore, substituting the values of all parameters,

$$\begin{aligned}\lambda_e &= 1.86 \times 10^{-11} \text{ m} \\ \lambda_p &= 4.35 \times 10^{-13} \text{ m} \\ \lambda_\alpha &= \frac{1}{2}\lambda_p = 2.17 \times 10^{-13} \text{ m}.\end{aligned}$$

(b) The number densities are $n = (N/V) = \rho/m$:

$$\begin{aligned}n_p &= \frac{6 \times 10^4}{1.7 \times 10^{-27}} = 3.59 \times 10^{31} \text{ m}^{-3} \\ n_\alpha &= \frac{1 \times 10^5}{4 \times 1.7 \times 10^{-27}} = 1.50 \times 10^{31} \text{ m}^{-3} \\ n_e &= n_p + 2n_\alpha = 6.58 \times 10^{31} \text{ m}^{-3}.\end{aligned}$$

The criterion for degeneracy, or for entering the quantum regime, is $(N/V)\lambda^3 > 1$, and

$$\begin{aligned}n_p\lambda_p^3 &= 2.9 \times 10^{-6} \\ n_\alpha\lambda_\alpha^3 &= 1.5 \times 10^{-7} \\ n_e\lambda_e^3 &= 0.42,\end{aligned}$$

so the protons and alpha particles are non-degenerate, i.e. fully in classical regime, while the electrons are weakly degenerate and so has to be considered as quantum particles (Fermions). I hope my use of calculator was OK here...

(c) Since the protons and alpha particles are classical and the electrons are only weakly quantum, it is reasonable to calculate their contribution to the pressure using the ideal gas law:

$$\begin{aligned}p &= (n_p + n_\alpha + n_e)k_B T \\ &= 11.7 \times 10^{31} \times 1.38 \times 10^{-23} \times 1.6 \times 10^7 = 2.6 \times 10^{16} \text{ Nm}^{-2}.\end{aligned}$$

The alternative (if you are reasonably unhappy interpreting nearly-overlapping electrons as ideal gas) is to treat it as Fermi gas and blatantly try the estimate of Fermi pressure (which we only know at $T \rightarrow 0$), $p_F = (\hbar^2/2m_e) * n_e^{5/3}$. The true answer will be somewhere in between, but clearly the ideal gas of protons and alpha particles will dominate.

The energy density of black body radiation is given by

$$u = \frac{\pi^2 k_B^4}{15 \hbar^3 c^3} T^4, \quad \text{so radiation pressure } p = \frac{u}{3} = 1.6 \times 10^{13} \text{ Nm}^{-2}.$$

The particle pressure at the centre of the sun is much larger than the radiation pressure, and therefore the particle pressure prevents gravitational collapse.

5. Helium-3

At temperatures below 0.4 K, a dilute solution of ^3He in liquid ^4He behaves like a gas of ^3He atoms moving freely *in vacuo* except that the effective mass of each ^3He atom is enhanced by a factor of about 2.4. The concentration of ^3He is 5 atomic percent and the density of the solution is 140 kg/m^3 . Sketch the temperature dependence of the heat capacity per ^3He atom at low temperatures. Calculate the Fermi temperature, T_F , and the coefficient γ of the specific heat at low temperatures, $c_V = \gamma T$.

[Answer: $T_F = \varepsilon_F/k_B = 0.33 \text{ K}$, $\gamma = 2.0 \times 10^{-22} \text{ J atom}^{-1} \text{ K}^{-2}$.]

Solution: For a degenerate Fermi gas the heat capacity for N particles in volume V is

$$C = \frac{\pi^2}{3} D(\varepsilon_F) k_B^2 T = \frac{\pi^2 N k_B^2}{2 \varepsilon_F} T, \quad (2)$$

where $\varepsilon_F = \hbar^2(3\pi^2 N/V)^{2/3}/2m^*$ is the Fermi energy, and m^* is the effective mass of the fermion “quasiparticles”. If the density of the mixture is 140 kg m^{-3} , then the average atomic mass of the mixture is 0.05 times the ^3He mass plus 0.95 times the ^4He mass = $6.61 \times 10^{-27} \text{ kg}$ per atom. The total number density is then $n_{\text{Tot}} = 2.12 \times 10^{28} \text{ atoms m}^{-3}$, and the number density of ^3He atoms is $n_{^3\text{He}} = 0.05 n_{\text{Tot}} = 1.06 \times 10^{27} \text{ atoms m}^{-3}$.

Considering the ^3He atoms as a Fermi gas we obtain

$$\varepsilon_F = 4.60 \times 10^{-24} \text{ J}, \quad T_F = \frac{\varepsilon_F}{k_B} = 0.33 \text{ K}. \quad (3)$$

The heat capacity is written as $C = \gamma T$, and from equations for C and ε_F we have

$$\frac{\gamma}{N} = 2.0 \times 10^{-22} \text{ J atom}^{-1} \text{ K}^{-2}.$$

6. Repulsion of Fermi particles

For Fermi particles at low temperature, examine the temperature change in (a) the Joule process: the gas expands in vacuum, and (b) the Joule-Kelvin process: the gas is forced through a valve while keeping it insulated so that no heat is exchanged with the environment. That is, find

$$\left(\frac{dT}{dV}\right)_U \quad \text{and} \quad \left(\frac{dT}{dp}\right)_H.$$

Argue how your result reflects the Fermi pressure at $T \rightarrow 0$, in both cases.

Solution: We need to recall from analytical thermodynamics:

$$\left(\frac{dT}{dV}\right)_U = \frac{1}{C_V} \left[p - T \left(\frac{dp}{dT}\right)_V \right] \quad \text{and} \quad \left(\frac{dT}{dp}\right)_H = \frac{1}{C_p} \left[T \left(\frac{dV}{dT}\right)_p - V \right]$$

At low temperature, $T \rightarrow 0$, one can ignore the T-terms in each bracket, so that

$$\left(\frac{dT}{dV}\right)_U = \frac{1}{C_V} [p_F] \quad \text{and} \quad \left(\frac{dT}{dp}\right)_H = -\frac{1}{C_p} [V]$$

with Fermi $C_V = (\pi^2 N k_B^2 / 2 \varepsilon_F) T$ and $p_F = \hbar^2 / 2m (N/V)^{5/3}$. At the core of low-T Joule process is the effective (Pauli-principle) repulsion of particles at low-T that leads to the Fermi pressure at $T \rightarrow 0$. In contrast, for the Joule-Kelvin process: $C_p \simeq N k_B$ (neglecting the vanishing C_V in comparison) and the result remains classical.

7. Bose gas at low temperature

Find the temperature dependence of chemical potential of the Bose gas at low temperature $T \rightarrow 0$ in 1- and in 2-dimensions. You know from the lectures that chemical potential μ_{Bose} is almost zero at large N , but here we want to specifically find its T-dependence, however small it might be.

Solution: In both cases, we need to use the N -integral in the momentum space:

$$\begin{aligned} \text{1D : } N &= \frac{2L}{2\pi\hbar} \int_0^\infty \frac{dp}{\exp[(p^2/2m - \mu)/k_B T] - 1} \approx \frac{2L}{2\pi\hbar} \int_0^\infty \frac{k_B T dp}{p^2/2m - \mu} = \frac{L k_B T \sqrt{m}}{\hbar \sqrt{2|\mu|}} \\ \text{2D : } N &= \frac{L^2}{(2\pi\hbar)^2} \int_0^\infty \frac{2\pi p dp}{\exp[(p^2/2m - \mu)/k_B T] - 1} = -\frac{L^2 m k_B T}{2\pi\hbar^2} \ln \left[1 - e^{\mu/k_B T} \right], \end{aligned}$$

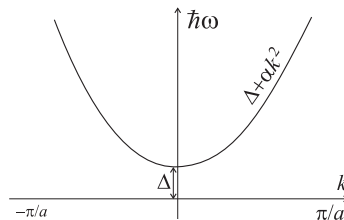
where L is the linear size of the system. The 1D integral is considerably simplified since at low temperatures $p^2/2m \simeq \mu \ll k_B T$ the integrand is a rapidly decaying function so we can Taylor-expand exponentials to the linear order, cancel 1, and find a simple algebraic integral that results (remember, μ is negative). The 2D integral is calculated directly after the p^2 substitution. Inverting both expressions we find μ :

$$\begin{aligned} \text{1D : } \mu &= -\frac{L^2 m^2 (k_B T)^2}{2\hbar^2 N^2}, \quad \text{for } k_B T \ll \hbar^2 N^2 / mL^2 \\ \text{2D : } \mu &= k_B T \ln \left[1 - \exp \left(\frac{-2\pi\hbar^2 N}{L^2 m k_B T} \right) \right]. \end{aligned}$$

You remember that in the lectures we got a simple estimate $\mu \simeq -k_B T / N$ from taking the low-T limit of Bose distribution, but now we did the proper counting (by integration) which is different in different dimensions. So in 1D μ is even smaller, $\sim (k_B T / N)^2$... In 2D it's exponentially small, at $T \rightarrow 0$ the limit is $\mu \simeq -k_B T e^{-2\pi\hbar^2 N / L^2 m k_B T}$. Notice that the 2D version has the high-T limit as well: expanding the exponential under the log, we have $\mu \simeq k_B T \ln (N \lambda^2 / L^2)$. We lost this classical limit in the 1D expression because to do the integral we chose to Taylor expand too early...

8. Spin waves

Spin waves in many ferromagnets show a gap at low energy, due to coupling of the orbital moments to the crystalline lattice. The resulting dispersion relation curves are typically as shown below.



Find and sketch the temperature dependence of the specific heat at low temperatures, assuming that the dispersion relation is isotropic.

Solution: We can treat the elementary excitations as a Bose gas in which N is not conserved (i.e., like black-body radiation, $\mu = 0$), and which has a dispersion relation $\varepsilon_k = \hbar\omega = \Delta + \alpha k^2$, where Δ is the energy gap at the origin. The average energy is given by

$$U = V \int_0^\infty \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \frac{4\pi k^2 dk}{(2\pi)^3} = \frac{V}{2\pi^2} \int_0^\infty \frac{(\Delta + \alpha k^2)}{e^{\beta(\Delta + \alpha k^2)} - 1} k^2 dk. \quad (4)$$

In the low temperature limit ($k_B T \ll \Delta$) we can approximate the integral as

$$\begin{aligned} U &\simeq \frac{V}{2\pi^2} \int_0^\infty e^{-\beta(\Delta + \alpha k^2)} (\Delta + \alpha k^2) k^2 dk = \frac{V}{2\pi^2} e^{-\beta\Delta} \left\{ \Delta \int_0^\infty e^{-\beta\alpha k^2} k^2 dk + \alpha \int_0^\infty e^{-\beta\alpha k^2} k^4 dk \right\} \\ &= \frac{V}{2\pi^2} e^{-\beta\Delta} \left\{ \frac{\Delta}{(\beta\alpha)^{3/2}} \int_0^\infty e^{-y^2} y^2 dy + \frac{\alpha}{(\beta\alpha)^{5/2}} \int_0^\infty e^{-y^2} y^4 dy \right\} \\ &= \frac{V}{8} \left(\frac{k_B T}{\alpha\pi} \right)^{3/2} e^{-\beta\Delta} \left\{ \Delta + \frac{3k_B T}{2} \right\} \end{aligned}$$

The important temperature dependence is contained in the $e^{-\beta\Delta}$ term, and this would certainly dominate experimental results for the heat capacity. This term is typical of a system with a gap between the ground state and first excited states (and you have seen it in the simple 2-level system already).

At temperatures where $k_B T \gg \Delta$, but still small compared with (say) the Curie temperature, the denominator in the integrand can be approximated as

$$\frac{1}{e^{\beta(\Delta + \alpha k^2)} - 1} \simeq \frac{1}{e^{\beta\alpha k^2} (1 + \beta\Delta) - 1} = \frac{1}{(e^{\beta\alpha k^2} - 1) \left(1 + \frac{\beta\Delta e^{\beta\alpha k^2}}{e^{\beta\alpha k^2} - 1} \right)} \simeq \frac{1}{e^{\beta\alpha k^2} - 1} \left(1 - \frac{e^{\beta\alpha k^2} \beta\Delta}{e^{\beta\alpha k^2} - 1} \right).$$

U can be rewritten as

$$\begin{aligned} U &\simeq \frac{V}{2\pi^2} \int_0^\infty \frac{(\Delta + \alpha k^2) k^2}{e^{\beta\alpha k^2} - 1} \left(1 - \frac{e^{\beta\alpha k^2} \beta\Delta}{e^{\beta\alpha k^2} - 1} \right) dk \\ &= \frac{V}{2\pi^2} \int_0^\infty \frac{\alpha k^2 k^2}{e^{\beta\alpha k^2} - 1} dk + \frac{V}{2\pi^2} \int_0^\infty \frac{\Delta k^2}{e^{\beta\alpha k^2} - 1} dk + 0(\beta\Delta) \\ &= \frac{\alpha V}{4\pi^2} \left(\frac{k_B T}{\alpha} \right)^{5/2} \int_0^\infty \frac{x^{3/2}}{e^x - 1} dx + \frac{V\Delta}{2\pi^2} \left(\frac{k_B T}{\alpha} \right)^{3/2} \int_0^\infty \frac{x^{1/2}}{e^x - 1} dx + 0(\beta\Delta). \end{aligned}$$

The first term varies with temperature as $T^{5/2}$; it is the standard ferromagnetic spin wave energy that we would have if there were no gap. The second term, which varies as $T^{3/2}$, comes from the offset of each spin-wave energy by Δ (for example the $k = 0$ spin-wave has no energy if $\Delta = 0$, so it wouldn't contribute to the thermal energy, but when $\Delta > 0$ it does contribute). When $k_B T/\alpha$ is large compared to Δ , the $T^{5/2}$ term dominates. The next largest term has an integrand which vanishes as $\beta\Delta$ everywhere except near $k \rightarrow 0$, where it is finite, but this is a small region of phase space so I'm ignoring it.

To make the sketch, take the derivative of U with respect to T . At low temperature the specific heat rises exponentially (signalling that there is a gap in the energy spectrum), then when $k_B T/\alpha \sim \Delta$ it crosses over to $T^{3/2}$ behaviour characteristic of a quadratic dispersion relation.

9. Black body radiation

A long air-filled coaxial transmission line, of length L and small diameter, is short circuited at each end. Show that, at room temperature and at a cyclic frequency $\nu = 10^9 \text{ Hz}$, the

mean energy of black body radiation between the conductors in a small frequency range $d\omega$ will be approximately

$$k_B T \frac{L}{\pi c} d\omega.$$

If the outer diameter is 1cm and the inner diameter 2mm, explain why it would be reasonable at 10^{12} Hz to replace this expression by one proportional to

$$k_B T \frac{V}{\pi^2 c^3} \omega^2 d\omega$$

where V is the volume between the conductors.

Solution: The question deals with Black-body radiation and, more generally, the relationship between the spectrum of excitations and the dimensionality of the system. The "long air-filled coaxial cable" acts as an EM cavity, at temperature T , with a spectrum of black-body radiation.

At $\nu = 10^9$ Hz, the wavelength, λ , is ≈ 0.3 m, which is greater than the diameter of the cable. Thus the system is essentially one-dimensional. In 1-D, the density of states is

$$g(\omega)d\omega = \frac{L}{\pi c} d\omega \quad (5)$$

and the internal energy, U is

$$U = \int \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \frac{L}{\pi c} d\omega. \quad (6)$$

We can approximate the Bose factor, $1/(e^{\hbar\omega/k_B T} - 1) \approx k_B T/\hbar\omega$, since we are in the high-temperature limit at this frequency and $\hbar\omega/k_B T \ll 1$. Thus, the energy in the frequency range $d\omega$ is $k_B T L d\omega/\pi c$.

At a frequency of $\nu = 10^{12}$ Hz, the wavelength $\lambda = 0.3$ mm, which is significantly smaller than the 4mm radial gap in the cable. It follows that the cable can support radial modes at this frequency alongside the longitudinal ones. Thus the system is approximately three-dimensional. With two polarisations at each \mathbf{k} -vector, the density of states is

$$g(\omega)d\omega = \frac{V\omega^2}{\pi^2 c^3} d\omega \quad (7)$$

and, as we are still in the high-temperature limit, the Bose factor is still $k_B T/\hbar\omega$. The energy in the frequency range $d\omega$ is, therefore, $k_B T V \omega^2 d\omega/\pi^2 c^3$.

10. Chemical potential

Write brief notes describing the chemical potential and examples of its use in thermodynamics and statistical mechanics. In your essay, include a sketch of μ as a function of (i) the number of particles per unit volume at constant temperature, and (ii) the temperature at constant number of particles per unit volume, in both the classical and quantum regimes.

Solution: The chemical potential μ appears as the conjugate variable of N in the thermodynamic potentials U , F , H , G , Φ , etc. From the thermodynamic potentials (e.g., from $dU = T dS - p dV + \mu dN$) we find a number of expressions for μ , such as $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$, but these are difficult to interpret intuitively except in special cases. For example, in general

we don't know how to change the energy at constant entropy, but for the special case of the Fermi gas, the Gibbs entropy expression for the entropy per energy level,

$$S_k = -k_B (n_k \ln n_k + (1 - n_k) \ln(1 - n_k)) \quad (8)$$

shows us that $\left(\frac{\partial S}{\partial N}\right)$ is zero at $n_k = 1 - n_k$, i.e., at $n_k = 1/2$, so if we add a particle at the energy level where $n_k = 1/2$, then we are adding energy at constant entropy, and so this energy level must be located at the chemical potential. But this is only possible below the degeneracy temperature, since at high temperatures the chemical potential of a Fermi gas is negative (i.e., there are no states for which $n_k = 1/2$ for a Fermi gas at high temperature). In the limit as $T \rightarrow 0$, $n_k = 1/2$ is located at the Fermi energy, so the Fermi energy and the chemical potential coincide at low temperature.

A more intuitive way of writing μ is as follows. The changes leading to equilibrium must be allowed by the Second Law of thermodynamics. Using $dU = T dS - p dV + \mu dN$ we get $\mu = -T \left(\frac{\partial S}{\partial N}\right)_{U,V}$, that is, the chemical potential is related to the change in entropy of a system when a particle is added at constant energy and volume. To illustrate the appeal of this expression, say we have two systems 1 and 2 in contact so that they can exchange particles, energy and volume.

$$\begin{aligned} dS = dS_1 + dS_2 &= \left(\frac{\partial S_1}{\partial U_1}\right)_{N_1, V_1} dU_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{N_1, U_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{U_1, V_1} dN_1 + \\ &\quad \left(\frac{\partial S_2}{\partial U_2}\right)_{N_2, V_2} dU_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{N_2, U_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{U_2, V_2} dN_2 \\ &= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1. \end{aligned}$$

We have used $dN_1 = -dN_2$, $dV_1 = -dV_2$ and $dU_1 = -dU_2$. The Law of Increase of entropy says that dS must be positive, so the first term tells us that energy flows from hot to cold, and the second term tells us that (for systems at equal temperature) the volume of the high pressure system will increase at the expense of the low pressure system. The last term is the one of interest here. To get it we used the expression for μ in terms of change of entropy with particle number. It tells us that particles flow from high to low chemical potential (for systems at equal temperature), i.e., dN_1 is negative if $\mu_1 > \mu_2$. The chemical potential controls particle flow just as the temperature controls energy flow.

Another useful way of writing the chemical potential for a pure phase is as the Gibbs free energy per particle, $\mu = G/N$. This is useful for describing phase equilibrium, because it can be shown (using the availability or otherwise) that the equilibrium of a system at constant temperature and pressure is determined by minimising the Gibbs free energy, and thus (again) that equilibrium involves equality of the chemical potentials of the phases involved. Among other things, we used this equality of chemical potentials at phase equilibrium to derive the Clausius-Clapeyron equation, from the fact that $d\mu = v dp - s dT$ for each phase as we move along the phase boundary, where v is the volume per molecule, and s is the entropy per molecule, in a given phase. Equating the changes in $d\mu$ produces the equation $dT/dp = \Delta v / \Delta s$, where Δv and Δs are the changes in the specific volume and entropy at the phase boundary. The chemical potential plays a similar role in the equilibrium properties of mixtures, where for example the change in chemical potential due to the addition of a solute to a solvent on one side of a semi-permeable membrane produces an osmotic pressure. Moreover, it is also central to chemical equilibrium, where the condition $\sum_i \nu_i \mu_i = 0$ can be derived from the minimum Gibbs free energy condition. The ν_i are the number of molecules of species i involved in a unit reaction.

The chemical potential is important in statistical mechanics whenever particles can move between subsystems. In an ideal gas the single-particle energy levels can be treated as

separate thermodynamic systems, which are in mutual equilibrium and have a common chemical potential. The statistical distribution of the energy eigenstates is then described by the Gibbs distribution: the probability of finding n particles in state i is

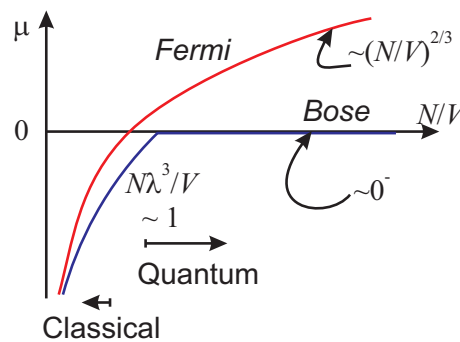
$$P(n_i) = \frac{(e^{-(\varepsilon_i - \mu)/k_B T})^n}{\Xi}, \quad (9)$$

where $\Xi = \sum_n (e^{-(\varepsilon_i - \mu)/k_B T})^n$ is the partition function for the state. The chemical potential therefore plays a central role in the occupation number distribution function. It can be set in two ways, either by equilibrium of the gas with a reservoir of particles which sets the chemical potential (this is the case for example in question 2, where the chemical potential of the two-dimensional gas adsorbed on the surface is set by the chemical potential of the three-dimensional gas, and it is also the case for a photon gas, where the absorption and emission of photons by the cavity walls sets the chemical potential to zero) or it may be set by the requirement that the total number of particles in the gas is N (for closed systems). The latter situation is encountered in standard treatments of Fermi and Bose gases, and of classical gases.

It should be noted that as well as containing terms that are related to the entropy, the chemical potential also contains terms that look like genuine potential energies, and in general particle equilibrium involves both kinds of terms. So for a classical ideal gas the chemical potential is

$$\mu = k_B T \left(\ln \left(\frac{N \lambda^3}{\sigma V} \right) - \ln Z_{\text{int}} \right) + \phi. \quad (10)$$

The first two terms, which come from the translational degrees of freedom of a classical gas and the internal degrees of freedom of the molecules, respectively, have to do with entropy, whereas the latter term is a potential energy per molecule, ϕ , which could for example be an electric potential if the molecules are charged, or a gravitational potential. General equilibrium involves particles flowing from high to low chemical potential. If the potential term is due to gravity, then this term tends to ‘want’ all the molecules to collect at the bottom of the system. However the entropic terms ‘want’ the molecules to spread out as much as possible. The final equilibrium represents a compromise between these two tendencies.



The sketch of μ plotted against N/V has the classical regime at small $(N \lambda^3 / V) \ll 1$ where $\mu = k_B T \ln (N \lambda^3 / \sigma V)$, hence for low values of N/V , μ is negative and diverges as $(N/V) \rightarrow 0$. When $N \lambda^3 / V \sim 1$, quantum effects become important. There is, of course, a difficult crossover region – and then in the deep quantum regime at $N \lambda^3 / V \gg 1$ we have: the Bose-Einstein condensation in Bose-particles case, which results in $\mu \simeq 0^-$; it stays there as the density increases further. In the Fermi case we get a degenerate Fermi gas, for which $\mu \approx \varepsilon_F$, the Fermi energy, which is positive and grows with density as $(N/V)^{2/3}$ in 3D.

