Statistical Mechanics: Set 1

1. Consider a lattice of N atoms at temperature T. In the absence of a magnetic field, each atom has a singlet ground state and an excited doublet that lies energy Δ above the ground state. An externally applied magnetic field splits the doublet by $2\mu H$, while leaving the mean energy of the doublet Δ above the ground state. The lower state of the doublet has the spin parallel to H.

Find the crystal's partition function. Hence calculate the magnetization as a function of H. Show that for $\mu H \ll k_{\rm B}T$ and $\beta = 1/(k_{\rm B}T)$, the susceptibility is $\chi = 2N\mu^2\beta{\rm e}^{-\beta\Delta}/(1 + 2{\rm e}^{-\beta\Delta})$.

2. The partition function of a rigid rotator is

$$Z = \sum_{j=0}^{\infty}(2j+1){\rm e}^{-\alpha\beta j(j+1)}.$$

Give an expression for α in terms of the rotator's moment of inertia I. Derive the heat capacity $C_{\rm rot}$ of a collection of N such rotators when (i) $\alpha\beta \ll 1$ and (ii) $\alpha\beta \gg 1$.

Given that the internuclear separation in HCl is $0.13\,$nm, sketch the form of $C_{\rm rot}$ as a function of T for N molecules of HCl.

What other contributions to the heat capacity are expected?

3. Two single-particle states are available, $|a\rangle$ and $|b\rangle$. List the two-particle states that are then available given that these states have to be either (i) symmetric, or (ii) antisymmetric, under exchange of the particles. Show that in either case the two-particle states are uniquely specified by giving two integers n_a and n_b that satisfy $n_a + n_b = 2$, where in case (ii) we have additionally n_a, $n_b \le 1$.

Rotons are spin-zero excitations in liquid ^{4}He, which may be created or destroyed singly. They have energy $\epsilon(p) = \Delta + (p - p_0)^2/2m$, where p is the roton momentum and Δ, p_0 and m are constants. Give, in the form of integrals over p, (i) the number N of rotons present in a volume V in thermal equilibrium at temperature T, and (ii) the corresponding free energy $\Omega \equiv -k_{\rm B}T\ln\mathcal{Z}$.

For temperatures very much less than both $\Delta/k_{\rm B}$ and $p_0^2/(2mk_{\rm B})$, show that

$$N = \frac{2(mk_{\rm B}T)^{1/2}}{(2\pi\hbar^2)^{3/2}}p_0^2V{\rm e}^{-\beta\Delta}$$

and obtain corresponding results for Ω and for the pressure P of the roton gas. Deduce, and comment on the equation of state of the gas in this low-temperature regime.

4. Consider a two-dimensional ideal bosonic gas at temperature T. Give, in the form of an integral, an expression for the number n of bosons present per unit area. Show that Bose-Einstein condensation does *not* take place for this two-dimensional gas. Show further that in the classical limit

$${\rm e}^{\beta\mu} = \frac{2\pi\hbar^2 n}{mk_{\rm B}T},$$

where m and μ are respectively the mass and the chemical potential of the particles and $\beta = 1/(k_{\rm B}T)$ as usual.

5. Einstein modelled a solid by treating each molecule as an independent three-dimensional harmonic oscillator of natural frequency ω. Write down the partition function for this model of N molecules.

In an improved model ω depends on the volume V and there is an additional term $(V - V_0)^2/(2KV_0^2)$, with V_0 a constant, in the free energy to account for the potential energy associated with the compressibility K of the solid. Given that

$$\frac{\mathrm{d}\ln\omega}{\mathrm{d}\ln V} = -\gamma \quad \text{a constant,}$$

show that when the solid is in equlibrium at zero pressure, the dilation $(V - V_0)/V_0$ (small) is proportional to the mean thermal energy of the Einstein model. Evaluate the constant of proportionality. What is the relationship between the dilation and pressure for small applied pressure?

6. Calculate the grand-canonical partition function $\mathcal{Z}$ for an ideal gas in the non-degenerate limit.

Consider the equilibrium between this gas and the 'gas' formed by molecules adsorbed on a surface. Suppose that the adsorbed molecules are free to move over the surface, and that the energy of such a molecule is

$$\frac{p^2}{2m} - \epsilon_0 + \tfrac{1}{2}m\omega^2 z^2,$$

where m is its mass, p its momentum, z is its distance from the surface and ϵ_0 and ω are constants. Calculate $\mathcal{Z}$ for this gas in the non-degenerate limit. Show that when the pressure of the three-dimensional gas is P, the mean number of adsorbed molecules per unit area is

$$n = P\left(\frac{2\pi\beta}{m\omega^2}\right)^{1/2} \mathrm{e}^{\beta\epsilon_0}, \quad \text{where} \quad \beta = \frac{1}{k_\mathrm{B}T}.$$

7. A Schottky defect is a vacancy in a crystal lattice that is associated with a surplus atom stuck on the crystal's surface. Assume that the density of these defects is low enough that we can neglect interactions between vacancies and between surplus atoms, and consider only the entropy S associated with the vacancies in a crystal with $N \gg 1$ sites. Use the microcanonical distribution to show that

$$S(n) = k_\mathrm{B}[N\ln N - n\ln n - (N-n)\ln(N-n)]$$

where the number n of defects is related to the energy ϵ per defect by

$$n = \frac{N}{\mathrm{e}^{\beta\epsilon} + 1}.$$

Obtain n independently from the canonical distribution.

Show that the contribution of the defects to the specific heat peaks at some temperature T_c, and estimate T_c.