TSP-2021/22 — Thermal and Statistical Physics (Part II)

Problem sheet 2: Equilibrium thermodynamics, basic statistical physics

1. **Multiphase mixtures**
   A substance A can exist as solid, liquid or gas. Its chemical potential μ in each of these phases depends on pressure p and temperature T. By considering the number of variables and the number of equations in the equilibrium conditions

   (i) $\mu_g(p,T) = \mu_\ell(p,T)$ for vapour-liquid coexistence, and
   (ii) $\mu_g(p,T) = \mu_\ell(p,T) = \mu_s(p,T)$ for vapour-liquid-solid coexistence

   show that in a $p-T$ phase diagram, vapour-liquid coexistence occurs along a line, whereas three-phase coexistence happens at a single point.

   We add a second substance B. Now, the chemical potentials also depend on the concentration of each component (A,B) within each phase s,ℓ,g. Three-phase coexistence of both substances requires

$$\begin{aligned}\mu_g^A(p,T,c_g^A) &= \mu_\ell^A(p,T,c_\ell^A) = \mu_g^A(p,T,c_s^A)\\ \mu_g^B(p,T,c_g^B) &= \mu_\ell^B(p,T,c_\ell^B) = \mu_g^B(p,T,c_s^B)\end{aligned}$$

   Note that $c_g^A + c_g^B = 1$ etc. By counting variables and constraints, show that three-phase coexistence for the mixture occurs along a line in the $p-T$ phase diagram.

   Generalise this argument to the equilibrium of P phases in a mixture of C components, and use it to determine the number of free thermodynamic variables (or thermodynamic degrees of freedom) that can be adjusted independently while preserving the coexistence of all the phases in all the components.

2. **Partition Function**
   The partition function of a system is

$$Z = \exp\left[aT^3V\right],$$

   where a is a positive constant. Obtain expressions for the Helmholtz free energy, the equation of state, the internal energy, the heat capacity at constant volume, and the chemical potential.

   Write the pressure as a function of the internal energy per unit volume. Can you identify the physical system that corresponds to such a partition function?

3. **Vacancies**
   A crystalline solid contains N identical atoms on N lattice sites, and N interstitial sites to which atoms may be transferred at the energy cost ε_c. If n atoms are on interstitial sites, show that the configurational entropy is $2k_B\ln(N!/n!\,(N-n)!)$.

   Assuming n/N is small, and that vacancies are very rare, show by minimising the total free energy that the equilibrium proportion of atoms on interstitial sites n/N is

$$\left\langle\frac{n}{N}\right\rangle = \frac{1}{1+\exp(\varepsilon_c/2k_BT)}.$$

4. **Zipper**
A zipper has N links; each link has a state in which it is closed with energy 0 and open with energy ϵ. We require, however, that the zipper can only unzip from the left end, and that the link number s can only open if all links to the left $(1, 2, \ldots, s-1)$ are already open.
(a) Show that the partition function is

$$Z = \frac{1 - \exp\left(-(N+1)\epsilon/k_B T\right)}{1 - \exp\left(-\epsilon/k_B T\right)}.$$

(b) Find the average number of open links in the low-temperature limit. The model is a very simplified model of the unwinding of two-stranded DNA molecules.

5. **Some partition functions**
Calculate the classical partition functions, and discuss the high- and low-temperature limits of:
(a) a one-dimensional simple harmonic oscillator, for which

$$E(p, x) = \frac{p^2}{2m} + \frac{1}{2}kx^2 \ ;$$

(b) a particle moving in three dimensions in a uniform gravitational field, for which

$$E(p, z) = \frac{p^2}{2m} + mgz \ .$$

(Note that a uniform gravitational field must necessarily be limited to a finite range in space)

6. **Relativistic gas**
Consider an ideal classical gas of volume V and temperature T, consisting of N indistinguishable particles in the extreme relativistic limit where the energy ϵ and momentum p of a particle are related by $\epsilon = cp$, where c is the speed of light.
(a) Calculate the partition function of the system Z, the equation of state, the entropy S, internal energy U, and the heat capacity C_V.
(b) Suppose that, in addition to its translational motion, each of the particles can exist in one of two states of energy Δ and $-\Delta$. Calculate Z, the equation of state, S, U, and C_V.

7. **Adsorption**
Helium atoms of mass m may be adsorbed from the vapour phase at pressure p onto a solid surface where they can move freely without interaction, behaving as a two-dimensional perfect gas. If the adsorption energy is Δ, then by treating the vapour as a particle reservoir for the helium atoms on the solid surface, and treating both sets of atoms as ideal classical gases, show that the number density per unit area of helium atoms on the surface is

$$n_{\text{ads}} = \left(\frac{p}{k_B T}\right)\left(\frac{2\pi\hbar^2}{mk_B T}\right)^{1/2} \exp\left(\frac{\Delta}{k_B T}\right).$$