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

Problem sheet I: questions 1-12

1. **Van der Waals gas**
Show that, for a van der Waals gas, the specific heat at constant volume, C_V, obeys

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0.$$

2. **Entropy of the monatomic gas**
The entropy of a monatomic ideal gas is given by the Sackur-Tetrode equation which can be written in the form:

$$S(U,V,N) = Nk_B \ln\left\{\alpha \frac{V}{N}\left(\frac{U}{N}\right)^{3/2}\right\},$$

where α is a constant to be derived later in the course.

Invert this expression to get $U(S,V,N)$. From this, obtain the equation of state expressing p as a function of V, N and T.

3. **Analytic thermodynamics**
Use a Maxwell relation and the chain rule to show that for any substance the rate of change of T with p in a reversible adiabatic compression is given by

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{T}{C_p}\right)\left(\frac{\partial V}{\partial T}\right)_p.$$

Find an equivalent expression for the adiabatic rate of change of T with V, and check that both results are valid for an ideal monatomic gas.

4. **Brief Notes**
Write brief notes on thermodynamic equilibrium in closed and open systems.

5. **Bubble**
Under what conditions is the Helmholtz free energy F a minimum for a system in equilibrium? The work corresponding to an increase in the surface area of a liquid is $dW = \Gamma\, dA$, where Γ is the surface tension, and A is the area of the surface.

Consider a bubble of air in a large container of liquid in equilibrium. Write the total Helmholtz free energy of the system as the sum of contributions from the air in the bubble, F_a, the surface of the bubble, F_s, and the surrounding liquid, F_l. Show that the pressure of the air inside the bubble is equal to $p_l + 2\Gamma/r$, where p_l is the pressure of the liquid.

6. **Superconductor**
The heat capacities of the superconducting and normal phases of a metal at low temperatures are given approximately by

$$\begin{aligned} C_s(T) &= V\alpha T^3 && \text{superconducting phase} \\ C_n(T) &= V\beta T^3 + V\gamma T && \text{normal phase,} \end{aligned}$$

where V is the volume and α, β, and γ are constants. Above a temperature T_c, the normal phase is stable. At low temperatures the superconducting phase is stable, but it can be suppressed in high magnetic fields, which enabled the experimental determination of $C_n(T)$ given above.

The latent heat for the transition is zero. What does this imply for the entropy of the normal and of the superconducting phase at T_c? Find an expression for T_c.

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

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

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, the pressure, and the chemical potential.

Can you identify the physical system that corresponds to such a partition function?

8. **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 $2k_B \ln(N!/n!\,(N-n)!)$.

Show that the equilibrium proportion of atoms on interstitial sites n/N is

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

9. **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. Find the partition function and the average number of open links in the low-T limit.

10. **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

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

11. **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.

12. **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

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