Statistical Physics
Exercise Sheet 8

Exercise 8.1 The Ideal Paramagnetic Gas and the Law of Mass Action

The goal of this exercise is to understand the statistical mechanics of a mixture of ideal gases undergoing chemical reactions. An application is an ideal gas where paramagnetic atoms may combine to form molecules whose magnetic moment vanishes.

(a) Consider r different substances $A_1, \ldots, A_r$ (e.g. $A_1 = \mathrm{H}_2$, $A_2 = \mathrm{O}_2$, and $A_3 = \mathrm{H_2O}$) that undergo s chemical reactions

$$\nu_1^\alpha A_1 + \cdots + \nu_r^\alpha A_r \;=\; 0\,,$$

where $\alpha = 1, \ldots, s$ and $\{\nu_i^\alpha\}$ are the *stoichiometric coefficients* of the reaction α (in the above example we have $s = 1$ and $\nu_1 = 2$, $\nu_2 = 1$, $\nu_3 = -1$).

Let N_i be the number of particles of the substance A_i. Now if the system is materially closed the set of possible variations in the number of particles is given by

$$dN_i = \sum_{\alpha=1}^{s} \nu_i^\alpha \, d\lambda^\alpha\,,$$

with independent variations $d\lambda^1, \ldots, d\lambda^s$. Show that, under constant temperature and pressure, the condition for thermodynamic equilibrium reads

$$\sum_{i=1}^{r} \nu_i^\alpha \mu_i \;=\; 0\,,$$

for each $\alpha = 1, \ldots, s$.

(b) Let the substance A_i be an ideal gas composed of point particles of mass m_i and of binding energy E_i. The Hamiltonian for the particles of type A_i then reads

$$H_i \;=\; \sum_{j=1}^{N_i} \left(\frac{\vec{p}_j^{\,2}}{2m_i} + E_i \right).$$

Compute the grand canonical partition function $\mathcal{Z}$ (fixed temperature, volume, and chemical potentials) of the system and show the *law of mass action*: At equilibrium one has

$$\prod_{i=1}^{r} \langle N_i \rangle^{\nu_i^\alpha} \;=\; f^\alpha(T, V, E_1, \ldots, E_r) \;=\; \prod_{i=1}^{r} \left(V a_i e^{-\beta E_i} \right)^{\nu_i^\alpha}\,,$$

for each $\alpha = 1, \ldots, s$. Here $a_i = (2\pi m_i k_B T)^{3/2}$.

(b) Consider now an ideal paramagnetic gas under the influence of an external magnetic field H (see also Section 3.5.4 in the lecture notes). The particles A_+ (resp. A_-) of mass m have a magnetic moment M parallel (resp. antiparallel) to the field. Furthermore, an A_+ and an A_- may combine to form a single molecule whose magnetic moment vanishes. The energy released in this reaction is E_b. The second possible "reaction" is a flip $A_\pm \mapsto A_\mp$. Use the above results to compute the relative magnetization per particle

$$\sigma \;=\; \frac{\langle N_+ \rangle - \langle N_- \rangle}{\langle N_+ + N_- + N_0 \rangle}\,.$$

Discuss the high and low temperature limits. How do the laws of mass action read?

Exercise 8.2 A Semiconductor at Low Temperature

Consider a simple model of a direct band semiconductor, where the band structure of the valence band is given by

$$\epsilon_v(\vec{k}) = -\frac{\hbar^2\vec{k}^2}{2m_v},$$

and of the conduction band by

$$\epsilon_c(\vec{k}) = E_g + \frac{\hbar^2\vec{k}^2}{2m_c},$$

where m_v and m_c are effective masses (band curvatures).

(a) Show that the number of electrons N satisfies

$$N = V\int_{\mathrm{BZ}} 2\frac{d^3k}{(2\pi)^3} = V\int_{\mathrm{BZ}} 2\frac{d^3k}{(2\pi)^3} f(\epsilon_c(\vec{k})) + V\int_{\mathrm{BZ}} 2\frac{d^3k}{(2\pi)^3} f(\epsilon_v(\vec{k})),$$

where f is the Fermi-Dirac distribution at temperature T and chemical potential μ, and BZ is the Briouillin zone of the crystal lattice. Hint: consider the limit $T \to 0$.

(b) In order to simplify calculations, we work in the low temperature regime $\mu \gg k_BT$ and $E_g - \mu \gg k_BT$. Use (a) to derive an expression for μ.

(c) Compute the intermal energy as well as the specific heat C_V. Assume for this purpose that that the lattice spacing is much smaller than the thermal wavelength of the band electrons. Interpret this result.