Thermodynamics

1 The rubber-band

Let us consider an elastic band with a fixed cross section as a thermodynamic system. The thermodynamic variables that characterize it are entropy S, length L and the mass (or number of moles) n. The expression of the differential of energy, dU is given by

$$dU = TdS + fdL + \mu dn, \tag{1}$$

where f is the tension acting on the band, and μ the chemical potential.

▷ **Q. 1-1** Derive the analog of the Gibbs-Duheim relation. One can observe experimentally that the tension f, when the length and the mass are constant, increases proportionnaly to temperature. This suggests that the equation of state is

$$U = cnT, \tag{2}$$

where c is a constant. Hookes's law on the other hand implies

$$f = \phi \frac{L - L_0}{n}, \tag{3}$$

where $L_0 = n\ell_0$ is the length at rest.

▷ **Q. 1-2** Show that ϕ is proportional to temperature.

▷ **Q. 1-3** Derive the expression of the entropy differential as a function of U, L and n.

▷ **Q. 1-4** Integrate this relation to obtain the entropy S in these variables.

▷ **Q. 1-5** Show that the rubber band contracts when being heated adiabatically. Is this common behavior for solids, explain ?

▷ **Q. 1-6** How does the length of the band change when being heated at constant tension ? Discuss also streching at constant temperature, and define work and heat for such a transformation.

2 Helmholz and Gibbs free energies for a simple magnetic system

The simplest magnetic system comprises N non-interacting spins $s_i = \pm 1$ which are placed in a magnetic field B. We will define Helmholz and Gibbs free energies, and show that they provide equivalent descriptions of the thermodynamics of the system in the thermodynamic limit, and we will in addition introduce the notion of large deviation to characterize rare fluctuations of the magnetization for this system. The total magnetization is denoted $M = \sum_i s_i$, and the magnetization per spin is $m = M/N$.

▷ **Q. 2-1** What is the partition function of this system and the Helmholz free energy $F_N(B)$? Verify that the average magnetization can be obtained as a derivative of $F_N(B)$. In the following, we shall mainly use the Helmholz free energy per spin defined as $f(B) = \lim_{N\to\infty} \frac{F_N(B)}{N}$.

▷ **Q. 2-2** Let us introduce the Legendre transform of $f(B)$, the Gibbs free energy per spin, such that $g(m) = f(B) + mB$ where $B = B(m)$ defined by the condition $m = -\partial f(B)/\partial B$. Calculate $g(m)$ and verify that the same equation of state can be obtained from $g(m)$ as from $f(B)$.

▷ **Q. 2-3** Calculate the entropy function $S(m)$ from the number of microscopic configurations compatible with the magnetization per spin m. Relate $S(m)$ to $g(m)$.

▷ **Q. 2-4** Evaluate from the previous question, the partition function as an integral over m using the saddle point approximation. Show that this compatible with the relation between Helmholz and Gibbs free energies obtained above in the thermodynamic limit when $N \to \infty$.

▷ **Q. 2-5** Let us define a probability distributions of the magnetization $P(M)$ to describe the fluctuations of such quantity, and let us assume that this probability behaves as

$$P(M) \simeq e^{-N\phi(m)}, \quad \text{for } N \to \infty, \tag{4}$$

where $\phi(m)$ represents the large deviation function of the magnetization. Evaluate this function in terms of Helmholz and Gibbs free energies. Under what conditions are the fluctuations described by this function gaussian ?