The Canonical Ensemble

1 Two-level systems with one degenerate level

Consider a set of N discernible particles, each capable of occupying an energy state $-\epsilon$ and q states grouped in energy around the value $+\epsilon$. Assume $q > 1$. In the limit of high temperatures:

- ☐ the total energy of the system is zero.
- ☐ the total energy of the system is positive and independent of q.
- ☐ the total energy of the system is positive and increases with q.

We calculate the canonical partition function Z_c:

$$Z_c = \sum_m e^{-\frac{E_m}{k_B T}} = e^{\frac{\epsilon}{k_B T}} + q e^{-\frac{\epsilon}{k_B T}}$$

So, the total energy of the system is

$$\begin{aligned} U &= \sum_m p_m E_m \qquad (1) \\ &= \sum_m \frac{e^{-\frac{E_m}{k_B T}}}{Z_c} E_m \qquad (2) \\ &= \epsilon \left(\frac{-e^{\frac{\epsilon}{k_B T}} + q e^{-\frac{\epsilon}{k_B T}}}{e^{\frac{\epsilon}{k_B T}} + q e^{-\frac{\epsilon}{k_B T}}} \right) \qquad (3) \\ &= \epsilon \left(1 - \frac{2}{1 + q e^{-2\frac{\epsilon}{k_B T}}} \right) \qquad (4) \end{aligned}$$

So in the limit of high temperatures, we have

$$\lim_{T \to +\infty} U = \epsilon \left(1 - \frac{2}{1+q} \right)$$

where we notice that U is positive $\forall q > 1$ and is an increasing function of q.

2 Polarization of nuclear spins

Consider a system of N independent and discernible protons. The magnetic moment associated with the proton spin is much smaller than that of the electron: it is given by

$$\mu_P = 2.79 \left(\frac{m_e}{M_p} \right) \mu_B,$$

where m_e is the mass of the electron, M_P is the mass of the proton, and μ_B is the Bohr magneton.

Let's set the temperature to $0.01K$. Calculate the magnetic field that must be applied to obtain a magnetization of about $\frac{3}{4}$ of the maximum possible magnetization.

Firstly, we notice that the maximum possible magnetization is

$$M_{\max} = N\mu_P$$

We know that the energy E_m of the system in a certain microstate of magnetization M_m is given by $E_m = -M_m B$. So, let's calculate the canonical partition function Z_c:

$$\begin{aligned} Z_c &= \sum_m e^{-\frac{E_m}{k_B T}} && (5) \\ &= \sum_m e^{\frac{M_m B}{k_B T}} && (6) \end{aligned}$$

We know that the total magnetization (per unit volume) is given by

$$\begin{aligned} \langle M \rangle &= k_B T \frac{\partial}{\partial B} \ln(Z_c) && (7) \\ &= \frac{k_B T}{Z_c} \frac{\partial}{\partial B} Z_c && (8) \\ &= \frac{k_B T}{Z_c} \left(\sum_m \frac{\partial}{\partial B} e^{\frac{M_m B}{k_B T}} \right) && (9) \\ &= \frac{1}{Z_c} \sum_m M_m e^{\frac{M_m B}{k_B T}} && (10) \end{aligned}$$

3 Fluctuations in the length of a spring

Take a spring with a rest length L_0 and stiffness K, and hang a mass M from one end. The system is in thermal equilibrium at temperature T, and we assume $L_0 \gg \sqrt{\frac{kT}{K}}$.

We study the thermal fluctuations in the length L of the spring, by measuring $\Delta = \langle L^2 \rangle - \langle L \rangle^2$. The quantity Δ:

- ☐ decreases when M increases.
- ☐ increases when M increases.
- ☐ is independent of M.

Let $x(t)$ be the position of mass M, with $x(0) = 0$. It is noted that $L(t) = L_0 + x(t)$. The equation of motion is

$$\ddot{x} = g - \frac{k}{M} x$$

We apply the Laplace transform with zero initial conditions:

$$s^2 X = \frac{g}{s} - \frac{k}{M} X$$

hence,

$$X(s) = \frac{g}{s\left(s^2 + \frac{k}{M}\right)} \implies x(t) = \frac{gM}{k}\left(1 - \cos\left(\sqrt{\frac{k}{M}} t\right)\right)$$

We conclude that

$$\begin{cases} \langle x \rangle &= \frac{gM}{k} \implies \langle L \rangle = L_0 + \frac{gM}{k} \implies \langle L \rangle^2 = L_0^2 + 2\frac{gM}{k} L_0 + \frac{g^2 M^2}{k^2} \\ \langle x^2 \rangle &= \frac{5g^2 M^2}{4k^2} \implies \langle L^2 \rangle = L_0^2 + 2L_0 \langle x \rangle + \langle x^2 \rangle = L_0^2 + 2\frac{gM}{k} L_0 + \frac{5g^2 M^2}{4k^2} \end{cases} \tag{11}$$

Therefore, $\Delta = \frac{g^2 M^2}{4k^2}$ increases as M increases.