Review Problems

1. The equation of state of one mole of a van der Waals gas is

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT,$$

where T is the temperature, P the pressure, v the molar volume, R the universal gas constant, and a and b two positive constants.

(i) Find the expression in terms of T and v of the calorimetric coefficient

$$\ell = T\left(\frac{\partial S}{\partial v}\right)_T,$$

where S is the entropy of the gas.

(ii) During an isothermal quasistatic expansion the molar volume goes from v_i to $v_f > v_i$. Give the expressions of the transfers of heat ΔQ and work ΔW in terms of T, v_i and v_f.

(iii) During the quasistatic isothermal expansion, what is the value of the total energy transfer ΔU? What is the sign of ΔU, and what does it mean?

2. You have two identical boxes of cookies. Each contains initially n cookies. Each time you want to eat a cookie, you select a box at random and pick a cookie from that box, without looking at the number of remaining cookies.

(i) When, for the first time, you discover that the selected box is empty, what is the probability $p(n, r)$ that the other box contains exactly r cookies?

(ii) Show that the expression found for $p(n, r)$ implies that

$$\sum_{r=0}^{n} \binom{2n-r}{n} \frac{1}{2^{2n-r}} = 1.$$

You are **not asked** to prove directly this formula.

3. A system consists of N noninteracting three-dimensional identical electric dipoles $\mathbf{p}_i$ $(i = 1, 2, \dots, N)$ in an external electric field $\mathbf{E}$. The energy of an electric dipole $\mathbf{p}$ in the field $\mathbf{E}$ is $-\mathbf{E} \cdot \mathbf{p}$.

(i) Assuming that the electric field points in the Oz direction, show that the partition function of the system of electric dipoles can be written

$$Z(\beta, E) = \left(\int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi} \mathrm{e}^{\beta E p \cos\theta} \sin\theta \, d\theta \, d\varphi \right)^N,$$

where $p = \sqrt{p_x^2 + p_y^2 + p_z^2}$, $E = ||\mathbf{E}||$, and $\beta = 1/kT$.

<u>Hint</u>: The Cartesian coordinates of an electric dipole $\mathbf{p}$ *in terms of its spherical coordinates* θ *and* φ *are*

$$\begin{aligned} p_x &= p \sin\theta \sin\varphi \\ p_y &= p \sin\theta \cos\varphi \\ p_z &= p \cos\theta, \end{aligned}$$

where $0 \leq \theta \leq \pi$ *and* $0 \leq \varphi < 2\pi$*.*
(ii) Find the expression of the Gibbs potential $G(\beta, E)$ defined by

$$G(\beta, E) = -\frac{1}{\beta} \log Z(\beta, E).$$

Hint: To calculate an integral of the form

$$\int_0^\pi \mathrm{e}^{a\cos\theta} \sin\theta \, d\theta,$$

where a *is a constant, use the change of variables* $u = \cos\theta$*.*
(iii) Show that the average value $\langle P_z \rangle$ of the projection on the direction of the electric field of the total electric dipole moment

$$\mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i$$

is given by

$$\langle P_z \rangle = Np\left(\frac{1}{\tanh(\beta E p)} - \frac{1}{\beta E p}\right).$$

(iv) Find the expression of the isothermal dielectric susceptibility

$$\chi_T = \left(\frac{\partial \langle P_z \rangle}{\partial E}\right)_T.$$

Verify that it satisfies the conditions imposed by the maximum entropy principle and Planck's formulation of the third principle.