Tarea 3: Ensambles Microcanónico y Canónico

Give Boltzmann's statistical definition of entropy and present its physical meaning briefly but clearly. A two-level system of $N = n_1 + n_2$ particles is distributed among two eigenstates 1 and 2 with eigenenergies E_1 and E_2 respectively. The system is in contact with a heat reservoir at temperature T. If a single quantum emission into the reservoir occurs, population changes $n_2 \to n_2 - 1$ and $n_1 \to n_1 + 1$ take place in the system. For $n_1 \gg 1$ and $n_2 \gg 1$, obtain the expression for the entropy change of

(a) the two level system, and of

(b) the reservoir, and finally

(c) from (a) and (b) derive the Boltzmann relation for the ratio n_1/n_2.

The three lowest energy levels of a certain molecule are $E_1 = 0, E_2 = \varepsilon, E_3 = 10\varepsilon$. Show that at sufficiently low temperatures (how low?) only levels E_1, E_2 are populated. Find the average energy E of the molecule at temperature T. Find the contributions of these levels to the specific heat per mole, C_v, and sketch C_v as a function of T.

2–5. Show that the entropy can be written as

$$S = -k \sum_j P_j \ln P_j$$

where P_j is given by Eq. (2–12).

2–7. Obtain the most probable distribution of N molecules of an ideal gas contained in two equal and connected volumes at the same temperature by minimizing the Helmholtz free energy for the two systems.

2–13. Show that for a particle confined to a cube of length a that

$$p_j = \frac{2}{3}\frac{E_j}{V}$$

By taking the ensemble average of both sides, we have

$$\bar{p} = \frac{2}{3}\frac{\bar{E}}{V}$$

If we use the fact that $\bar{E} = \frac{3}{2}NkT$ (to be proved in Chapter 5), we get the ideal gas equation of state.

2–14. We shall show in Chapter 5 that the partition function of a monatomic ideal gas is

$$Q(N, V, T) = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2} V^N$$

Derive expressions for the pressure and the energy from this partition function. Also show that the ideal gas equation of state is obtained if Q is of the form $f(T)V^N$, where $f(T)$ is any function of temperature.

2–15. In Chapter 11 we shall approximate the partition function of a crystal by

$$Q = \left(\frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}\right)^{3N} e^{U_0/kT}$$

where $h\nu/k \equiv \Theta_E$ is a constant characteristic of the crystal, and U_0 is the sublimation energy of the crystal. Calculate the heat capacity from this simple partition function and show that at high temperatures, one obtains the law of Dulong and Petit, namely, that $C_V \to 3Nk$ as $T \to \infty$.

2–16. In Chapter 13 of this author's textbook *Statistical Thermodynamics*, it is shown that the partition function of an ideal gas of diatomic molecules in an external electric field $\mathscr{E}$ is

$$Q(N, V, T, \mathscr{E}) = \frac{[q(V, T, \mathscr{E})]^N}{N!}$$

where

$$q(V, T, \mathscr{E}) = V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\left(\frac{8\pi^2 IkT}{h^2}\right)\frac{e^{-h\nu/2kT}}{(1-e^{-h\nu/kT})}\left(\frac{kT}{\mu\mathscr{E}}\right)\sinh\left(\frac{\mu\mathscr{E}}{kT}\right)$$

Here I is the moment of inertia of the molecule; ν is its fundamental vibrational frequency; and μ is its dipole moment. Using this partition function along with the thermodynamic relation,

$$dA = -S\,dT - p\,dV - M\,d\mathscr{E}$$

where $M = N\bar{\mu}$, where $\bar{\mu}$ is the average dipole moment of a molecule in the direction of the external field $\mathscr{E}$, show that

$$\bar{\mu} = \mu\left[\coth\left(\frac{\mu\mathscr{E}}{kT}\right) - \frac{kT}{\mu\mathscr{E}}\right]$$

Sketch this result versus $\mathscr{E}$ from $\mathscr{E} = 0$ to $\mathscr{E} = \infty$ and interpret it.

2–17. In Chapter 14 we shall derive an *approximate* partition function for a dense gas, which is of the form

$$Q(N, V, T) = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}(V - Nb)^N e^{aN^2/VkT}$$

where a and b are constants that are given in terms of molecular parameters. Calculate the equation of state from this partition function. What equation of state is this? Calculate the thermodynamic energy and the heat capacity and compare it to Problem 1–30.

Tarea 4: Ensambles Gran Canónico e Isotérmico-isobárico y Fluctuaciones

3–3. For a grand canonical ensemble show that

$$\left(\frac{\partial \bar{E}}{\partial V}\right)_{\gamma,\,\beta} + \beta\left(\frac{\partial \bar{p}}{\partial \beta}\right)_{\gamma,\,V} = -\bar{p}$$

Compare this to the thermodynamic equation (see Problem 1–31)

$$\left(\frac{\partial E}{\partial V}\right)_{\mu/T,\,1/T} + \frac{1}{T}\left(\frac{\partial p}{\partial(1/T)}\right)_{\mu/T,\,V} = -p$$

to suggest that $\beta = \text{const}/T$ for a grand canonical ensemble.

3–4. State and use Euler's theorem to show

$$p = kT\left(\frac{\partial \ln \Xi}{\partial V}\right)_{\mu,\,T} = kT\frac{\ln \Xi}{V}$$

3–6. Derive the principal thermodynamic connection formulas of the grand canonical ensemble starting from

$$pV = kT \ln \Xi$$

and

$$d(pV) - S\,dT + N\,d\mu + p\,dV$$

3–8. In the next chapter we shall see that the grand partition function of an ideal monatomic gas is

$$\Xi = e^{q\lambda}$$

where $q = (2\pi mkT/h^2)^{3/2}V$. Derive the thermodynamic properties of an ideal monatomic gas from Ξ.

3–9. Show that the partition function appropriate to an isothermal-isobaric ensemble is

$$\Delta(N, p, T) = \sum_E \sum_V \Omega(N, V, E)e^{-E/kT}\,e^{-pV/kT}$$

Derive the principal thermodynamic connection formulas for this ensemble.

3–10. In Problem 5–17 we shall show that the isothermal-isobaric partition function of an ideal monatomic gas is

$$\Delta = \left[\frac{(2\pi m)^{3/2}(kT)^{5/2}}{ph^3}\right]^N$$

Derive the thermodynamic properties of an ideal monatomic gas from Δ.

3–17. Show that

$$\overline{(E-\bar{E})^3} = k^2\left\{T^4\left(\frac{\partial C_V}{\partial T}\right) + 2T^3C_V\right\}$$

and that

$$\frac{\overline{(E-\bar{E})^3}}{\bar{E}^3} = 0(N^{-2})$$

for a canonical ensemble.

3–20. Derive an equation for the fluctuation in the volume in an isothermal-isobaric ensemble. In other words, derive an equation for $\overline{V^2} - \bar{V}^2$. Express your answer in terms of the isothermal compressibility, defined by

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{N,T}$$

Show that $\sigma_v/\bar{V}$ is of the order of $N^{-1/2}$.

3–22. Show that the fluctuation in energy in a grand canonical ensemble is

$$\sigma_E^2 = (kT^2C_V) + \left(\frac{\partial \bar{E}}{\partial \bar{N}}\right)_{T,V}\sigma_N^2$$

3–26. Show that

$$\left(\frac{\partial \mu}{\partial N}\right)_{V,T} = -\frac{V^2}{N^2}\left(\frac{\partial p}{\partial V}\right)_{N,T}$$