Exercise set 1

AI

1 Second law: axiomatic statement

An alternative statement of the second law (cf. D. Chandler, *Introduction to Modern Statistical Mechanics*) reads

> There is an extensive function of state $S(E, \mathbf{x})$, which is a monotonically increasing function of E, and if state B is adiabatically accessible from state A, then $S_B \geq S_A$.

Here $\mathbf{x}$ is a vector of extensive variables $(V, N, ...)$.

Starting from this statement, prove that for a process at temperature T, one finds $TdS \geq đQ$.

1.1 Principle of minimum internal energy

Using the above statement of the second law, prove the following corollary

> Among all the states with a specific entropy value, the state of equilibrium is that in which the internal energy is minimal

2 Equivalence of ensembles

Consider a system of N distinguishable particles, each of which can exist in one of two states separated by an energy ϵ. The state of the system can be specified by listing

$$\mathbf{n} = (n_1, n_2, \dots, n_N),$$

with $n_j = 0$ or 1. The energy of a given configurations is thus $E = \sum_{j=1}^{N} n_j \epsilon$.

a) Find the entropy in the microcanonical ensemble (fixed E and N), by exploiting the Boltzmann's expression $S = k_B \ln \Omega(E, N)$, where $\Omega(E, N)$ is the system phase space volume. Discuss the behaviour of S as a function of E. Hint: use the Stirling's formula $\ln M! \simeq M \ln M - M$.

b) Now consider the canonical ensemble (fixed T and N), and calculate the partition function, and the Helmholtz free energy A. By using the definition $A = E - TS$, and replacing E with its ensemble average, calculate the entropy S, and show that the result is the same as that obtained in the microcanonical ensemble.

3 Simple interacting system: Hard-spheres gas in one dimension

N particles of diameter ℓ can move on a line: as long as the distance between two particles is larger than ℓ, they do not interact. They are impenetrable, so the repulsive interaction diverges as soon as their distance is smaller or equal to ℓ.

The total potential energy of the system reads:

$$U(\{r_i\}) = \frac{1}{2} \sum_{i \neq j} \phi(r_i - r_j),$$

where

$$\phi(r) = \begin{cases} +\infty, & \text{if } |r| < \ell \\ 0, & \text{otherwise.} \end{cases}$$

Do the calculations in the constant (N, p, T) ensemble (nr. particles, pressure, temperature), and find the system partition function and the equation of state giving the volume as a function of the other variables $V(p, T)$. Hint: in the (N, p, T) ensemble, the partition function reads

$$\sum_{\text{states}} \mathrm{e}^{-\beta(H+pV)},$$

where H is the system Hamiltonian.

Here " $\sum_{\text{states}}$ " is an informal way to indicate the integral over the relevant variables in phase space.