Statistical Mechanics

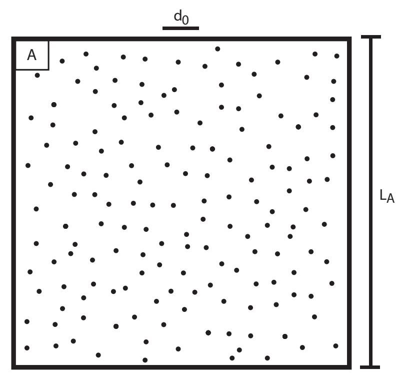
[**40 pts**] 1. A dilute gas of interacting molecules is contained in a large cubic box. The length of the sides of the box, L_{A}, is much larger than the average distance between the molecules, d_0: $L_{\mathrm{A}} \gg d_0$.

This system (denoted by $\mathcal{A}$) is isolated so that the total number of molecules and the total energy is conserved. The density of molecules at equilibrium is approximately uniform and well described by the average density $\rho = N_{\mathrm{A}}/L_{\mathrm{A}}^3$ where N_{A} is the total number of molecules in the box.

We consider two other systems with smaller cubic volumes contained within system $\mathcal{A}$:

- $\mathcal{B}$ has linear dimensions $L_{\mathrm{B}} = 0.5L_{\mathrm{A}} \gg d_0$
- $\mathcal{C}$ has linear dimensions $L_{\mathrm{C}} = d_0$.

The boundaries of $\mathcal{B}$ and $\mathcal{C}$ are open so that the number of molecules and energy within these volumes can fluctuate.



(a) Suppose we can monitor the number of molecules within system $\mathcal{B}$ (N_{B}) and system $\mathcal{C}$ (N_{C}) at any instant in time. Sketch a typical time series for $N_{\mathrm{B}}(t)$ and $N_{\mathrm{C}}(t)$. [**Remember to provide the scale for $N_{\mathrm{B}}(t)$ and $N_{\mathrm{C}}(t)$ in your sketch.**]

(b) Do you expect either system $\mathcal{B}$ or $\mathcal{C}$ to have the same thermodynamics as system $\mathcal{A}$? [**Briefly explain your reasoning.**]

(c) What is the name of the thermodynamic ensemble that most closely describes the system $\mathcal{A}$? Write down a thermodynamic relationship that determines the temperature T of system $\mathcal{A}$. [**Be sure to identify all statistical quantities in your expression.**]

(d) What is the name of the thermodynamic ensemble that most closely describes the system $\mathcal{B}$? Write down a thermodynamic relationship to determine the chemical potential $\mu(N, T, V)$ of system $\mathcal{B}$. [**Be sure to identify all statistical quantities in your expression.**]

(e) The chemical potential is an intensive thermodynamic quantity. What does this mean?

(f) For system $\mathcal{B}$, show that the relative fluctuations

$$\frac{\sqrt{\Delta^2 N}}{N} = \frac{\sqrt{\langle N^2 \rangle - \langle N \rangle^2}}{N} \tag{1}$$

vanish in the thermodynamic limit ($L \to \infty$ and $N \to \infty$ with ρ fixed).

[30 pts] 2. Consider a collection of N distinguishable, non-interacting two-level oscillators with energy levels $\epsilon = 0$ and $\epsilon = \epsilon_0$ at equilibrium with temperature T.
[Note parts (a) and (b) asks for a physical explanation for your answer, but no detailed calculation is required (or expected).]

(a) What is the entropy in the limits $k_{\mathrm{B}}T \ll \epsilon_0$ and $k_{\mathrm{B}}T \gg \epsilon_0$. Justify your answers.

(b) What is the heat capacity, C, in the limits $k_{\mathrm{B}}T \ll \epsilon_0$ and $k_{\mathrm{B}}T \gg \epsilon_0$. Justify your answers. Sketch C vs. $k_{\mathrm{B}}T/\epsilon_0$.

(c) Calculate the heat capacity and verify the limits given in part (b).

[30 pts] 3. Consider an ideal gas in equilibrium with a solid surface that has K adsorption sites which can be empty or occupied by a single molecule. Let the partition function for an occupied adsorption site be denoted by z_{s}.

(a) Using any ensemble you choose, find the equation of state and the chemical potential of the gas, μ_{g}.

(b) If the average number of adsorbed molecules is n, the fraction of occupied sites on the surface is $f = n/K$. Use the Grand Canonical Ensemble to calculate f as a function of the chemical potential of the surface, μ_{s}.

(c) Find the vapor pressure of the gas as function of f.