Homework Assignment 3

1. Classical ideal gas in various ensembles (10 points).

(a) Consider a dilute gas of N non-interacting particles of mass m in a fixed volume V, in equilibrium at a temperature T. The partition function for the *canonical ensemble* at constant T, V and N is

$$Z_N(T, V, N) = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N.$$

Calculate the free energy F and use it to compute the chemical potential of the gas. Write the chemical potential as a function of T and P.

(b) Consider a dilute gas of N non-interacting particles of mass m, in equilibrium at a temperature T and pressure P. Calculate the partition function $\mathcal{Z}$ for the *Gibbs canonical ensemble* at constant T, P and N, and its associated free energy G. Calculate the chemical potential as a function of T and P.

(c) Consider a dilute gas of non-interacting particles of mass m in a volume V, in equilibrium at a temperature T and a chemical potential μ. Calculate the partition function $\mathcal{Q}$ for the *grand canonical ensemble* at constant T, V and μ, and its associated free energy $\mathcal{G}$. Obtain an expression for the pressure as a function of T and μ. Then invert the relation to obtain the expression for μ.

Did you get the same chemical potential for all three choices of ensembles?

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2. Electric dipole in an external field II (10 points). As a follow-up from Pathria 3.35 in HW2, suppose that outside the vessel, the same diatomic gas is maintained at a constant pressure P_{ext}. Assume that external to the vessel the electric field is zero, whereas internal to the vessel the field is uniform with magnitude E. Now suppose that we drill a hole in the vessel to allow for particle exchange with the surroundings until the chemical equilibrium is reached (Fig 1). How will the
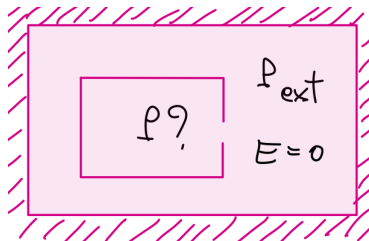

Figure 1:

pressure P in the vessel differ from P_{ext}?

(a) Use the partition function for the gaseous system in the *canonical ensemble*, the same one that

you found in the previous homework,

$$Z(N,V,T) = \frac{1}{N!} \left[\frac{V}{\lambda^3} \frac{8\pi^2 I k_B T}{h^2} \frac{\sinh(\beta \mu E)}{\beta \mu E} \right]^N,$$

to find P as a function of P_{ext}. **Hint**: What is the condition for chemical equilibrium? Which is greater? P or P_{ext}?

(b) Derive the same expression for P as a function of P_{ext} using the *grand canonical ensemble*.

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3. Linear polymer (10 points). A linear molecule consists of N atoms connected to each other in a chain in one dimension. Assume that $N \gg 1$ so that we can approximate $N - 1 \approx N$, for example. There are two possible lengths for each bond, a short length d_s, and a long length, d_l. The energy of a short bond is higher than the energy of a long bond by Δ. The molecule is held under a constant tensile force F (not to be confused with the free energy), and is in equilibrium with the surroundings at a temperature T.

(a) What is the partition function for constant T and F?

(b) Find the length L as a function of T and F. Investigate the behavior L as $T \to 0$, $T \to \infty$, and as $F \to 0$ and $F \to \infty$.