EXERCISE 7B: DIFFUSIVE EQUILIBRIUM AND CHEMICAL POTENTIAL

Objectives:

- Define the **chemical potential**, and chemical or diffusive equilibrium
- Determine the relative probabilities of microstates in the **grand canonical ensemble**
- Calculate and interpret the chemical potential of an ideal gas

References: Kittel & Kroemer, Ch. 5

1. *General conditions for equilibrium.* Consider two systems $\mathcal{A}_1$ and $\mathcal{A}_2$ that are allowed to exchange particles. We would like a way of quantifying which way particles must flow to establish **diffusive** or **chemical equilibrium**, just as their temperatures indicate which way heat must flow to establish thermal equilibrium. To this end, we define the chemical potential μ so that

$$dE = \tau d\sigma - pdV + \mu dN. \tag{1}$$

Let σ denote the entropy of the composite system $\mathcal{A}_1 + \mathcal{A}_2$, with fixed total energy $E = E_1 + E_2$, volume $V = V_1 + V_2$, and number of particles $N = N_1 + N_2$. Based on Eq. 1, derive a set of conditions for systems $\mathcal{A}_1$ and $\mathcal{A}_2$ to be in equilibrium.

a. Derive a condition for **thermal equilibrium** by maximizing σ with respect to exchange of energy between subsystems.

b. What additional conditions must hold for the system to be in…

i. …**mechanical equilibrium**?

ii. ... **chemical equilibrium**

c. Find expressions for the chemical potential μ in terms of ...

i. ... the entropy σ and temperature τ

ii. ... the Helmholtz free energy F

d. *Sign check.* Suppose two systems $\mathcal{A}_1$ and $\mathcal{A}_2$ that initially had different chemical potentials $\mu_2 > \mu_1$ are allowed to equilibrate at constant temperature τ. Which way do the particles tend to flow?

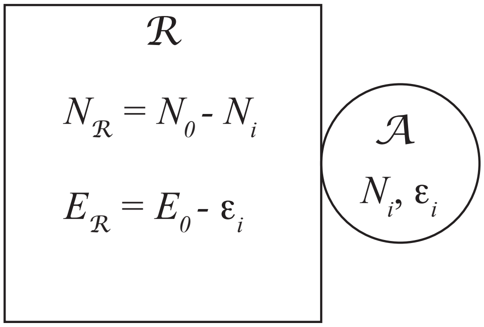

FIG. 1. A system $\mathcal{A}$ in thermal and diffusive contact with a reservoir $\mathcal{R}$. In microstate i, the system contains N_i particles and has energy ε_i.

2. *Grand canonical ensemble.* Consider a system $\mathcal{A}$ in thermal and diffusive contact with a reservoir $\mathcal{R}$ at temperature τ and chemical potential μ, as illustrated in Figure 1.

   a. Determine the equilibrium ratio P_1/P_2 of probabilities for finding the system in microstates 1 and 2, where the i^{th} microstate has N_i particles and energy ε_i.

b. Determine the probability P_i of finding the system in the i^{th} microstate.

c. Propose a definition for the **grand canonical partition function** (or **Gibbs sum**) $\mathfrak{z}$, and reexpress your result for P_i in terms of $\mathfrak{z}$.

d. Find an expression for the mean number of particles $\langle N \rangle$ in the system $\mathcal{A}$ in terms of $\mathfrak{z}$.

3. *Chemical potential of the ideal gas.* Recall that the free energy of a classical monatomic ideal gas is

$$F = N\tau \left[\ln\left(n\lambda_\tau^3\right) - 1\right], \tag{2}$$

where $\lambda_\tau = h/\sqrt{2\pi m\tau}$ and $n \equiv N/V$ is the number density.

a. Calculate the chemical potential of the ideal gas as a function of the number density n.

b. Does the chemical potential increase or decrease with increasing density? Explain.

c. Sketch μ/τ *vs.* $\ln(n)$ for the ideal gas at two different temperatures $\tau_1 < \tau_2$. Indicate within which region of your plot the ideal gas model is valid.

d. How do you interpret the sign of the chemical potential of the ideal gas?

e. What is the chemical potential of an ideal gas of atoms of mass m in a gravitational field? Express your answer in terms of the height z, the gravitational acceleration g, and the temperature τ (assumed to be uniform).

f. Find the equilibrium ratio $n(z_2)/n(z_1)$ of densities at two different heights.

g. What other method could you have used to obtain the result in f.?