

EXERCISE 8A: GASES OF IDENTICAL PARTICLES*Objectives:*

- Derive the **Bose-Einstein** and **Fermi-Dirac** distributions
- Recognize familiar limiting cases (ideal gas, Planck distribution)
- Analyze an ideal gas with internal degrees of freedom

References: Kittel & Kroemer, Ch. 6 (pp. 151-171)*Past results:*

- Grand canonical partition function (Gibbs sum): $\mathcal{Z} = \sum_{\text{asn}} e^{\beta(N\mu - \varepsilon_{s,N})}$
- $\langle N \rangle = \beta^{-1} \partial \ln \mathcal{Z} / \partial \mu$

In our treatment of ideal gases so far, we assumed the classical limit $n\lambda_\tau^3 \ll 1$, where n is the number density and λ_τ is the thermal de Broglie wavelength. Within the framework of the **grand canonical ensemble**, we can analyze the more general case without this constraint. However, it will now matter whether the particles are **fermions** or **bosons**.

1. *Quantum statistics.* Consider a single orbital of energy ε that is coupled to a reservoir of temperature τ and chemical potential μ . (We can consider additional orbitals later. In a non-interacting system, the energy of each orbital will be independent of the occupancy of the others.)
 - a. Suppose that the reservoir contains a single species of **fermions**. Write down the grand canonical partition function for the orbital and calculate the mean particle number $\langle N \rangle_\varepsilon$ occupying the orbital. Also calculate limiting values of $\langle N \rangle_\varepsilon$ for:
 - i. $\varepsilon < \mu$, $|\varepsilon - \mu| \gg \tau$
 - ii. $\varepsilon > \mu$, $|\varepsilon - \mu| \gg \tau$
 - iii. $|\varepsilon - \mu| \ll \tau$

- b. The occupancy from part a. is the **Fermi-Dirac** distribution function. Sketch it as a function of the energy ε for two different temperatures $\tau_1 < \tau_2$ at the same chemical potential μ . In this context, the chemical potential is called the **Fermi level**. Label the Fermi level on your plot.
- c. Now consider **bosons** instead. Write down the grand canonical partition function and calculate the mean number $\langle N \rangle_\varepsilon$ of bosons occupying the orbital.

- d. What constraint must be placed on the chemical potential for the number of bosons occupying the orbital to make physical sense?
- e. The occupancy from part c. is the **Bose-Einstein** distribution function. Where have you previously seen this function in this course (with $\mu = 0$), and what were the physical interpretations of ε and N ?
- f. Sketch the Bose-Einstein distribution function vs. $\varepsilon - \mu$ at fixed temperature τ . Add the Fermi-Dirac distribution function to the same plot. In what limit are the two distributions equivalent? In what regime do they look different? Explain.

- g. Consider now a set of many orbitals (such as the particle-in-a-box eigenstates). Let $f(\varepsilon)$ represent the average number of particles in an orbital of energy ε , and let ε_0 represent the energy of the ground state.
- i. Give a condition on the chemical potential μ for this system to be in the classical regime at temperature τ .
 - ii. In the classical regime, what statement can be made about the occupancies $f(\varepsilon)$?
2. *Revisiting the classical ideal gas.* Apply your results from above to the case where the orbitals are the eigenstates $\varepsilon_{\mathbf{n}}$ of a particle in a three-dimensional box of volume $V = L^3$. Consider a classical gas of N such atoms in the box of volume V .
- a. Express the total atom number N in terms of ...
 - i. ... the occupancies $f_{\mathbf{n}}$ of the individual orbitals.
 - ii. ... the energies $\varepsilon_{\mathbf{n}}$, chemical potential μ , and inverse temperature β .

- b. Based on a., determine the chemical potential as a function of density N/V and the thermal de Broglie wavelength λ_τ .

Hint: you have previously evaluated the following sum:

$$z_1^3 \equiv \sum_{\mathbf{n}} e^{-\beta \varepsilon_{\mathbf{n}}} = \frac{V}{\lambda_\tau^3}. \quad (1)$$

- c. Calculate the Helmholtz free energy $F(N, \tau)$ from the chemical potential. Does it match the result we previously derived for an ideal gas? In what ways is the present derivation different?

3. *Ideal gas with internal degrees of freedom.* Consider a classical gas of identical non-interacting molecules, each of which has internal (vibrational + rotational) energy ε_{int} . The total energy of a single molecule is then $\varepsilon_{\mathbf{n}} + \varepsilon_{\text{int}}$, where $\varepsilon_{\mathbf{n}}$ is the energy of the center-of-mass motion.

a. Since the gas is classical, it should not matter whether the molecules are bosons or fermions. Explain in words why $\mathfrak{z}_{\text{Bose}} \approx \mathfrak{z}_{\text{Fermi}}$ in the classical regime.

b. Write down the grand canonical partition function \mathfrak{z} for a single orbital \mathbf{n} in terms of the chemical potential μ and energies $\varepsilon_{\mathbf{n}}$, ε_{int} .

c. Re-express \mathfrak{z} in terms of the partition function

$$Z_{\text{int}} = \sum_{\text{int}} e^{-\beta \varepsilon_{\text{int}}} \quad (2)$$

associated with the internal degrees of freedom of a single molecule.

- d. Find the occupancy $f_{\mathbf{n}}$ of state \mathbf{n} at temperature β^{-1} in terms of Z_{int} , μ , and $\varepsilon_{\mathbf{n}}$.
- e. Recalling that we are assuming the gas to be in the classical regime, simplify your result from d.
- f. Determine the chemical potential as a function of density N/V and Z_{int} . Express it in terms of the result μ_0 for a monatomic ideal gas.

- g. Find the Helmholtz free energy in terms of the value F_0 for a monatomic ideal gas and an additional contribution F_{int} . Give the value and physical interpretation of F_{int} .

- h. *Starting point for next class:* Which of the following properties of the ideal gas are modified by the internal degrees of freedom, and how? Explain.
- i. The equation of state $p(N, \tau, V)$
 - ii. The entropy σ
 - iii. The heat capacities $C_V = \tau(\partial\sigma/\partial\tau)_V$ and $C_p = \tau(\partial\sigma/\partial\tau)_p$ at constant volume and constant pressure
 - iv. The isothermal and adiabatic compressibilities $\kappa_\tau = -V^{-1}(\partial V/\partial p)_\tau$ and $\kappa_\sigma = -V^{-1}(\partial V/\partial p)_\sigma$