EXERCISE 4B: STATISTICAL DERIVATION OF THE IDEAL GAS LAW

Objectives:

- Derive the **ideal gas law** from first principles (quantum and statistical mechanics)
- Calculate the **energy** and **entropy** of an ideal gas

Reading: Kittel & Kroemer, Ch. 3

Useful past results:

- $dF = -pdV - \sigma d\tau$
- $F = -\tau \ln Z$

1. *Partition function of an ideal gas.* Consider a gas of N non-interacting particles in a cubic box of volume $V = L^3$. Recall that the energy eigenstates of a single particle in a three-dimensional box are given by

$$\varepsilon(n_x, n_y, n_z) = \frac{\pi^2\hbar^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right). \tag{1}$$

   a. Let z_1 denote the partition function of a single particle in a one-dimensional box of length L (which we will calculate below). Find an expression for the partition function of N particles in a box of dimensions $L \times L \times L$ in terms of z_1...

      i. ...assuming that the particles are *distinguishable.*

      ii. ...assuming that the particles are *indistinguishable.*

b. Write out the partition function z_1 for a single particle in a 1D box and simplify it by approximating the sum as an integral.

c. The partition function z_1 can be expressed as $z_1 = L/\lambda_\tau$, where λ_τ is a temperature-dependent length-scale. What is the value of λ_τ? Can you give a physical interpretation for λ_τ?

d. Based on parts a.-c., write down the full partition function for the gas of N indistinguishable, non-interacting particles in terms of L, λ_τ, and N.

2. *Quantum mechanical derivation of the ideal gas law.*

   a. Calculate the Helmholtz free energy F of the ideal gas of $N \gg 1$ particles in a three-dimensional box of volume V.

   b. Calculate the pressure $p(N, T, V)$.

   c. While we are at it, let's also calculate the energy E of the ideal gas from the partition function Z.

3. *Entropy of the ideal gas.*

   a. Express the entropy of a generic system at known particle number N, temperature τ, and volume V as a derivative of the Helmholtz free energy $F(N, \tau, V)$.

   b. Calculate the entropy of a gas of N non-interacting *identical* particles. (*You already wrote down the Helmholtz free energy F in problem 2.*)

   Express your results in terms of N, V, and the **thermal de Broglie wavelength**

$$\lambda_\tau = \frac{h}{\sqrt{2\pi m \tau}}. \tag{2}$$

c. Your result from 3.b. is the Sackur-Tetrode equation for the entropy of a monatomic ideal gas. Subject it to a sanity check: does it violate any laws of thermodynamics? Explain.

d. In what parameter regime must the Sackur-Tetrode equation (3.b.) break down? *Why* does it break down?

e. *In summary:* what conditions must be satisfied for a gas to be considered **ideal**?

f. Estimate the thermal de Broglie wavelength for…

i. …nitrogen gas (28 amu) at room temperature. Compare your result with the typical intermolecular spacing at 1 atmosphere of pressure.

ii. …atomic sodium (23 amu) at a temperature of 100 nK.

iii. …an electron at room temperature. Compare your result with the lattice constant of a typical metal.