EXERCISE 5A: CLASSICAL STATISTICAL MECHANICS

Objectives:

- Apply the classical formulation of the partition function to an ideal gas particle
- Derive the **Maxwell-Boltzmann velocity distribution**
- Derive the **Equipartition Theorem**

Useful past results:

- Partition for a single particle in a 1D box: $z_1 = L/\lambda_\tau$
- Thermal de Broglie wavelength: $\lambda_\tau \equiv h/\sqrt{2\pi m\tau}$
- Gaussian integral $\int_{-\infty}^{\infty} du\, e^{-\alpha u^2} = \sqrt{\pi/\alpha}$.

Boltzmann's formulation of statistical mechanics predates quantum mechanics. How did Boltzmann describe microstates? Let $\mathbf{x}$ and $\mathbf{p}$ denote the position and momentum of a classical particle of mass m and $\mathcal{U}(\mathbf{x})$ its potential energy. Classically, the **partition function** in a D-dimensional system is given by

$$Z = \xi^{-D} \int d^D\mathbf{x} \int d^D\mathbf{p}\, e^{-\beta H(\mathbf{x},\mathbf{p})}, \tag{1}$$

where $H(\mathbf{x},\mathbf{p}) = \mathbf{p}^2/(2m) + \mathcal{U}(\mathbf{x})$ is the particle's total energy, $\beta = 1/\tau$ is the inverse temperature, and ξ is a normalization factor.

1. *A classical gas particle.*

   a. Calculate the partition function for a single particle in D dimensions confined to a box of volume L^D.

b. No classical physical quantities you calculate based on Z will depend on the normalization factor ξ. Nevertheless, determine the value of ξ by comparing the partition function Z calculated in Part a. to our previous quantum mechanical expression. How do you interpret your result?

c. Calculate the following quantities in D dimensions:

   i. The particle's mean energy E

   ii. The particle's rms velocity $v_{\mathrm{rms}} = \sqrt{\langle v_x^2 + v_y^2 + v_z^2 \rangle}$

d. Find the following probability distributions:

   i. …the distribution $P(v)$ for the particle's velocity v in $D = 1$ dimension. Sketch $P(v)$.

   ii. …the distribution $P(\mathbf{v})$ for the particle's velocity $\mathbf{v}$ in $D = 3$ dimensions.

   iii. …the distribution $P(|v|)$ for the particle's speed $|v|$ in $D = 3$ dimensions. Sketch $P(|v|)$.

e. Your result in d.iii. is the **Maxwell-Boltzmann** velocity distribution. Without doing detailed math, sketch analogous distribution functions for the speed of:
   i. A particle in $D = 1$ dimension
   ii. A particle in $D = 2$ dimensions

f. You could have done the entirety of this problem equally well starting from the quantum mechanical description of a particle in a box. Under what circumstances is it valid to use a classical description, in which the microstates are cells in phase space?

g. Under what circumstances might it be *advantageous* to use a classical description instead of a quantum mechanical one?

2. *Equipartition Theorem*
Consider quite generally a classical Hamiltonian of the form $H = \sum_{i=1}^{f} a_i u_i^2$, where u_i represent independent degrees of freedom, e.g., coordinates or their conjugate momenta.

   a. Give at least two examples of physical systems that can be described in the form above.

   b. Calculate the mean energy E for a system described by the generic Hamiltonian above at temperature $\tau = 1/\beta$.

      i. First, show that the partition function is of the form $Z \propto \beta^{\alpha}$. What is the value of the exponent α?

      ii. Calculate the mean energy E from the partition function.

c. Your derivation should show that each of the f degrees of freedom makes the same contribution to the energy. What is the energy per degree of freedom?

3. *Application of Equipartition: Gas of Diatomic Molecules*
   Apply the *equipartition theorem* to determine the mean energy and heat capacity of a dilute gas of N homonuclear diatomic molecules, accounting for translational, vibrational, and rotational degrees of freedom.

   a. Sketch the molecule, label its degrees of freedom, and write down the resulting total energy H. Don't worry about the precise numerical prefactors in H—just give the general form including all terms.

   b. Based on your sketch, what is the average energy $E(N, \tau)$ of the gas in the high-temperature limit?

c. Figure 1 shows the heat capacity C_V of a gas of H_2. Explain this graph as completely as possible. Label the values of the plateaus on the vertical scale.

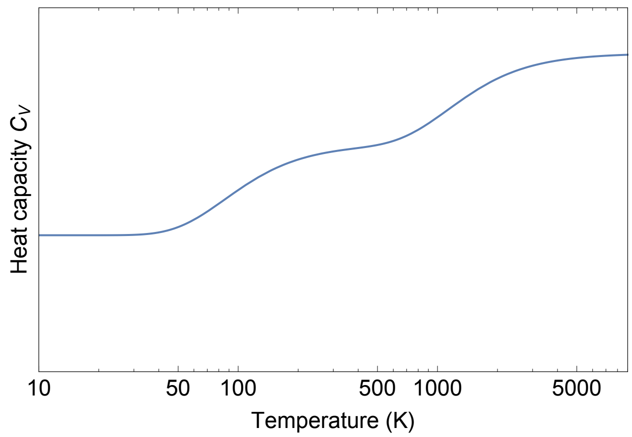

FIG. 1. Heat capacity of H_2 gas as a function of temperature T.