Non-interacting particles

1. **Rotating gas:** Consider a gas of N identical atoms confined to a spherical harmonic trap in three dimensions, i.e. the particles are subject to the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + \frac{K}{2} r_i^2 \right].$$

   (a) Show that the angular momentum of each particle $\vec{L}_i = \vec{r}_i \times \vec{p}_i$ is a conserved quantity, i.e. $\left\{ \vec{L}_i, \mathcal{H} \right\} = 0$. (Note that once interactions between particles are included, individual angular momenta are no longer conserved, while their sum $\vec{L} = \sum_{i=1}^{N} \vec{L}_i$ remains a conserved quantity.)

   (b) Since angular momentum is conserved, a generalized canonical distribution can be defined with probability

$$p[\mu \equiv \{\vec{p}_i, \vec{q}_i\}] = \frac{1}{Z(\beta, \vec{\Omega})} \exp\left(-\beta \mathcal{H}(\mu) - \beta \vec{\Omega} \cdot \vec{L}(\mu) \right).$$

   Compute the classical partition function for this gas of identical particles, assuming $\vec{\Omega} = \Omega \hat{z}$ with $\Omega < \sqrt{K/m}$.

   (c) Find the expectation value of angular momentum $\langle L_z \rangle$ in the above ensemble.

   (d) Write down the probability density of finding a particle at location (x, y, z), and hence obtain the expectation values $\langle x^2 \rangle$, $\langle y^2 \rangle$, and $\langle z^2 \rangle$

2. **Atomic/molecular hydrogen:** A container of volume V at temperature T contains N atoms of hydrogen, some forming hydrogen molecules. The gas is sufficiently dilute that interactions and quantum degeneracies can be ignored.

   (a) The Hamiltonian for N_1 hydrogen atoms is

$$H_a = \sum_{i=1}^{N_1} \frac{p_i^2}{2m}.$$

   Calculate the partition function $Z_a(N_1, T, V)$.

(b) The Hamiltonian for $N_2 = (N - N_1)/2$ hydrogen molecules is

$$H_m = \sum_{i=1}^{N_2} \left[\frac{p_i^2}{4m} + \frac{L_i^2}{2I} - \epsilon \right],$$

where ϵ is the energy gained on forming a molecule, the mass of the molecule is twice the atomic mass, and I is its moment of inertia. It is assumed that the temperature is such that the vibrational levels of the molecule are frozen, while the rotational levels are fully excited and can be treated classically (as in previous problem). Calculate the partition function $Z_m(N_2, T, V)$.

(c) Find the ratio n_m/n_a^2, where $n_a = N_a/V$ and $n_m = N_m/V$ are the densities of atomic and molecular hydrogen in equilibrium.

3. (Problem 7 of MK Ch. 4) **Molecular adsorption:** N diatomic molecules are stuck on a metal surface of square symmetry. Each molecule can either lie flat on the surface in which case it must be aligned to one of two directions, x and y, or it can stand up along the z direction. There is an energy cost of $\epsilon > 0$ associated with a molecule standing up, and zero energy for molecules lying flat along x or y directions.

(a) How many microstates have the smallest value of energy? What is the largest microstate energy?

(b) For *microcanonical* macrostates of energy E, calculate the number of states $\Omega(E, N)$, and the entropy $S(E, N)$.

(c) Calculate the heat capacity $C(T)$ and sketch it.

(d) What is the probability that a specific molecule is standing up?

(e) What is the largest possible value of the internal energy at any positive temperature?

4. (Problem 8 of MK Ch. 4) **Curie susceptibility:** Consider N non-interacting quantized spins in a magnetic field $\vec{B} = B\hat{z}$, and at a temperature T. The work done by the field is given by BM_z, with a magnetization $M_z = \mu \sum_{i=1}^{N} m_i$. For each spin, m_i takes only the $2s + 1$ values $-s, -s+1, ..., s-1, s$.

(a) Calculate the Gibbs partition function $\mathcal{Z}(T, B)$. (Note that the ensemble corresponding to the macrostate (T, B) includes magnetic work.)

(b) Calculate the Gibbs free energy $G(T, B)$, and show that for small B,

$$G(B) = G(0) - \frac{N\mu^2 s(s+1)B^2}{6k_B T} + \mathcal{O}(B^4).$$

(c) Calculate the zero field susceptibility $\chi = \partial M_z/\partial B|_{B=0}$, and show that is satisfies *Curie's law*

$$\chi = c/T.$$

(d) Show that, to leading order in B, $C_B - C_M = cB^2/T^2$ where C_B and C_M are heat capacities at constant B and M respectively.

5. (Problem 9 of MK Ch. 4) [*Optional*] **Langmuir isotherms:** An ideal gas of particles is in contact with the surface of a catalyst.

(a) Show that the chemical potential of the gas particles is related to their temperature and pressure via $\mu = k_B T \left[\ln \left((P/T)^{5/2}\right) + A_0\right]$, where A_0 is a constant.

(b) If there are $\mathcal{N}$ distinct adsorption sites on the surface, and each adsorbed particle gains an energy ϵ upon adsorption, calculate the grand partition function for the two dimensional gas with a chemical potential μ.

(c) In equilibrium, the gas and surface particles are at the same temperature and chemical potential. Show that the fraction of occupied surface sites is then given by $f(T, P) = P/(P + P_0(T))$. Find $P_0(T)$.

(d) In the grand canonical ensemble, the particle number N is a random variable. Calculate its characteristic function $\langle \exp(-ikN)\rangle$ in terms of $\mathcal{Q}(\beta\mu)$, and hence show that

$$\langle N^m \rangle_c = -(k_B T)^{m-1}\frac{\partial^m \mathcal{G}}{\partial \mu^m}|_T,$$

where $\mathcal{G}$ is the grand potential.

(e) Using the characteristic function, show that

$$\langle N^2 \rangle_c = k_B T \frac{\partial \langle N \rangle}{\partial \mu}|_T.$$

(f) Show that fluctuations in the number of adsorbed particles satisfy

$$\frac{\langle N^2 \rangle_c}{\langle N \rangle_c^2} = \frac{1-f}{\mathcal{N}f}$$

6. [*Optional*] **Disordered glass:** The heat capacity of many disordered materials vanishes linearly at low temperatures. A commonly used model such glassy materials materials is a collection of N non-interacting defects in thermal equilibrium at temperature T. Each defect is assumed to have two possible energies ϵ_i and $\epsilon_i + \delta_i$, with different values of ϵ_i and δ_i for each defect.

   (a) Compute the partition function $Z(T)$, the average energy $E(T)$, and the contribution to heat capacity $C(T)$ from these independent defects.

   (b) The number of defects with excitation energies between δ and $\delta + d\delta$ is given by $\rho(\delta)d\delta$, where $\rho(\delta)$ is the density of states of defects as a function of excitation energy. Assuming that $\rho(\delta)$ is uniformly distributed between energies of 0 and Δ, find the defect heat capacity $C(T)$, and comment on its behavior at low and high temperatures.

   (c) A uniform density of states may not be realistic. What feature of $\rho(\delta)$ will ensure $C \propto T$ at low temperatures?