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. $\{\vec{L}_i, \mathcal{H}\} = 0$. (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

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

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. Polar rods: Consider rod shaped molecules with moment of inertia $I$, and a dipole moment $\mu$. The contribution of the rotational degrees of freedom to the Hamiltonian is given by

$$\mathcal{H}_{\text{rot.}} = \frac{1}{2I} \left( p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) - \mu E \cos \theta \ ,$$

where $E$ is an external electric field. ($\phi \in [0, 2\pi]$, $\theta \in [0, \pi]$ are the azimuthal and polar angles, and $p_\phi$, $p_\theta$ are their conjugate momenta.)

(a) Calculate the contribution of the rotational degrees of freedom of each dipole to the classical partition function.
(b) Obtain the mean polarization \( P = \langle \mu \cos \theta \rangle \), of each dipole.

(c) Find the zero-field polarizability

\[
\chi_T = \frac{\partial P}{\partial E} \bigg|_{E=0}.
\]

(d) Calculate the rotational energy per particle (at finite \( E \)), and comment on its high and low temperature limits.

(e) Sketch the rotational heat capacity per dipole.

********

3. 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 \( \epsilon \) 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.

*******
4. **Fluctuation-induced dipole interactions**: The interaction between two dipole moments $\vec{D}_1$ and $\vec{D}_2$, at a separation $\vec{r} = r \hat{r}$ is given by

$$V(\vec{r}) = \frac{3}{r^3} \left( \vec{D}_1 \cdot \hat{r} \right) \left( \vec{D}_2 \cdot \hat{r} \right) - \left( \vec{D}_1 \cdot \vec{D}_2 \right).$$

(a) Consider permanent dipoles of fixed magnitude $|\vec{D}_1| = D_1$ and $|\vec{D}_2| = D_2$ which can point in any direction in three dimensions. Find the expression for the partition function $Z(r)$, obtained by integrating over all possible dipole orientations, at the lowest non-trivial order in $\beta V$. (Hint: Angular averages of vector components satisfy $\langle D_\alpha D_\beta \rangle_0 = D^2 \delta_{\alpha\beta}/3$.)

(b) The partition function $Z(r)$ can be interpreted as resulting from an effective fluctuation-induced potential $U(r)$. Find $U(r)$ at the lowest non-trivial order, and comment on its temperature dependence.

(c) Most atoms and molecules do not have a permanent dipole moment, but are polarizable, i.e. there is an energy cost of $D^2/(2\chi)$ to create a dipole moment of magnitude $D$. Now consider the dipolar interaction $V(r)$ emerging from two polarizable particles with polarizabilities $\chi_1$ and $\chi_2$. Repeat the calculation of $Z(r)$, including the energy costs of creating the dipoles.

(d) Find effective fluctuation-induced potential between polarizable particles at the lowest non-trivial order, and comment on its temperature dependence.

*****

5. **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 $\varepsilon > 0$ 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?

6. 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 $-s, -s+1, \cdots, s-1, s$.

(a) Calculate the Gibbs partition function $Z(T,B)$. (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 $B$,

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

(c) Calculate the zero field susceptibility $\chi = \partial M_z/\partial B|_{B=0}$, and show that it 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.

7. 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 $\mu = k_BT \left[ \ln \left( \frac{P}{T^{5/2}} \right) + A_0 \right]$, 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 $\epsilon$ upon adsorption, calculate the grand partition function for the two dimensional gas with a chemical potential $\mu$.

(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 $Q(\beta \mu)$, and hence show that

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

where $G$ is the grand potential.

(e) Using the characteristic function, show that

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

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

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

*******

8. One dimensional polymer: Consider a polymer formed by connecting $N$ disc shaped molecules into a one dimensional chain. Each molecule can align either along its long axis (of length $2a$) or short axis (length $a$). The energy of the monomer aligned along its shorter axis is higher by $\varepsilon$, i.e. the total energy is $H = \varepsilon U$, where $U$ is the number of monomers standing up.

(a) Calculate the partition function, $Z(T, N)$, of the polymer.

(b) Find the relative probabilities for a monomer to be aligned along its short or long axis.

(c) Calculate the average length, $\langle L(T, N) \rangle$, of the polymer.

(d) Obtain the variance, $\langle L(T, N)^2 \rangle_c$.

(e) What does the central limit theorem say about the probability distribution for the length $L(T, N)$?

*******

9. (Optional) Classical virial theorem: Let $\vec{X} = \{\vec{q}_i, \vec{p}_i\}$ denote any of the $6N$ coordinates in phase space, and consider any function $f(\vec{X})$. 

(a) Show that in a canonical ensemble governed by a Hamiltonian $\mathcal{H}(\bar{X})$
\[
\left\langle \frac{\partial f}{\partial X_i} \right\rangle = \beta \left\langle f \frac{\partial \mathcal{H}}{\partial X_i} \right\rangle,
\]
where $\beta = 1/(k_B T)$.

(b) Find the forms of the virial theorem obtained by substituting $f = q_i$ and $f = p_i$ in the general expression.

10. (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 $\epsilon_i$ and $\epsilon_i + \delta_i$, with different values of $\epsilon_i$ and $\delta_i$ 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 $\delta$ 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 $\Delta$, 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?