1. Consider a 1D hard-sphere gas with molecule diameter \(a\). Calculate the equation of state.

**Solution:**

\[
H = \sum_{i=1}^{N} \frac{\beta^2}{2m} + \sum_{i=2}^{N} V(x_i - x_{i-1})
\]

The partition function is given by

\[
Z = \frac{1}{\lambda N} \int_{0}^{L} d\delta_1 \int_{x_1}^{L-\delta_1} d\delta_2 \ldots \int_{x_{N-1}}^{L-\sum_{i=1}^{N-1} \delta_i} dx \sum_{i=1}^{N} e^{-\beta \sum_{i=1}^{N} V(x_i - x_{i-1})} \int_{-\infty}^{\infty} dp_1 \int_{-\infty}^{\infty} dp_2 \ldots \int_{-\infty}^{\infty} dp_N e^{-\frac{\beta^2}{2m} \sum_{i=1}^{N} \delta_i^2}
\]

We change variables to \(\delta_i = x_i - x_{i-1}\) which gives

\[
Z = \frac{1}{\lambda N} \int_{0}^{L} d\delta_1 \int_{x_1}^{L-\delta_1} d\delta_2 \ldots \int_{x_{N-1}}^{L-\sum_{i=1}^{N-1} \delta_i} dx \sum_{i=1}^{N} e^{-\beta \sum_{i=1}^{N} V(\delta_i)}
\]

where \(\lambda = \frac{\hbar}{\sqrt{2\pi mkT}}\)

We then define the Gibbs partition function as the Laplace transform of the partition function

\[
G = \int_{0}^{\infty} dLe^{-\beta PL} Z
\]

Since in the Gibbs partition function the value of \(L\) is taken from zero to infinity, the upper limits of the internal integrals will be taken to infinity, while the lower limit of the integrals will be \(a\). So

\[
G = \frac{1}{\lambda^N (\beta P)^2} \left[ \int_{a}^{\infty} d\delta e^{-\beta P \delta} \right]^{N-1} = \frac{1}{\lambda^N (\beta P)^{N+1}} e^{-\beta Pa} N^{-1}
\]

The mean length is given by

\[
L = -kT \frac{\partial \ln G}{\partial P} = \frac{(N+1)kT}{P} + (N - 1)a
\]

and the equation of state becomes

\[
|L - (N - 1)a| P = (N + 1)kT
\]

The excluded volume here is easily visualized and our intuition agrees with the exact calculation.

2. Consider a heteronuclear diatomic molecule with moment of inertia \(I\). In this problem, only the rotational motion of the molecule should be considered.

(a) Using classical statistical mechanics, calculate the specific heat \(C(T)\) of this system at temperature \(T\).

(b) In quantum mechanics, this system has energy levels \(E_j = \frac{\hbar^2}{2I} j(j+1)\), \(j = 0, 1, 2, \ldots\) Each level is \((2j+1)\)-fold degenerate. Using quantum statistical mechanics, find expressions for the partition function \(Z\) and the average energy \(\langle E \rangle\) of this system, as a function of temperature. Do not attempt to evaluate these expressions.

(c) By simplifying your expressions in (b), derive an expression for the specific heat \(C(T)\) that is valid at very low temperatures. In what range of temperatures is your expression valid?

(d) By simplifying your answer to (b), derive a high-temperature approximation to the specific heat \(C(T)\). What is the range of validity of your approximation?

**Solution:**

(a) The system has two rotational degrees of freedom, so \(\langle E \rangle = 2 \cdot \frac{1}{2} kT = kT\) and \(C = \frac{d\langle E \rangle}{dT} = k\)
(b) The partition function is \( Z = \sum_{j=0}^{\infty} (2j + 1) e^{-\beta E_j} \) and the average energy is \( \langle E \rangle = \frac{\sum_{j=0}^{\infty} E_j (2j+1) e^{-\beta E_j}}{\sum_{j=0}^{\infty} (2j+1) e^{-\beta E_j}} = -\frac{\partial \ln Z}{\partial \beta} \).

(c) As \( T \to 0 \) we keep only the first two terms in the partition function, so \( Z \approx 1 + 3 e^{-\beta E_1} \Rightarrow \ln Z \approx 3 e^{-\beta E_1} \).

The average energy is \( \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = 3E_1 e^{-E_1/kT} \) and the specific heat \( C = \frac{\partial^2 \langle E \rangle}{\partial T^2} = \frac{3k^2 T^2}{\beta^2} e^{-E_1/kT} \).

The validity of the above expression requires \( 5 e^{-\beta E_2} \ll 3 e^{-\beta E_1} \) and \( 3 e^{-\beta E_1} \ll 1 \), so \( kT \ll \hbar^2/I \).

\( \ln Z \approx \ln \beta + \text{const} \) so \( \langle E \rangle = 1/\beta = kT \). This is the classical result. Finally \( C = \frac{\partial \langle E \rangle}{\partial T} = k \).

3. 10^{10} weakly interacting spinless particles, each with the mass of the electron, are identical in appearance, but obey classical statistics. They are confined in a cubical box which is \( 10^{-6}\text{cm} \) on an edge. Each particle undergoes a potential interaction with the box which is of two sorts. One is attractive and leads to a bound state well which prevents the particle from escaping through the walls of the box. Find at what temperature the pressure in the box is one atm.

**Solution:**

\[ Z = \left( e^{U/kT} + \frac{4\pi V}{\hbar^2} \int_0^{\infty} e^{-p^2/2m k T} p^2 dp \right)^N, \] where \( U = 1eV \)

Thus \( Z = \left[ e^{U/kT} + V \left( \frac{2\pi m k T}{\hbar^2} \right)^{3/2} \right]^N \) and \( P = kT \frac{\partial}{\partial V} \log Z = \frac{NkT}{V} \left[ 1 + \frac{\hbar^3 e^{U/kT}}{V (2\pi m k T)^{1/2}} \right]^{-1} \).

Inverting the formula and plugging in the numbers gives us the required temperature.

4. An assembly of \( N \) particles of spin \( \frac{1}{2} \) are lined up on a straight line. Only nearest neighbors interact. When the spins of the neighbors are both up or down, their interaction is \( J \). When one is up and one is down, the interaction energy is \( -J \). What is the partition function of the assembly at temperature \( T \)?

**Solution:**

There are \( N \) spins, so \( N-1 \) pairs. Of these we have \( N_p \) parallel and \( N_a \) antiparallel. Since \( N_a + N_p = N - 1 \) the energy for a given configuration is

\[ E = J(N_p - N_a) = 2N_p + 1 - N \]

The partition function is

\[ Z = \sum e^{-E/kT} \]

There are \( \frac{(N-1)!}{N_a!N_p!} \) permutations, hence

\[ Z = 2 \sum \frac{(N-1)!}{N_a!N_p!} e^{-J(2N_p+1-N)/kT} = 2e^{J(N-1)/kT} \sum \frac{(N-1)!}{(N-1-N_p)!N_p!} e^{-2JN_p/kT} \]

The sum is just the expansion of \( 1 + e^{-2J/kT} \), so

\[ Z = 2e^{J(N-1)/kT} (1 + e^{-2J/kT})^{N-1} = 2^N \cosh(J/kT)^{N-1} \]

5. Assume a two level system consisting of \( N \) particles with energy gap \( \Delta \). The partition function is \( Z = (1 + e^{\Delta(-D/kT)})^N \). The average energy of the system is

\[ E = N \Delta \frac{\exp(-D/kT)}{1 + \exp(-D/kT)} \]

The number of particles in the excited state is

\[ n = N \frac{\exp(-D/kT)}{1 + \exp(-D/kT)} \]

For high temperature \( n \to N/2 \), while for low temperature \( n \to N \exp(-D/kT) \)
6. From thermodynamical principles, determine the vapor pressure $P_r$ for a very small droplet of liquid of radius $r$, in terms of the vapor pressure $P_\infty$ of a large body of the same liquid, having a negligible surface to volume ratio.

**Solution:**

$$G = M_1g_1 + M_2g_2 + 4\pi\gamma r^2$$

where $\gamma$ is the surface tension, $M_1$ is the mass of the droplet and $M_2$ the mass of its vapor. $g_1$ and $g_2$ are Gibbs energies per unit mass.

Setting $\delta G = 0$ we get

$$0 = \delta M_1(g_1 - g_2) + 8\pi\gamma r \frac{\partial r}{\partial M_1} = \delta M_1[g_1 - g_2 + 2\gamma/(\rho r)]$$

where $\rho$ is the mass density of the droplet. Hence in equilibrium $g_2 - g_2 = 2\gamma/(\rho r)$

For a given phase $V = \frac{\partial G}{\partial P}$, so $1/\rho = \frac{\partial g_2}{\partial P}$

Differentiating with respect to $P$ at constant temperature gives us

$$1/\rho_{vapor} - 1/\rho_{droplet} = -\frac{2\gamma}{\rho r^2} \frac{\partial r}{\partial P}$$

Assuming that $\rho_{vapor} \ll \rho_{droplet}$ and the vapor is a perfect gas

$$P \frac{\partial r}{\partial P} = -\frac{kT}{M} \frac{\rho r^2}{2\gamma}$$

Integrating, this gives $P = P_\infty exp(2M\gamma/\rho kTr)$