Problem 1

Consider a classical system of $N$ non-interacting diatomic molecules enclosed in a box of volume $V$ at temperature $T$. The Hamiltonian for a single molecule is,

$$H(p_1, p_2, r_1, r_2) = \frac{1}{2m}(p_1^2 + p_2^2) + \frac{1}{2}K|r_1 - r_2|^2,$$

where $p_1$, $p_2$, $r_1$, and $r_2$ are the momenta and coordinates of the two atoms in a molecule.

1.a) Find the partition function and the Helmholtz free energy of the system (Hint: the integration over phase space is easier if, in the integration over $d\mathbf{r}_1 d\mathbf{r}_2 (= d^3\mathbf{r}_1 d^3\mathbf{r}_2)$ one changes variables from the coordinates of the individual atoms, $(\mathbf{r}_1, \mathbf{r}_2)$, to the coordinates of the reduced system, $(\mathbf{R}, \mathbf{r})$, where $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ is the position vector of the center of mass of the two atoms, and $\mathbf{r} = (\mathbf{r}_1 - \mathbf{r}_2)$ is the relative distance between the two. In other words, apply what you know about the classical mechanics solution of a two-body problem!).

1.b) Find the specific heat at constant volume.

1.c) Find the mean square molecular diameter, $\langle |\mathbf{r}_1 - \mathbf{r}_2|^2 \rangle$.

Problem 2

A simple anti-ferromagnetic system consists of a chain of $N$ non-interacting and identical localized spin-1/2 dimers. The system is placed in an external magnetic field $\mathbf{B} = B\hat{Z}$ and is in contact with a heat reservoir at a fixed temperature $T$. The Hamiltonian for an individual dimer is given by the following expression,

$$H = JS(1) \cdot S(2) - \mu B (S_z(1) + S_z(2)),$$

where $J$ and $\mu$ are positive constants.

2.a) Obtain the eigenvalues and the eigenvectors of $H$.

2.b) Determine the partition function for the system (i.e. $N$ non-interacting and localized dimers) correct to second order in $B$, but correct to all orders in $T$.

2.c) Evaluate the expectation value of the magnetization $M = \mu\langle S_z(1) + S_z(2) \rangle$ to leading order in $B$. Justify your result in the limit $T \to 0$. 
2.d) Obtain the magnetic susceptibility defined as follows,

\[ \chi = \left( \frac{\partial \langle M \rangle}{\partial B} \right)_{T,B=0}. \]

You are told that the magnetic susceptibility is proportional to the variance in the magnetization. Is your answer consistent with this statement? Explain.

Problem 3

Consider a diluted gas of diatomic molecules. For most such systems, at temperatures above the normal boiling point of the fluid, the rotational energies are so closely spaced that they approximate a continuum, and classical statistical mechanics can be used. Let the mass of a molecule be \( M \) and the moment of inertia \( I \).

3.a) Express the rotational kinetic energy in terms of the two Euler angles \( \phi \) and \( \theta \), and show that in terms of the corresponding canonical momenta \( P_\phi \) and \( P_\theta \), it takes the form,

\[ K_{\text{rot}} = \frac{1}{2I} \left( P_\theta^2 + \frac{P_\phi^2}{\sin^2 \theta} \right). \]

(Hint: as in Problem 1, here too you are dealing with a diatomic molecule, i.e. a two-body system. Consider the suggestions given in Problem 1).

3.b) Ignoring the vibrations, write down the partition function.

3.c) Evaluate the partition function and show that the result is of the form,

\[ Z = \frac{V^N}{N!} \left( \frac{2\pi M k_B T}{\hbar^2} \right)^{3N/2} \left( \frac{8\pi^2 I k_B T}{\hbar^2} \right)^N. \]

3.d) Compute the internal energy and the entropy of this gas.

3.e) Using the expressions from (3.d), examine the behavior of the entropy at low temperatures. Does the obtained result agree with the third law of thermodynamics? Explain what happens at low temperatures.