Instructions:
• The exam consists of 10 short-answer problems (10 points each).
• Where possible, show all work; partial credit will be given if merited.
• Personal notes on two sides of an $8\frac{1}{2} \times 11$” page are allowed.
• Total time: 3 hours.

Unless otherwise noted, commonly used symbols are defined as follows:

- $P$: Pressure
- $T$: Absolute Temperature
- $R$: gas constant; $R = 8.314 \text{ J \cdot mole}^{-1} \cdot \text{Kelvin}^{-1}$
- $k$: Boltzmann’s constant; $k = \frac{R}{6.02 \times 10^{23}}$
- $\hbar$: Planck’s constant divided by $2\pi$
- $\beta$: $(kT)^{-1}$
- $S$: Entropy
- $V$: Volume
- $N$: Number of particles (Assume $N >> 1$)

Useful Relations and Constants:

$$\sum_{m=0}^{\infty} x^m = \frac{1}{1-x}; \ |x| < 1.$$  
$$\ln N! \sim N \ln N - N$$  
$$(1 + x)^\nu \simeq 1 + \nu x; \ |x| \ll 1$$  
$$\hbar = 6.626 \times 10^{-34} \text{ Js}$$  
$$m_e = 9.1 \times 10^{-31} \text{ kg}$$
**P1.** A vessel of fixed volume $V$ contains a noninteracting gas of $N$ diatomic molecules having mass $m$ and rotational inertia $I$ in equilibrium with the surroundings at a temperature $T$. The partition function is given by

$$Z = \left[ V \left( \frac{m k T}{2 \pi \hbar^2} \right)^{3/2} \left( \frac{2 k T}{\hbar^2} \right) \right]^N$$

Intramolecular vibrations are frozen out. What is the heat capacity at constant volume?

**P2.** A system consists of $N$ molecules in a solution of volume $V$ and at a temperature $T$. It is energetically favorable for the molecules to bond to one another end-to-end, forming polymers. It has been proposed by some investigators that, as a function of $T$, $V$, and $N$, the internal energy $U$ is adequately described by the function

$$U = -N \Delta \left( \frac{\sqrt{V} + 4V_0 e^{\beta \Delta}}{\sqrt{V} + 4V_0 e^{\beta \Delta} + \sqrt{V}} \right),$$

where $V_0$ is the volume of a single molecule and $\Delta$ is the binding energy per bond. If this proposal has any merit, $U$ must be extensive. Show that it is, or show that it is not.
P3. The allowed energy levels of a harmonic oscillator are given by

\[ E_n = \hbar \omega \left( n + \frac{1}{2} \right) \]

where \( n = 0, 1, 2, \ldots \) is a positive integer. Suppose that the harmonic oscillator is in thermal equilibrium at a temperature \( T \). Calculate the partition function and obtain from this an expression for the entropy \( S \). Show that your result is in agreement with the third law of thermodynamics.

P4. The partition function for a system of \( N \) atoms of mass \( m \) in a volume \( V \) in equilibrium at a temperature \( T \) is

\[ Z = \frac{V^N N!}{(2\pi m \hbar^2)^{3N}} \]

where \( \hbar = h/\sqrt{2\pi mkT} \). What is the Helmholtz free energy? What is the maximum amount of work that can be performed on the surroundings by the system if it is allowed to expand at constant temperature to twice its original volume?

P5. To first approximation, the conduction electrons in a metal are modeled as a noninteracting gas of spin-1/2 fermions, each having a charge \( -e \) and an effective mass \( m \). The electron density \( n = 10^{29} \text{m}^{-3} \) is large enough that the fermi gas is highly degenerate at room temperature, meaning that the states below the fermi surface are largely occupied; as a function of energy the fermi distribution function may be approximated by a step-function. Using the property that the chemical potential \( \mu \) is related to the number \( N \) of conduction electrons through an integral over single particle phase space,

\[ N = \frac{2}{(2\pi \hbar)^3} \int d^3x d^3p \frac{1}{e^{-\beta \mu} e^{\beta \frac{p^2}{2m}} + 1}, \]

show that the electrons at the fermi surface are moving with a speed

\[ v \simeq \frac{\hbar}{m} \left( 3\pi^2 n \right)^{1/3} = 1.7 \times 10^6 \text{m/s} \]

that is an order of magnitude higher than what one would expect from equipartition at room temperature.
**P6.** A cup of water initially at a temperature of 100 degrees Celsius is placed in contact with the environment at 25 degrees C and a constant pressure of 1 atm. Left alone, the water spontaneously cools to 25 C. If the cup contains 100 g of water and the heat capacity at constant pressure \( C_p = 4.186 \) J/g/deg is approximately constant, independent of temperature, what is the change in entropy of the water for this process? Explain how your result is consistent with the second law of thermodynamics.

**P7.** As a function of \( S \) and \( T \), the internal energy \( U \) of a system containing \( N \) particles is given by

\[
U = aN^{5/3} (V - bN)^{-2/3} \exp \left( \frac{2S}{3Nk} \right)
\]

where \( a \) and \( b \) are constants. Using the combined statement of the first and second laws,

\[
dU = TdS - PdV,
\]

find an equation for the pressure \( P \) as a function of \( T \) and \( V \).
P8. An insulating solid with volume $V$ contains $N$ spin-1/2 atoms, each having a magnetic moment $\vec{\mu} = -2\mu_0 \vec{S}$ where $\mu_0$ is the Bohr magneton and $\vec{S}$ is the spin. When the solid is placed between the poles of magnet, the magnetic field within the solid is uniform with strength $B$. Assuming that the spins are noninteracting, determine the partition function for the system at constant $T$ and $B$, and obtain from this an expression for the magnetization $M$. Sketch a graph showing $M$ as a function of $B$.

P9. The entropy of a system of $N$ spins in a magnetic field of strength $B$ is given by

$$S = Nk \left[ \ln 2 - \frac{(\beta \mu_0 B)^2}{2} \right]$$

in the temperature range of interest. Here $\mu_0$ is the Bohr magneton. Suppose that the system is thermally insulated from the surroundings and the magnetic field is slowly (reversibly) reduced from an initial value of $B_1$ to a final value $B_2$. If the temperature is initially $T_1$, what will be the final temperature $T_2$?

P10. Consider the system spin in P9. If the magnetic field is held constant, how much heat must be added to raise the temperature from an initial temperature $T_1$ to a final temperature $T_2$?