Please solve 4 out of 5 problems.

Problem 1 (25 points)
Even at low density, real gases do not quite obey the ideal gas law. A systematic way to account for deviations from ideal behavior is the virial expansion,

\[ PV = nRT \left( 1 + \frac{B(T)}{\frac{V}{n}} + \frac{C(T)}{\left(\frac{V}{n}\right)^2} + \ldots \right), \]

where the functions \( B(T) \), \( C(T) \), and so on are called the virial coefficients. When the density of the gas is fairly low, so that the volume per mole is large, each term in the series is much smaller than the one before. In many situations it is sufficient to omit the third term and concentrate on the second, whose coefficient \( B(T) \) is called the second virial coefficient (the first coefficient being 1).

(a) Think about the forces between molecules, and explain why we might expect \( B(T) \) to be negative at low temperatures but positive at high temperatures.

(b) Any proposed relation between \( P \), \( V \), and \( T \), like the ideal gas law or the virial equation, is called an equation of state. Another famous equation of state, which is qualitatively accurate even for dense fluids, is the van der Waals equation,

\[ \left( P + \frac{a n^2}{V^2} \right) (V - nb) = nRT, \]

where \( a \) and \( b \) are constants that depend on the type of gas. Calculate the second and third virial coefficients \( (B \) and \( C) \) for a gas obeying the van der Waals equation, in terms of \( a \) and \( b \). You may need the approximation, \( \frac{1}{(1-nb/V)} \approx 1 + \frac{nb}{V} + (nb/V)^2 \).
Problem 2 (25 points)
Functions encountered in physics are generally well enough behaved that their mixed partial derivatives do not depend on which derivative is taken first. Therefore, for instance,

\[ \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial S} \right) = \frac{\partial}{\partial S} \left( \frac{\partial U}{\partial V} \right), \]

where each \( \partial / \partial V \) is taken with \( S \) fixed, each \( \partial / \partial S \) is taken with \( V \) fixed, and \( N \) is always held fixed. From the thermodynamic identity (for \( U \)) you can evaluate the partial derivatives in parentheses to obtain

\[ \left( \frac{\partial T}{\partial V} \right)_S = -\left( \frac{\partial P}{\partial S} \right)_V, \]

a nontrivial identity called a Maxwell relation. Go through the derivation of this relation step by step. Then derive an analogous Maxwell relation from each of the other three thermodynamic identities (for \( H, F, \) and \( G \)).

Problem 3 (25 points)
[Boltzmann’s constant \( k = 1.38 \times 10^{-23} \text{J/K}, \text{amu} = 1.66 \times 10^{-27} \text{kg} \)]

For a planetary atmosphere in hydrostatic equilibrium, if the temperature gradient \( |dT/dz| \) exceeds a certain critical value, convection will occur. The condition for convection to occur is that a rising air mass must remain warmer than the surrounding air despite this adiabatic cooling.

(a) Assume that the atmosphere is an ideal gas with \( f \) degrees of freedom. Show that when an ideal gas expands adiabatically, the temperature and pressure are related by

\[ \frac{dT}{dP} = \frac{2}{f+2} \frac{T}{P} \]

(b) Assume the atmosphere is also in hydrostatic equilibrium; that is, \( dP = -g \rho dz \) where \( g \) is the gravitational acceleration and \( \rho \) is the density. For this case show that the temperature gradient, known as the adiabatic lapse rate, is given by

\[ \frac{dT}{dz} = -\left( \frac{2}{f+2} \right) \frac{g \bar{m}}{k} \]

where \( \bar{m} \) is the atmosphere’s average mass per molecule.

(c) The Earth’s atmosphere composed of approximately 20% \( \text{O}_2 \) and 80% \( \text{N}_2 \). Calculate its adiabatic lapse rate.
Problem 4 (25 points)
For a degenerate gas of \( N \) free electrons within volume \( V \), the density of states as a function of electron energy is:

\[
g(\varepsilon) = \frac{(2m)^{3/2}V}{2\pi^2 \hbar^3} \varepsilon^{1/2}
\]

At the temperature of absolute zero all accessible states are occupied by the \( N \) free electrons. The energy of the electron in the last available state is known as the Fermi energy and is given by

\[
\varepsilon_F = \frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} n^{2/3}
\]

where \( n \) is the electron density.

(a) Show that the total energy of this system is given by

\[
U_{\text{tot}} = \frac{3}{5} N\varepsilon_F
\]

(b) Even at absolute zero, such a system exerts a pressure \( P \) on its surroundings. To calculate this pressure, imagine that the volume increases by a small amount \( dV \). The electrons will do an amount of work \( PdV \) on their surroundings. Calculate the electron degeneracy pressure and show its dependence on \( n \) (the electron density).
Problem 5 (25 points)

Consider a classical particle moving in a one-dimensional potential well \( u(x) \) as shown in the Figure, where the higher the temperature the farther the particle will stray from the equilibrium point. The particle is in thermal equilibrium with a reservoir at temperature \( T \), so the probabilities of its various states are determined by Boltzmann statistics.

(a) Explain why the average position of the particle is given by

\[
\bar{x} = \frac{\int x e^{-\beta u(x)} \, dx}{\int e^{-\beta u(x)} \, dx},
\]

where each integral is over the entire \( x \) axis.

(b) If the temperature is reasonably low (but still high enough for classical mechanics to apply), the particle will spend most of its time near the bottom of the potential well. In that case we can expand \( u(x) \) in a Taylor series about the equilibrium point \( x_0 \):

\[
u(x) = u(x_0) + (x - x_0) \frac{du}{dx}\bigg|_{x_0} + \frac{1}{2}(x - x_0)^2 \frac{d^2u}{dx^2}\bigg|_{x_0} + \frac{1}{3!}(x - x_0)^3 \frac{d^3u}{dx^3}\bigg|_{x_0} + \cdots
\]

Show that the linear term must be zero, and that truncating the series after the quadratic term results in the trivial prediction \( \bar{x} = x_0 \).