Turn in this HW on or before Friday at 8pm.

1 Using Gibbs Free Energy

You are given the following Gibbs free energy:

$$G = -kTN \ln \left(\frac{aT^{5/2}}{p} \right),$$

where a is a constant (whose dimensions make the argument of the logarithm dimensionless).

(a) Compute the entropy.

(b) Work out the heat capacity at constant pressure C_p.

(c) Find the connection among V, p, N, and T, which is called the equation of state (Hint: find the volume as a partial derivative of the Gibbs free energy). Simplify the final expression as much as possible.

(d) Find the internal energy U from the expression for G that you were given in the main prompt. Simplify the final expression as much as possible.

2 Helmholtz Free Energy of a Van Der Waals Gas

The Helmholtz free energy of a van der Waals (vdW) gas can be written as:

$$F = -NkT \left\{ 1 + \ln \left[\frac{(V - Nb)T^{\frac{3}{2}}}{N} \right] \right\} - \frac{aN^2}{V}$$

Where a and b are constants.

(a) Derive the equation of state (relationship between p, T, and V) for this Helmholtz free energy. *Hint*: The starting equations for this problem include the thermodynamic identity, the definition of Helmholtz free energy, $F = U - TS$, and math identities such as the overlord equation.
Bonus point: Rearrange the vdW equation of state to highlight any similiarites with the ideal gas equation of state ($pV = NkT$). To highlight similarities, group together terms that have dimensions of pressure, group together terms that have dimension of volume, etc.

(b) Using your expression from part (a), sketch or plot $p(V)$ at various fixed temperatures. The volume axis should include Nb up to $6Nb$. Your plot can be dimensionless (i.e. V/Nb on the x axis). Select values of NkT and aN^2 that give curves with different shapes. Can you create a minima in pressure near $V = 2Nb$?

3 Ideal gas internal energy

In this problem, you will prove that the internal energy of an ideal gas depends on temperature, but not on volume, based soley on the ideal gas equation:

$$pV = Nk_BT \tag{1}$$

and of course your knowledge of thermodynamics. It's a pretty tricky proof, so I'll step you through it.

(a) To begin with, use the Helmholtz free energy $F = U - TS$ to show that

$$\left(\frac{\partial U}{\partial V}\right)_T = -p + T\left(\frac{\partial S}{\partial V}\right)_T \tag{2}$$

for *any* material.

(b) Now show that for any material

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V . \tag{3}$$

(c) Finally, show that for an ideal gas

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \tag{4}$$

Remember that the only statement we can assume about the ideal gas is $pV = Nk_BT$. We have not been given an expression for U.

4 Non-Ideal Gas

The equation of state of a gas that departs from ideality can be approximated by

$$p = \frac{NkT}{V}\left(1 + \frac{NB_2(T)}{V}\right),$$

where B_2 is called the second virial coefficient. B_2 is a function of T, so it is usually written as $B_2(T)$. The function $B_2(T)$ increases monotonically with temperature. Find $\left(\frac{\partial U}{\partial V}\right)_T$ and determine its sign.

5 Plastic Rod

Optional Practice

When stretched to a length L the tension force τ in a plastic rod at temperature T is given by its Equation of State

$$\tau = aT^2(L - L_o)$$

where a is a positive constant and L_o is the rod's unstretched length. For an unstretched rod (i.e. $L = L_o$) the heat capacity at constant length is $C_L = bT$ where b is a constant. Knowing the internal energy at T_o, L_o (i.e. $U(T_o, L_o)$) find the internal energy $U(T_f, L_f)$ at some other temperature T_f and length L_f.

(a) (1 point) Write an expression for the exact differential dU in terms of dT and dL (we've been calling this type of expression an "overlord equation").

(b) Show that the partial derivative $(\partial U/\partial L)_T = -aT^2(L - L_o)$.

(c) Integrate dU *very carefully* in the $T - L$ plane, keeping in mind that $C_L = bT$ holds *only* at $L = L_o$ to find $U(T_f, L_f) - U(T_0, L_0)$.