Homework 4 **Due October 2, 2017**

Solve each problem on separate sheets of paper, and clearly indicate the problem number and your name on each. Carefully and neatly document your answers. You may use a mathematical solver like Matlab or Mathematica. Use plotting software for all plots.

1 van der Waals CO_2 redux

Last homework you worked with the fundamental van der Waals equation:

$$s_{vdW}(u,v) = s_0 + R\ln(v-b) + cR\ln(u+a/v) \tag{1}$$

1. Construct the Helmholtz potential of a van der Waals fluid, $a_{vdW}(T,v)$. *Hints:* First differentiate to find the relationship between u and T.

2. Recall the example done in class of a piston separating two chambers of volumes 1 and $10\,L$, respectively, each containing 1 mole of ideal gas, the whole system held isothermal at $273\,K$. We showed in class that $-2.5\,kJ$ of work could be extracted by allowing the piston to adjust the volumes to $5\,L$ and $6\,L$. Compare the amount of work available from the same process and conditions if the fluid was van der Waals CO_2.

3. Compare the ideal and van der Waals CO_2 cases if the volumes started at 0.1 and $1.0\,L$ and ended at 0.5 and $0.6\,L$.

4. Take the same case of a system of total volume of $1.1\,L$, but now put 1 mole of van der Waals CO_2 fluid on one side of the piston and 1 mole of ideal gas on the other. If the piston was allowed to freely move, where would it end up?

2 Manipulating thermodynamic derivatives

As Prateek might say, the susceptibilities, c_P, α, and κ_T, are "awesome." Everything about a one component fluid can be expressed in terms of them, and for good reason! Here's some practice with them.

1. Express the derivative $\left(\frac{\partial T}{\partial v}\right)_h$ in terms of the three susceptibilities.

2. Determine the susceptibilities of a van der Waals fluid.

3. Plot $\left(\frac{\partial T}{\partial v}\right)_h$ vs. v for T from -50 to $50\,°C$ in $20\,°C$ increments for van der Waals CO_2. Under what conditions of temperature and volume is the derivative negative?

3 Practice with potentials

While a Carnot refrigerator sure would be efficient, in practice we don't like to wait an eternity for our 'fridges to get cold. Practical refrigerators use the Joule-Thomson effect and irreversible, isenthalpic expansion to create the cold we love. Let's see how cold we can make things with van der Waals CO_2.

1. Construct the enthalpy $h_{vdW}(T,v)$ of a van der Waals fluid.

2. Determine the change in temperature when van der Waals CO_2 is isenthalpically expanded from 10^{-4} to $10^{-3}\,m^3\,mol^{-1}$, starting from $10\,°C$.

3. A more reliable estimate of the change in temperature can be gotten from thermodynamic properties charts. Thermodynamic charts for CO_2 refrigerant are available at link. Use the pressure-enthalpy chart at the end of this document to determine the change in temperature for the same isenthalpic expansion as in the previous question.

4   A departure from ideality

The examples above assume the heat capacity of CO_2 to be a constant. More generally heat capacities are functions of temperature and pressure. (We'll learn why when we study statistical mechanics.) It's common to report heat capacities in a hypothetical ideal gas, pressure-independent limit, $c_p^{ig}(T)$. For instance, the molar heat capacity of ideal CO_2 is reported to be:

$$c_p^{ig}(t) = -11.401074 - 55.231532t + 5.149108t^2 - 0.29158t^3 + 0.110128t^{-2} + 115.93493t^{1/2}$$

where $t = T(K)/1000$.

1. Find the change in molar entropy of "ideal gas" CO_2 when heated from 290 to 350 K.

2. To find the real change in entropy, we would need to know the difference in entropy between the ideal gas and real states of CO_2 at identical T and v conditions. This difference is called a "departure function." To create this, we construct a hypothetical path between the real and ideal gas states, first expanding the van der Waals gas from v to $v \to \infty$, where it behaves ideally, and then compressing from ∞ to v as an ideal gas. Express $\left(\frac{\partial S}{\partial v}\right)_T$ in terms

of susceptibilities.

1. Construct $\left(\frac{\partial S}{\partial v}\right)_T$ for ideal CO_2.

2. Construct $\left(\frac{\partial S}{\partial v}\right)_T$ for van der Waals CO_2.

3. Construct the departure function $S^{vdW}(T, v) - S^{ig}(T, v)$ by appropriate integration. *Hint*: This difference is equivalent to *adding* S^{vdW} integrated along the path $v \to \infty$ and S^{ig} integrated along the path $\infty \to v$.

4. Use the departure function (twice) to compute the molar entropy change when van der Waals CO_2 is heated from 290 K and 1.0 L/mol to 350 K and 0.15 L/mol.