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   Just a little unstable

The energy minimum/entropy maximum principle places bounds on the stability of fundamental equations. What are the limits of stability with respect to T and v of the following fundamental equations?

1. A monatomic ideal gas:

$$f_{\text{ig}} = \{-RT \ln(v) - 1.5RT \ln(RT)\} + \{RT\}$$

2. A monatomic van der Waals gas:

$$f_{\text{vdW}} = \{-RT \ln(v - b) - 1.5RT \ln(RT)\} + \{RT - a/v\}$$

2   What passes for a law these days. . . .

The van der Waals equation obeys the law of corresponding states, so all van der Waals fluids exhibit the same vapor-liquid phase equilibrium when presented in reduced variables.

1. Use the following relationship to derive an expression for the van der Waals equation in terms of the reduced variable $v_R = v/v_c$, $T_R = T/T_c$, and $P_R = P/P_c$.

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = \left(\frac{\partial^2 f}{\partial v^2}\right)_{T=T_c} = 0$$

1. Plot the spinodal curve of a van der Waals fluid on a P_R, v_R diagram.

3   The two phases of van der Waals

Binodal curves are much trickier to find because they are determined by the equality of the three intensive variables rather than just by the curvature of the free energy. The "equal area construction" is a common numerical approach to finding the binodal points.

1. Use an equal area construction to compute the reduced saturation pressure and reduced vapor and liquid volumes at $T_r = 0.8, 0.85, 0.90, 0.95, 1$. You will want to use a numerical solver.

2. Plot the points on the same P_R, v_R diagram as the spinodal above.

3. (Bonus!) Find the latent entropy and latent enthalpy at $T_r = 0.8, 0.85, 0.90, 0.95, 1$, using the fact that:

$$\Delta s = \int_{v_l}^{v_g} \left(\frac{\partial s}{\partial v}\right)_T dv$$

   Comment on any trend you find. *Hint:* You'll want to apply a Maxwell relation to the partial derivative before evaluating.

4. (Bonus!) The van der Waals constants of H_2O are $a = 0.5609$ Pa m^{6}mol^{-2} and $b = 30.49 \times 10^{-6}$ m^{3}mol^{-1}. Use your results to estimate ΔH^{vap} of H_2O at 1 atm. How does the result compare to the experimental value of 40.64~kJ mol^{-1}?

4   Steam at the top of the mountain

The Clapeyron equation, and its cousin Clausius-Clapeyron, relate observable pressure and temperature at a phase boundary to the underlying latent quantities.

1. Determine the value of dT/dP for water at its normal boiling point ($1\,\mathrm{atm}$) of $373.1\,\mathrm{K}$ given that $\Delta H^{\mathrm{vap}}(373.1\ \mathrm{K}) = 40.65\,\mathrm{kJ/mol}$ and the densities of liquid and vapor are 0.9584 and $0.6010 \times 10^{-3}\,\mathrm{g\,mL^{-1}}$, respectively. Estimate the boiling point of water at $2\,\mathrm{atm}$.

2. A liquid boils at $95\,°\mathrm{C}$ at the top of a hill and at $105\,°\mathrm{C}$ at the bottom. It's latent heat of vaporization is $1000.0\,\mathrm{cal/mol}$. What is the height of the hill? *Hint:* How does pressure vary with altitude?

5   Qualitatively in phase

The triple point of oxygen (O_2) is at $54.3\mathrm{K}$ and $1.14\,\mathrm{torr}$; it's critical point is at $154.6\,\mathrm{K}$ and $37\,828\,\mathrm{torr}$; it's normal melting and boiling points are $-218.4\,°\mathrm{C}$ and $-182.9\,°\mathrm{C}$, respectively. Sketch the phase diagram of oxygen. Does it melt under applied pressure in the same way that water does?

6   Quantitatively in phase

Near the triple point the following equations describe the vapor pressure of liquid and solid NH_3:

$$\ln P^{\mathrm{sat}}(l) = 24.38\ \mathrm{Pa} - \frac{3063\ \mathrm{Pa\ K}}{T} \quad \ln P^{\mathrm{sat}}(s) = 27.92\ \mathrm{Pa} - \frac{3754\ \mathrm{Pa\ K}}{T}$$

1. What are the temperature and pressure at the triple point?

2. What is the latent heat of vaporization?

3. What is the latent heat of sublimation?

4. What is the latent heat of fusion at the triple point?

7   Are you sure? How sure?

The two state model allows a simple illustration of the principles of the microcanonical ensemble. A closed system is composed of an even number of two-state "atoms," each of which can have energy 0 or ϵ. The system is partitioned into two subsystems of equal size.
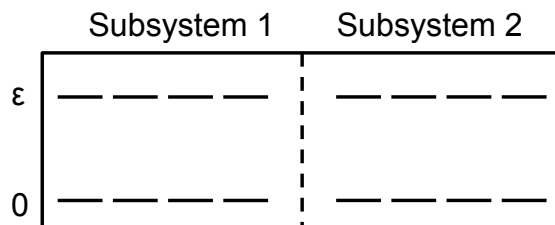
1. Suppose the system contains 8 atoms as in the figure above, and the total energy of the system is $U = 4\epsilon$. Determine the possible energies U_1 of subsystem 1 and their relative probabilities.

2. What fundamental assumption did you make to assess the probabilities?

3. The probability distribution you just calculated is called *binomial* (specifically, binomial with individual probability $p = 1/2$). As the sizes of the subsystems N_i and the total energy U grow proportionately, the probability distribution on U_1 becomes approximately *Gaussian* with mean $(1/2)N_1\epsilon$ and variance $\sigma^2 = N_1\epsilon^2$.

   (a) Calculate the ratio of the probability that $U_1 = 0.51U$ to $U_1 = 0.5U$ for $N_1 = 100$.

   (b) Calculate the ratio of the probability that $U_1 = 0.51U$ to $U_1 = 0.5U$ for $N_1 = 10^6$.

   (c) Calculate the ratio of the probability that $U_1 = 0.51U$ to $U_1 = 0.5U$ for $N_1 = 10^{20}$.

4. What do you think? As N_1 gets really big, what wil U_1 be? How certain are you?