Thermodynamics and Statistical Mechanics Homework Assignment 9

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Problem 1: SIR Model - A Coding Exercise

Code the SIR model for the dynamics of an epidemic using a programming language of your choice. Use parameters approximately relevant for this pandemic: mean recovery time about 10 days, and the basic reproduction number $R_0 = 3.5$ (note, these are not the real numbers, but more or less reasonable estimates.)

  a) Plot the fraction of infected x, the fraction of susceptible s and the fraction of recovered r people in the population as a function of the number of days starting from the day that $x = 10^{-4}$ (set this day to be time zero).

  b) After the epidemic comes to equilibrium what percent of the population will have been infected?

  c) Now consider a case in which a lock-down is ordered t_* days after day zero, bringing R_0 down to 0.5 from this day on. Calculate the percent of the population that have had the disease (i.e. recovered) at the time the epidemic reaches equilibrium if the lock-down was ordered (i) two weeks after day zero, (ii) three weeks after day zero (show graphs and give the final number). Suppose the population was the size of California (40 million) and the infection fatality rate (IFR) of the disease is 0.7%. What would be the approximate total number of fatalities in each of the above scenarios: unmitigated, lock-down (i), lock-down (ii)?

  d) Extend the model in some simple, but interesting direction. Explain your extension and what question it is trying to answer. Show a graph of a calculation that answers this question.
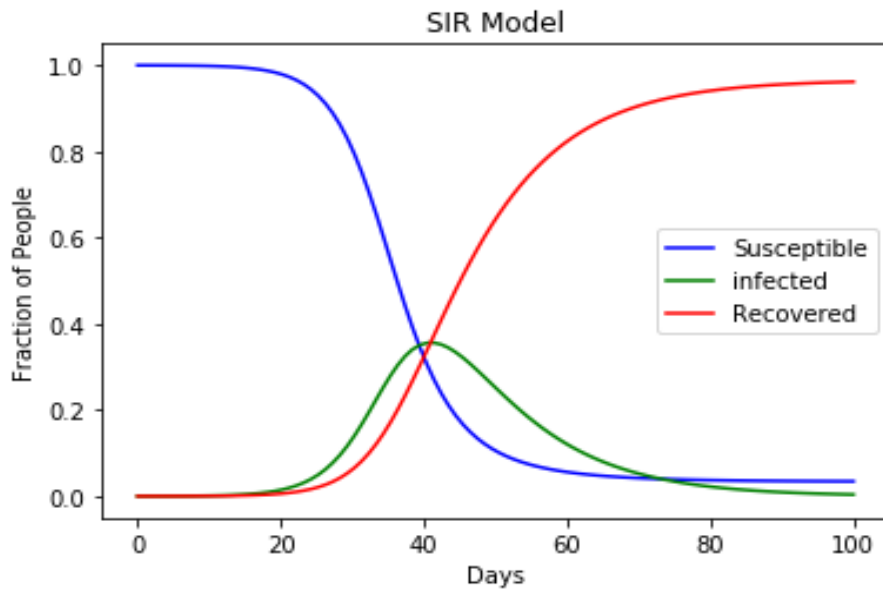
Solution

a)

Figure 1: Problem 9.1.a

b) At the equilibrium point, roughly 39% of the population will be infected.
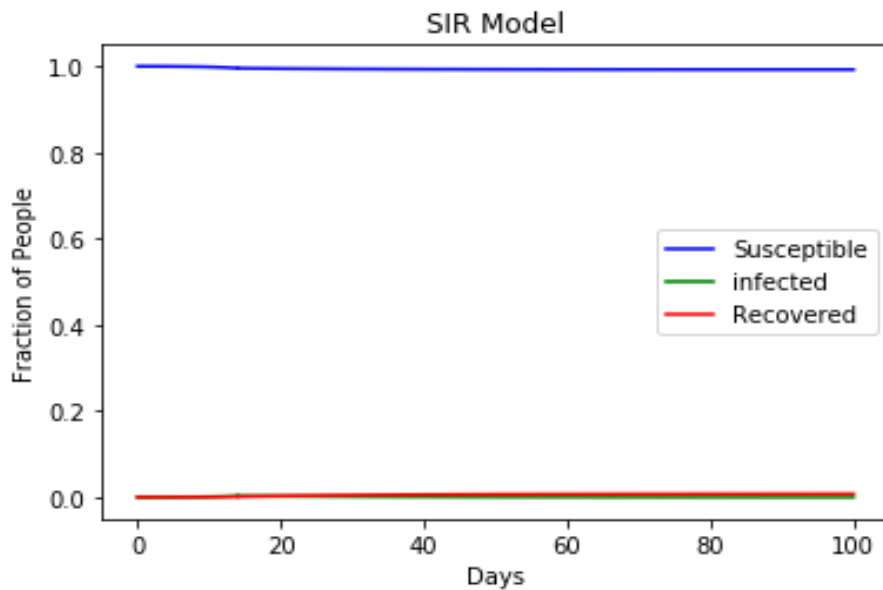**c)**i. About 0.13% of the population will have recovered at the equilibrium point.

Figure 2: Problem 9.1.c.i

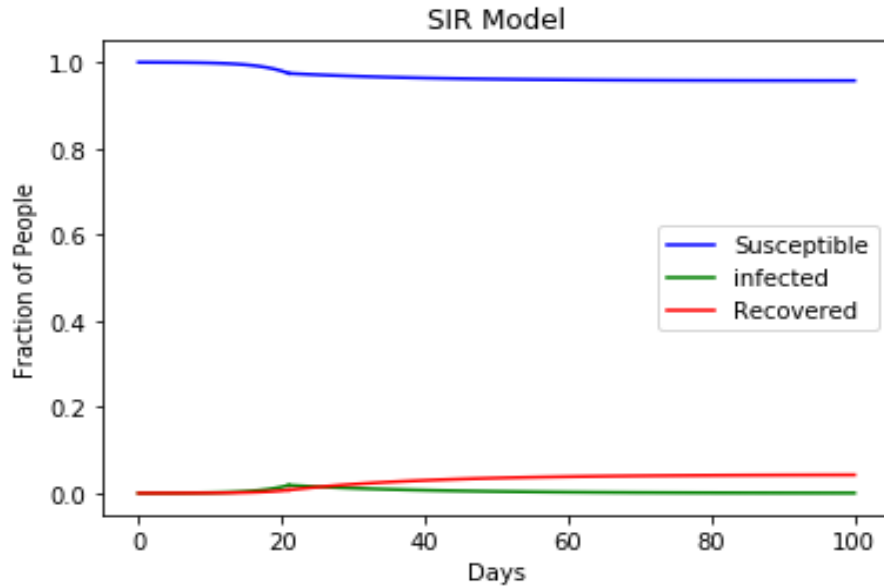ii. About 0.7% will have recovered at the equilibrium point.

Figure 3: Problem 9.1.c.ii

iii. If the disease was unmitigated, 268800 people can be expected to die. With lockdown (i), we can expect 2156 people to die. With lockdown (ii), we can expect 11760 people to die.

d) We can consider a situation where we lockdown after three weeks, for two weeks, and then reopen. Will the situation escalate or will it be reduced like the other lockdown situations? As we can see in the following graph, a temporary lockdown doesn't do too well in mitigating the spread of a disease.
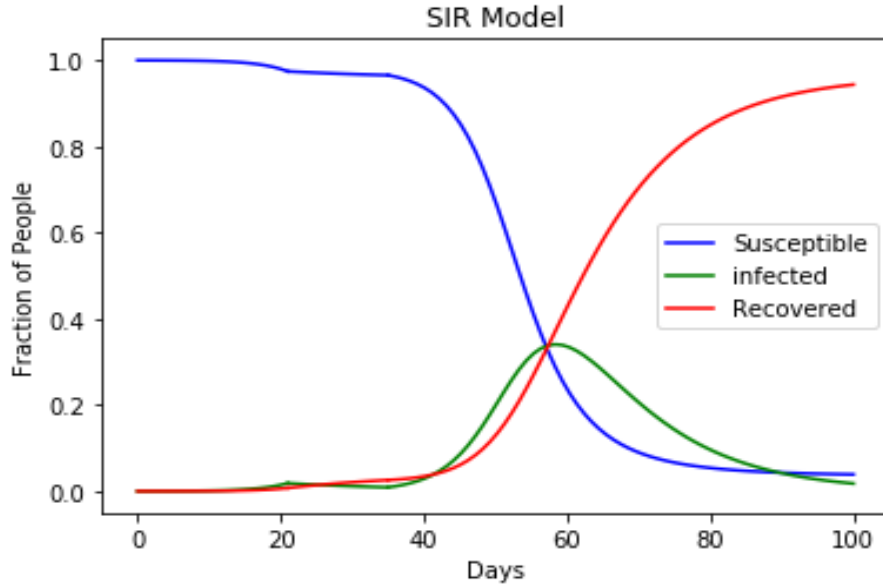
Figure 4: Problem 9.1.d.

Problem 2: Entropy, Energy, and Enthalpy of Van Der Waals Gas (Kittel 10.1)

a) Show that the entropy of the van der Waals gas is

$$\sigma = N\left(\ln\left(\frac{n_Q(V - Nb)}{N}\right) + \frac{5}{2}\right)$$

b) Show that the energy is

$$U = \frac{3}{2}N\tau - \frac{N^2 a}{V}$$

c) Show that the enthalpy $H = U + pV$ is

$$H(\tau, V) = \frac{5}{2}N\tau + \frac{N^2 b\tau}{V} - \frac{2N^2 a}{V}$$

$$H(\tau, p) = \frac{5}{2}N\tau + Nbp - \frac{2Nap}{\tau}$$

All results are given to first order in the van der Waals correction terms a, b.

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Solution

a) The Helmholtz free energy for a van der Waals gas is

$$F = -N\tau\left(\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 1\right) - \frac{N^2a}{V}$$

We can find the entropy by differentiating this with respect to the temperature to find

$$\sigma = -\frac{\partial F}{\partial \tau} = N\left(\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 1\right) + N\tau\frac{\partial}{\partial \tau}\left(\ln\left(\tau^{3/2}\right)\right)$$

$$= N\left(\ln\left(\frac{n_q(V - Nb)}{N}\right) + 1\right) + \frac{3N}{2}$$

$$= N\left(\ln\left(\frac{n_q(V - Nb)}{N}\right) + \frac{5}{2}\right)$$

b) We know that $U = \sigma\tau$ so

$$U - F + \sigma\tau$$

$$= -N\tau\left(\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 1\right) - \frac{N^2a}{V} + N\tau\left(\ln\left(\frac{n_Q(V - Nb)}{N}\right) + \frac{5}{2}\right)$$

$$U = \frac{3N\tau}{2} - \frac{N^2a}{V}$$

c) We will first need to pressure which can be found by differentiating the Helmholtz free energy by its volume.

$$p = -\frac{\partial F}{\partial V} = \frac{N\tau}{V - Nb} - \frac{N^2a}{V^2}$$

We can multiply this by V and add it to U to get

$$H = \frac{3N\tau}{2} - \frac{N^2a}{V} + \frac{N\tau V}{V - Nb} - \frac{N^2A}{V}$$

$$= \frac{3N\tau}{2} - \frac{2N^2a}{V} + \frac{N\tau}{1 - \frac{Nb}{V}}$$

We can Taylor expand that third term and ignore all terms of second order or higher to get

$$H(\tau, V) = \frac{5N\tau}{2} - \frac{2N^2a}{V} + \frac{N^2\tau b}{V}$$

$$H(\tau, p) = \frac{5N\tau}{2} - \frac{2Nap}{\tau} + Nbp$$

The last of which was found using

$$pV = N\tau$$

Problem 3: Calculation of dT/dp for Water (Kittel 10.2)

Calculate from the vapor pressure equation the value of dT/dp near $p = 1$ atm for the liquid-vapor equilibrium of water. The heat of vaporization at 100°C is 2260 J/g. Express the result in kelvin/atm.

Solution

The vapor pressure equation is

$$\frac{dp}{d\tau} = \frac{L}{\tau \Delta v} \approx \frac{Lp}{\tau^2} = \frac{1}{k}\frac{dp}{dT}$$

which leads us to

$$\frac{dp}{dT} = \frac{Lp}{kT^2}$$

This only deals with on molecule of water, but we want it in terms of moles so we need it in the form of

$$\frac{dp}{dT} = \frac{Lp}{RT^2}$$

Plugging in our values gives us

$$\frac{dp}{dT} \approx 0.035 \text{ atm/K}$$

or

$$\frac{dT}{dp} = 28.4 \text{ K/atm}$$

Problem 4: Heat of Vaporization of Ice (Kittel 10.3)

The pressure of water vapor over ice is 3.88 mmHg at -2°C and 4.58 mmHg at 0°C. Estimate in J/mol the heat of vaporization of ice at -1°C.

Solution

We can start off with the differential equation from the previous problem

$$\frac{dp}{dT} = \frac{pL}{RT^2}$$

We can integrate over both sides to get

$$L\frac{1}{T}\bigg|_{T_l}^{T_h} = R\ln(p)\big|_{p_h}^{p_l}$$

This gives us

$$L = R\frac{\ln\left(\frac{p_l}{p_h}\right)}{\frac{1}{T_h} - \frac{1}{T_l}}$$

Using l as the subscript for the lower temperature values and the subscript h for the higher temperature values. Plugging in our values gives us

$$L = 5.1 \times 10^4 \text{ J/mol}$$

Problem 5: Structure of the Gibbs Free Energy in the Liquid Gas Transition

a) Obtain the Gibbs free energy of a Van der Waals gas $G(P, \hat{T}, N, \hat{v})$ as a Legendre transform of the Helmholtz free energy derived in class (here $v = V/N$). For convenience I asked you to write it as a function of the scaled variables $\hat{T} = T/T_C$, $\hat{P} = P/P_c$, $\hat{v} = v/v_c$. The result you get should be of the form:

$$G(P, \hat{T}, N, \hat{v}) = AN\hat{\mu}(\hat{P}, \hat{T}, \hat{v})$$

where the function $\hat{\mu}(\hat{P}, \hat{T}, \hat{v})$ is independent of the parameters a and b. All the dependence on these parameters are in the unimportant scale factor of A.

Recall that at equilibrium G should only be a function of the externally imposed P, T, and N. The additional variable v adjusts by itself to minimize G. You will now plot G in various situations to see where the minima occur.

b) Choose some fixed temperature below T_C (e.g. $\hat{T} = 1/2$). Now produce computer plots of G versus v for three different values of pressure (i) a pressure a bit above the boiling point for the chosen T, (ii) approximately at the boiling point, (iii) a bit below the boiling point. On your plots (i) and (iii) indicate where is the meta stable state and where is the globally stable state (indicating for each one if it is a gas or a liquid). Similarly, mark the the unstable equilibrium state. In these plots, I suggest to scale the y-axis by AN, so that you actually plot the function $\hat{\mu}$ versus $\hat{v}$, which does not depend on the parameters a and b.

c) Make two other plots of G (or $\hat{\mu}$) versus $\hat{v}$ at the same temperature as above, but at pressures sufficiently below the boiling point, so that there is no meta-stable state.

d) Explore the behavior of G versus $\hat{v}$ close to the critical point. Show on plot for T a bit below T_c for $P = P_c$ ($\hat{P} = 1$) and on plot a bit above T_c for $P = P_c$.

Solution

a) We can start with the Helmholtz free energy of a van der Waals gas.

$$F = -N\tau(\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 1) - \frac{N^2 a}{V}$$

The Gibbs free energy is then

$$G = F + pV = -N\tau(\ln\left(\frac{n_Q(V - Nb)}{N}\right) + 1) - \frac{N^2 a}{V} + pV$$

Plugging in our reduced variables gives us

$$G = -N\frac{8a\hat{T}}{27b}(\ln(3\hat{v} - 1) + 1) - \frac{Na}{3b\hat{v}} + \frac{Na\hat{p}\hat{v}}{9b}$$

$$= AN\left(\frac{8\hat{T}}{27}(\ln(3\hat{v} - 1) + 1) + \frac{1}{3\hat{v}} - \frac{\hat{p}\hat{v}}{9}\right)$$

b) Plotting our curves gives us
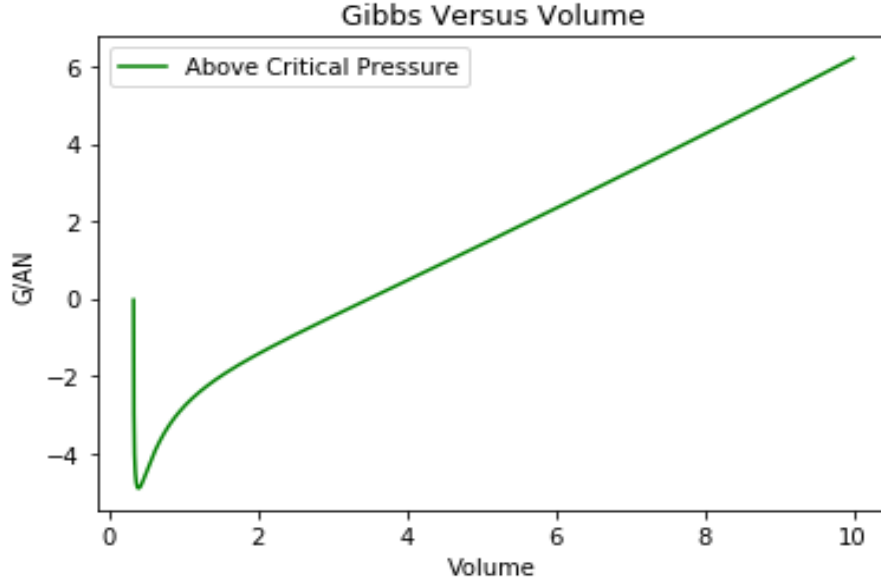
Figure 5: Problem 9.5.b.i
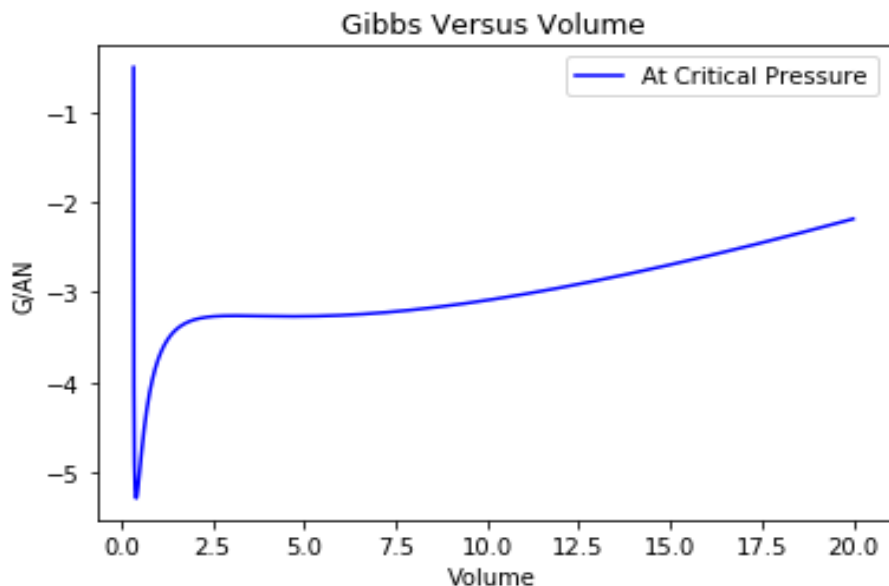
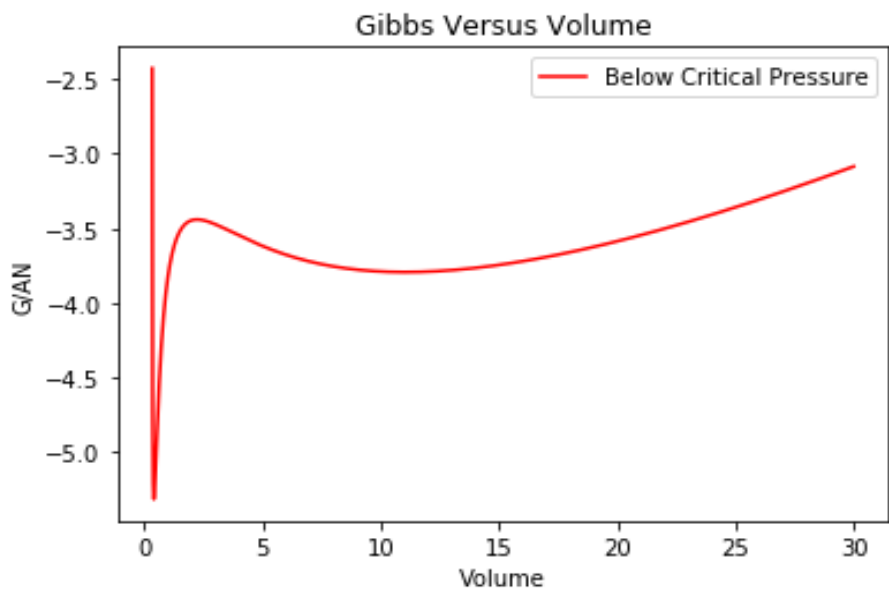Figure 6: Problem 9.5.b.ii

Figure 7: Problem 9.5.b.iii

As we can see, there are stable equilibrium for all curves at about $\hat{v} = 0.3$. Above the critical pressure yields no extra equilibria. At critical pressure, we have a metastable

equilibrium at around $\hat{v} = 3.5$ since it is an inflection point. At below the ciritical pressure, we get an unstable equilibrium at about $\hat{v} = 3$ and an extra stable equilibrium at about $\hat{v} = 11$.
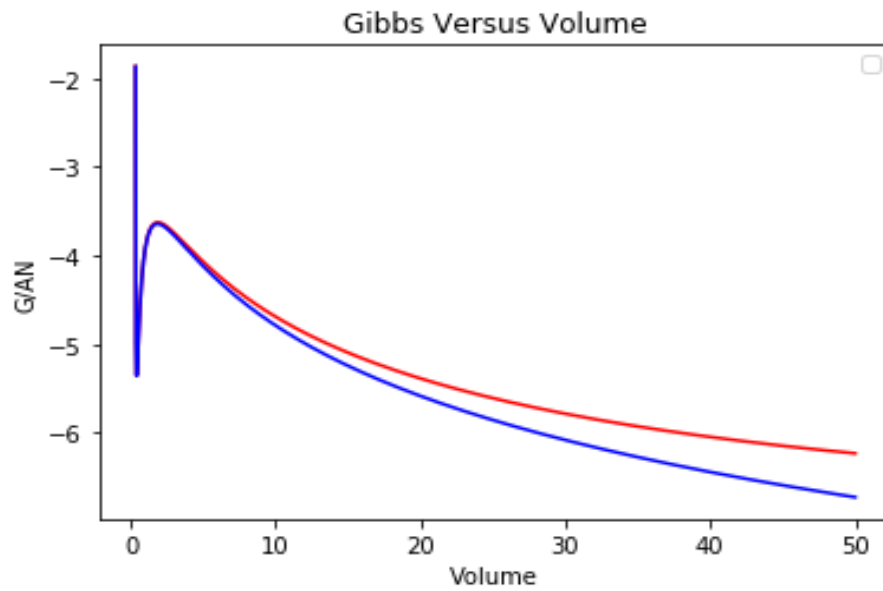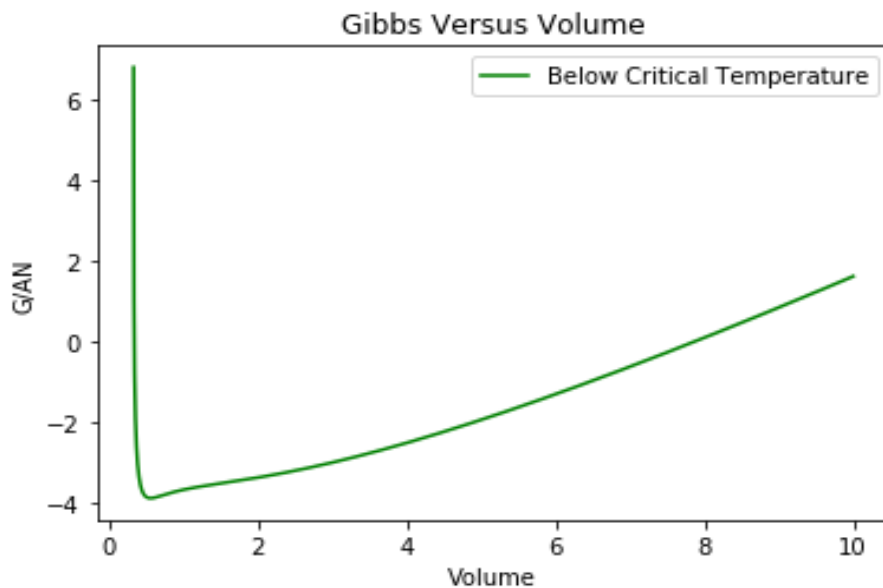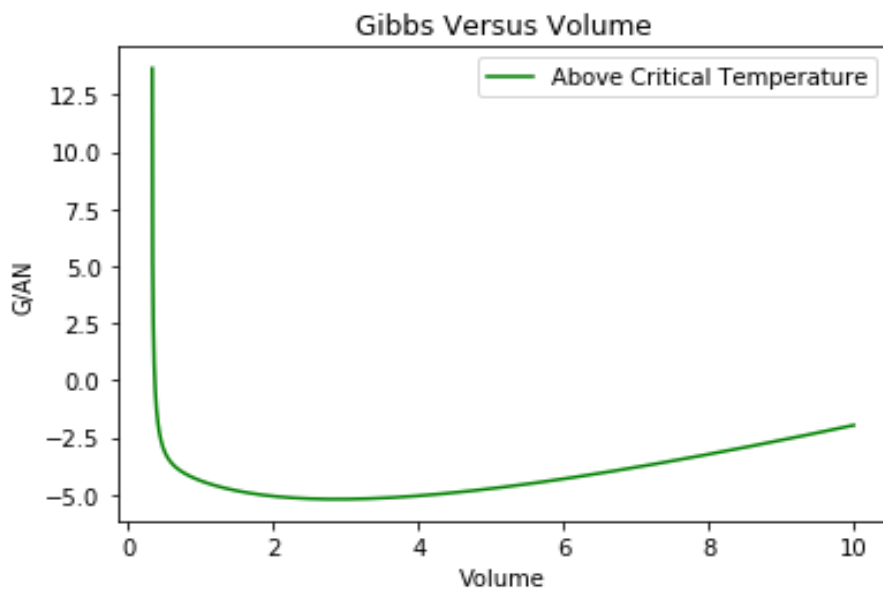
c)

Figure 8: Problem 9.5.c.

d)

Figure 9: Problem 9.5.d.i.

Figure 10: Problem 9.5.d.ii.