Reading:
1. Finish reading Fermi Chapter 4, pages 63-75. This section covers some examples of phase transitions, particularly the Clausius-Clapyron equation and the Van der Waals Eq. of State. Both are useful in the problems below.
2. Fermi Chapter 5, Thermodynamic Potentials. Read this as preparation for lectures to come.
3. Goodstein Section 1.2, part b), page 13 to 19. This section discusses the use of thermodynamic potentials for relating various partial derivatives. The section is a good backup to Fermi’s discussion (but very brief).

Comments:
At this point in the course, we very nearly have all the basic formalism in place to crank out results on any thermodynamic problem. We now know about the two fundamental functions of state, the internal energy, $U$, and the entropy, $S$, and we know about the 0th, 1st, and 2nd Law of thermodynamics.

The basic data which we require for solving actual problems are the Eqs. of State for any pair of work variables e.g., PV or HM, and the heat capacities along at least one special line, for each of the work pairs (see problem 1 below and related discussion in Goodstein for superconductors pages 39-41).

We are still missing a great deal of experience. Perhaps the most difficult part of the formal use of thermodynamics comes when we begin using partial differentials. Fermi has already used the mathematics of partial differentials several times; we will find that we run into arguments based on the nature of partial differentials quite often from here out. Some of the results are used so often that then have special names (keep your eyes peeled for the Maxwell Relations as we go on).

In this problem set, we consider some arguments which save us some work in calculations and we consider equations of state for various phases of matter beyond the ideal gas. In Problem 2, we investigate solid materials. Problem 3 covers the Van der Waals liquid-gas equation of state (much of this is discussed in Fermi Chapter 4) and Problem 4 touches on the phase transition for superconductors.

In each of these systems, the equation of state and/or the heat capacity can be more complicated than for the ideal gas which we have considered extensively. Our goal here is to use classical thermodynamics to relate the heat capacities and equations of state to general system behavior.
Problems:

1. Relationship between heat capacities.

One of the major goals in classical thermodynamics is to determine the minimum amount of experimental data necessary to determine the behavior of equilibrium systems in various situations. First, our calculations have required that we know (either experimentally or by some theory) the Equation of State, so that work can be calculated for various reversible paths. Second, we have required the Heat Capacities at constant volume and constant pressure. \( C_V \) and \( C_P \) are used along with the Eq. of State to help us calculate the internal energy change for the system. Then, once we know \( \Delta U \), we can calculate works and heats for any experimental situation. Similarly, the heat capacities are used in determining the entropy change, \( \Delta S \), so that spontaneous changes can be predicted.

Our goal in this problem is to show that we actually only need to know the Eq. of State and one of the two heat capacities. Once we know either of them, the other can be determined by general considerations. Here, we consider a PV system and the heat capacities \( C_V \) and \( C_P \). However, the results are easily extended to the case of more complicated systems (see Problem 4 below).

a) Use the fact that \( S \) is a function of state of the particular independent thermodynamic variables to write down equations for the total differential, \( dS \), under the conditions that \( S=S(V,T) \) and \( S=S(P,T) \). Then, use the fact that \( dQ=TdS \) along with the definition of the heat capacities to show that:

\[
C_V = T \left( \frac{\partial S}{\partial T} \right)_V \quad \text{and} \quad C_P = T \left( \frac{\partial S}{\partial T} \right)_P
\]

b) Now, our goal is to relate these two results to show that once you know the Eq. of State and the result for one of the partial derivatives above, then you can calculate the other. To do this, we begin by making use of the chain rule. For example, start with the equation from part a) for the total differential of the entropy assuming that it is a function of \( V \) and \( T \):

\[
dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV
\]

Then assume that you know the Eq. of State in the form \( V(P,T) \) and rewrite the total differential in terms of changes \( dT \) and \( dP \). Equate your result with the formal total differential from part a) to show that:

\[
C_P = C_V + T \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial V}{\partial T} \right)_T
\]

c) This result shows that the two heat capacities are related to each other. They are equal, but for the second term which depends upon a partial derivative of the
entropy function times another partial derivative which is calculated from the Eq.
of State. Our goal now is to show that the entropy partial can also be determined
from the Eq. of State! This result is typical of many that we will find as we go on,
namely, that many quantities which at first glance appear to be very difficult to get
experimentally, like changes in entropy with whatever, can be related to easily
measured changes of pressure or volume. The steps used next are typical of the
kind of argument:

First, again write down the total differential, \(dS\), for \(S=S(V,T)\). Next, write down
the total differential for the internal energy, \(dU\), for \(U=U(V,T)\) and use the 1st Law
to show that:

\[
\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V \quad \text{and} \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]
\]

Then apply the property of smooth functions, Fermi Eq. (83) to the second
derivatives of the entropy to show that:

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

This result is one of the so-called Maxwell relations that connect difficult to
measure quantities with easily measured ones. Then, show that:

\[
C_p = C_v + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p
\]

Thus, once we know the Eq. of State and \(C_v\), we can calculate \(C_p\). Generally, we
only need to have experimental data for one or the other heat capacity, not both.
This style of argument, based on total differentials and smoothness, is common.

2. Thermodynamics of solids.

As a change of pace from the ideal gas, let’s consider the case of solids. Many solids
are reasonably well described by the equation of state:

\[
V = V_0 \left(1 + \beta T - \kappa P\right)
\]

Here, the coefficients \(\beta\) and \(\kappa\), respectively referred to as the thermal expansion
coefficient and the isothermal compressibility, are themselves weak functions of
temperature, but for many materials, they can be approximated by constant values. It is
observed experimentally that \(\beta\) may be of either sign, but that \(\kappa\) is always found to be a
positive quantity for equilibrium systems.

Also, as long as the temperature is higher than roughly 150 K then, the heat capacity
of a solid at constant volume is approximately:
When investigating solids, we usually have a piece of the material which we investigate at fixed temperature and pressure. Thus, the independent variables for this problem are $P$ and $T$.

**a.** Imagine that you find a solid which has a negative value of $\kappa$. Think for awhile and then describe in words whether this type of material is a thermodynamic equilibrium state of matter or not. Be specific about why or why not. Try to think of an experiment you could do to test your opinions.

**b.** Use your results from Problem 1 to calculate $C_P$. What does the restriction on the sign of $\kappa$ imply for the relationship between $C_V$ and $C_P$? What does this relationship imply for the amount of heat required during isochoric vs. isobaric transitions?

**c.** Compare the value of $C_V$ above to that for the ideal gas. Fermi Eq. (29) shows that there is a term in the ideal gas internal energy function which goes as $C_V T$. There is an identical term for the solid's internal energy which dominates the temperature dependence of most materials near room temperature. Use the Equipartition Theorem (see the class notes) to determine the number of dynamical degrees of freedom (variables needed to describe the motion of the atom) per atom in the solid. Can you list what they are?

### 3. Van der Waals Equation of State.

One of the earliest efforts at predicting an equation of state from the atomic theory of matter was produced by Van der Waals for the case of liquids and gases. His equation can be written in a way which is suggestive of the ideal gas equation of state $PV=Nk_B T$. The Van der Waals equation is:

$$
(P + \frac{aN^2}{V^2}) (V - bN) = Nk_B T
$$

where $a$ and $b$ are constants which characterize the particular gas-liquid system. This equation can be arrived at from the ideal gas law by noting two facts about real gases and liquids: First, real atoms have a finite size. Second, the atoms have attractive interactions. Thus, rather than having the entire volume to inhabit, a gas molecule finds that $V$ is reduced somewhat due to the volume occupied by the other particles. In other words, $V \rightarrow (V - bN)$ where $b$ is the volume occupied by a single molecule. The $aN^2/N^2$ term causes $P$ to be smaller than it would be for the ideal gas due to the energy a molecule must use to escape the attractive potential of the others and cause outward pressure. Notice that my versions of the constants $a$ and $b$ are a bit different from Fermi's; mine are intended to reflect properties per atom, rather than per mole.
Fermi discusses the Van der Waals equation rather extensively in Chapter 4. He includes much of the physical discussion above and shows plots of the Eq. of State. Goodstein also shows a P-V plot of the van der Waals equation on page 446. The discussion below is intended to expand a bit on Fermi’s discussion.

As described in Fermi, the equation was designed by Van der Waals to be a correction to the ideal gas law (and it is), but it also predicts the appearance of a liquid phase. The general isotherm on the P-V plane shows both a local minimum and maximum where \( \left( \frac{\partial^2 P}{\partial V^2} \right)_T = 0 \) between these points, the system is unstable to gas-liquid phase separation. On one of the isotherms, at temperature \( T_c \), the two points occur at the same place, labeled as \( P_c \) and \( V_c \), where \( \left( \frac{\partial^2 P}{\partial V^2} \right)_T = 0 \) also.

a. Verify Fermi’s Equation (100) for the relationship between the critical values and the constants \( a \) and \( b \). Note that your results will be slightly different due to my different definition of the Eq. of State. Then, invert the equations to express \( a \) and \( b \) in terms of \( T_c \) and \( v_c = V_c/N \).

b. Express \( P_c \) in terms of \( T_c \) and \( v_c \).

c. Use the results from Problem Set 1 for the critical pressures and temperatures of the noble gases to produce a list of values for the constants \( a \) and \( b \) for each of these elements. Make a list of the values and convert these numbers to tell me the predicted radii of each atom and the typical interaction energy. Compare the predicted radii to actual data from somewhere (and reference it). (Extra Credit: Find some potential energy curves for the interaction between the noble gases. Do some backup reading in Kittel and Kroemer, say around page 287, to relate the value of \( a \) to the attractive potential between atoms. Compare your estimate of the interaction energy obtained from the experimental values of \( a \) to the actual attractive potential.)

d. Rewrite the van der Waals equation in terms of ‘reduced’ quantities \( t = T/T_c \), \( p = P/P_c \) and \( v = V/V_c \). Use Mathematica to plot your result on a p-v plane for several different reduced temperatures including \( t_c = 1 \).
Problem 1) Relationship between heat capacities.

There were several points to this problem. The first is that only the heat capacity (either one) and the Equation of State are required to integrate to find either of the basic functions of state, $U$ or $S$. The second point is that most of the manipulations which you use to solve the problem are common dodges for solving more general problems. For example, the trick used in part b) where we use $V(P,T)$ to rewrite a differential is a sneaky approach used frequently.

We will not pursue nearly as many of these formal partial derivative proofs as we would in a pure thermo class. However, it is important to see how a few of them work. Our approach will be to do the few which are necessary to show the most fundamental interrelations.

If we did happen to want to do more of these (some people love pain), then the Four Famous Formulae which I introduced in class are most important in streamlining the arguments. As an example, remember that one of the four formulae looked like this:

$$
\left( \frac{\partial x}{\partial y} \right)_w = \left( \frac{\partial x}{\partial y} \right)_z + \left( \frac{\partial x}{\partial z} \right)_y \frac{\partial y}{\partial z} \left( \frac{\partial z}{\partial y} \right)_w
$$

If you make the substitutions: $x=S$, $y=T$, $z=V$, and $W=P$, then we can immediately read off the result from part b):

$$
T \left( \frac{\partial S}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_V + T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p
$$

The FFFs don't really tell us anything new, but they often save us lots of formalism. Also, you notice that the FFFs don't get us to the final result. For that, you have to prove the equality between some obscure entropy derivative and a simple pressure derivative. As we shall see in class and in the reading, there is a second bag of tricks, referred to as the Maxwell Relations, which provide such derivative exchanges. There are again four basic Maxwell Relations (for PVT systems) and we prove one of them to finish this problem. However, once you have all four, they turn out to be really useful.

OK, so let's continue with the problem as given:
a) **Show how** $C_p$ and $C_v$ **are related to entropy derivatives.**

The relations proven in this part are often taken as basic definitions of the heat capacities. In many books, you will see the heat capacities only after the 2nd Law discussion. Here, we aim to take the experimental definition in terms of heat exchange, $dQ$, and temperature change, $dT$, and show how they relate to entropy changes. The arguments for both heat capacities are essentially identical. Following the suggested chain of reasoning we find:

$$
\begin{align*}
S(V,T) & \\
 dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\
S(P,T) & \\
 dS &= \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \\
\end{align*}
$$

but the heat is just $dQ=TdS$ so we have:

$$
\begin{align*}
 dQ &= T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV \\
C_v &= \left(\frac{dQ}{dT}\right)_V \\
C_v &= T \left(\frac{\partial S}{\partial T}\right)_V \\
C_p &= \left(\frac{dQ}{dT}\right)_P \\
C_p &= T \left(\frac{\partial S}{\partial T}\right)_P \\
\end{align*}
$$

As I said, these two final results are often taken as the fundamental definitions, but I prefer the ones in terms of heat.

b) **Work hard to do the job of one of the FFFs:**

In the intro to this problem, I showed how to get this the easy way, but one runs a risk with using the FFFs in that the arguments don't always appear to be transparent. Here's how you do it in a more direct way. The idea is to relate the two heat capacities through their definitions in terms of entropy. My suggestion is to start with the entropy vs. volume and temperature:
\[ dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV \]

The name of the game is to relate the quantities which depend upon volume and temperature to those which depend upon pressure and temperature so that we get a relation between \( C_p \) and \( C_v \). It is worth saying that these things get easier with practice, but a common trick is to rewrite the differentials by changing the "d-independent variable" of one to the "d-independent variable" of the other. In this case, if we change the \( dV \) to some mess of \( dP \) and \( dT \), we can rewrite \( dS(V,T) \) and compare it to the \( dS(P,T) \). This approach often yields interesting equalities.

OK, so given the equation of state, we can write down some form for the volume as a function of pressure and temperature, say \( V(P,T) \). Then,

\[ dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP \]

Plug this turkey into the \( dS(V,T) \) differential and we find:

\[ dS = \left[ \left( \frac{\partial S}{\partial T} \right)_V + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \right] dT + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T dP \]

Now here, we have a differential for entropy in terms of changes in pressure and temperature. If we equate terms with the formal differential for entropy with respect to pressure and temperature from part a), we find that the temperature term (multiplied by temperature) immediately yields the desired result:

\[ C_p = C_v + T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \]

As a bonus, which we don't use in this problem, we find that for a PVT system, the chain-rule for entropy works i.e.,

\[ \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial P} \right)_T \]

As I said, sometimes we the results we find are important and sometimes they are mundane.
c) Prove one of the Maxwell Relations

To finish the problem, we go after a modification of the b) result. Recall that our goal is to show that all we need is one heat capacity and the Eq. of State, to calculate the internal energy and entropy. The result in b) is almost there, except that there is an ugly entropy derivative.

The realization that we can get rid of this derivative in terms of one from the Eq. of State represents one of the great intellectual break-throughs of 19th century physics; we celebrate the magnitude of the achievement by naming the result for its inventor, J. Clerk Maxwell. Maxwell's accomplishments in electrodynamics are well known to most of you, but he made equally important contributions to thermodynamics and statistical mechanics. Einstein traced many of his inspirations in both relativity and in statistical mechanics to early arguments by Maxwell.

Our aim here is to prove one of the four Maxwell Relations. The others follow quickly once we have introduced the thermodynamic potentials. All of the Maxwell Relations are derived by looking at the second derivatives of the thermodynamic potentials and insisting that they are independent of order of differentiation.

Here's how this one works: Start with the equation from part a) for the heat differential:

\[ dQ = T \left( \frac{\partial S}{\partial T} \right)_V dT + T \left( \frac{\partial S}{\partial V} \right)_T dV \]

Next, recall from the 1st Law, that:

\[ dU = dQ - P dV \]

\[ = T \left( \frac{\partial S}{\partial T} \right)_V dT + \left[ T \left( \frac{\partial S}{\partial V} \right)_T - P \right] dV \]

However, we also know that the perfect differential of the internal energy is just:

\[ dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \]

so that we immediately find the pair of results:

\[ \left( \frac{\partial S}{\partial T} \right)_V = \frac{1}{T} \left( \frac{\partial U}{\partial T} \right)_V \quad \quad \left( \frac{\partial S}{\partial V} \right)_T = \frac{1}{T} \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] \]

The next step is to look at the second derivatives and insist that they are independent of order of differentiation. Remember, both the entropy and the internal energy have this property! So, we can rather quickly push through the results in parallel. First, take the appropriate cross derivatives of both sides:
If we equate the two entropy second derivatives, we have:
\[
\left( \frac{\partial}{\partial V} \left( \frac{\partial S}{\partial T} \right) \right)_T = \frac{1}{T} \left( \frac{\partial}{\partial V} \left( \frac{\partial U}{\partial T} \right) \right)_T = -\frac{1}{T^2} \left[ \left( \frac{\partial U}{\partial V} \right)_T + P \right] + \frac{1}{T} \left[ \left( \frac{\partial}{\partial T} \left( \frac{\partial U}{\partial V} \right)_T \right)_V + \left( \frac{\partial P}{\partial T} \right)_V \right]
\]

Recognizing the first bracket on the right as the entropy derivative with respect to volume and equating the two second derivatives of internal energy then leads immediately to the desired result:
\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V
\]

Plugging this relation into our result from b) completes the demonstration that once we know one heat capacity and the equation of state, then the other heat capacity can be calculated as:
\[
C_p = C_v + T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_p
\]
2. Thermodynamics of solids.

In this problem, we spend a little bit of time thinking about the thermodynamic description of the solid state. So far, we have played mostly with ideal gases. Some of the Fermi reading deals with non-ideal gases and liquids via the Van der Waals equation. In many cases, solids are rather well described as objects with a volume close to some basic volume, $V_0$, which can change volume slightly due to temperature and applied pressure. Then,

$$V = V_0 (1 + \beta T - \kappa P)$$

with the coefficients $\beta$ and $\kappa$, respectively referred to as the thermal expansion coefficient and the isothermal compressibility as described in the problem set. Again, both are weak functions of temperature (assumed constant here), $\beta$ may be of either sign, but $\kappa$ is always found to be a positive quantity for equilibrium systems.

AND, as long as the temperature is higher than roughly 150 K (so that quantum effects that we will consider later in the course can be neglected) then the heat capacity of a solid at constant volume is approximately:

$$C_v \approx 3 Nk_B$$

a) Why is $\kappa$ positive for equilibrium systems?

Perhaps a better question to ask is, "Why does a negative value of $\kappa$ imply that the solid is not in equilibrium?" To see why negative $\kappa$ is a disaster, think about finding an object with this type of compressibility (too bad for you):

Pick it up carefully. You are already in trouble, but let's imagine that you are dealing with a really small value of negative $\kappa$ so you don't know it yet. You want to investigate what happens as you apply pressure to the solid, so you go down to the machine shop and put the thing in a vise, and Clamp it....

The increased pressure on the object causes it to get bigger. The increase in volume causes the pressure from the fixed vise to increase. This causes the volume to get Bigger. The pressure goes up again, so the thing gets BIGGER... and

BIGGER...AND BIGGER...

BOOM!

Too bad you didn't get to publish. This result suggests that it was not an equilibrium solid, because when you poked it, it never came back to a nice equilibrium state.
There are many things you can find that behave in this way. For example, a brick of dynamite, or a jug full of mixed hydrogen and oxygen gas. Or perhaps you have seen superheated water in a microwave: You heat the water to a point above the boiling point. As soon as you touch the cup to take it out, the water leaps into ferocious boiling and expands suddenly. In most of these cases, the systems are metastable. For example, it is possible to poke dynamite gently and live. The superheated water is much more touchy. In each case, you can see that there is stored energy which is prevented from release by some type of energy barrier. However, if you ever get into the wrong region so that $\kappa$ is negative, the system is not going to come back.

b) $C_p$ and $C_v$ for solids.

From Problem 1, we have that:

$$C_p = C_v + T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p$$

From the equation of state, we have that:

$$P = -\frac{1}{\kappa} \left[ \left( \frac{V}{V_0} - 1 \right) - \beta T \right]$$

so that the required partial derivatives are just:

$$T \left( \frac{\partial P}{\partial T} \right)_v = \frac{\beta}{\kappa} T \quad \left( \frac{\partial V}{\partial T} \right)_p = \beta V_0$$

Plug and chug to find that:

$$C_p = 3Nk_B + \frac{\beta^2}{\kappa} V_0 T$$

Because all of the quantities in the second term are positive, it is apparent that the heat capacity at fixed pressure is always larger that the heat capacity at fixed volume.

Actually, this statement is general for equilibrium systems. Note that the requirement that compressibility be a positive quantity is generally true, independent of whether the system is solid or not. For the general system, the isothermal compressibility is defined as:
\[ \kappa_T \equiv -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \]

Similarly, the isobaric thermal expansion coefficient is more generally defined as:

\[ \beta_p = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \]

By doing some substitution and a bit of chain-ruling on the relation between the heat capacities (see for example Goodstein Eq. 1.2.108), we can show that in general,

\[ C_p - C_v = T \frac{\beta_p^2}{\kappa_T} V \]

so that \( C_p \) is always larger than \( C_v \), in equilibrium. Physically, what this says is that to raise the temperature at constant volume (isochoric heating) will require some amount of heat, but to raise the temperature by the same amount at constant pressure (isobaric heating) always requires more heat. The reason is that at constant pressure, we must add enough additional heat to do the work required to expand the material to its new volume.

c) **Equipartition Theorem for solids.**

The Equipartition Theorem says two things:

1. The internal energy will have a contribution for each atom of \( \frac{1}{2} k_B T \) for each dynamical degree of freedom for the atom.

2. The heat capacity at constant volume will have a contribution for each atom of \( \frac{1}{2} k_B \) for each dynamical degree of freedom for the atom.

The phrase 'dynamical degree of freedom' refers to the classical description of the motion of the atom. In the Lagrangian or the Hamiltonian which describes the motion of the atom, we will have a certain number of generalized coordinate and generalized velocities (for the Lagrangian formulation) or generalized momenta (for the Hamiltonian formulation). The coordinates and velocities/momenta are referred to as the dynamical degrees of freedom.

In the case of the ideal gas, there are no interaction potentials. Therefore, the Lagrangian and Hamiltonian only contain kinetic energy terms for each atom. Thus, there are three dynamical degrees of freedom for each atom (the three generalized velocity or momentum coordinates). Equipartition then says that we should expect \( \frac{1}{2} k_B T \) for each atom, in the internal energy, and \( \frac{1}{2} k_B \) per atom in the heat capacity at constant volume. Of course, these are just right for the ideal gas.
Now, in this problem, we don’t know the internal energy (yet, wait for PS 5), but we do know that the heat capacity is $3Nk_B$ or $3k_B$ per atom. From Equipartition, we see that there are predicted to be 6 dynamical degrees of freedom per atom in the solid.

What are they? Well, in a solid, the standard picture is that each atom is bound strongly to its nearest neighbors. This bonding makes the solid...Solid. OK, in the simplest picture, we think of each atom connected to its neighbors by springs. If you write down the Lagrangian of a mass connected by springs to the outside, you need 3 velocities or momenta for the kinetic energy terms and 3 generalized coordinates to describe the strength of the potential energy terms. Thus, you have 6 dynamical degrees of freedom.

3. Van der Waals Equation of State.

The Van der Waals equation of state was a breakthrough, developed by Johannes Diderik Van der Waals during his studies of gas-liquid coexistence. These studies eventually lead to his Nobel Prize in 1910. The equation remains interesting because it has parameters which come from a microscopic model, it is a simple analytical equation, and it actually does a pretty good job of describing the behavior of many real gases. Its prediction of a liquid state was a surprise to Van der Waals and makes the equation a good starting point in the description of phase transitions. The behavior that it predicts for liquids is not in as good agreement with experiment as is the case for the gases. The reason (see below) is that its description of the molecular interactions used in deriving the equation is very crude. Real liquids have properties which are sensitive to the details of the interactions. However, if there happened to be a material with the type of interactions (which I describe below) used in deriving the equation, it would behave much more like a Van der Waals liquid.

a) Solving for $a$ and $b$ via the critical point.

Mostly, everyone was able to trace the arguments in Fermi to verify his Eq. (100). My preferred approach is to note that the since the first two derivatives of pressure with respect to volume are zero at $T_C$, then we have two equations for the two unknowns, $a$ and $b$:

$$
\left( \frac{\partial P}{\partial V} \right)_{T_C} = -\frac{Nk_BT_C}{(V_C-bN)^2} - \frac{2aN^2}{V_C^2} = 0
$$

$$
\left( \frac{\partial^2 P}{\partial V^2} \right)_{T_C} = \frac{2Nk_BT_C}{(V_C-bN)^3} + \frac{6aN^2}{V_C^4} = 0
$$

Solve the first equation for $a$ to find that:
Plug into the second equation and solve for $b$. Then plug $b$ back into our result for $a$, and we are done. The results are:

$$a = \frac{V_c^3}{2N^2} \frac{Nk_BT_c}{(V_c - bN)^2}$$

In the result for $b$, I have defined the volume at the critical point per unit atom, $v_c$. Notice that in the original equation, the $b$ parameter was due to the finite volume occupied by an atom of the material. The equation then predicts that, as the volume is reduced, when it reaches three times the basic atomic volume, the material will reach the critical point (assuming we are on the critical isotherm). More about this below.

b) Relating the critical point parameters.

From a purely experimental point of view, it is not immediately obvious that the pressure, temperature and volume at which the critical point occurs are necessarily related. However, data from the noble gases indeed suggests, via the Law of Corresponding States (again, Van der Waals' invention which we saw in Problem Set 1) that they often are related. The Van der Waals equation provides a simple model in which we can investigate why.

In part a), we inverted the equation and solved for the two adjustable parameters, $a$ and $b$, in a way which allows us to fit the equation to actual data: Once we know the value of the critical temperature, the number of atoms, and the critical volume, then we have our $a$ and $b$ values. Then, the equation makes an actual prediction for the critical pressure. To see this, rewrite the equation to solve for the pressure:

$$P = \frac{Nk_BT}{(V-bN)} - \frac{aN^2}{V^2}$$

First, you can plug in the values of $a$ and $b$. Then, evaluate the equation at $T=T_c$ and $V=V_c$ to find the prediction:

$$P_c = \frac{3Nk_BT_c}{8V_c} = \frac{3k_BT_c}{8v_c}$$

There are two things to notice here:

1. Notice how much this result looks like the ideal gas equation of state. In fact, it would have been hard (impossible) to find any other combination of the basic parameters with units of pressure. However, the important point is the factor...
of 3/8 in front. It shows explicitly that the Van der Waals gas will be at a lower pressure than the ideal gas for a given \( N \), \( T \) and \( V \). This fact is due to the assumed atomic attractive potentials (see below).

2. Of course, we actually turn this critical pressure result upside down: In experiments, it is easiest to measure the critical temperature and pressure. We don't really know the 'size of atoms' in a gas. In fact, the modern concept of 'size' is rather complicated and depends upon the situation. However, once we know the critical pressure and temperature, then the Van der Waals equation allows us to determine \( v_c \) and, via the \( b \) parameter, a quantity referred to as the Van der Waals radius, an approximate radius for the atom. We'll do this in (c) below.

Let's just press here a bit longer and think about how physics is actually done. The result provides a rough tool for the experimentalist to investigate the atomic theory of matter: Suppose that you are Van der Waals, or a colleague who is interested in the work. It is the end of the 19th century, so nobody has a good idea about the size of Avogadro's number. This is a problem, because without a feeling for the number of atoms per mole, there is no way to calculate \( N \) for a given number of grams of material. Therefore, it is hard to figure out how to test the Van der Waals' prediction. You could toy with whether Van der Waals' work allows you to measure Avogadro's number, but without a known radius of the atoms, you are out of luck. Eventually, you get peeved and decide that you ought to be able to say something, so it strikes you that you could assume something and see what happens:

Suppose you assume that all atoms are roughly the same size. Then, the result above says that the critical pressure and the critical temperature should scale linearly with each other across all the known gas-liquid systems. Now we're talking! This kind of global prediction is worth a test. Let's take the data for the noble gases from Problem Set 1 and see how things go.

First, we collect the data. For the nobles, we have:

<table>
<thead>
<tr>
<th>Element</th>
<th>( P_{\text{crit}}(10^5 \text{Pa}) )</th>
<th>( T_{\text{crit}}(\text{K}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>26.2</td>
<td>44.4</td>
</tr>
<tr>
<td>Ar</td>
<td>48.6</td>
<td>151</td>
</tr>
<tr>
<td>Kr</td>
<td>55</td>
<td>210</td>
</tr>
<tr>
<td>Xe</td>
<td>58.9</td>
<td>290</td>
</tr>
</tbody>
</table>
Now let's do the plot. Here is the Mathematica code to plot it up:

```mathematica
pctclist = {{0, 0}, {44.4, 2.62}, {151, 4.86}, {210, 5.5}, {290, 5.89}};

ListPlot[pctclist,
  AxesOrigin -> {0, 0},
  Frame -> True,
  FrameLabel -> {"Tc", "Pc(MPa)"},
  Ticks -> Automatic]
```

Well, it doesn't look very linear... SO there's noting for it but to deduce that within the atomic picture, the size of atoms must vary. We press on to see what the equation says regarding the size and hope for more experiments with which to cross correlate the results.

c) Van der Waals radius and atomic interaction energies.

i) RADIUS

Let's assume that the atoms are spherical. Then, the volume of an atom is related to its radius by:

\[ V_{\text{atom}} = b = \frac{4}{3} \pi r^3 \]

or
\[ r = \left( \frac{3b}{4\pi} \right)^{\frac{1}{3}} \]

From our result for the critical pressure, we see that:

\[ P_c = \frac{3}{8} \frac{k_b T_c}{v_c} = \frac{1}{8} \frac{k_b T_c}{b} \]

or that, solving for \( b \), the Van der Waals radius becomes:

\[ r_{VDW} = \left( \frac{3k_b T_c}{32\pi P_c} \right)^{\frac{1}{3}} \]

Here are the results we find:

<table>
<thead>
<tr>
<th>Element</th>
<th>( P_{crit} )(10^5 Pa)</th>
<th>( T_{crit} )(K)</th>
<th>( r_{VDW} )(nm)</th>
<th>( r_{solid} )(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ne</td>
<td>26.2</td>
<td>44.4</td>
<td>0.191</td>
<td>0.222</td>
</tr>
<tr>
<td>Ar</td>
<td>48.6</td>
<td>151</td>
<td>0.234</td>
<td>0.265</td>
</tr>
<tr>
<td>Kr</td>
<td>55</td>
<td>210</td>
<td>0.251</td>
<td>0.286</td>
</tr>
<tr>
<td>Xe</td>
<td>58.9</td>
<td>290</td>
<td>0.273</td>
<td>0.310</td>
</tr>
</tbody>
</table>

The fourth column lists the radii deduced from X-ray measurements of the atomic spacing of the solid phases of each material (taken from Solid State Physics, by Neil Ashcroft and N. David Mermin). Notice that the trends are the same and that you can almost get one from the other with a fixed offset of 0.03 nm.

ii) INTERACTION ENERGY

The \( a \) term in the Van der Waals equation is somewhat more difficult to describe in a qualitative fashion. You have been told that it represents an effect due to the interactions between atoms, but to see why it is of the form seen in the equation requires a bit more analysis. Much of this analysis would be above the level of the course at this point (though not by the end). Goodstein discusses the origin of the term in Section 6.3, for those of you who would like a more complete description.

Qualitatively, you could reason like this: 1) I know that something interesting happens at the critical temperature. Below this temperature, if the atoms are squeezed into a sufficiently small volume, they form a liquid phase. 2) Formation
of the liquid phase means that the atoms no longer have the kinetic energy necessary to break loose from one another. 3) The only energy scale in the problem for describing this effect is $k_B T_c$. The kinetic energy at the critical point is some factor times $k_B T_c$. Similarly, the total interaction energy that a given atom feels is the sum of potentials from the atoms around it. AND this energy must be similar in magnitude to the kinetic energy at the critical point. Therefore, the interaction energy must also be some factor times $k_B T_c$. Any guess with this scale is OK with me.

c) **Scaled Van der Waals equation.**

In preparation for plotting any particular function, it is always useful to recast the function in terms of scaled variables. After all, the computer does not know anything about the units, so if you can choose meaningful scaled units, then your plot will usually show all the interesting behavior somewhere near unity in the scaled quantities.

To see this for the Van der Waals, let’s rewrite the equation in terms of the pressure, scaled by the critical pressure, the volume scaled by the critical volume, and temperature scaled by critical temperature. The dimensionless quantities are:

$$ p = \frac{P}{P_c}, \quad v = \frac{V}{V_c}, \quad t = \frac{T}{T_c} $$

If we stuff these into the equation, we can rewrite it as:

$$ P_c V_c \left( p + \frac{aN^2}{P_c V_c^2 v^2} \left( v - \frac{bN}{V_c} \right) \right) = N k_B T_c t $$

Plug in the value for $b$ and we get:

$$ \frac{P_c V_c}{N k_B T_c} \left( p + \frac{aN^2}{P_c V_c^2 v^2} \left( v - \frac{1}{3} \right) \right) = t $$

However, we already know that:

$$ \frac{P_c V_c}{N k_B T_c} = \frac{3}{8} \quad \text{and} \quad \frac{aN^2}{P_c V_c^2} = 3 $$

so the scaled equation becomes:
\[
\left( p + \frac{3}{v^2} \right) \left( v - \frac{1}{3} \right) = \frac{8}{3} t
\]

The plotting of this equation is then straight-forward, but many of you had difficulty understanding the results. Here is the Mathematica notebook I prepared for the plotting: