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:

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

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:
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\[ C_V = 3 N k_B \]

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 \( PV = N k_B T \). The Van der Waals equation is:

\[
\left( P + \frac{a N^2}{V^2} \right) (V - bN) = N k_B T
\]

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, \( V \to (V - bN) \) where \( b \) is the volume occupied by a single molecule. The \( aN^2/V^2 \) 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 \( \left( \frac{\partial P}{\partial V} \right)_T = 0 \) 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 \( t_c = 1 \).