Reading:
1. Fermi Chapter 5, Thermodynamic potentials. Finish reading this chapter.
2. Start plowing through the first chapter of Kittel and Kroemer.
3. Goodstein Section 1.2, parts b) through f), page 13 to 41. These sections cover the basic structure of classical thermodynamics which we will use as a target for our statistical arguments. Pay particular attention to the thermodynamic potentials and their proper variables.

Comments:

As you can tell, the reading is beginning to pull away from Fermi and move over to Kittel and Kroemer, and Goodstein. This move signals a redirection of the course from the nuts and bolts of calculating specific properties of thermal system, to a broader view of the formal structure of thermodynamics.

In lecture and in the reading, we are aiming at reaching a more general structure which we will then attempt to understand via the statistical properties of atoms and molecules. However, it is important to notice that this structure, based on functions of state like $U$ expressed in terms of its 'proper variables' $S$, $V$, and $N$, is still very much based on experimental observation. All of this formal structure follows from the 0th, 1st, and 2nd Laws i.e., it is profoundly experimental at the foundational level. Nothing in the microscopics prepares us for the fact that 'entropy increases'.

As an example, think about the derivation in class of the Euler Eq. for the internal energy:

$$U(S,V,N) = T(S,V,N)S - P(S,V,N)V + \mu(S,V,N)N$$

To get this result, we used two experimentally determined facts: 1) Internal energy is an extensive function of extensive variables. 2) The first partial derivatives of the internal energy with respect to each of the extensive variables yield only intensive quantities, $T$, -$P$, and $\mu$. Therefore, the Euler Eq. is constrained by experiment. We are only willing to consider internal energy functions which get the basic fact right. It is very important to recognize the extent to which we have insisted on building a function which will reproduce the experimental facts.

In this set, I ask you to work through the construction of the internal energy and entropy for two systems which you have worked with before. The first case is the ideal gas. The second is the solid, using the Eq. of State and heat capacity from Problem Set 4. In each case, you will exercise you thermodynamics formalism and will generate internal energy functions which we will try to understand statistically later in the course.
Problems:

1. Internal energy and entropy of solids.

On the last problem set, we considered the Eq. of State and the heat capacity of a typical solid. Again, for many solids, the Eq. of State looks like:

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

where, the coefficients \( \beta \) and \( \kappa \), are the thermal expansion coefficient and the isothermal compressibility. For this problem, assume that they are independent of temperature. Also, again assume that the heat capacity at constant volume is:

\[ C_v = 3 N k_B \]

a. Set up total differentials for the entropy and internal energy assuming that they are functions of \( V \) and \( T \). Use the Eq. of State and \( C_v \) to determine the coefficients in your total differentials. Explain how you can check whether these equations can be successfully integrated to yield functions of state. Verify, using this procedure, that your equations are going to work (at least in principle).

b. Now integrate your equations to find the internal energy and entropy as functions of \( V \) and \( T \). The reasoning here is similar to that used in Fermi 4.2 from Problem Set 3. However, this one will work.

c. Check your energy and entropy functions by taking the first partial derivatives with respect to \( T \) and \( V \). The temperature derivatives should yield things related only to \( C_v \). The volume derivatives can be compared with certain derivatives of the Eq. of State. Make the comparisons and verify that things are OK.

If you made it this far, you have gotten most of the experience which I would hope for, namely you have learned how to set up the differentials, check that they are going to work, and have then cranked out a result which can also be checked. At each step of this process, we have ways to stay on track. Remember how this works.

d. As an interesting fine point, look at your result for the internal energy as a function of the compressibility, \( \kappa \). For a hypothetical substance where \( \kappa = 0 \), what happens to your internal energy function and to your entropy function? (Hint: Something has gone horribly wrong.) From a physical point of view, we could say that there is always a finite compressibility (and hope that it is true). However, think about things from a mathematical viewpoint: What is the basic error in our calculation which leads to these crazy results?
2. \( U(S,V,N) \) for the ideal gas.

The ideal gas has often served as the first case to be considered anytime we have a new technique to play with. The ideal gas is popular in part because of the simplicity of the calculations and in part because it actually does a rather good job of describing the gaseous state of real matter. Our goal in this problem is to use the experimentally determined equation of state, \( PV = Nk_B T \), and heat capacity at constant volume, \( C_V \), to generate the energy function \( U(S,V,N) \) from which all other thermodynamic quantities can be determined.

In general, for a simple system of this type where \( V \) and \( T \) are the independent variables, the entropy should be \( S(V,T,N) \) and the internal energy should be \( U(V,T,N) \). Of course, the two functions must be related because the general arguments of classical thermodynamics tell us to expect to find an internal energy function \( U(S,V,N) \) from which all the system quantities including the equations of state can be determined via derivatives. Our goal in this problem is to find \( U(S,V,N) \) for the ideal gas as a simple example of the general case.

a. Under the general condition that \( U = U(V,T) \) and \( S = S(V,T) \), (we are ignoring the \( N \) dependence because we will hold \( N \) fixed) compare the formal total differential \( dS \) to the 1st Law equation:

\[
dS = \frac{1}{T} dU + \frac{P}{T} dV
\]

and show that:

\[
C_V \equiv T \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V
\]

and

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

The reasoning here is very much the same as from Problem 1 from Prob. Set 4, so this should be straight-forward.
b. The results from part a. can be used to integrate for the entropy function. First, for the ideal gas, we have seen that the heat capacity at constant volume is:

\[ C_V = \frac{3}{2} N k_B \]

*independent of volume.* Second, as a consequence \( U \) is independent of \( V \) for ideal gases. Use these facts and the results from part a. to integrate the total differential of \( S \). Show that:

\[ S = N k_B \ln \left( \frac{VT^{3/2}}{V_s T_s^{3/2}} \right) + S_s \]

where \( V_s, T_s \) and \( S_s \) are the temperature, volume and entropy at some standard condition. Invert the equation to find an expression for \( T(S,V,N) \). With this result, we have the first term of \( E=TS-PV+\mu N \) in terms of only \( S, V \) and \( N \).

c. Use the ideal gas equation of state and the results of part b. to express \( P(S,V,N) \). This gives us the second term for the energy.

d. If you consider the Euler equation (see Goodstein Eq. 1.2.34), \( U=TS-PV+\mu N \), which we also derived in class, then its total differential is written formally as \( dU=Tds+SdT-PdV+\mu dN+N\mu d \mu \). However, we also know from our arguments concerning heat and work that \( dE=Tds-PdV+\mu dN \). Thus, the remaining terms in the former equation must sum to zero. Therefore, we have a new equation typically referred to as the **Gibbs-Duhem equation** (also derived in class and in Goodstein Eq. 1.2.35). This is the equation which is usually applied to determine the chemical potential:

\[ d\mu = -\frac{S}{N} dT + \frac{V}{N} dP \]

Once we know \( S(T,P,N) \) and the equation of state which relates \( V \) and \( P \) then this equation can be integrated to get \( \mu \). Use the results above to show that:

\[ \mu = k_B T \ln \left[ e^{5/2} \frac{V_s T_s^{3/2}}{VT^{3/2}} \right] - T \frac{S_s}{N} \]

This result gives us the third term for \( U \).
e. Combine the results above in Euler's equation to show that the internal energy can be written as:

\[ U(S,V,N) = \frac{N\alpha_o}{V^{2/3}} e^{2S/3k_B N} \]

Write down a specific result for the constant \( \alpha_o \).

Now, recall that in class and in Fermi Eq. (29), we have seen that (aside from an arbitrary constant which I set to zero) the internal energy for an ideal gas is just given by \( U = C_V T \). Use the results of part b. for \( T(S,V,N) \) to show that this gives the same as the result we just derived by summing the terms of Euler's equation.

Thus, we could have avoided a good deal of trouble had we carefully determined that the internal energy for an ideal gas is simple enough that knowing temperature alone is sufficient to find the complete form of \( U(S,V,N) \)!

f. Demonstrate explicitly that the internal energy is extensive i.e., that:

\[ U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \]

When you do this part, think carefully about the constant \( \alpha_o \) from the standard state and how it scales with system size.

This problem is straight out of Goodstein. For those of you who don’t have Goodstein, I repeat the question here.

Use only the idea that the entropy is a function of energy, volume, and number of particles, $S(E,V,N)$, that the entropy increases for any process that can occur spontaneously, that it therefore is a maximum for any stable thermal equilibrium system, that entropy is proportional to the natural logarithm of the number of states available to the system, and the energy equation for the quantum energy levels of a particle in a box, to show the following:

a) Prove that a perfect gas in equilibrium must have uniform pressure and uniform chemical potential.

b) Show that for a perfect gas, $PV=\frac{2E}{3}$.

c) A system in either mechanical or thermodynamic equilibrium should resist changes. For example, a marble balanced on top of a sphere is not in equilibrium, since a small push will cause its state to change dramatically, and irreversibly, but a marble inside a spherical bowl is in equilibrium at the bottom. We have defined what we mean by equilibrium differently, however. Show that our definition of thermodynamic equilibrium, contained in supposition 1 on page 3, implies stability against small perturbations. Can the connection be made without using supposition 2?

Supposition 1: If we wait long enough, the initial conditions become irrelevant. This means that whatever the mechanism for changing state, however, the particles are able to redistribute energy and momentum among themselves, all memory of how the system started out must eventually get washed away by the multiplicity of possible events. When a system reaches this condition, it is said to be in equilibrium.

Supposition 2: For a system in equilibrium, all possible quantum states are equally likely. This second statement sounds like the absence of an assumption- It means, however, that a state in which all the particles have roughly the same energy has exactly the same probability as one in which most of the particles are nearly dead, and one particle goes buzzing madly about with most of the energy of the whole system. Would we not be better off assuming some more reasonable kind of behavior?