Thermal Physics

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Chapter 1

Spring 2018 Physics 441

Office hours David Roundy: TF 1-2, 401B Weniger (or possibly look for me in 477 Weniger) or upon request. My door is open when I’m in my office, and students are welcome to enter with questions.

Syllabus The syllabus is here.

Textbook Thermal Physics by Kittel and Kroemer. The textbook is not required, but the course will follow the text reasonably closely.

Course notes If you wish, you may download this entire website as an ebook, or as a PDF file.

Homework Homework will be due in class on Wednesday of each week (but not the first week of class). You should be able to start each homework the week before it is due. See the syllabus for details on homework grading. You may use the solutions (or any other resource you wish to use) but at the end of each problem, please cite what resources you used (students you worked with, whether you looked at the solutions, etc). Note that verbatim copying from any source is plagiarism. I recommend not using the solutions.

Introduction and course philosophy

This is your second course in thermal physics. Energy and Entropy took a thermodynamics-first approach, with primary emphasis on how you could measure something, and only later introducing how you could predict it. I strongly support this approach, but it is not the most common approach to thermal physics. I will teach this course in a more traditional order and approach, following the text of Kittel and Kroemer. This is the textbook that I used as an undergraduate. It’s an excellent book, but very much uses a more mathematical theory-first approach than I prefer.

Since this is now your second course in thermal physics, this should balance things out. With your Energy and Entropy background, you should be able to make physical connections with the math more easily. By organizing this course in this different way, I hope to broaden and deepen your understanding of thermal physics, while at the same time showing you a wide range of different physical systems.

Brief review of Energy and Entropy

Extensive/intensive (Schroeder 5.2)

If you consider two identical systems taken together (e.g. two cups of water, or two identical cubes of metal), each thermodynamic property either doubles or remains the same.

Extensive An extensive property, such as mass will double when you’ve got twice as much stuff.

Intensive An intensive property, such as density will be the same regardless of how much stuff you’ve got.
We care about extensivity and intensivity for several reasons. In one sense it functions like dimensions as a way to check our work. In another sense, it is a fundamental aspect of each measurable property, and once you are accustomed to this, you will feel very uncomfortable if you don’t know whether it is extensive or intensive.

**How to measure things**

**Volume** Measure dimensions and compute it. *(extensive)*

**Pressure** Force per area. Can equalize if systems can exchange volume. *(intensive) (Schroeder 1.2)*

**Temperature** Find something that depends on temperature, and calibrate it. Alternatively use an ideal gas. Equalizes when systems are in contact. *(intensive)*

**Energy** Challenging... measure work and heat (e.g. by measuring power into resistor). *(extensive)*

\[
W = - \int pdV \quad (1.1)
\]

**Entropy** *(extensive)* Measure heat for a quasistatic process and find

\[
\Delta S = \int \frac{dQ}{T} \quad (1.2)
\]

*(Schroeder 3.2)*

**Derivatives** Measure changes of one thing as the other changes, with the right stuff held fixed.

**First Law** *(Energy conservation, Schroeder 1.4)*

\[
dU = dQ + dW \quad (1.3)
\]

**Second Law** *(Entropy increases, Schroeder 2.3)*

\[
\Delta S_{\text{system}} + \Delta S_{\text{environment}} \geq 0 \quad (1.4)
\]

**Thermodynamic identity** *(Schroeder 3.4)*

\[
dU = TdS - pdV \quad (1.5)
\]

**Thermodynamic potentials** *(Schroeder 1.6, 5.1)*

**Helmholtz free energy**

\[
F = U - TS \quad (1.6)
\]

\[
dF = dU - TdS - SdT = -SdT - pdV \quad (1.7)
\]

**Enthalpy**

\[
H = U + pV \quad (1.9)
\]

\[
dH = dU + pdV + Vdp = TdS + Vdp \quad (1.10)
\]

**Gibbs free energy**

\[
G = H - TS \quad (1.12)
\]

\[
g = U - TS + pV \quad (1.13)
\]

\[
dG = dH - TdS - SdT = -SdT + Vdp \quad (1.14)
\]

**Statistical entropy** *(Schroeder 2.6, Problem 6.43)*

Boltzmann formulation (microcanonical or for large N):

\[
S(E) = k_B \ln g \quad (1.16)
\]
Gibbs formulation (always true):

\[ S(E) = -k_B \sum_{i} P_i \ln P_i \]  
\[ (1.17) \]

Boltzmann ratio (Schroeder 6.1)

\[ \frac{P_i}{P_j} = e^{\frac{E_i - E_j}{k_BT}} \]  
\[ (1.18) \]

\[ P_i = \frac{e^{\frac{E_i}{k_BT}}}{\sum_{j} e^{\frac{E_j}{k_BT}}} \]  
\[ (1.19) \]

Thermal averages (Schroeder 6.2)

The average value of any quantity is given by the weighted average

\[ \langle X \rangle = \sum_{i} P_i X_i \]  
\[ (1.20) \]
Chapter 2

Week 1: Gibbs entropy approach

The only reference in the text is (Schroeder Problem 6.43).

There are two different approaches for deriving the results of statistical mechanics. These results differ in what fundamental postulates are taken, but agree in the resulting predictions. The textbook takes a traditional microcanonical Boltzmann approach.

This week, before using that approach, we will reach the same results using the Gibbs formulation of the entropy (sometimes referred to as the “information theoretic entropy”), as advocated by Jaynes. Note that Boltzmann also used the more general Gibbs entropy, even though it doesn’t appear on his tombstone.

Microstates vs. macrostates

You can think of a microstate as a quantum mechanical energy eigenstate. As you know from quantum mechanics, once you have specified an energy eigenstate, you know all that you can about the state of a system. Note that before quantum mechanics, this was more challenging. You can define a microstate classically, and people did so, but it was harder. In particular, the number of microstates classically is generally both infinite and non-countable, since any real number for position and velocity is possible. Quantum mechanics makes this all easier, since any finite (in size) system will have an infinite but countable number of microstates.

When you have a non-quantum mechanical system (or one that you want to treat classically), a microstate represents one of the “primitive” states of the system, in which you have specified all possible variables. In practice, it is common when doing this to specify what we might call a “mesostate”, but call it a microstate. E.g. you might hear someone describe a microstate of a system of marbles in urns as defined by how many marbles of each color are in each urn. Obviously there are many quantum mechanical microstates corresponding to each of those states.

Small White Boards Write down a description of one particular macrostate.

A macrostate is a state of a system in which we have specified all the properties of the system that will affect any measurements we may care about. For instance, when defining a macrostate of a given gas or liquid, we could specify the internal energy, the number of molecules (or equivalently mass), and the volume. We need to specify all three properties (if we want to ask, for instance, for the entropy), because otherwise we won’t have a unique answer. For different sorts of systems there are different ways that we can specify a macrostate. In this way, macrostates have a flexibility that real microstates do not. E.g. I could argue that the macrostate of a system of marbles in urns would be defined by the number of marbles of each color in each urn. After all, each macrostate would still correspond to many different energy eigenstates.
Probabilities of microstates

The name of the game in statistical mechanics is determining the probabilities of the various microstates, which we call \( \{ P_i \} \), where \( i \) represents a microstate. I will note here the term **ensemble**, which refers to a set of microstates with their associated probabilities. We define ensembles according to what constraints we place on the microstates, e.g. in this discussion we will constrain all microstates to have the same volume and number of particles, which defines the **canonical ensemble**. Next week/chapter we will discuss the microcanonical ensemble (which also constrains all microstates to have identical energy), and other ensembles will follow. Today’s discussion, however, will be largely independent of which ensemble we choose to work with, which generally depends on what processes we wish to consider.

Normalization

The total probability of all microstates added up must be one.

\[
\sum_i P_i = 1
\]

(2.1)

This may seem obvious, but it is very easy to forget when lost in algebra!

From probabilities to observables

If we want to find the value that will be measured for a given observable, we will use the weighted average. For instance, the internal energy of a system is given by:

\[
U = \sum_i P_i E_i
\]

(2.2)

where \( E_i \) is the energy eigenvalue of a given microstate. The \( \langle E_i \rangle \) notation simply denotes a weighted average of \( E \). The subscript in this notation is optional.

This may seem wrong to you. In quantum mechanics, you were taught that the outcome of a measurement was always an eigenvalue of the observable, **not** the expectation value (which is itself an average). The difference is in how we are imagining performing a measurement, and what the size of the system is thought to be.

In contrast, imagine measuring the mass of a liter of water, for instance using a balance. While you are measuring its mass, there are water molecules leaving the glass (evaporating), and other water molecules from the air are entering the glass and condensing. The total mass is fluctuating as this occurs, far more rapidly than the scale can tip up or down. It reaches balance when the weights on the other side balance the *average* weight of the glass of water.

The process of measuring pressure and energy are similar. There are continually fluctuations going on, as energy is going back and forth between your system and the environment, and the process of measurement (which is slow) will end up measuring the average.

In contrast, when you perform spectroscopy on a system, you do indeed see lines corresponding to discrete eigenvalues, even though you are using a macroscopic amount of light on what may be a macroscopic amount of gas. This is because each photon that is absorbed by the system will be absorbed by a single molecule (or perhaps by two that are in the process of colliding). Thus you don’t measure averages in a direct way.

In thermal systems such as we are considering in this course, we will consider the kind of observable where the average value of that observable is what is measured. This is why statistics are relevant!

Energy as a constraint

Energy is one of the most fundamental concepts. When we describe a macrostate, we will (almost) al-
ways need to constrain the energy. For real systems, there are always an infinite number of microstates with no upper bound on energy. Since we never have infinite energy in our labs or kitchens, we know that there is a practical bound on the energy.

We can think of this as applying a mathematical constraint on the system: we specify a $U$, and this disallows any set of probabilities $\{P_i\}$ that have a different $U$.

**Small Group Question** Consider a system that has just three microstates, with energies $-\epsilon$, 0, and $\epsilon$. Construct three sets of probabilities corresponding to $U = 0$.

I picked an easy $U$. Any “symmetric” distribution of probabilities will do. You probably chose something like:

\[
\begin{array}{c|c|c}
E_i & -\epsilon & 0 & \epsilon \\
P_i & 0 & 1 & 0 \\
P_i & 1/3 & 1/3 & 1/3 \\
\end{array}
\]

**Question** Given that each of these answers has the same $U$, how can we find the correct set of probabilities are for this $U$? Vote on which you think most likely!

The most “mixed up” would be ideal. But how do we define mixed-up-ness? The “mixed-up-ness” of a probability distribution can be quantified via the Gibbs formulation of entropy:

\[
S = -k \sum_{i} P_i \ln P_i 
\]

\[
= \sum_i P_i (-k \ln P_i) 
\]

\[
= \langle -k \ln P_i \rangle 
\]

So entropy is a kind of weighted average of $-\ln P_i$.

The Gibbs entropy expression (sometimes referred to as the information theory entropy, or Shannon entropy) can be shown to be the only possible entropy function (of $\{P_i\}$) that has a reasonable set of properties:

1. It must be extensive. If you subdivide your system into uncorrelated and noninteracting subsystems (or combine two noninteracting systems), the entropy must just add up. Solve problem 2 on the homework this week to show this. (Technically, it must be additive even if the systems interact, but that is more complicated.)

2. The entropy must be a continuous function of the probabilities $\{P_i\}$. Realistically, we want it to be analytic.

3. The entropy shouldn’t change if we shuffle around the labels of our states, i.e. it should be symmetric.

4. When all microstates are equally likely, the entropy should be maximized.

5. All microstates have zero probability except one, the entropy should be minimized.

**Note** The constant $k$ is called Boltzmann’s constant, and is sometimes written as $k_B$. Kittel and Kroemer prefer to set $k_B = 1$ in effect, and defines $\sigma$ as $S/k_B$ to make this explicit. I will include $k_B$ but you can and should keep in mind that it is just a unit conversion constant. Note also that changing the base of the logarithm in effect just changes this constant.

How is this mixed up?

**Small Group Question** Compute $S$ for each of the above probability distributions.

**Answer**

\[
\begin{array}{c|c|c|c|c}
E_i & -\epsilon & 0 & \epsilon & S \\
P_i & 0 & 1 & 0 & 0 \\
P_i & 1/3 & 1/3 & 1/3 & \ln 2 \\
P_i & 1/3 & 1/3 & 1/3 & \ln 3 \\
\end{array}
\]

You can see that if more states are probable, the entropy is higher. Or alternatively you could say that if the probability is more “spread out”, the entropy is higher.
Maximize entropy

The correct distribution is that which maximizes the entropy of the system, its Gibbs entropy, subject to the appropriate constraints. Yesterday we tackled a pretty easy 3-level system with \( U = 0 \). If I had chosen a different energy, it would have been much harder to find the distribution that gave the highest entropy.

**Small Group Question** Find the probability distribution for our 3-state system that maximizes the entropy, given that the total energy is \( U \).

**Answer** We have two constraints,

\[
\sum_{\mu} P_{\mu} = 1 \tag{2.7}
\]
\[
\sum_{\mu} P_{\mu}E_{\mu} = U \tag{2.8}
\]

and we want to maximize

\[
S = -k \sum_{\mu} P_{\mu} \ln P_{\mu}, \tag{2.9}
\]

Fortunately, we’ve only got three states, so we write down each sum explicitly, which will make things easier.

\[
P_{-} + P_{0} + P_{+} = 1 \tag{2.10}
\]
\[
-\epsilon P_{-} + \epsilon P_{+} = U \tag{2.11}
\]
\[
P_{+} = P_{-} + \frac{U}{\epsilon} \tag{2.12}
\]
\[
P_{-} + P_{0} + \frac{U}{\epsilon} = 1 \tag{2.13}
\]
\[
P_{0} = 1 - 2P_{-} - \frac{U}{\epsilon} \tag{2.14}
\]

Now that we have all our probabilities in terms of \( P_{-} \) we can simplify our entropy:

\[
-\frac{S}{k} = P_{-} \ln P_{-} + P_{0} \ln P_{0} + P_{+} \ln P_{+} \tag{2.16}
\]
\[
= P_{-} \ln P_{-} + (P_{+} + \frac{U}{\epsilon}) \ln (P_{-} + \frac{U}{\epsilon})
\]
\[
+ (1 - 2P_{-} - \frac{U}{\epsilon}) \ln (1 - 2P_{-} - \frac{U}{\epsilon}) \tag{2.17}
\]

Now we can maximize this entropy by setting its derivative to zero!

\[
-\frac{dS}{dP_{-}} = 0 \tag{2.18}
\]
\[
= \ln P_{-} + 1 - 2 \ln (1 - 2P_{-} - \frac{U}{\epsilon}) - 2
\]
\[
+ \ln (P_{-} + \frac{U}{\epsilon}) + 1 \tag{2.19}
\]
\[
= \ln \left( \frac{P_{-} (P_{+} + \frac{U}{\epsilon})}{(1 - 2P_{-} - \frac{U}{\epsilon})^{2}} \right) \tag{2.21}
\]

\[
1 = \frac{P_{-} (P_{+} + \frac{U}{\epsilon})}{(1 - 2P_{-} - \frac{U}{\epsilon})^{2}} \tag{2.22}
\]

And now it is just a polynomial equation... 

\[
P_{-} (P_{-} + \frac{U}{\epsilon}) = (1 - 2P_{-} - \frac{U}{\epsilon})^{2} \tag{2.23}
\]
\[
P_{-}^{2} + \frac{U}{\epsilon} P_{-} = 1 - 4P_{-} - 2\frac{U}{\epsilon} + 4P_{-}^{2} + 4P_{-} \frac{U}{\epsilon} + \frac{U^{2}}{\epsilon^{2}} \tag{2.24}
\]

At this stage I’m going to stop. Clearly you could keep going and solve for \( P_{-} \) using the quadratic equation, but we wouldn’t learn much from doing so. The point here is that we can solve for the three probabilities given the internal energy constraint. However, doing so is a major pain, and the result is not looking promising in terms of simplicity. There is a better way!

**Lagrange multipliers**

If you have a function of \( N \) variables, and want to apply a single constraint, one approach is to use the...
constraint to algebraically eliminate one of your variables. Then you can set the derivatives with respect to all remaining variables to zero to maximize. This is what you presumably did in the last activity. However, in many cases this isn’t feasible. And when there are many variables, it is almost universally inconvenient. A nicer approach for maximization under constraints is the method of Lagrange multipliers.

The idea of Lagrange multipliers is to introduce an additional variable (called the Lagrange multiplier) rather than eliminating one. This may seem counter-intuitive, but it allows you to create a new function that can be maximized by setting its derivative with to all \( N \) variables to zero, while still satisfying the constraint.

Suppose we have a situation where we want to maximize \( F \) under some constraints:

\[
F = F(w, x, y, z) \quad (2.25)
\]
\[
f_1(w, x, y, z) = C_1 \quad (2.26)
\]
\[
f_2(w, x, y, z) = C_2 \quad (2.27)
\]

We define a new variable \( L \) as follows:

\[
L = F + \lambda_1(C_1 - f_1(w, x, y, z)) + \lambda_2(C_2 - f_2(w, x, y, z)) \quad (2.28)
\]

Note that \( L = F \) provided the constraints are satisfied, since the constraint means that \( f_1(x, y, z) - C_1 = 0 \). We then maximize \( L \) by setting its derivatives to zero:

\[
\left( \frac{\partial L}{\partial w} \right)_{w,x,y,z} = 0 \quad (2.29)
\]
\[
= \left( \frac{\partial F}{\partial w} \right)_{w,x,y,z} - \lambda_1 \frac{\partial f_1}{\partial w} - \lambda_2 \frac{\partial f_2}{\partial w} \quad (2.30)
\]
\[
\left( \frac{\partial L}{\partial x} \right)_{w,y,z} = 0 \quad (2.31)
\]
\[
= \left( \frac{\partial F}{\partial x} \right)_{w,y,z} - \lambda_1 \frac{\partial f_1}{\partial x} - \lambda_2 \frac{\partial f_2}{\partial x} \quad (2.32)
\]
\[
\left( \frac{\partial L}{\partial y} \right)_{w,x,z} = 0 \quad (2.33)
\]
\[
= \left( \frac{\partial F}{\partial y} \right)_{w,x,z} - \lambda_1 \frac{\partial f_1}{\partial y} - \lambda_2 \frac{\partial f_2}{\partial y} \quad (2.34)
\]
\[
\left( \frac{\partial L}{\partial z} \right)_{w,x,y} = 0 \quad (2.35)
\]
\[
= \left( \frac{\partial F}{\partial z} \right)_{w,x,y} - \lambda_1 \frac{\partial f_1}{\partial z} - \lambda_2 \frac{\partial f_2}{\partial z} \quad (2.36)
\]

This gives us four equations. But we need to keep in mind that we also have the two constraint equations:

\[
f_1(x, y, z) = C_1 \quad (2.37)
\]
\[
f_2(x, y, z) = C_2 \quad (2.38)
\]

We now have six equations and six unknowns, since \( \lambda_1 \) and \( \lambda_2 \) have also been added as unknowns, and thus we can solve all these equations simultaneously, which will give us the maximum under the constraint. We also get the \( \lambda \) values for free.

The meaning of the Lagrange multiplier

So far, this approach probably seems pretty abstract, and the Lagrange multiplier \( \lambda_i \) seems like a strange number that we just arbitrarily added in. Even were there no more meaning in the multipliers, this method would be a powerful tool for maximization (or minimization). However, as it turns out, the multiplier often (but not always) has deep physical meaning. Examining the Lagrangian \( L \), we can see that

\[
\left( \frac{\partial L}{\partial C_1} \right)_{w,x,y,z,C_2} = \lambda_1 \quad (2.39)
\]

so the multiplier is a derivative of the lagrangian with respect to the corresponding constraint value. This doesn’t seem to useful.
More importantly (and less obviously), we can now think about the original function we maximized \( F \) as a function (after maximization) of just \( C_1 \) and \( C_2 \). If we do this, then we find that

\[
\left( \frac{\partial F}{\partial C_1} \right)_{C_2} = \lambda_1 \tag{2.40}
\]

I think this is incredibly cool! And it is a hint that Lagrange multipliers may be related to Legendre transforms.

**Maximizing entropy**

When maximizing the entropy, we need to apply two constraints. We must hold the total probability to 1, and we must fix the mean energy to be \( U \). This time I'm going to call my Lagrange multipliers \( \alpha_k \) and \( \beta_k \) so as to reduce the number of subscripts required and also to make all the Boltzmann constants go away.

\[
L = S + \alpha k_B \left( 1 - \sum_i P_i \right) + \beta k_B \left( U - \sum_i P_i E_i \right) \tag{2.41}
\]

where \( \alpha \) and \( \beta \) are the two Lagrange multipliers. I’ve added here a couple of factors of \( k_B \) mostly to make the \( k_B \) in the entropy disappear. We want to maximize this, so we set its derivatives to zero:

\[
\frac{\partial L}{\partial P_i} = 0 \tag{2.43}
\]

\[
= -k_B \ln P_i - k_B \alpha - \beta k_B E_i \tag{2.44}
\]

\[
\ln P_i = -1 - \alpha - \beta E_i \tag{2.45}
\]

\[
P_i = e^{-1-\alpha-\beta E_i} \tag{2.46}
\]

So now we know the probabilities in terms of the two Lagrange multipliers, which already tells us that the probability of a given microstate is exponentially related to its energy. At this point, it is convenient to invoke the normalization constraint...

\[
1 = \sum_i P_i \tag{2.47}
\]

\[
= \sum_i e^{-1-\alpha-\beta E_i} \tag{2.48}
\]

\[
= e^{-1-\alpha} \sum_i e^{-\beta E_i} \tag{2.49}
\]

\[
e^{1+\alpha} = \sum_i e^{-\beta E_i} \tag{2.50}
\]

Where we define the normalization factor as

\[
Z \equiv \sum_i \text{all states} e^{-\beta E_i} \tag{2.52}
\]

which is called the partition function. Putting this together, the probability is

\[
P_i = \frac{e^{-\beta E_i}}{Z} \tag{2.53}
\]

\[
= \frac{\text{Boltzmann factor}}{\text{partition function}} \tag{2.54}
\]

At this point, we haven’t yet solved for \( \beta \), and to do so, we’d need to invoke the internal energy constraint:

\[
U = \sum_i E_i P_i \tag{2.55}
\]

\[
U = \sum_i E_i e^{-\beta E_i} \tag{2.56}
\]

As it turns out, \( \beta = \frac{1}{k_B T} \). This follows from my claim that the Lagrange multiplier is the partial derivative with respect to the constant value.
\[ k_B \beta = \left( \frac{\partial S}{\partial U} \right)_{\text{Normalization}=1} \]  

However, I did not prove this to you. I will leave demonstrating this as a homework problem.

**Homework for week 1 (PDF)**

1. **Energy, Entropy, and Probabilities**  
   The goal of this problem is to show that once we have maximized the entropy and found the microstate probabilities in terms of a Lagrange multiplier \( \beta \), we can prove that \( \beta = \frac{1}{kT} \) based on the statistical definitions of energy and entropy and the thermodynamic definition of temperature embodied in the thermodynamic identity.

   The internal energy and entropy are each defined as a weighted average over microstates:

   \[ U = \sum_i E_i P_i \quad S = -k_B \sum_i P_i \ln P_i \]  

   We saw in class that the probability of each microstate can be given in terms of a Lagrange multiplier \( \beta \) as

   \[ P_i = \frac{e^{-\beta E_i}}{Z} \quad Z = \sum_i e^{-\beta E_i} \]  

   Put these probabilities into the above weighted averages in order to relate \( U \) and \( S \) to \( \beta \). Then make use of the thermodynamic identity

   \[ dU = TdS - pdV \]  

   to show that \( \beta = \frac{1}{kT} \).

2. **Gibbs entropy is extensive**  
   Consider two non-interacting systems \( A \) and \( B \). We can either treat these systems as separate, or as a single combined system \( AB \). We can enumerate all states of the combined by enumerating all states of each separate system. The probability of the combined state \((i_A, j_B)\) is given by \( P_{ij}^{AB} = P_i^A P_j^B \). In other words, the probabilities combine in the same way as two dice rolls would, or the probabilities of any other uncorrelated events.

   a) Show that the entropy of the combined system \( S_{AB} \) is the sum of entropies of the two separate systems considered individually, i.e. \( S_{AB} = S_A + S_B \). This means that entropy is extensive. Use the Gibbs entropy for this computation. You need make no approximation in solving this problem.

   b) Show that if you have \( N \) identical non-interacting systems, their total entropy is \( NS_1 \) where \( S_1 \) is the entropy of a single system.

   **Note**  
   In real materials, we treat properties as being extensive even when there are interactions in the system. In this case, extensivity is a property of large systems, in which surface effects may be neglected.

3. **Boltzmann probabilities**  
   Consider the three-state system with energies \((-\epsilon, 0, \epsilon)\) that we discussed in class.

   a) At infinite temperature, what are the probabilities of the three states being occupied?

   b) At very low temperature, what are the three probabilities?

   c) What happens to the probabilities if you allow the temperature to be negative?
Chapter 3

Week 2: Entropy and Temperature
(K&K 2, Schroeder 6)

This week we will be following Chapter 2 of Kittel and Kroemer, which uses a microcanonical approach (or Boltzmann entropy approach) to relate entropy to temperature. This is an alternative derivation to the Gibbs approach we used last week, and it can be helpful to have seen both. In a few ways the Boltzmann approach is conceptually simpler, while there are a number of other ways in which the Gibbs approach is simpler.

Fundamental assumption

The difference between these two approaches is in what is considered the fundamental assumption. In the Gibbs entropy approach we assumed that the entropy was a “nice” function of the probabilities of microstates, which gave us the Gibbs formula. From there, we could maximize the entropy to find the probabilities under some set of constraints.

The Boltzmann approach makes what is perhaps simpler assumption, which is that if only microstates with a given energy are permitted, then all of the microstates with that energy are equally probable. (This scenario with all microstates having the same energy is the microcanonical ensemble.) Thus the macrostate with the most corresponding microstates will be most probable macrostate. The number of microstates corresponding to a given macrostate is called the multiplicity $g(E,V)$. In this approach, multiplicity (which did not show up last week!) becomes a fundamentally important quantity, since the macrostate with the highest multiplicity is the most probable macrostate.

Outline of the week One or two topics per day:

1. Quick version showing the conclusions we will reach.
2. Finding the multiplicity of a paramagnet (Chapter 1).
3. Combining two non-interacting systems; defining temperature.
4. Central limit theorem and how “large $N$” does its magic.

Quick version

This quick version will tell you all the essential physics results for the week, without proof. The beauty of statistical mechanics (whether following the text or using the information-theory approach of last week) is that you don’t actually need to take on either faith or experiment the connection between the statistical theory and the empirical definitions used in thermodynamics.
Entropy

The multiplicity sounds sort of like entropy (since it is maximized), but the multiplicity is not extensive (nor intensive), because the number of microstates for two identical systems taken together is the square of the number of microstates available to one of the single systems. This naturally leads to the Boltzmann definition of the entropy, which is

\[ S(E, V) = k_B \ln g(E, V). \] (3.1)

The logarithm converts the multiplicity into an extensive quantity, in a way that is directly analogous to the logarithm that appears in the Gibbs entropy.

For large systems (e.g. systems composed of ~ \(10^{23}\) particles), the most probable configuration is essentially the same as any remotely probable configuration. This comes about due for the same reason that if you flip \(10^{23}\) coins, you will get \(5 \times 10^{22} \pm 10^{12}\) heads. On an absolute scale, that’s a lot of uncertainty in the number of heads that would show up, but on a fractional scale, you’re pretty accurate if you assume that 50\% of the flips will be heads.

Temperature

From Energy and Entropy (and last week), you will remember that \(dU = TdS - pdV\), which tells us that \(T = \left( \frac{\partial U}{\partial S} \right)_V\). If we assume that only states with one particular energy \(E\) have a non-zero probability of being occupied, then \(U = E\), i.e. the thermodynamic internal energy is the same as the energy of any allowed microstate. Then we can replace \(U\) with \(E\) and conclude that

\[ T = \left( \frac{\partial E}{\partial S} \right)_V \] (3.2)

\[ \frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_V \] (3.3)

\[ = \left( \frac{\partial k_B \ln g(E, V)}{\partial E} \right)_V \] (3.4)

\[ = k_B \frac{1}{g} \left( \frac{\partial g}{\partial E} \right)_V \] (3.5)

From this perspective, it looks like our job is to learn to solve for \(g(E)\) and from that to find \(S(E)\), and once we have done these tasks we will know the temperature (and soon everything else).

Differentiable multiplicity The above assumes that \(g(E)\) is a differentiable function, which means that the number of microstates must be a continuous function of energy! This highlights one of the distinctions between the microcanonical approach and our previous (cannonical) Gibbs approach.

In reality, we know from quantum mechanics that any system of finite size has a finite number of eigenstates within any given energy range, and thus \(g(E)\) cannot be either continuous or differentiable. Boltzmann, of course, did not know this, and assumed that there were an infinite number of microstates possible within any energy range, and would strictly speaking interpret \(g(E)\) in terms of a volume of phase space.

The resolution to this conundrum is to invoke large numbers, and to assume that we are averaging \(g(E)\) over a range of energies in which there are many, many states. For real materials with \(N \approx 10^{23}\), this assumption is pretty valid. Much of this chapter will involve learning to work with this large \(N\) assumption, and to use it to extract physically meaningful results. In the Gibbs approach this large \(N\) assumption was not needed.

As Kittel discusses towards the end of the chapter, we only really need to know \(g(E)\) up to some
constant factor, since a constant factor in \( g \) becomes a constant additive change in \( S \), which doesn’t have any physical impact.

The “real” \( g(E) \) is a smoothed average over a range of energies. In practice, doing this can be confusing, and so we tend to focus on systems where the energy is always an integer multiple of some constant. Thus a focus on spins in a magnetic field, and harmonic oscillators.

**Multiplicity of a paramagnet**

So now the question becomes how to find the number of microstates that correspond to a given energy \( g(E) \). Once we have this in an analytically tractable form, we can everything else we might care for (with effort).

This is essentially a counting problem, and much of what you need is introduced in Chapter 1. We will spend some class time going over one example of computing the multiplicity. Consider a paramagnetic system consisting of spin \( \frac{1}{2} \) particles that can be either up or down. Each spin has a magnetic moment in the \( \hat{z} \) direction of \( \pm m \), and we are interested in the total magnetic moment \( \mu_{\text{tot}} \), which is the sum of all the individual magnetic moments. Note that the magnetization \( M \) used in electromagnetism is just the total magnetic moment of the material divided by its volume.

\[
M \equiv \frac{\mu_{\text{tot}}}{V} \quad (3.6)
\]

**Note** It is confusingly common to refer to the total magnetic moment as the magnetization. Given either a numerical value or an expression, it’s usually easy to tell what you’ve got by checking the dimensions.

**Small Group Question** Work out how many ways a system of 4 spins can have any possible magnetization of enumerating all the microstates corresponding to each magnetization.

Now find a mathematical expression that will tell you the multiplicity of a system with an even number \( N \) spins and just one \( \uparrow \) spin. Then find the multiplicity for two \( \uparrow \) spins, and for three \( \uparrow \) spins.

Now find a mathematical expression that will tell you the multiplicity of a system with an even number \( N \) spins and total magnetic moment \( \mu_{\text{tot}} = 2sm \) where \( s \) is an integer. We call \( s \) the **spin excess**, since \( N_s = \frac{1}{2}N + s \). Alternatively, you could write your expression in terms of the number of up spins \( N_\uparrow \) and the number of down spins \( N_\downarrow \).

**Answer** We can enumerate all spin microstates:

\[
\begin{align*}
\mu_{\text{tot}} &= -4m \quad \text{g}=1 \\
\mu_{\text{tot}} &= -2m \quad \text{g}=4 \\
\mu_{\text{tot}} &= 0 \quad \text{g}=6 \\
\mu_{\text{tot}} &= 2m \quad \text{g}=4 \\
\mu_{\text{tot}} &= 4m \quad \text{g}=1
\end{align*}
\]

To generalize this to \( g(N, s) \), we need to come up with a systematic way to count the states that have the same spin excess \( s \). Clearly if \( s = \pm N/2 \), \( g = 1 \), since that means that all the spins are pointed the same way, and there is only one way to do that.

\[
g(N, s = \pm \frac{1}{2}N) = 1 \quad (3.7)
\]

Now if we have just one spin going the other way, there are going to be \( N \) ways we could manage that:

\[
g \left( \frac{1}{2}N - 1 \right) = N \quad (3.8)
\]

Now when we go to flip it so we have two spins up, there will be \( N - 1 \) ways to flip the second spin. But then, when we do this we will end up counting every possibility twice, which means that we will need to divide by two.
When we get to adding the third \( \uparrow \) spin, we’ll have \( N - 2 \) spins to flip. But now we have to be even more careful, since for the same three up-spins, we have several ways to reach that microstate. In fact, we will need to divide by \( 6 \), or \( 3 \times 2 \) to get the correct answer (as we can check for our four-spin example).

\[
g( N, s = \pm \left( \frac{1}{2} N - 2 \right) ) = \frac{N(N - 1)(N - 2)}{3!} \quad (3.10)
\]

At this stage we can start to see the pattern, which comes out to

\[
g( N, s ) = \frac{N!}{\left( \frac{1}{2} N + s \right)! \left( \frac{1}{2} N - s \right)!} = \frac{N!}{N\uparrow! N\downarrow!} \quad (3.11)
\]

\[
\text{Stirling’s approximation}
\]

As you can see, we now have a bunch of factorials. Once we compute the entropy, we will have a bunch of logarithms of factorials.

\[
N! = \prod_{i=1}^{N} i \quad (3.13)
\]

\[
\ln N! = \ln \left( \prod_{i=1}^{N} i \right) = \sum_{i=1}^{N} \ln i \quad (3.15)
\]

So you can see that the log of a factorial is a sum of logs. When the number of things being summed is large, we can approximate this sum with an integral. This may feel like a funny business, particularly for those of you who took my computational class, where we frequently used sums to approximate integrals! But the approximation can go both ways. In this case, if we approximate the integral as a sum we can find an analytic expression for the factorial:

\[
\ln N! \approx \sum_{i=1}^{N} \ln i \quad (3.16)
\]

\[
\approx \int_{1}^{N} \ln x \, dx \quad (3.17)
\]

\[
= x \ln x - x \bigg|_{1}^{N} \quad (3.18)
\]

\[
= N \ln N - N + 1 \quad (3.19)
\]

At this point, we should recognize that the 1 that we see is much smaller than the other two terms, and is actually likely to be wrong. Importantly, there is a larger error being made here, which we can see if we zoom into the upper end of our integral. We are missing \( \frac{1}{2} \ln N! \). The reason is that our integral went precisely to \( N \), but if we imagine a midpoint rule picture (or trapezoidal rule) we are missing half of that last point. This gives us:

\[
\ln N! \approx \left( N + \frac{1}{2} \right) \ln N - N \quad (3.20)
\]

We could find the constant term correctly (it is not 1), but that is more work, and even the \( \frac{1}{2} \) above is usually omitted when using Stirling’s approximation, since it is much smaller than the others when \( N \gg 0 \).

\textbf{Entropy of our spins}

I’m going to use a different approach than the text to find the entropy of this spin system when there are many spins and the spin excess is relatively small.
\[ S = k \ln g(N, s) \]  
\[ = k \ln \left( \frac{N!}{\left(\frac{N}{2} + s\right)! \left(\frac{N}{2} - s\right)!} \right) \]  
\[ = k \ln \left( \frac{N!}{N!} \right) \]  
\[ = k \ln \left( \frac{N!}{(h + s)! (h - s)!} \right) \]  
(3.21)  
(3.22)  
(3.23)  
(3.24)

With these indexes, each sum can go from \( k = 1 \) to \( k = s \), which will enable us to combine our sums into one.

\[ \frac{S - S_0}{k} = -s \sum_{k=1}^{s} \ln(h + k) + s \sum_{k=1}^{s} \ln(h + 1 - k) \]  
\[ = s \sum_{k=1}^{s} \left( \ln(h + 1 - k) - \ln(h + k) \right) \]  
(3.31)  
(3.32)

At this stage, I’m going to define for convenience \( h \equiv \frac{1}{2}N \), just to avoid writing so many \( \frac{1}{2} \). I’m also going to focus on the \( s \) dependence of the entropy.

\[ \frac{S}{k} = \ln(N!) - \ln(N_1!) - \ln(N_2!) \]  
\[ = \ln N! - \ln(h + s)! - \ln(h - s)! \]  
\[ = \ln N! - \sum_{i=1}^{h+s} \ln i - \sum_{i=1}^{h-s} \ln i \]  
(3.25)  
(3.26)  
(3.27)

At this point, if you’re anything like me, you’re thinking “I could turn that difference of logs into a log of a ratio!” Sadly, this doesn’t turn out to help us. Instead, we are going to start trying to get the \( h \) out of the way in preparation for taking the limit as \( s \ll h \).

\[ \frac{S(s) - S_0}{k_B} = -\sum_{i=1}^{h+s} \ln i - \sum_{i=1}^{h-s} \ln i + \sum_{i=1}^{h} \ln i + \sum_{i=1}^{h} \ln i \]  
\[ = -\sum_{i=h+1}^{h+s} \ln i + \sum_{j=h-s+1}^{h} \ln j \]  
(3.28)  
(3.29)

where I have changed the sums to account for the difference between the sums with \( s \) and those without. At this stage, our indices are starting to feel a little inconvenient given the short range we are summing over, so let’s redefine our index or summation so the sums will run up to \( s \). In preparation for this, at the last step, I renamed one of my dummy indexes.

\[ \frac{S - S_0}{k} \approx s \sum_{k=1}^{s} \left( \frac{k - 1}{h} - \frac{k}{h} \right) \]  
\[ = -\frac{2}{h} \sum_{k=1}^{s} \left( k - \frac{1}{2} \right) \]  
\[ = -\frac{4}{N} \sum_{k=1}^{s} \left( k - \frac{1}{2} \right) \]  
(3.35)  
(3.36)  
(3.37)
converting sum to integral where \( s = 5 \)

\[
\int_0^s x \, dx = \frac{1}{2} s^2 \quad (3.38)
\]

has the same value as the sum, since the area under the orange curve (which is the sum) is equal to the area under the blue curve (which is the integral).

The geometric way to solve this looks visually very much the same as the integral picture, but instead of computing the area from the straight line, we cut the stair-step area “half” and fit the two pieces together such that they form a rectangle with width \( s/2 \) and height \( s \).

Taken together, this tells us that when \( s \ll N \)

\[
S(N, s) \approx S(N, s = 0) - k \frac{4}{N} s^2 \quad (3.39)
\]

\[
= S(N, s = 0) - k \frac{2s^2}{N} \quad (3.40)
\]

This means that the multiplicity is gaussian:

\[
S = k \ln g 
\]

\[
g(N, s) = e^{\frac{S(N,s)}{k}} 
\]

\[
= e^{\frac{S(N,s=0)}{k} - \frac{2s^2}{N}} 
\]

\[
= g(N, s = 0)e^{-\frac{2s^2}{N}} 
\]

Thus the multiplicity (and thus probability) is peaked at \( s = 0 \) as a gaussian with width \( \sim \sqrt{N} \). This tells us that the width of the peak increases as we increase \( N \). However, the excess spin per particle decreases as \( \sim \frac{1}{\sqrt{N}} \). So that means that our fractional polarization becomes far more sharply peaked as we increase \( N \).

**Thermal contact**

Suppose we put two systems in contact with one another. This means that energy can flow from one system to the other. We assume, however, that the contact between the two systems is weak enough that their energy eigenstates are unaffected. This is a bit of a contradiction you’ll need to get used to: we treat our systems as non-interacting, but assume there is some energy transfer between them. The reasoning is
that the interaction between them is very small, so
to that we can treat each system separately, but energy
can still flow.

We ask the question: “How much energy will each
system end up with after we wait for things to settle
down?” The answer to this question is that energy
will settle down in the way that maximizes the number
of microstates.

Let us consider two simple systems: a 2-spin param-
agnet, and a 4-spin paramagnet.

**System A** A system of 3 spins each with energy ±1.
This system has the following multiplicity found
from Pascal’s triangle:

\[
\begin{array}{cccc}
1 & 1 & 1 & 1 \\
1 & 2 & 1 & 1 \\
1 & 3 & 3 & 1 \\
-3 & -1 & 1 & 3
\end{array}
\]

**System B** A system of 4 spins each with energy ±1.
This system has the following multiplicity found
from Pascal’s triangle:

\[
\begin{array}{cccccc}
1 & 1 & 1 & 1 & 1 & 1 \\
1 & 2 & 1 & 1 & 1 & 1 \\
1 & 3 & 3 & 1 & 1 & 1 \\
1 & 4 & 6 & 4 & 1 & 1 \\
-4 & -2 & 0 & 2 & 4 & 4
\end{array}
\]

**Question** What is the total number of microstates
when you consider systems A and B together as
a combined system? Answer

We need to multiply the numbers of microstates
for each system separately, because for each mi-
crostate of A, it is possible to have B be in any
of its microstates. So the total is \(2^3 \cdot 2^4 = 128\).

Since we have two separate systems here, it is mean-
ingful to ask what the probability is for system A to
have energy \(E_A\), given that the combined system has
energy \(E_{AB}\).

**Small group question** What is the multiplicity of
the combined system if the energy is 3, i.e.
\(g_{AB}(E_{AB} = 3)\)?

**Answer** To solve this, we just need to multiply the
multiplicities of the two systems and add up all
the energy possibilities that total 3:

\[
g_{AB}(E_{AB} = 0) = g_A(-1)g_B(4) + g_A(1)g_B(2) + g_A(3)g_B(0)
\]

\[
= 3 \cdot 1 + 3 \cdot 4 + 1 \cdot 6
\]

\[
= 21
\]

**Small group question** What is the probability
that system A has energy 1, if the combined
energy is 3?

**Answer** To solve this, we just need to multiply the
multiplicities of the two systems, which we al-
ready found and divide by the total number of
microstates:

\[
P(E_A = 1 | E_{AB} = 3) = \frac{g_A(1)g_B(2)}{g_{AB}(3)}
\]

\[
= \frac{3 \cdot 4}{21}
\]

\[
= \frac{4}{7}
\]

which shows that this is the most probable dis-
tribution of energy between the two subsystems.

Given that these two systems are able to exchange
energy, they ought to have the same temperature.
To find the most probable energy partition between
the two systems, we need to find the partition that
maximizes the multiplicity of the combined system:

\[
g_{AB}(E_A) = g_A(E_A)g_B(E_{AB} - E_A)
\]

\[
0 = \frac{dg_{AB}}{dE_A}
\]

\[
= \frac{g_A'}{g_B} - \frac{g_B'}{g_A}
\]

\[
\frac{g_A'}{g_A} = \frac{g_B'}{g_B}
\]

\[
1 \frac{\partial g_A(E_A)}{\partial E_A} = \frac{1}{g_B(E_B)} \frac{\partial g_B(E_B)}{\partial E_B}
\]

This tells us that the “thing that becomes equal” when
the two systems are in thermal contact is this strange
ratio of the derivative of the multiplicity with respect to energy divided by the multiplicity itself. You may be able to recognize this as what is called a logarithmic derivative.

\[
\frac{\partial}{\partial E_A} \ln(g_A(E_A)) = \frac{1}{g_A(E_A)} \frac{\partial g_A(E_A)}{\partial E_A}
\]  

(3.56)

thus we can conclude that when two systems are in thermal contact, the thing that equalizes is

\[
\beta = \left( \frac{\partial \ln g}{\partial E} \right)_V
\]  

(3.57)

At this stage, we haven’t shown that \( \beta = \frac{1}{kT} \), but we have shown that it should be a function of \( T \), since \( T \) is also a thing that is equalized when two systems are in thermal contact.

By dimensional reasoning, you can recognize that this could be \( \frac{1}{kT} \), and we’re just going to leave this at that.

**Homework for week 2 (PDF)**

1. **Entropy and Temperature** (K&K 2.1) Suppose \( g(U) = CU^{3N/2} \), where \( C \) is a constant and \( N \) is the number of particles.
   a) Show that \( U = \frac{3}{2} N k_B T \).
   b) Show that \( \left( \frac{\partial S}{\partial U} \right)_N \) is negative. This form of \( g(U) \) actually applies to the ideal gas.

2. **Paramagnetism** Find the equilibrium value at temperature \( T \) of the fractional magnetization

\[
\frac{\mu_{\text{tot}}}{Nm} = \frac{2\langle s \rangle}{N}
\]  

(3.58)

of a system of \( N \) spins each of magnetic moment \( m \) in a magnetic field \( B \). The spin excess is \( 2s \). The energy of this system is given by

\[
U = -\mu_{\text{tot}} B
\]  

(3.59)

where \( \mu_{\text{tot}} \) is the total magnetization. Take the entropy as the logarithm of the multiplicity \( g(N, s) \) as given in (1.35 in the text):

\[
S(s) \approx k_B \log g(N, 0) - k_B \frac{2s^2}{N}
\]  

(3.60)

for \( |s| \ll N \), where \( s \) is the spin excess, which is related to the magnetization by \( \mu_{\text{tot}} = 2sm \).

**Hint:** Show that in this approximation

\[
S(U) = S_0 - k_B \frac{U^2}{2m^2 B^2 N},
\]  

(3.61)

with \( S_0 = k_B \log g(N, 0) \). Further, show that \( \frac{1}{kT} = -\frac{U}{m^2 B^2 N} \), where \( U \) denotes \( \langle U \rangle \), the thermal average energy.

3. **Quantum harmonic oscillator**
   a) Find the entropy of a set of \( N \) oscillators of frequency \( \omega \) as a function of the total quantum number \( n \). Use the multiplicity function:

\[
g(N, n) = \left( \frac{N + n - 1}{N - 1} \right)!
\]  

(3.62)

and assume that \( N \gg 1 \). This means you can make the Stirling approximation that \( \log N! \approx N \log N - N \). It also means that \( N - 1 \approx N \).

b) Let \( U \) denote the total energy \( n \hbar \omega \) of the oscillators. Express the entropy as \( S(U, N) \). Show that the total energy at temperature \( T \) is

\[
U = \frac{N \hbar \omega}{e^{\frac{kT}{\hbar \omega}} - 1}
\]  

(3.63)

This is the Planck result found the hard way. We will get to the easy way soon, and you will never again need to work with a multiplicity function like this.
Chapter 4

Week 3: Boltzmann distribution and Helmholtz (K&K 3, Schroeder 6)

This week we will be deriving the Boltzmann ratio and the Helmholtz free energy, continuing the microcanonical approach we started last week. Last week we saw that when two systems were considered together in a microcanonical picture, the energy of each system taken individually is not fixed. This provides our stepping stone to go from a microcanonical picture where all possible microstates have the same energy (and equal probability) to a canonical picture where all energies are possible and the probability of a given microstate being observed depends on the energy of that state.

We ended last week by finding that the following quantity is equal in two systems in thermal equilibrium

\[ \beta = \left( \frac{\partial \ln g}{\partial E} \right)_V \quad (4.1) \]

where \( g(E) \) is the multiplicity in the microcanonical ensemble. To more definitively connect this with temperature, we will again consider two systems in thermal equilibrium using a microcanonical ensemble, but this time we will make one of those two systems huge. In fact, it will be so huge that we can treat it using classical thermodynamics, i.e. we can conclude that the above equation applies, and we can assume that the temperature of this huge system is unaffected by the small change in energy that could happen due to differences in the small system.

Let us now examine the multiplicity of our combined system, making \( B \) be our large system:

\[ g_{AB}(E) = \sum_{E_A} g_A(E_A) g_B(E_{AB} - E_A) \quad (4.2) \]

We can further find the probability of any particular energy being observed from

\[ P_A(E_A|E_{AB}) = \frac{g_A(E_A) g_B(E_{AB} - E_A)}{\sum_{E'_A} g_A(E'_A) g_B(E_{AB} - E'_A)} \quad (4.3) \]

where we are counting how many microstates of the combined system have this particular energy in system \( A \), and dividing by the total number of microstates of the combined system to create a probability. So far this is identical to what we had last week. The difference is that we are now claiming that system \( B \) is huge. This means that we can approximate \( g_B \). Doing so, however requires some care.

**Warning wrong!** We might be tempted to simply Taylor expand \( g_B \).
\[ g_B(E_{AB} - E_A) \approx g_B(E_{AB}) - \beta g_B(E_{AB})E_A + \cdots \]  
(4.4)

\[ \approx g_B(E_{AB})(1 - \beta E_A) \]  
(4.5)

This however, would be wrong unless \( \beta E_A \ll 1 \).

One way to see that this expansion must have limited range is that if \( \beta E_A \geq 1 \) then we will end up with a negative multiplicity, which is meaningless. The trouble is that we only assumed that \( E_A \) was small enough not to change the temperature (or \( \beta \)), which does not mean that \( \beta E_A < 1 \). Thus this expansion is guaranteed to fail.

When we run into this problem, we can consider that \( \ln g(E) \) is generally a smoother function than \( g(E) \). Based on the Central Limit Theorem, we expect \( g(E) \) to typically have a Gaussian shape, which is one of our analytic functions that is least well approximated by a polynomial. In contrast, \( \ln g \) will be parabolic (to the extent that \( g \) is Gaussian), which makes it a prime candidate for a Taylor expansion.

**Right way** The right way to do this is to Taylor expand the \( \ln g \) (which will be entropy), since the derivative of \( \ln g \) is the thing that equilibrates, and thus we can assume that this derivative won’t change much when we make a small change to a large system.

\[ \ln g_B(E_{AB} - E_A) \approx \ln g_B(E_{AB}) - \beta E_A + \cdots \]  
(4.6)

\[ g_B(E_{AB} - E_A) \approx g_B(E_{AB})e^{-\beta E_A} \]  
(4.7)

Now we can plug this into the probability equation above to find that

\[ P_A(E_A) = \frac{g_A(E_A)g_B(E_{AB})e^{-\beta E_A}}{\sum_{E_A'} g_A(E_A')g_B(E_{AB})e^{-\beta E_A'}} \]  
(4.8)

\[ = \frac{g_A(E_A)e^{-\frac{E_A}{k_BT}}}{\sum_{E_A'} g_A(E_A')e^{-\frac{E_A'}{k_BT}}} \]  
(4.9)

Now this looks a bit different than the probabilities we saw previously (two weeks ago), because this is the probability that we see an energy \( E_A \), not the probability for a given microstate, and thus it has the factors of \( g_A \), and it sums over energies rather than microstates. To find the probability of a given microstate, we just need to divide the probability of its energy by the number of microstates at that energy, i.e. drop the factor of \( g \):

\[ P_i^A = \frac{e^{-\beta E_i}}{Z} \]  
(4.10)

\[ Z = \sum_{E} g(E)e^{-\beta E} \]  
(4.11)

\[ = \sum_{E} e^{-\beta E} \]  
(4.12)

This is all there is to show the Boltzmann probability distribution from the microcanonical picture: Big system with little system, treat big system thermodynamically, count microstates.

**Note** We still haven’t shown (this time around) that \( \beta = \frac{1}{k_BT} \). Right now \( \beta \) is just still a particular derivative that equalizes when two systems are in thermal equilibrium.

**Internal energy**

Now that we have the set of probabilities expressed again in terms of \( \beta \), there are a few things we can solve for directly, namely any quantities that are directly defined from probabilities. Most specifically, the internal energy
\[ U = \sum_i P_i E_i \]  
(4.13)

\[ = \sum_i E_i e^{-\beta E_i} \]  
(4.14)

\[ = \frac{1}{Z} \sum_i E_i e^{-\beta E_i} \]  
(4.15)

Now doing yet another summation will often feel tedious. There are a couple of ways to make this easier. The simplest is to examine the sum above and notice how very similar it is to the partition function itself. If you take a derivative of the partition function with respect to \( \beta \), you will find:

\[ \left( \frac{\partial Z}{\partial \beta} \right)_V = \sum_i e^{-\beta E_i} (-E_i) \]  
(4.16)

\[ = -UZ \]  
(4.17)

\[ U = -\frac{1}{Z} \left( \frac{\partial Z}{\partial \beta} \right)_V \]  
(4.18)

\[ = -\left( \frac{\partial \ln Z}{\partial \beta} \right)_V \]  
(4.19)

**Big Warning** In this class, I do not want you beginning any solution (either homework or exam) with a formula for \( U \) in terms of \( Z \)! This step is not that hard, and you need to do it every time. What you need to remember is definitions, which in this case is how \( U \) comes from probability. The reasoning here is that I’ve all too often seen students who years after taking thermal physics can only remember that there is some expression for \( U \) in terms of \( Z \). It is easier and more correct to remember that \( U \) is a weighted average of the energy.

**Pressure**

How do we compute pressure? So far, everything we have done has kept the volume fixed. Pressure tells us how the energy changes when we change the volume, i.e. how much work is done. From Energy and Entropy, we know that

\[ dU = TdS - pdV \]  
(4.20)

\[ p = -\left( \frac{\partial U}{\partial V} \right)_S \]  
(4.21)

So how do we find the pressure? We need to find the change in internal energy when we change the volume at fixed entropy.

**Small white boards** How do we keep the entropy fixed when changing the volume?

**Answer** Experimentally, we would avoid allowing any heating by insulating the system. Theoretically, this is less easy. When we consider the Gibbs entropy, if we could keep all the probabilities fixed while expanding, we would also fix the entropy! In quantum mechanics, we can show that such a process is possible using time-dependent perturbation theory. Under certain conditions, if you perturb a system sufficiently slowly, it will remain in the “same” eigenstate it was in originally. Although the eigenstate changes, and its energy changes, they do so continuously.

If we take a derivative of \( U \) with respect to volume while holding the probabilities fixed, we obtain the following result:

\[ p = -\left( \frac{\partial U}{\partial V} \right)_S \]  
(4.22)

\[ = -\left( \frac{\partial \sum_i E_i P_i}{\partial V} \right)_S \]  
(4.23)

\[ = -\sum_i P_i \frac{dE_i}{dV} \]  
(4.24)

\[ = -\sum_i e^{-\beta E_i} \frac{dE_i}{dV} \]  
(4.25)

So the pressure is just a weighted sum of derivatives.
of energy eigenvalues with respect to volume. We can apply the derivative trick to this also:

\[ p = \frac{1}{\beta Z} \left( \frac{\partial Z}{\partial V} \right)_\beta \]  
\[ = \frac{1}{\beta} \left( \frac{\partial \ln Z}{\partial V} \right)_\beta \]  
\[ (4.26) \]

Now we have an expression in terms of \( \ln Z \) and \( \beta \).

**Helmholtz free energy**

We saw a hint above that \( U \) somehow relates to \( \ln Z \), which hinted that \( \ln Z \) might be something special, and now \( \ln Z \) also turns out to relate to the pressure somehow. Let’s put this into thermodynamics language.\(^1\)

\[ U = - \left( \frac{\partial \ln Z}{\partial \beta} \right)_V \]  
\[ (4.28) \]

\[ d \ln Z = -U d\beta + \left( \frac{\partial \ln Z}{\partial V} \right)_\beta dV \]  
\[ (4.29) \]

\[ d \ln Z = -U d\beta + \beta p dV \]  
\[ (4.30) \]

We can already see the work in here. So now we’re going to try a switch to a \( dU \) rather than a \( d\beta \), since we know something about \( dU \).

\[ d(\beta U) = U d\beta + \beta dU \]  
\[ (4.31) \]

\[ d \ln Z = - (d(\beta U) - \beta dU) + \beta p dV \]  
\[ = \beta dU - d(\beta U) + \frac{p}{\beta} dV \]  
\[ (4.33) \]

\[ \beta dU = d (\ln Z + \beta U) - \beta p dV \]  
\[ (4.34) \]

\[ dU = \frac{1}{\beta} d (\ln Z + \beta U) - p dV \]  
\[ (4.35) \]

Comparing this result with the thermodynamic identity tells us that

\[ S = k_B \ln Z + U/T \]  
\[ (4.36) \]

\[ F \equiv U - TS \]  
\[ (4.37) \]

\[ = U - T (k_B \ln Z + U/T) \]  
\[ (4.38) \]

\[ = U - k_B T \ln Z + U \]  
\[ (4.39) \]

\[ = -k_B T \ln Z \]  
\[ (4.40) \]

That was a bit of a differentials slog, but got us the same result without assuming the Gibbs entropy. It did, however, demonstrate a not-quite-contradiction, in that the expression we found for the entropy is not mathematically equal to the Boltzmann entropy. It approaches the same thing for large systems, although I won’t prove that now.

**Small groups** Consider a system with \( g \) eigenstates, each with energy \( E_0 \). What is the free energy?

**Answer** We begin by writing down the partition function

\[ Z = \sum_i e^{-\beta E_i} \]  
\[ (4.41) \]

\[ = g e^{-\beta E_0} \]  
\[ (4.42) \]

Now we just need a log and we’re done.

\[ F = -kT \ln Z \]  
\[ (4.43) \]

\[ = -kT \ln (g e^{-\beta E_0}) \]  
\[ (4.44) \]

\[ = -kT (\ln g + \ln e^{-\beta E_0}) \]  
\[ (4.45) \]

\[ = E_0 - Tk \ln g \]  
\[ (4.46) \]

This is just what we would have concluded about the free energy if we had used the Boltzmann expression for the entropy in this microcanonical ensemble.

Waving our hands, we can understand \( F = -kT \ln Z \) in two ways:

1. If there are more accessible microstates, \( Z \) is bigger, which means \( S \) is bigger and \( F \) must be more negative.

\(^1\)Of course, we already talked last week about \( F = -kT \ln Z \), but that was done using the Gibbs entropy, which we’re pretending we don’t yet know...
2. If we only consider the most probable energies, to find the energy from $Z$, we need the negative logarithm, and a $kT$ to cancel out the $\beta$.

**Using the free energy**

Why the big deal with the free energy? One way to put it is that it is relatively easy to compute. The other is that once you have an analytic expression for the free energy, you can solve for pretty much anything else you want.

Recall:

\[
F \equiv U - TS
\]

\[
dF = dU - SdT - TdS
\]

\[
= -SdT - pdV
\]

\[
-S = \left( \frac{\partial F}{\partial T} \right)_V
\]

\[
-p = \left( \frac{\partial F}{\partial V} \right)_T
\]

Thus by taking partial derivatives of $F$ we can find $S$ and $p$ as well as $U$ with a little arithmetic. You have all seen the Helmholtz free energy before so this shouldn’t be much of a surprise. Practically, the Helmholtz free energy is *why* finding an analytic expression for the partition function is so valuable.

In addition to the “fundamental” physical parameters, we can also find response functions, such as heat capacity or compressibility which are their derivatives. Of particular interest is the heat capacity at fixed volume. The heat capacity is vaguely defined as:

\[
C_V \equiv \left( \frac{\partial Q}{\partial T} \right)_V
\]

which is a nice equation, but can be a nuisance because we often don’t know $U$ as a function of $T$, which is not one of its natural variables. We can also go back to our Energy and Entropy relationship between heat and entropy where $\bar{d}Q = TdS$, and use that to find the ratio that defines the heat capacity:

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

Note that this could also have come from a manipulation of the previous derivative of the internal energy. However, the “heat” reasoning allows us to recognize that the heat capacity at constant pressure will have the same form when expressed as an entropy derivative. This expression is also convenient when we compute the entropy from the Helmholtz free energy, because we already know the entropy as a function of $T$.

**Ideal gas with just one atom**

Let us work on the free energy of a particle in a 3D box.

**Small groups (5 minutes)** Work out (or write down) the energy eigenstates for a particle confined to a cubical volume with side length $L$. You may either use periodic boundary conditions or an infinite square well. When you have done so, write down an expression for the partition function.

**Answer** The energy is just the kinetic energy, given by...
\[ T = \frac{\hbar^2 k_B}{2m} \] (4.55)

The allowed values of \( k \) are determined by the boundary conditions. If we choose periodic boundary conditions, then

\[ k_x = \frac{2\pi}{L} \quad n_x = \text{any integer} \quad (4.56) \]

and similarly for \( k_y \) and \( k_z \), which gives us

\[ E_{n_x n_y n_z} = \frac{2\pi^2 \hbar^2}{mL^2} (n_x^2 + n_y^2 + n_z^2) \quad (4.57) \]

where \( n_x, n_y, \) and \( n_z \) take any integer values. If we chose the infinite square well boundary conditions instead, our integers would be positive values only, and the prefactor would differ by a factor of four.

From this point, we just need to sum over all states to find \( Z \), and from that the free energy and everything else! So how do we sum all these things up?

\[ Z = \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty}^{\infty} \sum_{n_z=-\infty}^{\infty} e^{-\beta \frac{2\pi^2 \hbar^2}{mL^2} (n_x^2 + n_y^2 + n_z^2)} \]

\[ = \sum_{n_x} \sum_{n_y} \sum_{n_z} e^{-\beta \frac{2\pi^2 \hbar^2}{mL^2} n_x^2} e^{-\beta \frac{2\pi^2 \hbar^2}{mL^2} n_y^2} e^{-\beta \frac{2\pi^2 \hbar^2}{mL^2} n_z^2} \]

\[ = \left( \sum_{n_x} e^{-\beta \frac{2\pi^2 \hbar^2}{mL^2} n_x^2} \right)^3 \quad (4.58) \]

This gives us a very easy integral.

\[ Z = \left( \int_{-\infty}^{\infty} e^{-x^2} \, dx \right)^3 \quad (4.64) \]

So there we have our partition function for a single atom in a big box. Let’s go on to find exciting things!
First off, let’s give a name to the nasty fraction to the \( \frac{3}{2} \) power. It has dimensions of inverse volume, or number per volume, and it has \( \hbar \) in it (which makes it quantum) so let’s call it \( n_Q \), since I use \( n = N/V \) for number density.

\[
n_Q = \left( \frac{k_B T m}{2\pi \hbar^2} \right)^{\frac{3}{2}} \quad (4.68)
\]

\[
F = -kT \ln Z = -kT \ln (V n_Q) \quad (4.69)
\]

\[
\frac{\partial F}{\partial V} T = \frac{kT}{V} \quad (4.70)
\]

This looks like (and is) a very simple formula, but you need to keep in mind that \( n_Q \) depends on temperature, so it’s not quite as simple as it looks. Now that we have the Helmholtz free energy, we can solve for the entropy, pressure, and internal energy pretty quickly.

**Small groups** Solve for the entropy, pressure, and internal energy.

\[
S = -\left( \frac{\partial F}{\partial T} \right)_V = k \ln (V n_Q) + \frac{kT}{V} \frac{d n_Q}{d T} \quad (4.71)
\]

\[
S = k \ln (V n_Q) + \frac{kT}{V} \left\{ \frac{3 n_Q}{2} \right\} \quad (4.72)
\]

\[
S = k \ln (V n_Q) + \frac{3}{2} k_B \quad (4.73)
\]

\[
U = F + TS = -kT \ln (V n_Q) + kT \ln (V n_Q) + \frac{3}{2} k_B T \quad (4.75)
\]

\[
U = \frac{3}{2} k_B T \quad (4.76)
\]

The pressure derivative gives a particularly simple result.

\[
p = -\left( \frac{\partial F}{\partial V} \right)_T = \frac{kT}{V} \quad (4.78)
\]

**Ideal gas with multiple atoms**

Extending from a single atom to several requires just a bit more subtlety. Naively, you could just argue that because we understand extensive and intensive quantities, we should be able to go from a single atom to \( N \) atoms by simply scaling all extensive quantities. That is almost completely correct (if done correctly).

The entropy has an extra term (the “entropy of mixing”), which also shows up in the free energy. Note that while we may think of this “extra term” as an abstract counting thing, it is physically observable, provided we do the right kind of experiment (which turns out to need to involve changing \( N \), so we won’t discuss it in detail until we talk about changing \( N \) later).

There are a few different ways we could imagine putting \( N \) non-interacting atoms together. I will discuss a few here, starting from simplest, and moving up to the most complex.

**Different atoms, same box** One option is to consider a single box with volume \( V \) that holds \( N \) different atoms, each of a different kind, but all with the same mass. In this case, each microstate of the system will consist of a microstate for each atom. Quantum mechanically, the wave function for the entire state with \( N \) atoms will separate and will be a product of \( N \) single-particle states (or orbitals)

\[
\Psi_{\text{microstate}}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \prod_{i=1}^{N} \phi_{n_{x_i}, n_{y_i}, n_{z_i}}(\vec{r}_i) \quad (4.80)
\]
and the energy will just be a sum of different energies. The result of this will be that the partition function of the entire system will just be the product of the partition functions of all the separate non-interacting systems (which happen to all be equal). This is mathematically equivalent to what already happened with the three $x$, $y$ and $z$ portions of the partition function.

$$Z_N = Z_1^N$$ (4.81)

$$F_N = NF_1$$ (4.82)

This results in simply scaling all of our extensive quantities by $N$ except the volume, which didn’t increase when we added more atoms.

This result sounds great, in that it seems to be perfectly extensive, but when we look more closely, we can see that it is actually not extensive!

$$F_N = -NkT \ln(Vn_Q)$$ (4.83)

If we double the size of our system, so $N \rightarrow 2N$ and $V \rightarrow 2V$, you can see that the free energy does not simply double, because the $V$ in the logarithm doubles while $n_Q$ remains the same (because it is intensive). So there must be an error here, which turns out to be caused by having treated all the atoms as distinct. If each atom is a unique snowflake, then it doesn’t quite make sense to expect the result to be extensive, since you aren’t scaling up “interchangeable” things.

Identical atoms, but different boxes We can also consider saying all atoms are truly identical, but each atom is confined into a different box, each with identical (presumably small) size. In this case, the same reasoning as we used above applies, but now we also scale the total volume up by $N$. This is a more natural application of the idea of extensivity.

This is taking the idea of extensivity to an extreme: we keep saying that a system with half as much volume and half as many atoms is “half as much” until there is only one atom left. You would be right to be skeptical that putting one atom per box hasn’t resulted is an error.

Identical atoms, same box This is the picture for a real ideal gas. All of our atoms are the same, or perhaps some fraction are a different isotope, but who cares about that? Since they are all in the same box, we will want to write the many-atom wavefunction as a product of single-atom wavefunctions (sometimes called orbitals). Thus the wave function looks like our first option of “different atoms, same box”, but we have fewer distinct microstates, since swapping the quantum numbers of two atoms doesn’t change the microstate.

How to remove this duplication, which is sort of a fundamental problem when our business is counting microstates? Firstly, we will consider it vanishingly unlikely for two atoms to be in the same orbital (when we study Bose condensation, we will see this assumption breaking down). Then we need to figure out exactly how many times we counted each orbital, so we can correct our number of microstates (and our partition function). That number is equal to the number of permutations of $N$ distinct numbers, which is $N!$, if we can assume that there is negligible probability that two atoms are in an identical state. Thus we have a corrected partition function.
This answer is extensive, because now we have a ratio of $V$ and $N$ in the logarithm. So yay.

We now have the true free energy for an ideal gas at high enough temperature.

**Small groups (10-15 minutes)** Given this free energy, solve for $S$, $U$, and $p$.

**Answer** This is very similar to what we did with just one atom, but now it will give us the true answer for the monatomic ideal gas.

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

$$= -Nk\ln\left(\frac{n}{n_Q}\right) - 1 - NkT\frac{\partial}{\partial T}\ln n_Q$$

$$= -Nk\ln\left(\frac{n}{n_Q}\right) + Nk + \frac{3}{2}Nk$$

$$= -Nk\ln\left(\frac{n}{n_Q}\right) + \frac{5}{2}Nk$$

This is called the Sackur-Tetrode equation. The quantum mechanics shows up here ($\hbar^2/m$), even though we took the classical limit, because the entropy of a truly classical ideal gas has no minimum value. So quantum mechanics sets the zero of entropy. Note that the zero of entropy is a bit tricky to measure experimentally (albeit possible). The zero of entropy is in fact set by the Third Law of Thermodynamics, which you probably haven’t heard of.

Now we can solve for the internal energy:

$$U = F + TS$$

$$= NkT\left(\ln\left(\frac{n}{n_Q}\right) - 1\right) - NkT\ln\left(\frac{n}{n_Q}\right) + \frac{5}{2}NkT$$

$$= \frac{3}{2}NkT$$

This is just the standard answer you’re familiar with. You can notice that it doesn’t have any quantum mechanics in it, because we took The pressure is easier than the entropy, since the volume is only inside the log:

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$= \frac{NkT}{V}$$

This is the ideal gas law. Again, the quantum mechanics has vanished in the classical limit.

**Homework for week 3 (PDF)**

*For each problem, please let me know how long the problem took, and what resources you used to solve it!*

1. **Free energy of a two state system (K&K 3.1, modified)**

   a) Find an expression for the free energy as a function of $T$ of a system with two states, one at energy 0 and one at energy $\varepsilon$.

   b) From the free energy, find expressions for the internal energy $U$ and entropy $S$ of the system.

   c) Plot the entropy versus $T$. Explain its asymptotic behavior as the temperature becomes high.
d) Plot the $S(T)$ versus $U(T)$. Explain the maximum value of the energy $U$.

2. Magnetic susceptibility Consider a paramagnet, which is a material with $n$ spins per unit volume each of which may each be either “up” or “down”. The spins have energy $\pm mB$ where $m$ is the magnetic dipole moment of a single spin, and there is no interaction between spins. The magnetization $M$ is defined as the total magnetic moment divided by the total volume. Hint: each individual spin may be treated as a two-state system, which you have already worked with above.

\[ M = n m \tanh \left( \frac{mB}{kT} \right) \]  

(4.104)

where $n$ is the number of spins per unit volume. The figure shows what this magnetization looks like.

\[ \text{Figure 4.1: Plot of magnetization vs. B field} \]

a) Find the Helmholtz free energy of a paramagnetic system (assume $N$ total spins) and show that $F_N/kT$ is a function of only the ratio $x \equiv mB/kT$.

b) Use the canonical ensemble (i.e. partition function and probabilities) to find an exact expression for the total magnetization $M$ and the susceptibility

\[ \chi \equiv \left( \frac{\partial M}{\partial B} \right)_T \]  

(4.103)

as a function of temperature and magnetic field for the model system of magnetic moments in a magnetic field. The result for the magnetization is

\[ M = n m \tanh \left( \frac{mB}{kT} \right) \]  

(4.104)

\[ \text{Figure 4.1: Plot of magnetization vs. B field} \]

3. Free energy of a harmonic oscillator A one-dimensional harmonic oscillator has an infinite series of equally spaced energy states, with $\varepsilon_n = n \hbar \omega$, where $n$ is an integer $\geq 0$, and $\omega$ is the classical frequency of the oscillator. We have chosen the zero of energy at the state $n = 0$ which we can get away with here, but is not actually the zero of energy! To find the true energy we would have to add a $\frac{1}{2} \hbar \omega$ for each oscillator.

\[ \frac{S}{k_B} = \frac{\hbar \omega}{kT} \ln \left( \frac{1}{1 - e^{-\frac{\hbar \omega}{kT}}} \right) \]  

(4.106)

This entropy is shown in the nearby figure, as well as the heat capacity.

4. Energy fluctuations (K&K 3.4, modified) Consider a system of fixed volume in thermal contact with a reservoir. Show that the mean square fluctuations in the energy of the system is

\[ \langle (\varepsilon - \langle \varepsilon \rangle)^2 \rangle = k_B T^2 \left( \frac{\partial U}{\partial T} \right)_V \]  

(4.107)
Here $U$ is the conventional symbol for $\langle \varepsilon \rangle$. **Hint:** Use the partition function $Z$ to relate $\left( \frac{\partial U}{\partial T} \right)_V$ to the mean square fluctuation. Also, multiply out the term $(\cdots)^2$.

5. **Quantum concentration** (K&K 3.8) Consider one particle confined to a cube of side $L$; the concentration in effect is $n = L^{-3}$. Find the kinetic energy of the particle when in the ground state. There will be a value of the concentration for which this zero-point quantum kinetic energy is equal to the temperature $kT$. (At this concentration the occupancy of the lowest orbital is of the order of unity; the lowest orbital always has a higher occupancy than any other orbital.) Show that the concentration $n_0$ thus defined is equal to the quantum concentration $n_Q$ defined by (63):

$$n_Q \equiv \left( \frac{MkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \quad (4.108)$$

within a factor of the order of unity.

6. **One-dimensional gas** (K&K 3.11) Consider an ideal gas of $N$ particles, each of mass $M$, confined to a one-dimensional line of length $L$. Find the entropy at temperature $T$. The particles have spin zero.
Chapter 5

Week 4: Thermal radiation and Planck distribution (K&K 4, Schroeder 7.4)

This week we will be tackling things that reduce to a bunch of simple harmonic oscillators. Any system that classically reduces to a set of normal modes each with its own frequency falls in this category. We will start with just an ordinary simple harmonic oscillator, and will move on to look at radiation (photons) and sound in solids (phonons).

Harmonic oscillator

You will recall that the energy eigenvalues of a single simple harmonic oscillator are given by

\[ E_n = (n + \frac{1}{2})\hbar\omega \]  

(5.1)

Note The text uses \( s \) rather than \( n \) for the quantum number, but that is annoying, and on the blackboard my \( s \) looks too much like my \( S \), so I’ll stick with \( n \). The text also omits the zero-point energy. It does make the math simpler, but I think it’s worth seeing how the zero-point energy goes away to start with.

We will begin by solving for the properties of a single simple harmonic oscillator at a given temperature. You already did this once using multiplicities, but it’s easier this way.

\[ Z = \sum_{n=0}^{\infty} e^{-\left(n + \frac{1}{2}\right)\beta\hbar\omega} \]  

(5.2)

\[ = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} \]  

(5.3)

Now the sum is actually a harmonic (or geometric) sum, which has a little trick to solve:

\[ Z = e^{-\frac{1}{2}\beta\hbar\omega} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n \]  

(5.4)

\[ \xi = e^{-\beta\hbar\omega} \]  

(5.5)

The trick involves multiplying the series by \( \xi \) and subtracting:
\[ \Xi = \sum_{n=0}^{\infty} \xi^n \]  
\[ = 1 + \xi + \xi^2 + \cdots \]  
\[ \xi \Xi = \xi + \xi^2 + \cdots \]  
\[ \Xi - \xi \Xi = 1 \]  
\[ \Xi = \frac{1}{1 - \xi} \]  

Thus we find that the partition function is simply

\[ Z = \frac{e^{-\frac{1}{2} \beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \]  

This gives us the free energy

\[ F = -kT \ln Z \]  
\[ = -kT \ln \left( \frac{e^{-\frac{1}{2} \beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \right) \]  
\[ = \frac{1}{2} \hbar \omega + kT \ln \left( 1 - e^{-\beta \hbar \omega} \right) \]  

We can see now that the ground state energy just ends up as a constant that we add to the free energy, which is what you probably would have guessed. Kittel was able to omit this constant simply by redefining the zero of energy.

**Small groups** Solve for the high temperature limit of the free energy.

**Answer** At high temperatures, \( \beta \hbar \omega \ll 1 \), which means

\[ e^{-\beta \hbar \omega} = 1 - \beta \hbar \omega + \frac{1}{2} (\beta \hbar \omega)^2 + \cdots \]  
\[ \ln(1 - e^{-\beta \hbar \omega}) = \ln \left( \beta \hbar \omega - \frac{1}{2} (\beta \hbar \omega)^2 + \cdots \right) \]  
\[ F \approx \frac{1}{2} \hbar \omega + kT \ln \left( \frac{\hbar \omega}{kT} \right) \]  

So far this doesn’t tell us much, but from it we can quickly tell the high temperature limits of the entropy and internal energy:

\[ S \approx -k \ln \left( \frac{\hbar \omega}{kT} \right) - kT \frac{kT}{\hbar \omega} \left( \frac{\hbar \omega}{kT} \right) - \frac{1}{2} \left( \frac{\hbar \omega}{kT} \right)^2 \]  
\[ = k \left( \ln \left( \frac{kT}{\hbar \omega} \right) + 1 \right) \]  

The entropy increases as we increase temperature, as it always must. The manner in which \( S \) increases logarithmically with temperature tells us that the number of accessible microstates must be proportional to \( \frac{\hbar \omega}{kT} \).

\[ S = - \left( \frac{\partial F}{\partial T} \right)_V \]  
\[ = -k \ln \left( 1 - e^{-\beta \hbar \omega} \right) + kT \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \frac{\hbar \omega}{kT} \]  
\[ = -k \ln \left( 1 - e^{-\beta \hbar \omega} \right) + \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \frac{\hbar \omega}{T} \]  

**Planck distribution**

Finally, we can find the internal energy and the average quantum number (or number of “phonons”). The latter is known as the Planck distribution.

\[ U = F + TS \]  
\[ = \frac{1}{2} \hbar \omega + T \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \frac{\hbar \omega}{T} \]  

\[ U = \langle n \rangle + \frac{1}{2} \frac{\hbar \omega}{T} \]  
\[ \langle n \rangle \approx \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \]  
\[ \approx \frac{1}{e^{\beta \hbar \omega} - 1} \]  

So far, all we’ve done is a straightforward application of the canonical formalism from last week: we com-
computed a partition function, took a log, and from that found the entropy and internal energy.

**Small groups** Solve for the high-temperature and low-temperature limits of the internal energy and/or the average number of quanta $\langle n \rangle$.

**High temperature answer** First we consider $\frac{kT}{\hbar \omega} \gg 1$ or $\beta \hbar \omega \ll 1$. In this case, the exponential is going to be very close to one, and we can use a power series approximation for it.

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1} \quad (5.29)$$

$$\approx \frac{1}{1 + \beta \hbar \omega + \frac{1}{2} (\beta \hbar \omega)^2 + \cdots} - 1 \quad (5.30)$$

$$= \frac{kT}{\hbar \omega} \frac{1}{1 + \frac{1}{2} \beta \hbar \omega + \cdots} \quad (5.31)$$

$$= kT \frac{1}{\frac{1}{\hbar \omega} (1 - \frac{1}{2} \beta \hbar \omega + \cdots)} \quad (5.32)$$

$$\approx kT \frac{1}{\hbar \omega} - \frac{1}{2} \quad (5.33)$$

The first term is our equipartition term: $\frac{1}{2} kT$ each for the kinetic and potential energy. The second term is our next-order correction, which you need not necessarily include. There would be a next term which would be proportional to $1/T$, but we have omitted.

**Low temperature answer** At low temperature $\beta \hbar \omega \gg 1$, and we would rather look the other representation:

$$\langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1} \quad (5.29)$$

$$\approx \frac{1}{(1 + \beta \hbar \omega + \frac{1}{2} (\beta \hbar \omega)^2 + \cdots} - 1 \quad (5.30)$$

$$= \frac{kT}{\hbar \omega} \frac{1}{1 + \frac{1}{2} \beta \hbar \omega + \cdots} \quad (5.31)$$

$$= kT \frac{1}{\hbar \omega} (1 - \frac{1}{2} \beta \hbar \omega + \cdots) \quad (5.32)$$

$$\approx kT \frac{1}{\hbar \omega} - \frac{1}{2} \quad (5.33)$$

because now the exponentials are small (rather than large), which means we can expand the denominator as a power series.

$$\langle n \rangle = e^{-\beta \hbar \omega} \left( 1 + e^{-\beta \hbar \omega} + \cdots \right) \quad (5.36)$$

$$\approx e^{-\beta \hbar \omega} + e^{-2\beta \hbar \omega} \quad (5.37)$$

Once again, I kept one more term than is absolutely needed. Clearly at low temperature we have a very low number of quanta, which should be no shock. I hope you all expected that the system would be in the ground state at very low temperature.

**Summing over microstates**

I realized that we haven’t spent much time talking about how to sum over microstates. Once you “get it,” summing over microstates is very easy. Unfortunately, this makes it less obvious that this requires teaching, and I have a tendency to skim over this summation. A nice example of this was the second homework, which involved the paramagnet again. You needed to find the partition function for $N$ dipoles. After spending a week working with multiplicities, it would be very natural to take the

$$Z = \sum_{\mu} e^{-\beta E_{\mu}} \quad (5.38)$$

and think of the $\mu$ as having something to do with spin excess, and to think that this sum should involve multiplicities. You can write a solution here using multiplicities and summing over all possible energies, but that is the hard way. The easy way only looks easy once you know how to do it. The easy way involves literally summing over every possible sequence of spins.

$$Z = \sum_{s_1 = \pm 1} \sum_{s_2 = \pm 1} \cdots \sum_{s_N = \pm 1} e^{-\beta E(s_1, s_2, \ldots, s_N)} \quad (5.39)$$

This may look messy, but things simplify when we consider the actual energy (unless we try to simplify that by expressing it in terms of $N_\uparrow$ or the spin excess).

$$E(s_1, s_2, \ldots, s_N) = -s_1 mB - s_2 mB - \cdots - s_N mB \quad (5.40)$$
Now this may look pretty nasty, but it's actually beautiful, because each $s_i$ has a separate term that is added together, which means that it separates! I'll use fewer words for a bit...

$$Z = \sum_{s_1 = \pm 1} \sum_{s_2 = \pm 1} \cdots \sum_{s_N = \pm 1} e^{\beta (s_1 mB + s_2 mB + \cdots + s_N mB)}$$

(5.41)

$$= \sum_{s_1 = \pm 1} \sum_{s_2 = \pm 1} \cdots \sum_{s_N = \pm 1} e^{\beta s_1 mB} e^{\beta s_2 mB} \cdots$$

(5.42)

$$= \sum_{s_1 = \pm 1} e^{\beta s_1 mB} \sum_{s_2 = \pm 1} e^{\beta s_2 mB} \cdots \sum_{s_N = \pm 1} e^{\beta s_N mB}$$

(5.43)

$$= \left( \sum_{s_1 = \pm 1} e^{\beta s_1 mB} \right) \cdots \left( \sum_{s_N = \pm 1} e^{\beta s_N mB} \right)$$

(5.44)

$$= \left( \sum_{s = \pm 1} e^{\beta s mB} \right)^N$$

(5.45)

$$= \left( \sum_{s = \pm 1} e^{\beta s mB} \right)^N$$

(5.46)

The important steps above were

1. Writing the sum over states as a nested sum over every quantum number of the system.
2. Breaking the exponential into a product, which we can do because the energy is a sum of terms each of which involve just one quantum number.
3. Doing each sum separately, and finding the result as the product of all those sums.

Note that the final result here is a free energy that is just $N$ times the free energy for a system consisting of a single spin. And thus we could alternatively do our computation for a system with a single spin, and then multiply everything that is extensive by $N$. The latter is a valid shortcut, but you should know why it gives a correct answer, and when (as when we have identical particles) you could run into trouble.

**Black body radiation**

Researchers in 1858-1860 realized that materials emitted light in strict proportion to their ability to absorb it, and hence a perfectly black body would be emit the most radiation when heated. Planck and others realized that we should be able to use thermal physics to predict the spectrum of black body radiation. A key idea was to recognize that the light itself should be in thermal equilibrium.

One example of a “black body” is a small hole in a large box. Any light that goes into the hole will bounce around so many times before coming out of the hole, that it will all be absorbed. This leads to the idea of studying the radiation in a closed box, which should match that of a black body, when it is in thermal equilibrium.

**Eigenstates of an empty box**

So what are the properties of an empty box? Let’s assume metal walls, and not worry too much about details of the boundary conditions, which shouldn’t make much difference provided the box is pretty big. The reasoning is basically the same as for a particle in a 3D box: the waves must fit in the box. As for the particle in a box, we can choose either periodic boundary conditions or put nodes at the boundaries. I generally prefer periodic (which gives both positive and negative $\vec{k}$), rather than dealing with sine waves (which are superpositions of the above). A beautiful thing about periodic boundary conditions is that your set of $\vec{k}$ vectors is independent of the Hamiltonian, so this looks very much like the single atom in a box we did last week.

$$k_x = n_x \frac{2\pi}{L} \quad n_x = \text{any integer} \quad (5.47)$$

and similarly for $k_y$ and $k_z$, which gives us
\[ \omega(\vec{k}) = c|\vec{k}| \quad (5.48) \]
\[ \omega_{n_xn_yn_z} = \frac{2\pi c}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} \quad (5.49) \]

where now we need to be extra-careful to remember that in this expression \( n_x \) is not a number of photons, even though \( n \) is a number of photons. Fortunately, we will soon be done with our \( n_x \), once we finish summing. The possible energies of a single mode are those of a simple harmonic oscillator, so for each of the \( n_x,n_y,n_z \) triples there is a different quantum number \( n \), and an energy given by

\[ E_n = \left( n + \frac{1}{2} \right) \hbar \omega \quad (5.50) \]

In your homework, you will use a summation over all the normal modes to solve for the thermodynamic properties of the vacuum, and will show that

\[ F = \frac{8\pi V(kT)^4}{\hbar^2 c^3} \int_0^\infty \ln (1 - e^{-\xi}) \xi^2 d\xi \quad (5.51) \]
\[ = -\frac{8\pi^5 V(kT)^4}{45} \frac{1}{\hbar^3 c^3} \quad (5.52) \]
\[ = -\frac{\pi^2 V(kT)^4}{45} \frac{1}{\hbar^3 c^3} \quad (5.53) \]

provided the box is big enough that \( \frac{\hbar c}{kT} \ll 1 \). At first this looks freaky, because the free energy is always negative while you know that the energy is always positive. This just means that entropy is dominating the free energy.

The entropy is given by

\[ S = \frac{32\pi^5}{45} kV \left( \frac{kT}{\hbar c} \right)^3 \quad (5.54) \]
\[ = \frac{4\pi^2}{45} kV \left( \frac{kT}{\hbar c} \right)^3 \quad (5.55) \]

which is a comfortingly positive quantity, and the energy is

\[ \frac{U}{V} = \frac{8\pi^5 (kT)^4}{15 \hbar^3 c^3} \quad (5.56) \]
\[ = \frac{\pi^2 (kT)^4}{15 \hbar^3 c^3} \quad (5.57) \]

which is also nicely positive.

Note also that these quantities are also nicely extensive, as you would hope.

Knowing the thermodynamic properties of the vacuum is handy, but doesn’t tell us yet about the properties of a black body. To do that we’ll have to figure out how much of this radiation will escape through a little hole.

**Sefan-Boltzmann law of radiation**

To find the radiation power, we need do a couple of things. One is to multiply the energy per volume by the speed of light, which would tell us the energy flux through a hole if all the energy were passing straight through that hole. However, there is an additional geometrical term we will need to find the actual magnitude of the power, since the radiation is travelling equally in all directions. This will give us another dimensionless factor.

If we define the velocity as \( c\hat{k} \) where \( c \) is the speed of light and \( \hat{k} \) is its direction, the power flux (or intensity) in the \( \hat{z} \) direction will be given by the energy density times the average value of the positive \( \hat{z} \) component of the velocity. When \( v_z < 0 \), the light doesn’t come out the hole at all. This average can be written as
\[ I = \frac{U}{V} \int_0^{2\pi} \int_0^\pi v_z \sin \theta d\theta d\phi \tag{5.58} \]
\[ = \frac{U}{V} \int_0^{2\pi} \int_0^\pi c \cos \theta \sin \theta d\theta d\phi \tag{5.59} \]
\[ = \frac{U c}{V} \int_0^1 \xi d\xi \tag{5.60} \]
\[ = \frac{U c}{V} \int_0^\infty \xi d\xi \tag{5.61} \]
\[ = -6\pi \frac{(kT)^4}{h^3c^2} \int_0^\infty \ln (1 - e^{-\xi}) \xi^2 d\xi \tag{5.62} \]

This is the famous Stefan-Boltzmann law of radiation. Since the constants are all mostly a nuisance, they are combined into the Stefan-Boltzmann constant:

\[ I \equiv \text{power radiated per area of surface} \tag{5.63} \]
\[ = \sigma_B T^4 \tag{5.64} \]
\[ \sigma_B = -6\pi \frac{k^4_B}{h^3c^2} \int_0^\infty \ln (1 - e^{-\xi}) \xi^2 d\xi \tag{5.65} \]

**Side note** Why is this \( T^4 \) law important for incandescent light bulbs? The resistivity of a metal increases with temperature. In a light bulb, if you have a bit of wire that is a bit hotter than the rest, its resistivity will be higher, and that will cause it to have more Joule heating, and get hotter. If nothing else came into play, we’d have a feedback loop, and the hot bit would just keep getting hotter, and having higher resistivity, until it vaporized. Boom. Fortunately, the power of light radiated from that hot bit of wire will increase faster than its resistivity goes up (because \( T^4 \) is serious!), preventing the death spiral, and saving the day!

**Planck radiation law**

Having found the total power radiated, a fair question is how much of that power is at each possible frequency. This defines the black body spectrum. Each mode has an occupancy \( \langle n \rangle \) that is the same as that of the harmonic oscillator from Monday. But the power radiated also depends on how many modes there are at a given frequency. This may be more clear if we solve for the internal energy in a different way:

\[ U = \sum_j \langle n_j \rangle h\omega_j \tag{5.66} \]
\[ = \sum_j \frac{h\omega_j}{e^{\beta h\omega_j} - 1} \tag{5.67} \]
\[ \approx \int \int \int \frac{hc}{e^{\frac{hc}{kT} \sqrt{n_x^2 + n_y^2 + n_z^2}} - 1} d\omega_x d\omega_y d\omega_z \tag{5.68} \]
\[ = \int_0^\infty \frac{hc}{e^{\frac{hc}{kT} n} - 1} 4\pi n^2 dn \tag{5.69} \]

Now we can transform the integral from \( n \) to \( \omega \) via \( \omega_n = c2\pi/L \).
Kirchoff law

Surface temperature

Phonons in solids

Much of the same physics that we have considered here applies also to phonons in solids. For smallish $\vec{k}$, the frequency of a phonon is proportional to $|\vec{k}|$, with the speed of sound as the proportionality constant. We won’t have time for this in class.

Debye theory

The key thing Debye realized was that unlike light, the phonon $\vec{k}$ has a maximum value.

Homework for week 4 (PDF)

1. **Radiation in an empty box** As discussed in class, we can consider a black body as a large box with a small hole in it. If we treat the large box a metal cube with side length $L$ and metal walls, the frequency of each normal mode will be given by:

$$\omega_{n_x n_y n_z} = \frac{\pi c}{L} \sqrt{n_x^2 + n_y^2 + n_z^2}$$  \hspace{1cm} (5.73)

where each of $n_x$, $n_y$, and $n_z$ will have positive integer values. This simply comes from the fact that a half wavelength must fit in the box. There is an additional quantum number for polarization, which has two possible values, but does not affect the frequency. Each normal mode is a harmonic oscillator, with energy eigenstates $E_n = n\hbar\omega$ where we will not include the zero-point energy $\frac{1}{2}\hbar\omega$, since that energy cannot be extracted from the box. (See the Casimir effect for an example where the zero point energy of photon modes does have an effect.)

Note This is a slight approximation, as the boundary conditions for light are a bit more complicated. However, for large $n$ values this gives the correct result.

a) Show that the free energy is given by

$$F = 8\pi \frac{V(kT)^4}{\hbar^3 c^3} \int_0^\infty \ln \left(1 - e^{-\xi}\right) \xi^2 d\xi$$ \hspace{1cm} (5.74)

$$= -\frac{8\pi^5}{45} \frac{V(kT)^4}{\hbar^3 c^3}$$ \hspace{1cm} (5.75)

$$= -\frac{\pi^2}{45} \frac{V(kT)^4}{\hbar^3 c^3}$$ \hspace{1cm} (5.76)

provided the box is big enough that $\frac{\hbar c}{kT} \ll 1$. Note that you may end up with a slightly different dimensionless integral that numerically evaluates to the same result, which would be fine. I also do not expect you to solve this definite integral analytically, a numerical confirmation is fine. However, you must manipulate your integral until it is dimensionless and has all the dimensionful quantities removed from it!

b) Show that the entropy of this box full of photons at temperature $T$ is

$$S = \frac{32\pi^5}{45} kV \left(\frac{kT}{\hbar c}\right)^3$$ \hspace{1cm} (5.77)

$$= \frac{4\pi^2}{45} kV \left(\frac{kT}{\hbar c}\right)^3$$ \hspace{1cm} (5.78)

c) Show that the internal energy of this box full of photons at temperature $T$ is

$$\frac{U}{V} = \frac{8\pi^5}{15} \frac{(kT)^4}{\hbar^3 c^3}$$ \hspace{1cm} (5.79)

$$= \frac{\pi^2}{15} \frac{(kT)^4}{\hbar^3 c^3}$$ \hspace{1cm} (5.80)

2. **Surface temperature of the earth** (K&K 4.5)

Calculate the temperature of the surface of the
Earth on the assumption that as a black body in thermal equilibrium it reradiates as much thermal radiation as it receives from the Sun. Assume also that the surface of the Earth is a constant temperature over the day-night cycle. Use the sun’s surface temperature $T_\odot = 5800\, \text{K}$; and the sun’s radius $R_\odot = 7 \times 10^{10}\, \text{cm}$; and the Earth-Sun distance of $1.5 \times 10^{11}\, \text{cm}$.

3. **Pressure of thermal radiation** (modified from K&K 4.6) We discussed in class that

$$p = -\left(\frac{\partial F}{\partial V}\right)_T$$  \hspace{1cm} (5.81)

Use this relationship to show that

a) $$p = -\sum_j \langle n_j \rangle \hbar \left(\frac{d\omega_j}{dV}\right),$$  \hspace{1cm} (5.82)

where $\langle n_j \rangle$ is the number of photons in the mode $j$;

b) Solve for the relationship between pressure and internal energy.

4. **Heat shields** (K&K 4.8) A black (nonreflective) plane at high temperature $T_h$ is parallel to a cold black plane at temperature $T_c$. The net energy flux density in vacuum between the two planes is $J_U = \sigma_B (T_h^4 - T_c^4)$, where $\sigma_B$ is the Stefan-Boltzmann constant used in (26). A third black plane is inserted between the other two and is allowed to come to a steady state temperature $T_m$. Find $T_m$ in terms of $T_h$ and $T_c$, and show that the net energy flux density is cut in half because of the presence of this plane. This is the principle of the heat shield and is widely used to reduce radiant heat transfer. *Comment:* The result for $N$ independent heat shields floating in temperature between the planes $T_u$ and $T_l$ is that the net energy flux density is $J_U = \sigma_B \frac{r_u^4 - r_l^4}{N+1}$. 

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Chapter 6

Week 5: Chemical potential and Gibbs distribution (K&K 9, Schroeder 7.1)

This week be looking at scenarios where the number of particles in a system changes. We could technically always manage to solve problems without doing such a system, but allowing \( N \) to change is often a lot easier, just as letting the energy change made things easier. In both case, we enable ourselves to consider a smaller system, which tends to be both conceptually and mathematically simpler.

The atmosphere

Let's talk about the atmosphere for a moment. Each atmosphere has a potential energy. We can solve this problem using the canonical ensemble as we have learned. We will consider just one atom, but now with gravitational potential energy as well as kinetic energy. This time around we'll do this classically rather than quantum mechanically. We can work out the probability of this atom having any particular momentum and position.

\[
P_1(\vec{p}, \vec{r}) = \frac{e^{-\beta \left( \frac{p^2}{2m} + mgz \right)}}{Z_1} = \frac{e^{-\beta \frac{p^2}{2m} - \beta mgz}}{Z_1} \tag{6.1}
\]

This tells us that the probability of this atom being at any height drops exponentially with height. If we extend this to many atoms, clearly the density must drop exponentially with height. This week we'll be looking at easier approaches to explain this sort of phenomenon. You can see the obvious fact that potential energy will affect density, and hence pressure. We will be generalizing the idea of potential energy into what is called chemical potential.

Chemical potential

Imagine for a moment what happens if you allow just two systems to exchange particles as well as energy. Clearly they will exchange particles for a while, and then things will settle down. If we hold them at fixed temperature, their combined Helmholtz free energy will be maximized. This means that the derivative
of the Helmholtz free energy with respect to $N$ must be equal on both sides. This defines the chemical potential.

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V}$$

(6.3)

This expands our total differential of the free energy

$$dF = -SdT - pdV + \mu dN$$

(6.4)

which also expands our understanding of the thermodynamic identity

$$dU = TdS - pdV + \mu dN$$

(6.5)

which tells us that the chemical potential is also

$$\mu = \left( \frac{\partial U}{\partial N} \right)_{S,V}$$

(6.6)

The chemical potential expands our set of thermodynamic variables, and allows all sorts of nice excitement. Specifically, we now have three extensive variables that the internal energy depends on, as well as their derivatives, the temperature, pressure, and chemical potential.

**Note** In general, there is one chemical potential for each kind of particle, thus the word “chemical” in chemical potential. Thus the “three” I discuss is actually a bit flexible.

**Internal and external**

The chemical potential is in fact very much like potential energy. We can distinguish between external chemical potential, which is basically ordinary potential energy, and internal chemical potential, which is the chemical potential that we compute as a property of a material. We’ll do a fair amount of computing of the internal chemical potential this week, but keep in mind that the total chemical potential is what becomes equal in systems that are in equilibrium. The total chemical potential at the top of the atmosphere, is equal to the chemical potential at the bottom. If it were not, then atoms would diffuse from one place to the other.

**Ideal gas chemical potential**

Recall the Helmholtz free energy of an ideal gas is given by

$$F = NF_1 + k_B T \ln N!$$

$$= -Nk_B T \ln \left( V \left( \frac{mk_B T}{2\pi \hbar^2} \right)^{\frac{3}{2}} \right) + k_B TN (\ln N - 1)$$

(6.7)

$$= -Nk_B T \ln (VN_Q) + k_B TN (\ln N - 1)$$

(6.8)

$$= Nk_B T \ln \left( \frac{N}{Vn_Q} \right) - NkT$$

(6.9)

To find the chemical potential, we just need to take a derivative.

**Small groups** Find the chemical potential of the ideal gas.

**Answer**

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{V,T}$$

(6.11)

$$= k_B T \ln \left( \frac{N}{Vn_Q} \right)$$

(6.12)

$$= k_B T \ln \left( \frac{n}{n_Q} \right)$$

(6.13)

where the number density $n$ is given by $n \equiv N/V$.

This equation can be solved to find the density in terms of the chemical potential:
This might remind you of the Boltzmann relation. In fact, it's very closely related to the Boltzmann relation. We do want to keep in mind that the $\mu$ above is the internal chemical potential. The total chemical potential is given by the sum of the internal chemical potential and the external chemical potential, and that total is what is equalized between systems that are in diffusive contact.

$$\mu_{tot} = \mu_{int} + mgz$$

$$= k_B T \ln \left( \frac{n}{n_Q} \right) + mgz$$

We can solve for the density now, as a function of position.

$$k_B T \ln \left( \frac{n}{n_Q} \right) = \mu_{tot} - mgz$$

$$n = n_Q e^{-\beta (\mu_{tot} - mgz)}$$

This is just telling us the same result we already knew, which is that the density must drop exponentially with height.

**Interpreting the chemical potential**

The chemical potential can be challenging to understand intuitively, for myself as well as for you. The ideal gas expression

$$n = n_Q e^{\beta \mu}$$  \hspace{1cm} (6.14)

can help with this. This tells us that the density increases as we increase the chemical potential. Particles spontaneously flow from high chemical potential to low chemical potential, just like heat flows from high temperature to low. This fits with the idea that at high $\mu$ the density is high, since I expect particles to naturally flow from a high density region to a low density region.

The distinction between internal and external chemical potential allows us to reason about systems like the atmosphere. Where the external chemical potential is high (at high altitude), the internal chemical potential must be lower, and there is lower density. This is because particles have already fled the high-$\mu$ region to happier locations closer to the Earth.

**Gibbs factor and sum**

Let’s consider how we maximize entropy when we allow not just microstates with different energy, but also microstates with different *number of particles.* The problem is the same was we dealt with the first week. We want to maximize the entropy, but need to fix the total probability, the average energy and now the average number.

$$\langle N \rangle = N = \sum_i P_i N_i$$

$$\langle E \rangle = U = \sum_i P_i E_i$$

$$1 = \sum_i P_i$$

Now let’s construct a lagrangian with three lagrange multipliers to maximize the entropy.

$$\mathcal{L} = -k \sum_i P_i \ln P_i + k \alpha \left( 1 - \sum_i P_i \right)$$

$$+ k \beta \left( U - \sum_i P_i E_i \right)$$

$$+ k \gamma \left( N - \sum_i P_i N_i \right)$$ 

(6.23)
Now we maximize this.

\[ 0 = -\frac{1}{k} \frac{\partial \mathcal{L}}{\partial P_i} \]
\[ = \ln P_i + 1 + \alpha + \beta E_i + \gamma N_i \]  
\[ P_i = e^{-1 - \alpha - \beta E_i - \gamma N_i} \]

Examine this total differential, we can see that

\[ \mu T = \left( \frac{\partial S}{\partial N} \right)_{U,V} \]

Great, now as before we’ll want to apply the normalization constraint first.

\[ 1 = \sum_i P_i \]
\[ = \sum_i e^{-1 - \alpha - \beta E_i - \gamma N_i} \]
\[ = e^{-1 - \alpha} \sum_i e^{-\beta E_i - \gamma N_i} \]
\[ e^{-1 - \alpha} = \frac{1}{\sum_i e^{-\beta E_i - \gamma N_i}} \]

Thus we find that the probability of a given microstate is

\[ P_i = \frac{-\beta E_i - \gamma N_i}{Z} \]
\[ Z \equiv \sum_i e^{-\beta E_i - \gamma N_i} \]

Now we can zap this with \( d \) to find its derivatives:

\[ dS = k\beta dU + k\gamma dN + kN d\gamma + k \frac{dZ}{Z} \]

Putting \( dS \) together gives

\[ dS = k\beta dU + k\gamma dN \]
Thus, we conclude that

\[ k\gamma = -\frac{\mu}{T} \]  
\[ \gamma = -\beta\mu \]  
(6.44)  
(6.45)

**Actual Gibbs sum (or grand sum)**

Putting this interpretation for \( \gamma \) into our probabilities we find the Gibbs factor and **Gibbs sum** (or **grand sum** or **grand partition function**) to be:

\[ P_j = -\frac{\beta (E_j - \mu N_j)}{Z} \]  
(6.46)

\[ Z = \sum_i e^{-\beta (E_i - \mu N_i)} \]  
(6.47)

where you must keep in mind that the sums are over all microstates (including states with different \( N \)). We can go back to our expressions for internal energy and number

\[ U = \sum_i P_i E_i \]  
(6.48)

\[ = \frac{1}{Z} \sum_i E_i e^{-\beta (E_i - \mu N_i)} \]  
(6.49)

\[ N = \sum_i P_i N_i \]  
(6.50)

\[ = \frac{1}{Z} \sum_i N_i e^{-\beta (E_i - \mu N_i)} \]  
(6.51)

We can now use the derivative trick to relate \( U \) and \( N \) to the Gibbs sum \( Z \), should we so desire.

**Small groups** Work out the partial derivative tricks to compute \( U \) and \( N \) from the grand sum.

**Answer** Let’s start by exploring the derivative with respect to \( \beta \) which worked so nicely with the partition function.

\[ \frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{1}{Z} \sum_i (E_i - \mu N_i) e^{-\beta (E_i - \mu N_i)} \]  
(6.52)

\[ = -U + \mu N \]  
(6.53)

Now let’s examine a derivative with respect to \( \mu \).

\[ \frac{1}{Z} \frac{\partial Z}{\partial \mu} = \frac{1}{Z} \sum_i (\beta N_i) e^{-\beta (E_i - \mu N_i)} \]  
(6.54)

\[ = \beta N \]  
(6.55)

Arranging these to find \( N \) and \( U \) is not hard.

**Small groups** Show that

\[ \frac{\partial N}{\partial \mu} \bigg|_{T,V} > 0 \]  
(6.56)

**Answer**

\[ N = \sum_i N_i P_i \]  
(6.57)

\[ = kT \frac{1}{Z} \left( \frac{\partial Z}{\partial \mu} \right)_\beta \]  
(6.58)

So the derivative we seek will be

\[ \left( \frac{\partial N}{\partial \mu} \right)_{T,V} = kT \left( \frac{\partial^2 Z}{\partial \mu^2} \right)_\beta \]  
(6.59)

\[ = \sum_i N_i \left( \frac{\partial P_i}{\partial \mu} \right)_\beta \]  
(6.60)

\[ = \sum_i N_i \left( \beta N_i P_i - \frac{P_i}{Z} \left( \frac{\partial Z}{\partial \mu} \right)_\beta \right) \]  
(6.61)

\[ = \sum_i N_i (\beta N_i P_i - \beta \langle N \rangle P_i) \]  
(6.62)
We can simplify this the notation by expressing things in terms of averages, since we’ve got sums of $P_i$ times something.

$$= \beta \langle N_i (N_i - \langle N \rangle) \rangle$$  \hspace{1cm} (6.63)

$$= \beta \left( \langle N^2 \rangle - \langle N \rangle^2 \right)$$  \hspace{1cm} (6.64)

$$= \beta \left( \langle N - \langle N \rangle \rangle^2 \right)$$  \hspace{1cm} (6.65)

This is positive, because it is an average of something squared. The last step is a common step when examining variances of distributions, and relies on the fact that $\langle N - \langle N \rangle \rangle = 0$.

Euler integrals

There is a nice trick we can use to better understand the chemical potential, and how it relates to the Gibbs free energy. This involves reasoning about how internal energy changes when all the extensive variables are changed simultaneously, and connects with Euler’s homogeneous function theorem. You can prove this mathematically (it’s not excessively hard), but I’ll hand-wave my way through it, which I think leads to better understanding anyhow.

Suppose we have a glass of water. We will define our “system” to be all the water within a particular cubic centimeter of water within the glass. If I change my system to consist of two cubic centimeters of water within the same glass, clearly $T$, $p$, and $\mu$ will not change. In fact, I can scale the volume however I like in this way (up to the volume of the whole glass) without ever changing these intensive variables. What happens to $U$ when we do this? Since it is extensive, clearly it must also scale with the volume. Since

$$dU = TdS - pdV + \mu dN$$  \hspace{1cm} (6.66)

we could show that there is in fact only one function that scales in precisely this way. We could imagine integrating this differential starting with a very small volume up to a large one, scaling all extensive quantities in the same way. The result of that integral would be

$$U = TS - pV + \mu N$$  \hspace{1cm} (6.67)

which is in fact true. It often is unhelpful, since we can’t use this expression to find any useful partial derivatives, for instance, and once we have analytic expressions for all six of these properties, we’re probably already done. But there is one cool trick we could do, which is to examine the Gibbs free energy:

$$G \equiv U - TS + pV$$  \hspace{1cm} (6.68)

$$= \mu N$$  \hspace{1cm} (6.69)

which tells us that the chemical potential is just the Gibbs free energy per particle. If we have several chemical species, this expression just becomes

$$G = \sum_i \mu_i N_i$$  \hspace{1cm} (6.70)

so each chemical potential is a partial Gibbs free energy per molecule.

Side note There is another interesting thing we can do with the relationship that

$$U = TS - pV + \mu N$$  \hspace{1cm} (6.71)

and that involves zapping it with $d$. This tells us that

$$dUTdS + SdT - pdV - Vdp + \mu dN + N d\mu$$  \hspace{1cm} (6.72)

which looks downright weird, since it’s got twice as many terms as we normally see. This tells us that the extra terms must add to zero:
0 = SdT − Vdp + Ndp \quad (6.73)

This relationship tells us just how \( T, p \) and \( \mu \) must change in order to keep our extensive quantities extensive and our intensive quantities intensive.

### Absolute activity

The total activity is defined as

\[ \lambda = e^{\beta \mu} \quad (6.74) \]

The text discusses this a little, pointing out that you could write the Gibbs sum with a \( \lambda^N \) instead of an \( e^{\beta \mu N} \). This doesn’t particularly excite me. But activity is somewhat interesting because it is very much like the concentration. Remember for an ideal gas

\[ n = n_Q e^{\beta \mu} \quad (6.75) \\
= n_Q \lambda \quad (6.76) \]

so you can think of activity as a kind of concentration (or number density) in weird units (keeping in mind that the weird units are temperature dependent). In fact, in chemistry classes, activity is often written in square brackets, e.g. as \([\text{H}_2\text{O}]\). In introductory classes this is often used as concentration, but technically it is activity.

The equation for chemical equilibrium is related to the change in Gibbs free energy for a reaction. Consider, for instance the chemical reaction

\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \quad (6.77) \]

The equilibrium constant for this reaction is given by

\[ K = \frac{[\text{H}_2\text{O}]^2}{[\text{O}_2][\text{H}_2]^2} \quad (6.78) \\
= \frac{\lambda_H^2 \lambda_O^2}{\lambda_H^2 \lambda_O^2} \quad (6.79) \\
= e^{\beta \mu_{\text{H}_2\text{O}}} \quad (6.80) \\
= e^{\beta (2\mu_{\text{H}_2\text{O}} - 2\mu_{\text{H}_2} - \mu_{\text{O}_2})} \quad (6.81) \\
= e^{\beta (G_{\text{products}} - G_{\text{reactants}})} \quad (6.82) \]

which tells us that the equilibrium constant is just determined by \( \Delta G \) for the reaction.

However, as is often the case, this relationship is backwards from what we expect. We expect a reaction to proceed forward if the products have a lower Gibbs free energy than the reactants, and this is telling us the opposite. As usual, when we get a minus sign error like this, it is because I have failed to distinguish between “internal” and “external” chemical potential (and thus Gibbs free energy, and also activity).

In this case, looking at chemistry, the distinction we need is between the “chemical” Gibbs free energy, which we can think of as “external”, and the “physical” Gibbs free energy (and chemical potential, and activity), which we can think of as “internal”. The activity used in chemistry is the “internal” activity (in contrast to the “total” activity), which does not include in effect the Gibbs free energy of a single isolated molecule. The internal chemical potential thus only contains effects of concentration, etc.

**Why include this mistake?** You might be wondering: why include in the notes this mistake? I failed to distinguish between internal and external chemical potential, but why not fix that before starting the problem? I thought about doing that, but decided that it would be more helpful for you to see how that thinking comes about. This was indeed a genuine error I made, and it took me some time to find the solution, and significant puzzlement and frustration. Seeing how a mistake is made and how it is resolved,
I think can be effective in learning how to resolve your own mistakes.

All right, so how would we approach this problem more systematically? We would define

\[
[H_2O] \equiv e^{\beta \mu_{H_2O,\text{int}}} = e^{\beta G_{H_2O,\text{int}}/N}
\]

(6.83)

(6.84)

So then the rate constant is given by

\[
K = \frac{[H_2O]^2}{[O_2][H_2]^2} = e^{\beta(2\mu_{H_2O,\text{int}} - 2\mu_{H_2,\text{int}} - \mu_{O_2,\text{int}})}
\]

(6.85)

(6.86)

Now we will want to write the internal chemical potential in terms of the total chemical potential and the external potential (which remember is the one used in chemistry). I will use \(G^o\) to represent the free energy of formation, which is the free energy of an isolated molecule, which we are calling the “external” free energy. Note that because \(G^o\) is per atom (in real chemistry it is per mole), it is an intensive quantity, and we don’t need to divide by \(N\) to get the chemical potential (since \(N = 1\)).

\[
\mu_{\text{tot}} = \mu_{\text{int}} + \mu_{\text{ext}}
\]

(6.87)

\[
\mu_{\text{int}} = \mu_{\text{tot}} - G^o
\]

(6.88)

Putting this into our \(K\) (and taking a log to avoid writing exponentials), we get

\[
\ln \frac{K}{\beta} = 2(\mu_{H_2O,\text{tot}} - G^o_{H_2O})
\]

\[
- 2(\mu_{H_2,\text{tot}} - G^o_{H_2})
\]

\[
- (\mu_{O_2,\text{tot}} - G^o_{O_2})
\]

(6.89)

(6.90)

Now the Gibbs free energies are looking promising here, but you might be unhappy about all these total chemical potentials hanging around. They might seem extra confusing (since chemical potential still probably seems weird and mysterious). Actually, they are quite simple to handle, and the key is the word equilibrium in equilibrium constant. This constant defines what is going on when the system is in chemical equilibrium. That means that no molecules are spontaneously doing the reaction in either direction. What defines a spontaneous change of molecule number? A difference in total chemical potential! So this difference must be zero. Yay for vanishing terms we dislike!

\[
K = e^{\beta(2G^o_{H_2} + G^o_{O_2} - 2G^o_{H_2O})}
\]

(6.91)

\[
e^{-\beta(2G^o_{H_2O} - 2G^o_{H_2} - G^o_{O_2})}
\]

(6.92)

\[
e^{-\beta(G^o_{\text{products}} - G^o_{\text{reactants}})}
\]

(6.93)

So now we’ve got our sign right, so if the products have lower free energy than the reactants, we have a high rate constant (and lots of products).

**Take-home points** I hope you found interesting this little side expedition into chemistry. All you need for this class is the definition of activity, and even that isn’t terribly important—it’s just a definition. I find fascinating where these fundamental chemistry relations come from, and also that the relationship between concentrations arises from an ideal gas approximation! Which is why it is only valid in the limit of low concentration, and why the solvent is typically omitted from the equilibrium constant, since its activity is essentially fixed.
Homework for week 5 (PDF)

1. **Centrifuge** (K&K 5.1) A circular cylinder of radius $R$ rotates about the long axis with angular velocity $\omega$. The cylinder contains an ideal gas of atoms of mass $M$ at temperature $T$. Find an expression for the dependence of the concentration $n(r)$ on the radial distance $r$ from the axis, in terms of $n(0)$ on the axis. Take $\mu$ as for an ideal gas.

2. **Potential energy of gas in gravitational field** (K&K 5.3) Consider a column of atoms each of mass $M$ at temperature $T$ in a uniform gravitational field $g$. Find the thermal average potential energy per atom. The thermal average kinetic energy is independent of height. Find the total heat capacity per atom. The total heat capacity is the sum of contributions from the kinetic energy and from the potential energy. Take the zero of the gravitational energy at the bottom $h = 0$ of the column. Integrate from $h = 0$ to $h = \infty$. You may assume the gas is ideal.

3. **Active transport** (K&K 5.4) The concentration of potassium $K^+$ ions in the internal sap of a plant cell (for example, a fresh water alga) may exceed by a factor of $10^4$ the concentration of $K^+$ ions in the pond water in which the cell is growing. The chemical potential of the $K^+$ ions is higher in the sap because their concentration $n$ is higher there. Estimate the difference in chemical potential at 300K and show that it is equivalent to a voltage of 0.24V across the cell wall. Take $\mu$ as for an ideal gas. Because the values of the chemical potential are different, the ions in the cell and in the pond are not in diffusive equilibrium. The plant cell membrane is highly impermeable to the passive leakage of ions through it. Important questions in cell physics include these: How is the high concentration of ions built up within the cell? How is metabolic energy applied to energize the active ion transport?

David adds You might wonder why it is even remotely plausible to consider the ions in solution as an ideal gas. The key idea here is that the ideal gas entropy incorporates the entropy due to position dependence, and thus due to concentration. Since concentration is what differs between the cell and the pond, the ideal gas entropy describes this pretty effectively. In contrast to the concentration dependence, the temperature-dependence of the ideal gas chemical potential will be almost entirely incorrect.

4. **Gibbs sum for a two level system** (Modified from K&K 5.6)

a) Consider a system that may be unoccupied
with energy zero, or occupied by one particle in either of two states, one of energy zero and one of energy $\varepsilon$. Find the Gibbs sum for this system is in terms of the activity $\lambda \equiv e^{\beta \mu}$. Note that the system can hold a maximum of one particle.

b) Solve for the thermal average occupancy of the system in terms of $\lambda$.

c) Show that the thermal average occupancy of the state at energy $\varepsilon$ is

$$\langle N(\varepsilon) \rangle = \frac{\lambda e^{-\frac{\varepsilon}{\beta}T}}{Z_{\varepsilon}}$$  \hspace{1cm} (6.94)

d) Find an expression for the thermal average energy of the system.

e) Allow the possibility that the orbitals at 0 and at $\varepsilon$ may each be occupied each by one particle at the same time; Show that

$$Z = 1 + \lambda + \lambda e^{-\frac{\varepsilon}{\beta}T} + \lambda^2 e^{-2\frac{\varepsilon}{\beta}T} \hspace{1cm} (6.95)$$

$$= (1 + \lambda) (1 + e^{-\frac{\varepsilon}{\beta}T}) \hspace{1cm} (6.96)$$

Because $Z$ can be factored as shown, we have in effect two independent systems.

5. **Carbon monoxide poisoning** (K&K 5.8) In carbon monoxide poisoning the CO replaces the O$_2$ adsorbed on hemoglobin (Hb) molecules in the blood. To show the effect, consider a model for which each adsorption site on a heme may be vacant or may be occupied either with energy $\varepsilon_A$ by one molecule O$_2$ or with energy $\varepsilon_B$ by one molecule CO. Let $N$ fixed heme sites be in equilibrium with O$_2$ and CO in the gas phases at concentrations such that the activities are $\lambda(O_2) = 1 \times 10^{-5}$ and $\lambda(CO) = 1 \times 10^{-7}$, all at body temperature 37°C. Neglect any spin multiplicity factors.

a) First consider the system in the absence of CO. Evaluate $\varepsilon_A$ such that 90 percent of the Hb sites are occupied by O$_2$. Express the answer in eV per O$_2$.

b) Now admit the CO under the specified conditions. Fine $\varepsilon_B$ such that only 10% of the Hb sites are occupied by O$_2$. 

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Chapter 7

Week 6: Ideal gas (K&K 6, Schroeder 6.7)

Midterm on Monday

Topics are everything through week 4, including week 3 homework, which was due in week 4. Problems should be similar to homework problems, but designed to be completed in class. The exam will be closed notes. You should be able to remember the fundamental equations:

\[ dU = TdS - pdV \quad (7.1) \]
\[ F = U - TS \quad (7.2) \]
\[ dF = -SdT - pdV \quad (7.3) \]
\[ P_i = \frac{e^{-\beta E_i}}{Z} \quad (7.4) \]
\[ Z = \sum_i e^{-\beta E_i} \quad (7.5) \]
\[ U = \sum_i E_i P_i \quad (7.6) \]
\[ F = -kT \ln Z \quad (7.7) \]
\[ S = -k \sum_i P_i \ln P_i \quad (7.8) \]

If you need a property of a particular system (the ideal gas, the simple harmonic oscillator), it will be given to you. There is no need, for instance, to remember the Stefan-Boltzmann law or the Planck distribution.

Quantum mechanics and orbitals

Kittel uses the term orbital to refer to an energy eigenstate (or wave function) of a one-particle system. How do things differ when we have more than one particle?

Suppose we have three particles (and ignore spin for a moment). The wave function would be written as \( \Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots) \). This function in general has nothing to do with any single-particle orbitals. Orbitals arise when we consider a Hamiltonian in which there are no interactions between particles:

\[ \hat{H} = \frac{\hat{p}_1^2}{2m} + V(\vec{r}_1) + \frac{\hat{p}_2^2}{2m} + V(\vec{r}_2) + \cdots \quad (7.10) \]

When our Hamiltonian is separable in this way (i.e. the particles don’t interact, and there are no terms that involve both \( \vec{r}_1 \) and \( \vec{r}_2 \)), we can use separation of variables in the solution, and we obtain a wave function that is a product of orbitals:

\[ |i_1, i_2, i_3, \cdots\rangle = \phi_{i_1}(\vec{r}_1)\phi_{i_2}(\vec{r}_2)\phi_{i_3}(\vec{r}_3) \cdots \quad (7.11) \]
Assuming the potential and mass are the same for every particle, these orbitals are eigenstates of the following single-particle eigenvalue equation:

\[
\left( \frac{\hat{p}^2}{2m} + V(r) \right) \phi_i(r) = \varepsilon_i \phi_i(r)
\]  

(7.12)

There is a catch, however, which arises if the particles are truly indistinguishable (as is the case for electrons, protons, atoms of the same isotope, etc.). In this case, there is a symmetry which means that permuting the labels of our particles cannot change any probabilities:

\[
|\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots)|^2 = |\Psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \cdots)|^2
\]  

(7.13)

\[
= |\Psi(\vec{r}_2, \vec{r}_3, \vec{r}_1, \cdots)|^2
\]  

(7.14)

The simple product we wrote above doesn’t have this symmetry, and thus while it is an eigenfunction of our eigenvalue equation, it cannot represent the state of a real system of identical particles. Fortunately, this is pretty easy to resolve: permuting the labels doesn’t change the energy, so we have a largish degenerate subspace in which to work. We are simply required to take a linear combination of these product states which does have the necessary symmetry.

The above equation, while true, does not tell us what happens to the wave function when we do a permutation, only to its magnitude. As it turns out, there are two types of symmetry possible: bosons and fermions.

This isn’t a quantum class, so I won’t say much more, but we do need to connect with the orbitals picture. When we have non-interacting fermions, their energy eigenstates can be written using a Slater determinant, which is just a convenient way to write the proper antisymmetric linear combination of all possible product states with the same set of orbitals:

\[
\Psi_{i_1 i_2 i_3 \cdots}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots) = \frac{1}{\sqrt{N!}} \begin{vmatrix}
\phi_{i_1}(\vec{r}_1) & \phi_{i_1}(\vec{r}_1) & \phi_{i_1}(\vec{r}_1) & \cdots \\
\phi_{i_2}(\vec{r}_1) & \phi_{i_2}(\vec{r}_1) & \phi_{i_2}(\vec{r}_1) & \cdots \\
\phi_{i_3}(\vec{r}_1) & \phi_{i_3}(\vec{r}_1) & \phi_{i_3}(\vec{r}_1) & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{vmatrix}
\]  

(7.16)

This relies on the properties of a determinant, which changes sign if you swap two rows or two columns. This means that if two of your orbitals are the same, the result will be zero, so the “occupancy” of any orbital is either 0 or 1. Note that the \( N! \) is required in order to ensure that the wave function is normalized provided the orbitals are orthonormal.

**Bosons**

Bosons have integer spin, and differ from fermions in that their sign does not change when you interchange particles.

\[
\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \cdots) = \Psi(\vec{r}_2, \vec{r}_1, \vec{r}_3, \cdots)
\]  

(7.17)

The wavefunction for noninteracting bosons looks very much like the Slater determinant above, only with a special version of the determinant that has all + signs. The bosons can have as many particles as they want in a given orbital. In the limiting case where all particles are in the same orbital, a single product of orbitals satisfies the required symmetry.

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Fermi-Dirac distribution

Let us now consider a set of non-interacting fermions. These fermions have a Hamiltonian with a set of single-particle energy eigenvalues given by \( \varepsilon_i \). How do we find the probability of any given many-body microstate? As always, the probability of any given microstate is given by the Boltzmann distribution, but given that are particles are non-interacting, we’d prefer to deal with just one at a time. As it turns out, dealing with one particle at a time is not really possible, but in a grand canonical ensemble we can deal with a single orbital at a time with much greater ease. We can think of each orbital as a separate system, and ask how many particles it has! Particles can now be exchanged between orbitals just like they were between systems last week.

Now that we are thinking of an orbital as a system, we can pretty easily write down all the possible states of that system: it is either occupied or unoccupied. The latter case has 0 energy, and also \( N = 0 \), while the former case has energy \( \varepsilon_i \) and \( N = 1 \). Summing over these gives the Gibbs sum

\[
Z = 1 + e^{-\beta(\varepsilon_i - \mu)} \tag{7.18}
\]

**Small groups** Find the energy and the average occupancy \( \langle N \rangle \) of the orbital

**Answer** If we want to find \( \langle N \rangle \) of the system, we can do that in the usual way Finding is basically the same

\[
\langle N \rangle = \sum_i N_i P_i \tag{7.19}
\]

\[
= \frac{0 + e^{-\beta(\varepsilon_i - \mu)}}{Z} \tag{7.20}
\]

\[
= \frac{e^{-\beta(\varepsilon_i - \mu)}}{1 + e^{-\beta(\varepsilon_i - \mu)}} \tag{7.21}
\]

\[
= \frac{1}{1 + e^{\beta(\varepsilon_i - \mu)}} \tag{7.22}
\]

Finding the energy is basically the same, since the energy is proportional to the occupancy:

\[
\langle E \rangle = \sum_i E_i P_i \tag{7.23}
\]

\[
= 0 + \varepsilon_i e^{-\beta(\varepsilon_i - \mu)} \tag{7.24}
\]

\[
= \varepsilon_i \langle N \rangle \tag{7.25}
\]

The average occupancy of an orbital is called the Fermi-Dirac function, and is normally written as:

\[
f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1} \tag{7.26}
\]

Whenever you are looking at non-interacting fermions, \( f(\varepsilon) \) will be very helpful.

**Small groups** Sketch the Fermi-Dirac function.

When talking about electrons, we often refer to the chemical potential \( \mu \) as the Fermi level. Kittel also defines the Fermi energy \( \varepsilon_F \) as the Fermi level when the temperature is zero, i.e.

\[
\varepsilon_F \equiv \mu(T = 0) \tag{7.27}
\]

At zero temperature, all the orbitals with energy less than \( \varepsilon_F \) are occupied, while all the orbitals with higher energy are unoccupied.

**Actual electrons** You might (or might not) be wondering how we can talk about electrons as non-interacting particles. After all, they are charged particles, which naturally repel each other rather strongly. Indeed, a Slater determinant is a terrible approximation for an energy eigenstate for any many-electron system. So why are we bothering talking about orbitals and the Fermi-Dirac distribution that relies on orbitals being an actual thing?

I’m not going to thoroughly explain this, but rather just give a few hints about why what we’re doing might be reasonable. The key idea is that what we are really interested in is the behavior
of excited states of our many-body system. (The ground state is also very interesting, e.g. if you want to study vibrations or phonons, but not in terms of the thermal behavior of the electrons themselves.) Fortunately, even though the electrons really do interact with one another very strongly, it is possible to construct a picture of elementary excitations that treats these excitations as not interacting with one another. In this kind of a picture, what we are talking about are called quasiparticles. These represent an excitation of the many-body state. And it turns out that in many cases (particularly for solids) we can represent a given excited state of the many-body system as a sum of the energy of a bunch of non-interacting quasiparticles. When this breaks down, we invent new names like exciton to represent an excitation in which more than one quasiparticle are interacting.

**Bose-Einstein distribution**

The same ideas apply to bosons as to fermions: we can treat each orbital as a separate system in the grand canonical ensemble. In this case, however, the occupancy \( N \) can have any (non-negative) value.

**Small groups** Solve for the Gibbs sum for an orbital with energy \( \varepsilon \), and solve for the \( \langle N \rangle \) for a single orbital occupied by bosons.

**Answer** The Gibbs sum will be

\[
Z = \sum_{N=0}^{\infty} e^{-\beta(N\varepsilon - \mu)N} \tag{7.28}
\]

\[
= \sum_{n=0}^{\infty} \left( e^{-\beta(\varepsilon - \mu)} \right)^N \tag{7.29}
\]

\[
= \sum_{n=0}^{\infty} \left( e^{-\beta(\varepsilon - \mu)} \right)^N \tag{7.30}
\]

This looks suspiciously like a simple harmonic oscillator. The same harmonic summation trick applies, and we see that

\[
Z = 1 + e^{-\beta(\varepsilon - \mu)} + \left( e^{-\beta(\varepsilon - \mu)} \right)^2 + \cdots \tag{7.31}
\]

\[
e^{-\beta(\varepsilon - \mu)} Z = e^{-\beta(\varepsilon - \mu)} + \left( e^{-\beta(\varepsilon - \mu)} \right)^2 + \cdots \tag{7.32}
\]

Subtracting the two gives

\[
\left( 1 - e^{-\beta(\varepsilon - \mu)} \right) Z = 1 \tag{7.33}
\]

\[
Z = \frac{1}{1 - e^{-\beta(\varepsilon - \mu)}} \tag{7.34}
\]

Solving for the average occupancy \( \langle N \rangle \) is again more tedious than for a fermion:

\[
\langle N \rangle = \sum_i N_i p_i \tag{7.35}
\]

\[
= \frac{1}{Z} \sum_{N=0}^{\infty} N e^{-\beta(\varepsilon - \mu)N} \tag{7.36}
\]

\[
= \frac{1}{Z} \frac{\partial Z}{\partial \mu} \left( \frac{1}{\beta} \right) \tag{7.37}
\]

\[
= - \frac{1 - e^{-\beta(\varepsilon - \mu)}}{(1 - e^{-\beta(\varepsilon - \mu)})^2} \left( e^{-\beta(\varepsilon - \mu)} \right) \left( \frac{1}{\beta} \right) \tag{7.38}
\]

\[
= \frac{e^{-\beta(\varepsilon - \mu)}}{1 - e^{-\beta(\varepsilon - \mu)}} \tag{7.39}
\]

\[
f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} \tag{7.40}
\]

This turns out to be just the Planck distribution we already saw, only with a chemical potential as reference. Why does this bosonic system look like a simple harmonic oscillator? Since the particles are non-interacting, we have the same set of energy eigenvalues, which is to say an equally spaced series of states. This is conversely related to why we can describe solutions to the simple harmonic oscillator as bosonic phonons.

This expression, the Bose-Einstein distribution, tells us that at low temperatures, we could end up seeing
a lot of particles in low energy states (if there are any eigenvalues below \( \mu \)), in contrast to the Fermi-Dirac distribution, which never sees more than one particle per state.

Classical ideal gas

We are now prepared to talk about a gas in the classical limit. In the classical limit, there is no difference in behavior between fermions and bosons. This happens when the probability of finding a particle in a particular orbital is \( \ll 1 \). And this happens when \( \beta(\varepsilon - \mu) \gg 1 \) for all orbitals, i.e. when \( \mu \) is very negative. When this is the case, both the Fermi-Dirac distribution and the Bose-Einstein distribution become identical.

\[
\langle N \rangle = \sum_{\text{orbitals}} f(\varepsilon_i) = \sum_{\text{orbitals}} e^{-\beta(\varepsilon_i - \mu)} = e^{\beta\mu} \sum_{\text{orbitals}} e^{-\beta(\varepsilon_i)} = e^{\beta\mu} Z_1
\]

\[
N = e^{\beta\mu} n_Q V
\]

where \( Z_1 \) is the partition function for a single particle in a box, which we derived a few weeks ago to be \( n_Q V \) where \( n_Q \equiv \left( \frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \). Thus we can once again find the expression we found last week, where

\[
e^{\beta\mu} = \frac{1}{n_Q V} \frac{N}{n_Q}
\]

We can solve for the chemical potential

\[
\mu = kT \left( \ln N - \ln V - \frac{3}{2} \ln(kT) + \frac{3}{2} \ln \left( \frac{2\pi\hbar^2}{m} \right) \right)
\]

Thus it decreases as volume increases or as the temperature increases. We can further find the free energy by integrating the chemical potential. This is again redundant when compared with the approach we already solved for this. Remember that

\[
dF = -SdT - pdV + \mu dN
\]

\[
\mu = \left( \frac{\partial F}{\partial N} \right)_{V,T}
\]

Note that this must be an integral at fixed \( V \) and \( T \):
\[ F = \int_0^N \mu dN \quad (7.52) \]

\[ = \int_0^N kT (\ln N - \ln V - \ln n_Q) dN \quad (7.53) \]

\[ = kT (N \ln N - N - N \ln V - N \ln n_Q) \quad (7.54) \]

\[ = NkT \left( \ln \left( \frac{n}{n_Q} \right) - 1 \right) \quad (7.55) \]

Small groups Solve for the entropy of the ideal gas (from this free energy).

Answer

\[ -S = \left( \frac{\partial F}{\partial T} \right)_{V,N} \quad (7.56) \]

\[ = Nk \left( \ln \left( \frac{n}{n_Q} \right) - 1 \right) - \frac{NkT}{n_Q} \frac{\partial n_Q}{\partial T} \quad (7.57) \]

\[ = Nk \left( \ln \left( \frac{n}{n_Q} \right) - 1 \right) - \frac{NkT}{n_Q} \frac{3nQ}{nQ} \quad (7.58) \]

\[ -S = Nk \left( \ln \left( \frac{n}{n_Q} \right) - \frac{5}{2} \right) \quad (7.59) \]

\[ S = Nk \left( \ln \left( \frac{n}{n_Q} \right) + \frac{5}{2} \right) \quad (7.60) \]

This expression for the entropy is known as the Sackur-Tetrode equation.

Small groups Solve for the pressure of the ideal gas (from the free energy)

Answer

\[ p = - \left( \frac{\partial F}{\partial V} \right)_{T,N} \quad (7.61) \]

\[ = \frac{NkT}{V} \quad (7.62) \]

That was pretty easy, once we saw that \( n_Q \) was independent of volume. This expression is known as the ideal gas law.

Small groups Solve for the internal energy of the ideal gas

Answer

\[ U = F + TS \quad (7.63) \]

\[ = \frac{3}{2} NkT \quad (7.64) \]

Also pretty familiar.

Small groups Solve for the heat capacity at constant volume of the ideal gas

Answer

\[ C_V = \left( \frac{\partial U}{\partial T} \right)_{V,N} \quad (7.65) \]

\[ = T \left( \frac{\partial S}{\partial T} \right)_{V,N} \quad (7.66) \]

\[ = \frac{3}{2} Nk \quad (7.67) \]

This one is relatively easy.

Small groups Solve for the heat capacity at constant pressure of the ideal gas

Answer

\[ C_p = T \left( \frac{\partial S}{\partial T} \right)_{p,N} \quad (7.68) \]

\[ = T \left( \frac{\partial \ln \left( \frac{n}{n_Q} \right) + \frac{5}{2}}{\partial T} \right)_{p,N} \quad (7.69) \]

This one requires one (small) step more. We have to convert the volume into a pressure in the free energy expression.

\[ C_p = T \left( \frac{\partial \ln \left( \frac{n}{n_Q} \right) + \frac{5}{2}}{\partial T} \right)_{p,N} \quad (7.70) \]

\[ = NkT \left( \frac{\partial \ln \left( \frac{n}{n_Q} \right) + \frac{5}{2}}{\partial T} \right)_{p,N} \quad (7.71) \]

\[ = NkT \left( \frac{\partial \ln \left( \frac{Vn_Q}{N} \right)}{\partial T} \right)_{p,N} \quad (7.72) \]

\[ = NkT \left( \frac{\partial \ln \left( \frac{NkT}{p} \right)}{\partial T} \right)_{p,N} \quad (7.73) \]
At this point we peek inside and see that \( n_Q \propto T^{\frac{3}{2}} \) and can complete the derivative

\[
C_p = \frac{5}{2} N k \quad (7.74)
\]

This has been a series of practice computations involving the ideal gas. The results are useful for some of your homework, and the process of finding these properties is something you will need to know for the final exam. Ultimately, pretty much everything comes down to summing and integrating to find partition functions, and then taking derivatives (and occasional integrals) to find everything else.

**Homework for week 6 (PDF)**

1. **Derivative of Fermi-Dirac function** (K&K 6.1) Show that 
   
   \[
   -\frac{\partial f}{\partial \epsilon} \bigg|_{\epsilon = \mu} = \frac{1}{4kT} \n
   \]
   
   Thus the lower the temperature, the steeper the slope of the Fermi-Dirac function.

2. **Symmetry of filled and vacant orbitals** (K&K 6.2) Show that

   \[
   f(\mu + \delta) = 1 - f(\mu - \delta) \quad (7.75)
   \]

   Thus the probability that an orbital \( \delta \) above the Fermi level is occupied is equal to the probability an orbital \( \delta \) below the Fermi level is vacant. A vacant orbital is sometimes known as a hole.

3. **Distribution function for double occupancy statistics** (K&K 6.3) Let us imagine a new mechanics in which the allowed occupancies of an orbital are 0, 1, and 2. The values of the energy associated with these occupancies are assumed to be 0, \( \epsilon \), and 2\( \epsilon \), respectively.

   a) Derive an expression for the ensemble average occupancy \( \langle N \rangle \), when the system composed of this orbital is in thermal and diffusive contact with a reservoir at temperature \( T \) and chemical potential \( \mu \).

   b) Return now to the usual quantum mechanics, and derive an expression for the ensemble average occupancy of an energy level which is doubly degenerate; that is, two orbitals have the identical energy \( \epsilon \). If both orbitals are occupied the total energy is 2\( \epsilon \). How does this differ from part (a)1?

4. **Entropy of mixing** (Modified from K&K 6.6) Suppose that a system of \( N \) atoms of type \( A \) is placed in diffusive contact with a system of \( N \) atoms of type \( B \) at the same temperature and volume.

   a) Show that after diffusive equilibrium is reached the total entropy is increased by \( 2Nk \ln 2 \). The entropy increase \( 2Nk \ln 2 \) is known as the entropy of mixing.

   b) If the atoms are identical (\( A = B \)), show that there is no increase in entropy when diffusive contact is established. The difference has been called the Gibbs paradox.

   c) Since the Helmholtz free energy is lower for the mixed \( AB \) than for the separated \( A \) and \( B \), it should be possible to extract work from the mixing process. Construct a process that could extract work as the two gases are mixed at fixed temperature. You will probably need to use walls that are permeable to one gas but not the other.

   **Note** This course has not yet covered work, but it was covered in Energy and Entropy, so you may need to stretch your memory to finish part (c).

5. **Ideal gas in two dimensions** (K&K 6.12)

   a) Find the chemical potential of an ideal monatomic gas in two dimensions, with \( N \) atoms confined to a square of area \( A = L^2 \). The spin is zero.

   b) Find an expression for the energy \( U \) of the gas.
c) Find an expression for the entropy $\sigma$. The temperature is $kT$.

6. **Ideal gas calculations** (K&K 6.14) Consider one mole of an ideal monatomic gas at 300K and 1 atm. First, let the gas expand isothermally and reversibly to twice the initial volume; second, let this be followed by an isentropic expansion from twice to four times the original volume.

   a) How much heat (in joules) is added to the gas in each of these two processes?
   
   b) What is the temperature at the end of the second process?
   
   c) Suppose the first process is replaced by an irreversible expansion into a vacuum, to a total volume twice the initial volume. What is the increase of entropy in the irreversible expansion, in J/K?
Chapter 8

Week 7: Fermi and Bose gases (K&K 7, Schroeder 7))

This week we will look at Fermi and Bose gases. These consist of noninteracting fermions or bosons. There is no point studying these at high temperatures and/or low densities, since that is just where they are identical to the classical ideal gas, which we covered last week. So we’ll be low-temperature all week. What happens at low temperatures, and where do we see these gases in real life?

The Fermi gas is most widely seen in metals and semiconductors. In both cases, the electrons (or possibly holes) can be sufficiently dense that “low temperature” corresponds to room temperature or even far above. Now, you might wonder in what insane world it makes sense to think of the electrons in a metal as “noninteracting.” If so, you could read my little note about “actual electrons” towards the end of the section on the Fermi-Dirac distribution. In any case, it is reasonable and useful to treat metals as a non-interacting Fermi gas. Room temperature is pretty low, as it turns out, from the perspective of the electrons in a metal, and it’s not hard to get things colder than room temperature.

Bose gases at effectively low temperatures are less commonly found, and thus in some ways are more cool. Partly this is because there are fewer boson particles. You need to look at atoms with integer spin, such as $^4$He. The “new” quantum thing that Bose gases do is to condense at low temperatures. This condensate is similar to a superfluid, but not the same thing. It is also analogous to superconductivity, but again, not the same thing. The first actual Bose-Einstein condensate wasn’t formed until 1995, out of rubidium atoms at 170 nanokelvins. So “low temperature” in this case was actually pretty chilly.

Density of (orbital) states

We have found ourselves often writing summations over all the orbitals, such as

\[
N = \sum_{n_x} \sum_{n_y} \sum_{n_z} f(\varepsilon_{n_x n_y n_z}) \tag{8.1}
\]

\[
= \iiint f(\varepsilon_{n_x n_y n_z}) dn_x dn_y dn_z \tag{8.2}
\]

\[
= \int_{0}^{\infty} f(\varepsilon(n)) 4\pi n^2 dn \tag{8.3}
\]

Then we make the integral dimensionless, etc. This can be tedious to do over and over again. In the classical limit we can often use a derivative trick to write an answer as a derivative of a sum we have already solved, but that that doesn’t work at low temperatures (i.e. the quantum limit). There is another approach, which is to solve for the density of states and then use that. (Note that while it is called...
“density of states” it is more accurately described as a density of orbitals, since it refers to the solutions to the one-particle problem.

The density of states is the number of orbitals per unit energy at a given energy. So basically it does two things for us. First, it turns the 3D integral into a 1D integral. Secondly, it converts from an “n” integral into an energy integral. This isn’t as nice as a dimensionless integral, but we can still do that ourselves later.

We use a density of states by converting

\[
\sum_{n_x} \sum_{n_y} \sum_{n_z} F(\varepsilon_{n_x n_y n_z}) = \int d\varepsilon F(\varepsilon) D(\varepsilon) \quad (8.4)
\]

where \( F \) is any function of the orbital energy \( \varepsilon \). You can see why it is convenient, particularly because the density of states is often itself a very simple function.

Finding the density of states

Kittel gives a method for finding the density of states which involves first integrating to find the number of states under a given energy \( \varepsilon \), and then taking a derivative of that. This is a perfectly find approach, but I think a simpler method involves just using a Dirac \( \delta \)-function.

\[
\mathcal{D}(\varepsilon) = \sum_{i} \delta(\varepsilon_i - \varepsilon) \quad (8.5)
\]

where you do need to be certain to turn the summation correctly into an integral before making use of the \( \delta \)-function.

Small groups Solve for the density of states of an electron gas (or of any other spin-\( \frac{1}{2} \) gas, which will have the same expression. You need to know that

\[
\varepsilon_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) \quad (8.6)
\]

where \( n_x \) and the other range from 1 to \( \infty \). This corresponds to hard-wall boundary conditions, since we’re putting a half-wavelength in the box. You should also keep in mind that each combination of \( n_x, n_y, \) and \( n_z \) will correspond to two orbitals, one for each possible spin state.

I should also perhaps warn you that when integrating \( \delta \)-functions you will always want to perform a change of variables such that the integration variable is present inside the \( \delta \)-function and is not multiplied by anything.

Answer

\[\mathcal{D}(\varepsilon) = 2 \sum_{n_x=1}^{\infty} \sum_{n_y} \sum_{n_z} \delta \left( \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) - \varepsilon \right) \quad (8.7)\]

\[\mathcal{D}(\varepsilon) = 2 \int \int \int_0^\infty \delta \left( \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) - \varepsilon \right) dn_x dn_y dn_z \quad (8.8)\]

\[\mathcal{D}(\varepsilon) = \frac{2}{8} \int \int \int_{-\infty}^\infty \delta \left( \frac{\hbar^2 \pi^2}{2m L^2} (n_x^2 + n_y^2 + n_z^2) - \varepsilon \right) dn_x dn_y dn_z \quad (8.9)\]

At this point I have converted to an integral over all “space”. Now we’ll switch into spherical coordinates before doing a change of variables. Actually, it is useful (although I don’t expect students to come up with this), to switch into \( k \)-space before going into an energy integral. \( \vec{k} \equiv \frac{\pi}{L} \vec{n} \)

\[\mathcal{D}(\varepsilon) = \left( \frac{L}{2\pi} \right)^3 \int \int \int_{-\infty}^\infty \delta \left( \frac{\hbar^2 k^2}{2m} - \varepsilon \right) d^3k \quad (8.10)\]

I hope that \( \vec{k} \) as a vector feels more comfortable to you than a vector of quantum numbers \( \vec{n} \). In

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any case, we now want to do a change of variables into spherical coordinates

\[ D(\epsilon) = 2 \left( \frac{L}{2\pi} \right)^3 \int_0^\infty \delta \left( \frac{\hbar^2 k^2}{2m} - \epsilon \right) 4\pi k^2 dk \]  

(8.11)

At this point I’d like to pause and point out that an integral over momenta will always end up looking basically like this (except in some cases the \( \epsilon(k) \) will be different), and this is an acceptable starting point for your solutions on homework or an exam. If we have fewer dimensions, we may have an area or line element rather than a volume derivative in \( k \) space, and we would have fewer factors of \( \frac{L}{\pi} \). Now we can do a change of variables into an energy variable:

\[ \epsilon = \frac{\hbar^2 k^2}{2m} \quad \quad d\epsilon = \frac{\hbar^2}{m} dk \]  

(8.12)

\[ k^2 = \frac{2m}{\hbar^2} \epsilon \quad \quad kdk = m \frac{\hbar^2}{\hbar^2} d\epsilon \]  

(8.13)

And now putting all these things into our integral we find

\[ D(\epsilon) = \frac{V}{\pi^2} \int_0^\infty \delta (\epsilon - \epsilon) \sqrt{\frac{2m}{\hbar^2}} \frac{m}{\hbar^2} d\epsilon \]  

(8.14)

\[ = \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \delta (\epsilon - \epsilon) \epsilon^{\frac{1}{2}} d\epsilon \]  

(8.15)

And now our integral is in a form where we can finally make use of the delta function! If we had not transformed it in this way (as I suspect is a common error), we would get something with incorrect dimensions! 😞

And that is the density of states for a non-relativistic particle in 3 dimensions. For your homework, you will get to solve for the properties of a highly relativistic particle, which has the same density of states as a photon (apart from a factor of two due to polarization, and any factor due to spin).

**Common error** A very common error which I made myself when writing these notes is to forget the factor of two due to spin. Of course, if you have a spin \( \frac{3}{2} \) fermion, it would be a factor of four. One advantage of using a density of states is that it already includes this factor, so you no longer need to remember it! 😊

### Using the density of states

Once we have the density of states, we can solve for various interesting properties of quantum (or classical) gases. The easiest thing to do is a fermi gas at zero temperature, since the Fermi-Dirac function turns into a step function at that limit. We can start by solving for the Fermi energy of a fermi gas, which is equal to the chemical potential when the temperature is zero. We do this by solving for the number assuming we know \( \epsilon_F \), and then backwards solving for \( \epsilon_F \). I will do a couple of extra steps here to remind you how this relates to what we did last week.

\[ N = \sum \text{all orbitals} f(\epsilon_i) \]  

(8.17)

\[ = \sum \text{all orbitals} \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \]  

(8.18)

\[ = \int_0^{\epsilon_F} D(\epsilon) \delta(\epsilon - \mu) - 1 d\epsilon \]  

(8.19)

\[ = \int_{\epsilon_F}^{\epsilon_F} D(\epsilon) d\epsilon \]  

(8.20)

In the last step, I made the assumption that \( T = 0 \), so I could turn the Fermi-Dirac function into a step function.
function, which simply changes the bounds of the integral. It is all right to start with this assumption, when doing computations at zero temperature. Now I’ll put in the density of states.

\[
N = \int_0^{\varepsilon_F} \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon^{\frac{3}{2}} d\varepsilon \tag{8.21}
\]

\[
= \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^{\varepsilon_F} \varepsilon^{\frac{3}{2}} d\varepsilon \tag{8.22}
\]

\[
= \frac{V}{2\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{2}{3} \varepsilon_F^{\frac{3}{2}} \tag{8.23}
\]

Now we can just solve for the Fermi energy!

\[
\varepsilon_F = \left( \frac{N}{V} 3\pi^2 \right)^{\frac{1}{3}} \tag{8.24}
\]

\[
= \frac{\hbar^2}{2m} \left( \frac{N}{V} 3\pi^2 \right)^{\frac{1}{3}} \tag{8.25}
\]

This is the energy of the highest occupied orbital in the gas, when the temperature is zero. As you will see, many of the properties of a metal (which is the Fermi gas that you use on an everyday basis) depend fundamentally on the Fermi energy. For this reason, we also like to define other properties of electrons at the Fermi energy: momentum, velocity (technically speed, but it is called Fermi velocity), and even “temperature”.

\[
k_F = \left( \frac{N}{V} 3\pi^2 \right)^{\frac{1}{3}} \tag{8.26}
\]

\[
p_F = \hbar k_F \tag{8.27}
\]

\[
= \hbar \left( \frac{N}{V} 3\pi^2 \right)^{\frac{1}{3}} \tag{8.28}
\]

\[
v_F = \frac{p_F}{m} \tag{8.29}
\]

\[
= \frac{\hbar}{m} \left( \frac{N}{V} 3\pi^2 \right)^{\frac{1}{3}} \tag{8.30}
\]

\[
T_F = \frac{\varepsilon_F}{k_B} \tag{8.31}
\]

The text contains a table of properties of metals at the Fermi energy for a number of simple metals. I don’t expect you to remember them, but it’s worth having them down somewhere so you can check the reasonableness of an answer from time to time. Basically, they all come down to

\[
\varepsilon_F \sim 4\text{eV} \text{ (with } \sim \times 2 \text{ variation)} \tag{8.32}
\]

\[
k_F \sim 10^8\text{cm}^{-1} \tag{8.33}
\]

\[
v_F \sim 10^8\text{cm s}^{-1} \tag{8.34}
\]

Biographical sidenote My PhD advisor insisted that I memorize these numbers (and a few more) prior to my oral exam. He said that experimentalists think that theorists don’t know anything about the real world, and hence it is important to be able to estimate things. Sure enough, on my exam I had to estimate the frequency of radiation that passes unabsorbed through at typical superconductor (which is in the microwave band).

Units sidenote My advisor also insisted that I memorize these results in cgs units rather than SI (i.e. mks) units, since that is what any faculty would be comfortable with. You may have noticed that Kittel preferentially uses cgs units, although not exclusively. Berkeley (where Kittel taught) was one of the last hotbeds of cgs units, and as a result all of my physics courses used Gaussian units (which is synonymous with cgs).
Before we move on, it is worth showing you how we can simplify the density of states now that we know what the Fermi energy is:

\[
D(\varepsilon) = \frac{V}{(2\pi)^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon^{\frac{3}{2}} \quad (8.35)
\]

\[
= \frac{3}{2} N \varepsilon_F^{-\frac{3}{2}} \varepsilon^{\frac{3}{2}} \quad (8.36)
\]

There is nothing particularly deep here, but this is somewhat more compact, and often the factors of \(\varepsilon_F\) will end up canceling out.

**Small groups** Solve for the internal energy at zero temperature of a Fermi gas.

**Answer** We just need to do a different integral.

\[
U = \int_{0}^{\varepsilon_F} D(\varepsilon) \varepsilon d\varepsilon \quad (8.37)
\]

\[
= \frac{3}{2} N \varepsilon_F^{-\frac{3}{2}} \int_{0}^{\varepsilon_F} \varepsilon^{\frac{5}{2}} \varepsilon d\varepsilon \quad (8.38)
\]

\[
= \frac{3}{2} N \varepsilon_F^{-\frac{3}{2}} \frac{2}{5} \varepsilon_F^{\frac{3}{2}} \quad (8.39)
\]

\[
= \frac{3}{5} N \varepsilon_F \quad (8.40)
\]

We generally find when looking at Fermi gasses that things with dimensions of energy end up proportional to the Fermi energy. The \(N\) we could also have predicted, in order to end up with an extensive internal energy.

**Fermi gas at finite temperature**

The Fermi gas is more exciting (and more... thermal?) when the temperature is not precisely zero. Let’s start with the heat capacity at low temperatures, which is one area where metals inherently differ from semiconductors and insulators.

We are looking at a metal with \(n\) electrons per unit volume, at temperature \(T\), where \(kT \ll \varepsilon_F\). We are looking to find out the heat capacity \(C_V\).

**Small whiteboards** How would you approach this?

**Answers** Remember that

\[
C_V = \left( \frac{\partial U}{\partial T} \right)_{V,N} = T \left( \frac{\partial S}{\partial T} \right)_{V,N} \quad (8.41)
\]

which means that we need either \(S\) or \(U\) in order to find the heat capacity at fixed volume. We could do either, but given what we know about the electron gas, \(U\) is easier to find.

We can find \(U\) by integrating with the density of states and the Fermi-Dirac distribution. This is a new variant of our usual

\[
U = \sum_i P_i E_i \quad (8.42)
\]

In this case, we will instead sum over all orbitals the energy contribution of each orbital, again in effect treating each orbital as a separate system.

\[
U = \sum_i f(\varepsilon_i) \varepsilon_i \quad (8.43)
\]

\[
= \int \varepsilon f(\varepsilon) D(\varepsilon) d\varepsilon \quad (8.44)
\]

Remember that for an electron gas

\[
D(\varepsilon) = \frac{V}{(2\pi)^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \varepsilon^{\frac{3}{2}} \quad (8.45)
\]

\[
= \frac{3}{2} N \varepsilon_F^{-\frac{3}{2}} \sqrt{\varepsilon} \quad (8.46)
\]

Sometimes one or the other of these may be more convenient.
Hand-waving version of heat capacity

We can begin with a hand-waving version of solving for the heat capacity. We look at the Fermi-Dirac function at both finite and zero temperature, and we can note that the red and blue shaded areas, representing the probability of orbitals being unoccupied below $\varepsilon_F$ and the probability of excited orbitals above $\varepsilon_F$ being occupied are equal (this was your homework).

To find the energy, of course, we need the Fermi-Dirac function times the density of states. You might think that the red and blue areas will now be unequal, since we are multiplying the blue region by a larger density of states than the red region. However, provided the number of electrons is fixed (as is usual), the chemical potential must shift such that the two areas are equal.

So how do we find the heat capacity? We can work out a rough equation for the internal energy change (relative to zero), and then take a derivative. Now the width of the red and blue regions is $\sim kT$. We know this from your first homework problem last week, where you showed that the slope at the chemical potential is $\frac{1}{\varepsilon_F}$. A steeper slope means a proportionately wider region that is neither zero nor one.

Heat capacity without so much waving

To find the heat capacity more carefully, we could set up this integral, noting that the Fermi-Dirac function is the only place where temperature dependence arises:

$$ U(T) - U(0) \sim \text{(\# electrons excited)} (\Delta \text{energy}) $$

$$ \sim (D(\varepsilon_F)kT)(kT) $$

$$ C_V = \left( \frac{\partial U}{\partial T} \right)_{N,V} $$

$$ \sim D(\varepsilon_F)k^2T $$

which tells us that the heat capacity vanishes at low temperatures, and is proportional to $T$, which is a stark contrast to insulators, for which $C_V \propto T^3$ as predicted by the Debye model.
\[ C_V = \left( \frac{\partial U}{\partial T} \right)_{N,V} \quad (8.51) \]

\[ = \int_0^\infty \varepsilon D(\varepsilon) \frac{\partial f}{\partial T} d\varepsilon \quad (8.52) \]

\[ = \int_0^\infty \varepsilon D(\varepsilon) \frac{(\varepsilon - \varepsilon_F)e^{\beta(\varepsilon - \varepsilon_F)}}{(e^{\beta(\varepsilon - \varepsilon_F)} + 1)^2} \frac{1}{kT^2} d\varepsilon \quad (8.53) \]

where in the last stage I assumed that the chemical potential would not be changing significantly over our (small) temperature range. An interesting question is what the shape of \( \frac{\partial f}{\partial T} \) is. The exponential on top causes it to drop exponentially at \( \varepsilon - \varepsilon_F \gg kT \), while the exponential on the bottom causes it to drop at low energies where \( \varepsilon_F - \varepsilon \gg kT \). This makes it sharply peaked, provided \( kT \ll \varepsilon_F \), which can justify evaluating the density of states at the Fermi energy.

We can also for the same reason set the bounds on the integral to be all energies

\[ C_V \approx D(\varepsilon_F) \int_{-\infty}^\infty \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} d\varepsilon \quad (8.54) \]

Now we have an integral that we would love to make dimensionless, but which has an annoying \( \varepsilon \) that does not have \( \varepsilon_F \) subtracted from it. Let’s look at even and oddness. The ratio does not look either very even or very odd, but we can make it do so by multiplying by \( e^{-\beta(\varepsilon - \varepsilon_F)} \) top and bottom.

\[ C_V \approx \frac{D(\varepsilon_F)}{kT^2} \int_{-\infty}^\infty \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} \frac{1}{e^{-\beta(\varepsilon - \varepsilon_F)} + 1} d\varepsilon \quad (8.55) \]

\[ = \frac{D(\varepsilon_F)}{kT^2} \int_{-\infty}^\infty \frac{1}{e^{\beta(\varepsilon - \varepsilon_F)} + e^{-\beta(\varepsilon - \varepsilon_F)}} d\varepsilon \quad (8.56) \]

Now we can do a change of variables

\[ \xi = \beta(\varepsilon - \varepsilon_F) \quad d\xi = \beta d\varepsilon \quad (8.57) \]

This makes our integral almost dimensionless:

\[ C_V = \frac{D(\varepsilon_F)}{kT^2} \int_{-\infty}^\infty \left( kT\xi + \varepsilon_F \right)^{\text{odd}} (kT\xi) \frac{1}{e^\xi + e^{-\xi} + 2} kT d\xi \quad (8.58) \]

\[ = \frac{D(\varepsilon_F)k^2T}{kT} \int_{-\infty}^\infty \frac{\xi^2}{e^\xi + e^{-\xi} + 2} d\xi \quad (8.59) \]

So here is our answer, expressed in terms of a dimensionless integral. Wolfram alpha tells me this integral is \( \frac{\pi^2}{3} \).

**Bose gas**

\[ f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} - 1} \quad (8.60) \]

The divergence of the Bose-Einstein distribution means that \( \mu \) must be always less than the minimum orbital energy, i.e. \( \mu < 0 \). As before, the total number is given by

Figure 8.3: Bose function for finite temperature

\[ f(\varepsilon) \]
\[
N = \int_0^\infty f(\varepsilon) D(\varepsilon) d\varepsilon \\
= (V \cdots) \int_0^\infty f(\varepsilon) \varepsilon^{\frac{1}{2}} d\varepsilon \tag{8.61}
\]

where in the second step I assumed a three-dimensional gas, and omitted the various constants in the density of states for brevity.

\[
N_{\text{ground}} = N - \int_0^\infty f(\varepsilon, \mu = 0) D(\varepsilon) d\varepsilon \tag{8.63}
\]

When \(N_{\text{ground}} > 0\) according to this formula, we say that we have a Bose-Einstein condensate. The temperature at which this transition happens (for a fixed density) is the Bose-Einstein transition temperature. Your last homework this week is to solve for this transition temperature.

**Homework for week 7 (PDF)**

1. **Energy of a relativistic Fermi gas** (Slightly modified from K&K 7.2) For electrons with an energy \(\varepsilon \gg mc^2\), where \(m\) is the mass of the electron, the energy is given by \(\varepsilon \approx pc\) where \(p\) is the momentum. For electrons in a cube of volume \(V = L^3\) the momentum takes the same values as for a non-relativistic particle in a box.

   a) Show that in this extreme relativistic limit the Fermi energy of a gas of \(N\) electrons is given by

   \[
   \varepsilon_F = \hbar \pi c \left( \frac{3n}{\pi} \right)^{\frac{1}{2}} \tag{8.64}
   \]

   where \(n \equiv \frac{N}{V}\) is the number density.

   b) Show that the total energy of the ground state of the gas is

   \[
   U_0 = \frac{3}{4} N \varepsilon_F \tag{8.65}
   \]

2. **Pressure and entropy of degenerate Fermi gas** (K&K 7.3)
a) Show that a Fermi electron gas in the ground state exerts a pressure

\[ p = \frac{(3\pi^2)^{\frac{2}{3}}}{5} \frac{\hbar^2}{m} \left( \frac{N}{V} \right)^{\frac{2}{3}} \]  \hspace{1cm} (8.66)

In a uniform decrease of the volume of a cube every orbital has its energy raised: The energy of each orbital is proportional to \( \frac{1}{L^2} \) or to \( \frac{1}{V^{\frac{1}{3}}} \).

b) Find an expression for the entropy of a Fermi electron gas in the region \( kT \ll \varepsilon_F \). Notice that \( S \to 0 \) as \( T \to 0 \).

3. Mass-radius relationship for white dwarfs (Modified from K&K 7.6)
Consider a white dwarf of mass \( M \) and radius \( R \). The dwarf consists of ionized hydrogen, thus a bunch of free electrons and protons, each of which are fermions. Let the electrons be degenerate but nonrelativistic; the protons are nondegenerate.

a) Show that the order of magnitude of the gravitational self-energy is

\[ -\frac{GM^2}{R}, \] where \( G \) is the gravitational constant. (If the mass density is constant within the sphere of radius \( R \), the exact potential energy is \(-\frac{5}{3} \frac{GM^2}{R}\)).

b) Show that the order of magnitude of the kinetic energy of the electrons in the ground state is

\[ \frac{\hbar^2 N^{\frac{2}{3}}}{mR^2} \approx \frac{\hbar^2 M^{\frac{2}{3}}}{mM_H^2R^2} \] \hspace{1cm} (8.67)

where \( m \) is the mass of an electron and \( M_H \) is the mass of a proton.

c) Show that if the gravitational and kinetic energies are of the same order of magnitude (as required by the virial theorem of mechanics), \( M^{\frac{2}{3}}R \approx 10^{20} \text{g}^{\frac{1}{3}} \text{cm} \).

d) If the mass is equal to that of the Sun \( (2 \times 10^{33} \text{g}) \), what is the density of the white dwarf?

e) It is believed that pulsars are stars composed of a cold degenerate gas of neutrons (i.e. neutron stars). Show that for a neutron star \( M^{\frac{2}{3}}R \approx 10^{17} \text{g}^{\frac{1}{3}} \text{cm} \). What is the value of the radius for a neutron star with a mass equal to that of the Sun? Express the result in km.

4. Fluctuations in a Fermi gas (K&K 7.11)
Show for a single orbital of a fermion system that

\[ \langle (\Delta N)^2 \rangle = \langle N \rangle \left( 1 + \langle N \rangle \right) \] \hspace{1cm} (8.68)

if \( \langle N \rangle \) is the average number of fermions in that orbital. Notice that the fluctuation vanishes for orbitals with energies far enough from the chemical potential \( \mu \) so that \( \langle N \rangle = 1 \) or \( \langle N \rangle = 0 \).

5. Einstein condensation temperature (Roundy problem)
Starting from the density of free particle orbitals per unit energy range

\[ D(\varepsilon) = \frac{V}{4\pi^2} \left( \frac{2M}{\hbar^2} \right)^{\frac{2}{3}} \varepsilon^{\frac{2}{3}} \] \hspace{1cm} (8.69)

show that the lowest temperature at which the total number of atoms in excited states is equal to the total number of atoms is

\[ T_E = \frac{1}{k_B} \frac{\hbar^2}{2M} \left( \frac{N}{V} \int_0^{\infty} \frac{4\pi^2}{\varepsilon^{\frac{2}{3}}} d\xi \right)^{\frac{2}{3}} \] \hspace{1cm} (8.70)

The infinite sum may be numerically evaluated to be 2.612. Note that the number derived by integrating over the density of states, since the density of states includes all the states except the ground state.

Note: This problem is solved in the text itself. I intend to discuss Bose-Einstein condensation in class, but will not derive this result.
Chapter 9

Week 8: Work, heat, and cycles
(K&K 8, Schroeder 4)

This week we will be zooming through chapters 8 of Kittel and Kroemer. Chapter 8 covers heat and work, which you learned about during Energy and Entropy. Hopefully this will be a bit of review and catch-up time, before we move on to phase transitions.

Heat and work

As we reviewed in week 1, heat and work for a quasistatic process are given by

\[ Q = \int TdS \] \hspace{1cm} (9.1)
\[ W = -\int pdV \] \hspace{1cm} (9.2)

But we can often make use of the First Law in order to avoid computing both of these (if we know how to find the internal energy):

\[ \Delta U = Q + W \] \hspace{1cm} (9.3)

and we can add to that the results from this class:

\[ pV = NkT \] \hspace{1cm} (9.4)
\[ U = \frac{3}{2}NkT \] \hspace{1cm} (9.5)

\[ S = Nk \left( \ln \left( \frac{nQ}{n} \right) + \frac{5}{2} \right) \] \hspace{1cm} (9.6)
\[ F = NkT \left( \ln \left( \frac{n}{nQ} \right) - 1 \right) \] \hspace{1cm} (9.7)
\[ n = nQe^{-\beta\mu} \] \hspace{1cm} (9.8)
\[ nQ = \left( \frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \] \hspace{1cm} (9.9)

\[ (9.10) \]

Let us consider a simple cycle in which we start with the gas at temperature \( T_C \).

1. Adiabatically compress the gas until it reaches temperature \( T_H \).
2. Expand a gas to twice its original volume at fixed temperature \( T_H \).
3. Expand the gas at fixed entropy until its temperature reaches \( T_C \).
4. Finally go back to the original volume at fixed temperature $T_C$.

**Small groups** Solve for the heat and work on each of these steps. In addition find the total work done.

**Answer** We can solve this problem most easily by working out the heat at each step.

1. Since the process is adiabatic, $Q_1 = 0$. To find the work, we just need to know $\Delta U = \frac{3}{2}Nk\Delta T$. So the work must be $W = \frac{3}{2}Nk(T_H - T_C)$.

2. Now we are increasing the volume, which will change the entropy. Since the temperature is fixed, $Q = T\Delta S$, and we can find $\Delta S$ easily enough from the Sackur-Tetrode entropy: $\Delta S = Nk\ln 2$. Since the internal energy doesn’t change, the heat and work are opposite. $Q = -W = NkT_H \ln 2$.

3. Now we are again not changing the entropy, and thus not heating the system, so $W = \Delta U$, and the work done is equal and opposite of the work done on step #1. $W = \frac{3}{2}Nk(T_C - T_H)$.

4. This will be like step 2, but now the temperature is different, and since we are compressing the work is negative: $Q = -W = NkT_C \ln \frac{1}{2} = -NkT_C \ln 2$.

Putting these all together, the total work done is

$$W = NkT_H \ln 2 - NkT_C \ln 2$$

(9.11)

$$= \ln 2Nk(T_H - T_C)$$

(9.12)

which has lost energy due to heating our engine as it expanded in step 2), and a cool place at $T_C$, which got heated up when we compressed our gas at step 4. In addition, over the entire cycle some work was done.

![Figure 9.1: Carnot engine energy and entropy flow diagram.](image)

The energy we put in is all the energy needed to keep the hot side hot, which is the $Q$ for step 2.

$$Q_H = NkT_H \ln 2$$

(9.13)

The efficiency is the ratio of what we get out to what we put in, which gives us

$$\varepsilon = \frac{W}{Q_H}$$

(9.14)

$$= \frac{\ln 2Nk(T_H - T_C)}{NkT_H \ln 2}$$

(9.15)

$$= 1 - \frac{T_C}{T_H}$$

(9.16)

This is just the famous Carnot efficiency.
Note I could have made this an easier problem if I had changed the statement to expand at fixed temperature until the entropy changed by a given $\Delta S$. Then we would not have had to use the Sackur-Tetrode equation at all, and our result would have been true for any material, not just an ideal gas!

We could also have run this whole cycle in reverse. That would look like the next figure. This is how a refrigerator works. If you had an ideal refrigerator and an ideal engine with equal capacity, you could operate them both between the inside and outside of a room to achieve nothing. The engine could precisely power the refrigerator such that no net heat is exchanged between the room and its environment.

Figure 9.2: Carnot fridge energy and entropy flow diagram.

Naturally, we cannot create an ideal Carnot engine or an ideal Carnot refrigerator, because in practice a truly reversible engine would never move. However, it is also very useful to know these fundamental limits, which can guide real heat engines (e.g. coal or nuclear power plants, some solar power plants) and refrigerators or air conditioners. Another use of this ideal picture is that of a heat pump, which is a refrigerator in which you cool the outside in order to heat your house (or anything else). A heat pump can thus be more efficient than an ordinary heater. Just looking at the diagram for a Carnot fridge, you can see that the heat in the hot location exceeds the work done, precisely because it also cools down the cold place.

Homework for week 8 (PDF)

1. Heat pump (K&K 8.1)
   a) Show that for a reversible heat pump the energy required per unit of heat delivered inside the building is given by the Carnot efficiency:
   \[
   \frac{W}{Q_H} = \eta_C = \frac{T_H - T_C}{T_H} \tag{9.17}
   \]
   What happens if the heat pump is not reversible?
   b) Assume that the electricity consumed by a reversible heat pump must itself be generated by a Carnot engine operating between the even hotter temperature $T_{HH}$ and the cold (outdoors) temperature $T_C$. What is the ratio $\frac{Q_{HH}}{Q_H}$ of the heat consumed at $T_{HH}$ (i.e. fuel burned) to the heat delivered at $T_H$ (in the house we want to heat)? Give numerical values for $T_{HH} = 600$ K; $T_H = 300$ K; $T_C = 270$ K.
   c) Draw an energy-entropy flow diagram for the combination heat engine-heat pump, similar to Figures 8.1, 8.2 and 8.4 in the text (or the equivalent but sloppier) figures in the course notes. However, in this case we will involve no external work at all, only energy and entropy flows at three temperatures, since the work done is all generated from heat.

2. Photon Carnot engine (Modified from K&K 8.3)
   In our week on radiation, we saw that the Helmholtz free energy of a box of radiation at temperature $T$ is
\[ F = -8\pi \frac{V(kT)^4 \pi^4}{h^3c^3} \frac{1}{45} \]  

(9.18)

From this we also found the internal energy and entropy

\[ U = 24\pi \frac{(kT)^4 \pi^4}{h^3c^3} \frac{V}{45} \]  

(9.19)

\[ S = 32\pi kV \left( \frac{kT}{hc} \right)^3 \frac{\pi^4}{45} \]  

(9.20)

Given these results, let us consider a Carnot engine that uses an empty metallic piston (i.e. a photon gas).

a) Given \( T_H \) and \( T_C \), as well as \( V_1 \) and \( V_2 \) (the two volumes at \( T_H \)), determine \( V_3 \) and \( V_4 \) (the two volumes at \( T_C \)).

b) What is the heat \( Q_H \) taken up and the work done by the gas during the first isothermal expansion? Are they equal to each other, as for the ideal gas?

c) Does the work done on the two isentropic stages cancel each other, as for the ideal gas?

d) Calculate the total work done by the gas during one cycle. Compare it with the heat taken up at \( T_H \) and show that the energy conversion efficiency is the Carnot efficiency.

3. **Light bulb in a refrigerator** (K&K 8.7) A 100W light bulb is left burning inside a Carnot refrigerator that draws 100W. Can the refrigerator cool below room temperature?
Chapter 10

Week 9: Phase transformations (K&K 10, Schroeder 5.3)

We will be ending this class by looking at phase transformations, such as the transformation from liquid to solid, or from liquid to gas. The existence of phase transformations—which are ubiquitous in nature—requires interactions between particles, which up to now we have neglected. Hence, we will be reverting to a thermodynamics approach, since incorporating interactions into statistical mechanics is not so easy.

One of the key aspects for most phase transformations is **coexistence**. It is possible to have both ice and liquid water in equilibrium with each other, coexisting happily. The existence of coexistence in fact breaks some assumptions that we have made. For instance, starting way back in Energy and Entropy, we have assured you that you could describe the state of a system using practically any pair of state variables (or triple, now that we include \( N \)). However, if ice and water are coexisting, then there must be an ambiguity, because at that temperature and pressure the system could be either ice or water, which are different!

For your online edification (probably not much in class), I include here a phase diagram of water, which includes not only the liquid, vapor and solid phases, but also a dozen or so different crystal phases that you can reach at some combination of high pressure or low temperature.

A phase diagram of an ordinary pure material will have two interesting points, and three interesting lines.

---

**Figure 10.1: Phase diagram of water (high resolution), from Wikipedia**
The two interesting points are the triple point (at which solid, liquid, and vapor can all coexist), and the critical point, at which the distinction between liquid and vapor vanishes. The three lines represent coexistence between solid and gas (or vapor), coexistence between liquid and gas, and coexistence between liquid and solid.

**Coexistence**

To understand a phase transformation, we first need to understand the state of coexistence.

**Question** If we view the liquid and solid here as two separate systems that are in equilibrium with each other, what can you tell me about those two systems?

**Answer** They must be at the same temperature (since they can exchange energy), they must be at the same pressure (since they can exchange volume), and least obvious they must be at the same chemical potential, since they can exchange molecules.

The first two properties define why we can draw the coexistence as a line on a pressure-temperature diagram, since when the two phases coexist they must have the same pressure and temperature. If we drew a volume-temperature diagram, the coexisting phases would not lie at the same point. The final property, that the chemical potentials must be identical, may seem obvious in retrospect. This also means that the Gibbs free energy per particle of the two phases must be equal (since this is equal to the chemical potential).

**Clausius-Clapeyron**

When you look at the phase diagram in its usual pressure versus temperature representation, you can now think of the lines as representing the points where two chemical potentials are equal (e.g. the chemical potential of water and ice). A natural question would be whether you could predict the slopes of these curves? Or alternatively, does knowing the slopes of these curves tell you anything about the materials in question?

We can begin by considering two very close points on the liquid-vapor curve, separated by $dp$ and $dT$. We know that

\[
\mu_g(T, p) = \mu_l(T, p) \quad (10.1)
\]

\[
\mu_g(T + dT, p + dp) = \mu_l(T + dT, p + dp) \quad (10.2)
\]

We can now expand the small difference in terms of differentials

\[
\mu_g(T, p) + \left( \frac{\partial \mu_g}{\partial T} \right)_{p,N} dT + \left( \frac{\partial \mu_g}{\partial p} \right)_{T,N} dp = \mu_l(T, p) + \left( \frac{\partial \mu_l}{\partial T} \right)_{p,N} dT + \left( \frac{\partial \mu_l}{\partial p} \right)_{T,N} dp \quad (10.3)
\]

We can now collect the two differentials and find their ratio.

\[
\left( \frac{\partial \mu_g}{\partial T} \right)_{p,N} - \left( \frac{\partial \mu_l}{\partial T} \right)_{p,N} dT = \left( \frac{\partial \mu_l}{\partial p} \right)_{T,N} - \left( \frac{\partial \mu_g}{\partial p} \right)_{T,N} dp \quad (10.4)
\]

Thus the derivative of the coexistence curve is given by

\[
dp = \frac{\partial \mu_g}{\partial T} - \frac{\partial \mu_l}{\partial T} \left( \frac{\partial \mu_g}{\partial p} \right)_{T,N} \left( \frac{\partial \mu_l}{\partial p} \right)_{T,N} \quad (10.5)
\]

\[
dp = - \frac{\partial \mu_l}{\partial T} - \frac{\partial \mu_g}{\partial T} \left( \frac{\partial \mu_l}{\partial p} \right)_{T,N} \left( \frac{\partial \mu_g}{\partial p} \right)_{T,N} \quad (10.6)
\]
Small groups Find an expression for these derivatives to express this ratio in terms of thermal variables that are more comfortable. You will want to make use of the fact we derived a few weeks ago, which says that the chemical potential is the Gibbs free energy per particle, where $G = U - TS + pV$.

**Answer**

\[
G = U - TS + pV \quad (10.7)
\]

\[
= \mu N \quad (10.8)
\]

\[
dG = dU - TdS - SdT + pdV - Vdp \quad (10.9)
\]

\[
= -SdT + Vdp + \mu dN \quad (10.10)
\]

\[
Nd\mu = -SdT + Vdp + \mu dN \quad (10.11)
\]

\[
d\mu = -\frac{S}{N}dT + \frac{V}{N}dp + \frac{\mu}{N}dN \quad (10.12)
\]

From this differential we can see that

\[
-\frac{S}{N} = \left( \frac{\partial \mu}{\partial T} \right)_{p,N} \quad (10.13)
\]

\[
\frac{V}{N} = \left( \frac{\partial \mu}{\partial p} \right)_{T,N} \quad (10.14)
\]

Thus we can put these into the ratios above, and we will find that the $N$s will cancel, and the minus sign on the entropy will cancel the minus sign that was out front.

\[
\frac{dp}{dT} = \frac{s_g - s_l}{v_g - v_l} \quad (10.15)
\]

This looks like a bit of a nuisance having all these $N$ values on the bottom. It looks cleaner if we just define $s = \frac{S}{N}$ as the specific entropy (or entropy per atom) and $v = VN$ as the specific volume (or volume per atom). Thus we have

\[
\frac{dp}{dT} = \frac{s_g - s_l}{v_g - v_l} \quad (10.16)
\]

This is the famous Clausius-Clapeyron equation, and is true for any phase coexistence curve in the pressure-temperature phase diagram.

We can further expand this by interpreting the change in entropy as a latent heat. If the entropy changes discontinuously, since the phase transformation happens entirely at a single temperature, we can use the relationship between heat and entropy to find that

\[
Q = T\delta S \quad (10.17)
\]

We call the heat needed to change from one phase to another the latent heat $L$, which gives us that

\[
\frac{dp}{dT} = \frac{L}{T\Delta V} \quad (10.18)
\]

This equation can be a bit tricky to use right, since you could get the direction of $\Delta V$ wrong. The one with entropy and volume is easier, since as long as both changes are in the same direction (vapor minus liquid or vice versa) it is still correct.

From Clausius-Clapeyron we can see that so long as the volume increases as the entropy also increases, the coexistence curve will have a positive slope.

**Question** When would the slope ever be negative?

It requires a high-entropy phase that also has lower volume!

**Answer** Ice and water! Water has higher entropy, but also has lower volume than ice (i.e. is more dense). This is backwards from most other materials, and causes the melting curve to slope up and to the left for ice.

van der Waals

When we talk about phase transformations, we require some sort of system in which there are interactions between particles, since that is what leads to a phase
transformation. We can either do this from the bottom up, by constructing a system in which there are interactions and then solving for the properties of that system, or we could use a more empirical approach, in which we use an approximate set of equations of state (or a free energy) that behaves much like a real system.

The van der Waals fluid is sort of in between these two approaches. I will describe how we would “derive” the van der Waals free energy in a slightly hand-waving manner, and then we will use it as an effectively empirical system that we can use to explore how a phase transition might happen. The van der Waals fluid in essence is a couple of corrections to the ideal gas law, which together add enough interactions to give a plausible description of a liquid-vapor phase transition.

Small white boards What kind of interactions might exist in a real gas that are ignored when we treat it as an ideal gas?

Answer Repulsion and attraction! ~ Atoms will have a very high energy if they sit on top of another atom, but atoms that are at an appropriate distance will feel an attractive interaction.

In fluids, attraction and repulsion tend to be treated very differently. Repulsion tends to primarily decrease entropy rather than increasing energy, because the atoms can simply avoid being on top of each other. In contrast, attraction often has little effect on entropy (except when there is a phase transformation), but can decrease the energy. It has little effect on entropy because the attraction is often very weak, so it doesn’t (much) affect where the atoms are, but does affect the energy, provided the atoms are close enough.

Building up the free energy: repulsion

Let’s start by looking at the ideal gas free energy:

\[
F_{\text{ideal}} = -NkT \left( \ln \left( \frac{nQV}{N} \right) + 1 \right)
\]  

This free energy depends on both volume and temperature (also \( N \), but let’s keep that fixed). The temperature dependence is out front and in \( nQ \). The volume dependence is entirely in the logarithm. When we add the repulsive interaction, we can wave our hands a bit and argue that the effect of repulsion is to keep atoms from sitting too close to one another, and that results in each atom having less volume it could be placed in. The volume available for a given atom will be the total volume \( V \), minus the volume occupied by all the other atoms, which we can call \( Nb \) where \( N \) is the number of atoms, and \( b \) is the excluded volume per atom. You might argue (correctly) that the excluded volume should be \((N - 1)b\), but we will be working in the limit of \( N \gg 1 \) and can ignore that fine distinction. Making this substitution gives us

\[
F_{\text{with repulsion}} = -NkT \left( \ln \left( \frac{nQ(V - Nb)}{N} \right) + 1 \right)
\]  

This free energy is going to be higher than the ideal gas free energy, because we are making the logarithm lesser, but there is a minus sign out front. That is good, because we would hardly expect including repulsion to lower the free energy.

In your homework you will (incidentally) show that this free energy gives an internal energy that is identical to the ideal gas free energy, which bears out what I said earlier about repulsion affecting the entropy rather than the energy.

Adding attraction: mean field theory

When we want to add in attraction to the free energy, the approach we will use is called mean field theory. I prefer to talk about it as first-order thermodynamic perturbation theory. (Actually, mean field theory is often more accurately described as a poor approximation to first-order perturbation theory, as it is common in mean-field theory to ignore any correlations in the reference fluid.) You know perturbation theory from quantum mechanics, but
the fundamental ideas can be applied to any theory, including statistical mechanics.

The fundamental idea of perturbation theory is to break your Hamiltonian into two terms: one that you are able to solve, and a second term that is small. In this case, in order to derive (or motivate?) the van der Waals equation, our reference would be the system with repulsion only, and the perturbation would be the attraction between our atoms. We want to solve this purely classically, since we don’t know how to solve the energy eigenvalue equation with interactions between particles included.

Classically, we would begin by writing down energy, and then we would work out the partition function by summing over all possible microstates in the canonical ensemble. A logarithm would then tell us the free energy. The energy will be

\[ E = \sum_{\text{all atoms}} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{ij} U(|\vec{r}_i - \vec{r}_j|) \]  

(10.21)

where \( U(r) \) is an attractive pair potential, which is to say, a potential energy of interaction between each pair of atoms. The first term is the kinetic energy (and is the same for the ideal gas), while the second term is a potential energy (and is zero for the ideal gas). The partition function is then

\[ Z = \frac{V^N}{N!} \int d^3 r_1 \int d^3 r_2 \cdots \int d^3 r_N \]

\[ \frac{1}{V^N} \int d^3 p_1 \int d^3 p_2 \cdots \int d^3 p_N e^{-\beta \left( \sum \frac{p_i^2}{2m} + \frac{1}{2} \sum U(|\vec{r}_i - \vec{r}_j|) \right)} \]  

(10.22)

\[ = \frac{1}{N!} \int d^3 p_1 \int d^3 p_2 \cdots \int d^3 p_N e^{-\beta \left( \sum \frac{p_i^2}{2m} \right)} \]

\[ \int d^3 r_1 \int d^3 r_2 \cdots \int d^3 r_N e^{-\beta \left( \frac{1}{2} \sum U(|\vec{r}_i - \vec{r}_j|) \right)} \]  

(10.23)

At this point I will go ahead and split this partition function into two factors, an ideal gas partition function plus a correction factor that depends on the potential energy of interaction.

\[ Z = \frac{V^N}{N!} \int d^3 p_1 \int d^3 p_2 \cdots \int d^3 p_N e^{-\beta \left( \sum \frac{p_i^2}{2m} \right)} \]

\[ \frac{1}{V^N} \int d^3 r_1 \int d^3 r_2 \cdots \int d^3 r_N e^{-\beta \left( \frac{1}{2} \sum U(|\vec{r}_i - \vec{r}_j|) \right)} \]  

(10.24)

\[ = Z_{\text{ideal}} \frac{1}{V^N} \int d^3 r_1 \int d^3 r_2 \cdots \int d^3 r_N e^{-\beta \left( \frac{1}{2} \sum U(|\vec{r}_i - \vec{r}_j|) \right)} \]  

(10.25)

\[ = Z_{\text{ideal}} Z_{\text{config}} \]  

(10.26)

Now we can express the free energy!

\[ F = -kT \ln Z \]

\[ = -kT \ln (Z_{\text{ideal}} Z_{\text{config}}) \]

(10.27)

\[ = F_{\text{ideal}} - kT \ln Z_{\text{config}} \]  

(10.28)

So we just need to approximate this excess free energy (beyond the ideal gas free energy). Let’s get to the approximation bit.

\[ Z_{\text{config}} = \int \frac{d^3 r_1}{V} \cdots \int \frac{d^3 r_N}{V} e^{-\beta \left( \frac{1}{2} \sum U(|\vec{r}_i - \vec{r}_j|) \right)} \]  

(10.30)

\[ \approx \int \frac{d^3 r_1}{V} \cdots \int \frac{d^3 r_N}{V} \left( 1 - \sum_{ij} \frac{\beta}{2} U(r_{ij}) \right) \]  

(10.31)

At this point I have used a power series approximation on the exponentials, under the assumption that our attraction is sufficiently small. Now we can write this sum in a simpler manner, taking account of the symmetry between the different particles.
At this stage, I’ve gotten things way simpler. Note also, that I did something wrong. I assumed that the potential was always small, but the repulsive part of the potential is not small. But we’ll ignore that for now. Including it properly would be doing this right, but instead we’ll use the approach that lead’s to the van der Waals equation of state. To continue...

\[ F_{\text{excess}} = -kT \ln Z_{\text{conf}} \]  
\[ = -kT \ln \left( 1 - \frac{\beta N^2}{2} \int \frac{d^3r}{V} U(r) \right) \]  
\[ \approx kT \frac{\beta N^2}{2} \int \frac{d^3r}{V} U(r) \]  
\[ = \frac{N^2}{2} \int \frac{d^3r}{V} U(r) \]  
\[ \equiv -\frac{N^2}{V} a \]  

where I’ve defined \( a \equiv -\frac{1}{2} \int d^3r U(r) \). The minus sign here is to make \( a \) a positive quantity, given that \( U(r) < 0 \). Putting this together with the ideal gas free energy modified to include a simple repulsion term, we have the van der Waals free energy:

\[ F_{\text{vdW}} = -NkT \left( \ln \left( \frac{nQ(V-Nb)}{N} \right) + 1 \right) - \frac{N^2}{V} a \]

**van der Waals and liquid-vapor phase transition**

Let’s start by looking at the pressure as a function of volume according to the van der Waals equation:

\[ p = -\left( \frac{\partial F}{\partial V} \right)_{T,N} \]  
\[ = \frac{NkT}{V-Nb} - \frac{N^2}{V^2} a \]  

This equation is the van der Waals equation of state, which is often rewritten to look like:

\[ (p + \frac{N^2}{V^2} a) (V-Nb) = NkT \]

as you can see it is only slightly modified from the ideal gas law, provided \( a \ll p \) and \( Nb \ll V \).

**Answer**

\[ p = -\left( \frac{\partial F}{\partial V} \right)_{T,N} \]  
\[ = \frac{NkT}{V-Nb} - \frac{N^2}{V^2} a \]  

Clearly the pressure will diverge as the volume is decreased towards \( Nb \), which puts a lower bound on the volume. This reflects the fact that each atom takes \( b \) volume, so you can’t compress the fluid smaller than that. At larger volumes, the pressure will definitely be positive and decreasing, since the attractive term dies off faster than the first term. However, if \( a \) is sufficiently large (or \( T \) is sufficiently small), we may find that the second term dominates when the volume is not too large.

We can also rewrite this pressure to express it in terms of the number density \( n \equiv \frac{N}{V} \), which I find a little more intuitive than imagining the volume changing:

\[ n = \frac{N}{V} \]  
\[ a = -\frac{1}{2} V \int d^3r U(r) \]  
\[ \equiv -\frac{1}{V} a \]  
\[ p = \frac{NkT}{V-Nb} - \frac{N^2}{V^2} a \]  
\[ = \frac{kT}{N} - \frac{N^2}{V^2} a \]  
\[ = \frac{kT}{N-Nb} - \frac{N^2}{V^2} a \]  
\[ = \frac{kT}{N} - \frac{N^2}{V^2} a \]  
\[ = \frac{kT}{N-Nb} - \frac{N^2}{V^2} a \]  

**van der Waals equation of state**

**Small groups** Solve for the van der Waals pressure, as a function of \( N \), \( V \), and \( T \) (and of course, also \( a \) and \( b \)).
So this tells us that as we increase the density from zero, the pressure will begin by increasing linearly. It will end by approaching infinity as the density approaches \( \frac{1}{b} \). In between, the attractive term may or may not cause the pressure to do something interesting.

\[ p = \frac{kT}{n - b} - n^2 a \quad (10.46) \]
\[ = kT \frac{n}{1 - nb} - n^2 a \quad (10.47) \]

This equation is kind of nice, but it’s still pretty confusing because it has three different constants (other than \( n \)) in it. We can reduce that further by rewriting it in terms of the packing fraction \( \eta \equiv \frac{nb}{V} \), which is the fraction of the volume that is filled with atoms.

\[ p = \frac{kT}{b} \eta \frac{1}{1 - \eta} - \frac{a}{b^2} \eta^2 \quad (10.48) \]

We now see that there are just two “constants” to deal with, \( \frac{kT}{b} \) and \( \frac{a}{b^2} \) each of which have dimensions of pressure. The former, of course, depends on temperature, and the ratio between them (i.e. \( \frac{kT}{a} \)) will fully determine the shape of our pressure curve (in terms of density).

Clearly something interesting is happening at low temperatures. This is a phase transition. But how do we find out what the density (or equivalently, volume) of the liquid and solid are? You already know that the pressure, temperature and chemical potential must all be equal when two phases are in coexistence. From this plot we can identify triples of densities where the temperature and pressure are both identical. Which corresponds to the actual phase transition?

**Question** How might you determine from this van der Waals equation of state or free energy where the phase transformation happens?

**Answer** As before, we need to have identical pressure, temperature and chemical potential. So we need to check which of these equal pressure states have the same chemical potential.

**Common tangent**

Most approaches require us to work with the Helmholtz free energy rather than the pressure equation. If we plot the Helmholtz free energy versus volume (with number fixed) the pressure is the nega-
tive slope. We also need to ensure that the chemical potential (or Gibbs free energy) is identical at the two points.

\[ kT_b = 0.26 \]

So for two points to have the same Gibbs free energy (at pressure \( p \)), their Helmholtz free energy (at fixed temperature) must pass through a line with slope equal to the pressure. If those two points also have that pressure as their slope, then they have both equal slope and equal chemical potential, and are our two coexisting states. This is the common tangent construction.

The common tangent construction is very commonly used when looking at multiple crystal structures, when you don’t even know which ones are stable in the first place.

**Note** The common tangent construction also works when we plot \( F \) versus \( n \) or \( N \).

**Gibbs free energy**

Another approach to solve for coexistence points is to plot the Gibbs free energy versus pressure, each of which can be computed easily from the Helmholtz free energy. When we plot the Gibbs free energy versus pressure, we find that there is a crossing and a little loop. This loop corresponds to metastable and unstable states, and the crossing point is where the two phases (liquid and vapor, in our case) coexist.

\[ dG = -SdT + Vdp \]  

This tells us that the slope of the \( G \) versus \( p \) curve (at fixed temperature) is just the volume of the system. Since the volume can vary continuously (at least in the Helmholtz free energy we constructed), this slope must continuously change.
as we follow the path. That explains why we have pointy points, since the slope must be the same on both sides of the curve. The points thus represent the states where the pressure has an extremum, as we change the volume. In between those two extrema is the range where increasing volume causes the pressure to increase. These states are mechanically unstable, and thus cannot be observed.

Examples of phase transitions

I'd like to spend just a bit of time talking about the wide variety of different phase transitions that can and do happen, before we discuss how these transitions can be understood in a reasonably unified way through Landau theory.

**Liquid-vapor**

The liquid-vapor transition is what we just discussed. The only fundamental difference between liquid and vapor is the density of the fluid.

**Melting/freezing**

Melting and freezing is similar to the liquid-vapor transition, with the difference however, that there cannot be a critical point, since we cannot go from solid to liquid without a phase transition.

**Sublimation**

Sublimation is very much like melting. Its major difference happens because of the difference between a gas and a liquid, which means that there is no temperature low enough that there will not be a gas in equilibrium with a solid at low pressure.

**Solid/solid**

Solid-solid phase transitions are interesting in that different solid phases have different crystal symmetries which make it both possible and reasonable to compute (and possibly even observe) properties for different phases at the same density and pressure.

**Ferromagnetism**

A ferromagnetic material (such as iron or nickel) will spontaneously magnetize itself, although the magnetized regions do break into domains. When the material is heated above a given temperature (called the Curie temperature) it is no longer ferromagnetic, but instead behaves as an ordinary paramagnetic material. This is therefore a phase transitions.

**Ferroelectrics**

A ferroelectric material is a material that has a spontaneous electric dipole polarization at low temperatures. It behaves very much like an electrical analogue of a ferromagnetic material.

**Antiferromagnetism**

An antiferromagnetic material (such as nickel oxide) will have different atoms with oppositely polarized spin. This is less easy to observe by elementary school children than ferromagnetism, but is also a distinct phase, with a phase transition in which the spins become disordered.

**Superconductivity**

A superconductor at low temperatures has zero electrical resistivity. At higher temperature it is (for ordinary superconductors) an ordinary metal. Lead is a classic example of a superconductor, and has a transition temperature of 7.19K. You see high-$T_c$ superconductors in demos more frequently, which have transition temperatures up to 134K, but are more
complicated in terms of their cause and phase diagram.

**Superfluidity**

A superfluid (and helium 4 is the classic example) has zero viscosity at low temperatures. For helium this transition temperature is \( 2.17 \text{K} \).

**Bose-Einstein condensation**

The transition to having a macroscopic occupation in the ground state in a gas of bosons is another phase transition.

**Mixing of binary systems**

In binary systems (e.g. salt and water, or an alloy of nickel and iron) there are many of the same phase transitions (e.g. liquid/gas/solid), but now we have an additional parameter which is the fraction of each component in the phase. Kittel and Kroemer have a whole chapter on this kind of phase transition.

**Landau theory**

There are so many kinds of phase transitions, you might wonder whether they are all different, or if we can understand them in the same (or a similar) way. Landau came up with an approach that allows us to view the whole wide variety of phase transitions in a unified manner.

The key idea is to identify an **order parameter** \( \xi \), which allows us to distinguish the two phases. This order parameter ideally should also be something that has interactions we can control through some sort of an external field. Examples of order parameters:

- **Liquid-vapor** volume or density
- **Ferromagnetism** magnetization
- **Ferroelectrics** electric polarization density

**Superconductivity or superfluidity** quantum mechanical amplitude (including phase)

**Binary mixtures** fraction of components

The key idea of Landau is to express a Helmholtz free energy as a function of the order parameter:

\[
F_L(\xi, T) = U(\xi, T) - TS(\xi, T) \tag{10.52}
\]

Now at a given temperature there is an equilibrium value for the order parameter \( \xi_0 \), which is determined by minimizing the free energy, and this equilibrium order parameter defines the actual Helmholtz free energy.

\[
F(T) = F_L(\xi_0, T) \leq F_L(\xi, T) \tag{10.53}
\]

So far this hasn’t given us much. Landau theory becomes powerful is when we expand the free energy as a power series in the order parameter (and later as a power series in temperature).

**A continuous phase transition**

To make things concrete, let us assume an order parameter with inversion symmetry, such as magnetization or electrical polarization. This means that \( F_L \) must be an even function of \( \xi \), so we can write that

\[
F_L(\xi, T) = g_0(T) + \frac{1}{2}g_2(T)\xi^2 + \frac{1}{4}g_4(T)\xi^4 + \cdots \tag{10.54}
\]

The entire temperature dependence is now hidden in the coefficients of the power series. A simple example where we could have a phase transition, would be if the sign of \( g_2 \) changed at some temperature \( T_0 \). In this case, we could do a power series expansion of our coefficients around \( T_0 \), and we would have something like:
where I am ignoring the temperature dependence of $g_4$, under the assumption that it doesn’t do anything too fancy near $T_0$. I’m leaving $g_0(T)$ alone, because it causes no trouble, and will be useful later. I’m also going to assume that $α$ and $g_4(T_0)$ are positive. Now we can solve for the order parameter that minimizes the free energy by setting its derivative to zero.

\[
\left( \frac{∂F_L}{∂ξ} \right)_T = 0
\]

\[
= α(T - T_0)ξ + g_4(T_0)ξ^3
\]

This has two solutions:

\[
ξ = 0 \quad ξ^2 = (T_0 - T) \frac{α}{g_4(T_0)}
\]

If $T > T_0$ there is only one (real) solution, which is that the order parameter is zero. Thus when $T > T_0$, we can see that

\[
F(T) = g_0(T)
\]

exactly, since $ξ = 0$ causes all the other terms in the Landau free energy to vanish.

In contrast, when $T < T_0$, there are two solutions that are minima ($±\sqrt{(T_0 - T)α/g_4(T_0)}$), and one maximum at $ξ = 0$. In this case the order parameter continuously (but not smoothly) goes to zero. This tells us that the free energy at low temperatures will be given by

\[
F(T) = g_0(T) - \frac{α^2}{4g_4(T_0)}(T - T_0)^2
\]

Small groups  Solve for the entropy of this system when the temperature is near $T_0$.

**Answer** We can find the entropy from the free energy by considering its total differential

\[
dF = -SdT - pdV
\]

which tells us that

\[
-S = \left( \frac{∂F}{∂T} \right)_V
\]

Let’s start by finding the entropy for $T < T_0$:

\[
S_ < = -\frac{dg_0}{dT} - \frac{α^2}{2g_4(T_0)}(T_0 - T)
\]

When the temperature is high, this is easier:

\[
S_ > = -\frac{dg_0}{dT}
\]

This tells us that the low-temperature has an extra-low entropy relative to what it would have had without the phase transition. However, the entropy is continuous, which means that there is no latent heat associated with this phase transition, which is called a **continuous phase transition**. An older name for this kind of phase transition (used in the text) is a **second order phase transition**. Currently “continuous” is preferred for describing phase transitions with no latent heat, because they are not always actually **second order** as is this example.

Examples of continuous phase transitions include ferromagnets and superconductors.

An abrupt phase transition

To get an abrupt phase transition with a nonzero latent heat (as for melting or boiling), we need to consider a scenario where $g_4 < 0$ and $g_6 > 0$. This gives us two competing local minima at different values for the order parameter. (Note that an abrupt
phase transition is also known as a first order phase transition.)

\[ F_L = g_0(T) + \frac{1}{2} \alpha(T - T_0) \xi^2 - \frac{1}{4} |g_4(T)| \xi^4 + \frac{1}{6} g_6 \xi^6 + \cdots \]  
\tag{10.65}

**Small groups if we have time** Find the solutions for the order parameter, and in particular find a criterion for the phase transition to happen.

**Answer** We want to find minima of our free energy...

\[ \frac{\partial F_L}{\partial \xi} = 0 \]  
\tag{10.66}

\[ = \alpha(T - T_0) \xi - |g_4(T)| \xi^3 + g_6 \xi^5 \]  
\tag{10.67}

One solution is \( \xi = 0 \). Otherwise,

\[ 0 = \alpha(T - T_0) - |g_4(T)| \xi^2 + g_6 \xi^4 \]  
\tag{10.68}

which is just a quadratic. It has solutions when

\[ \xi^2 = |g_4(T)| \pm \sqrt{|g_4(T)|^2 - 4g_6 \alpha(T - T_0)} \]  
\tag{10.69}

Note that this has four solutions. Two have \( \xi < 0 \), and show up because our free energy is even. One of the other solutions is a local maximum, and the final solution is a local minimum. For this to have a real solution, we would need for the thing in the square root to be positive, which means

\[ g_4(T)^2 \geq 4g_6 \alpha(T - T_0) \]  
\tag{10.70}

It would be tempting to take this as an equality when we are at the phase transition. However, that is just the point at which there is a local minimum, but we are looking for a global minimum (other than \( \xi = 0 \)). This global minimum will require that

\[ F_L(\xi > 0) < F_L(\xi = 0) \]  
\tag{10.71}

which leads us to conclude that

\[ \frac{1}{2} \alpha(T - T_0) \xi^2 - \frac{1}{4} |g_4(T)| \xi^4 + \frac{1}{6} g_6 \xi^6 < 0 \]  
\tag{10.72}

We can plug in the criterion for an extremum in the free energy at nonzero \( \xi \) to find:

\[ \frac{1}{2} (|g_4(T)| \xi^2 - g_6 \xi^4) \xi^2 - \frac{1}{4} |g_4(T)| \xi^4 + \frac{1}{6} g_6 \xi^6 < 0 \]  
\tag{10.73}

\[ \frac{1}{4} |g_4(T)| \xi^4 - \frac{1}{3} g_6 \xi^6 < 0 \]  
\tag{10.74}

\[ \frac{1}{4} |g_4(T)| - \frac{1}{3} g_6 \xi^2 < 0 \]  
\tag{10.75}

At this point we would want to make use of the solution for \( \xi^2 \) above that used the quadratic equation. We would then have eliminated \( \xi \) from the equation, and could solve for a relationship between \( |g_4(T)| \), \( g_6 \), and \( \alpha(T - T_0) \).

**Homework for week 9 (PDF)**

1. **Vapor pressure equation** (David) Consider a phase transformation between either solid or liquid and gas. Assume that the volume of the gas is way bigger than that of the liquid or solid, such that \( \Delta V \approx V_g \). Furthermore, assume that the ideal gas law applies to the gas phase. **Note: this problem is solved in the textbook, in the section on the Clausius-Clapeyron equation.**

   a) Solve for \( \frac{dp}{dT} \) in terms of the pressure of the vapor and the latent heat \( L \) and the temperature.

   b) Assume further that the latent heat is roughly independent of temperature. Integrate to find the vapor pressure itself as a
function of temperature (and of course, the latent heat).

Note that this is a rather coarse approximation, since the latent heat of water varies by about 10% between 0°C and 100°C. Still, you will see a pretty cool result, that is roughly accurate (and good enough for the problems below).

2. Entropy, energy, and enthalpy of van der Waals gas (K&K 9.1) In this entire problem, keep results to first order in the van der Waals correction terms $a$ and $b$.

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

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

(10.76)

b) Show that the energy is

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

(10.77)

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

$$H(T, V) = \frac{5}{2} NkT + \frac{N^2bkT}{V} - 2\frac{N^2a}{V}$$

(10.78)

$$H(T, p) = \frac{5}{2} NkT + Nbp - \frac{2Nap}{kT}$$

(10.79)

3. Calculation of $\frac{dT}{dp}$ for water (K&K 9.2) Calculate based on the Clausius-Clapeyron equation the value of $\frac{dT}{dp}$ near $p = 1$ atm for the liquid-vapor equilibrium of water. The heat of vaporization at 100°C is 2260 J g$^{-1}$. Express the result in kelvin/atm.

4. Heat of vaporization of ice (Modified K&K 9.3) The pressure of water vapor over ice is 518 Pa at −2°C. The vapor pressure of water at its triple point is 611 Pa, at 0.01°C (see Wikipedia water data page). Estimate in J mol$^{-1}$ the heat of vaporization of ice just under freezing. How does this compare with the heat of vaporization of water?
Chapter 11

Review

Topics are everything that has been covered on homework. Problems should be similar to homework problems, but short enough to be completed during the exam. The exam will be closed notes. You should be able to remember the fundamental equations.

Equations to remember

Most of the equations I expect you to remember date back from Energy and Entropy, with a few exceptions.

**Thermodynamic identity** The thermodynamic identity, including the chemical potential:

\[ dU = TdS - pdV + \mu dN \]  
(11.1)

You should be able from this to extract relationships such as \( \mu = \left( \frac{\partial U}{\partial N} \right)_{S,V} \).

**Thermodynamic potentials** You need to know the Helmholtz and Gibbs free energies.

\[ F = U - TS \]  
(11.2)
\[ G = U - TS + pV \]  
(11.3)
\[ dF = -SdT - pdV + \mu dN \]  
(11.4)
\[ G = U - TS + pV \]  
(11.5)
\[ dG = -SdT + Vdp + \mu dN \]  
(11.6)

You don’t need to remember their differentials, but you do need to be able to find them quickly and use them, e.g. to find out how \( \mu \) relates to \( F \) as a derivative. I’ll point out that by remembering how to find the differentials, you also don’t need to remember the sign of \( U - TS \), since you can figure it out from the thermodynamic identity by making the \( TdS \) term cancel.

**Heat and work** You should remember the expressions for differential heat and work

\[ dQ = TdS \]  
(11.7)
\[ dW = -pdV \]  
(11.8)
and you should be able to use these expressions fluently, including integrating to find total heat or work, or solving for entropy given heat:

\[ dS = \frac{dQ}{T} \]  
(11.9)

**Efficiency** You should know that efficiency is defined as “what you get out” divided by “what you put in”, and that for a heat engine this comes down to

\[ \epsilon = \frac{W_{\text{net}}}{Q_H} \]  
(11.10)

**Entropy** You should remember the Gibbs expression for entropy in terms of probability.

\[ S = -k \sum_i P_i \ln P_i \]  
(11.11)
Boltzmann probability You should be comfortable with the Boltzmann probability, able to predict properties of systems using them.

\[ P_i = \frac{e^{-\beta E_i}}{Z} \quad (11.12) \]
\[ Z = \sum_i e^{-\beta E_i} \quad (11.13) \]
\[ F = -kT \ln Z \quad (11.14) \]

Derivative trick You may need to remember the derivative trick for turning a summation into a derivative of another summation in order to complete a problem. More particularly, I want you not to use an expression for \( U \) in terms of \( Z \) that comes from the derivative trick, without writing down the three lines of math (or so) required to show that it is true.

Thermal averages You should remember that the internal energy is given by a weighted average:

\[ U = \sum_i E_i P_i \quad (11.15) \]

And similarly for other variables, such as \( N \) in the grand canonical ensemble.

Chemical potential You should remember that the chemical potential is the Gibbs free energy per particle.

\[ \mu = \frac{G}{N} \quad (11.16) \]

You should also be able to make a distinction between internal and external chemical potential to solve problems such as finding the density as a function of altitude (or in a centrifuge), if I give you the expression for the chemical potential of an ideal gas (or other fluid).

Gibbs factor and sum You should be comfortable with the Gibbs sum and finding probabilities in the grand canonical ensemble.

\[ P_i = \frac{e^{-\beta (E_i - \mu N_i)}}{Z} \quad (11.17) \]
\[ Z = \sum_i e^{-\beta (E_i - \mu N_i)} \quad (11.18) \]

Incidentally, in class we didn’t cover the grand potential (or grand free energy), but that is what you get if you try to find a free energy using the Gibbs sum like the partition function.

Fermi-Dirac, Bose-Einstein, and Planck distributions You should remember these distributions

\[ f_{FD}(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \quad (11.19) \]
\[ f_{BE}(\epsilon) = \frac{1}{e^{\beta(\epsilon - \mu)} - 1} \quad (11.20) \]

and should be able to use them to make predictions for properties of non-interacting systems of fermions and bosons. This also requires remembering how to reason about orbitals as essentially independent systems within the grand canonical ensemble. You should remember that the Planck distribution for photons (or phonons) is the same as the Bose-Einstein distribution, but with \( \mu = 0 \). This comes about because photons and phonons are bosons, but are a special kind of boson that has no conservation of particle number.

Density of states You should remember how to use a density of states together with the above distributions to find properties of a system of non-interacting fermions or bosons

\[ \langle X(\epsilon) \rangle = \int D(\epsilon) f(\epsilon) X(\epsilon) d\epsilon \quad (11.21) \]

As special cases of this, you should be able to find \( N \) (or given \( N \) find \( \mu \)) or the internal energy. We had a few homeworks where you found entropy from the density of states, but I think that was a bit too challenging/confusing to put on the final exam.

Conditions for coexistence You should remember that when two phases are in coexistence, their
temperatures, pressures, and chemical potentials must be identical, and you should be able to make use of this.

**Equations not to remember**

If you need a property of a particular system (the ideal gas, the simple harmonic oscillator), it will be given to you. There is no need, for instance, to remember the Stefan-Boltzmann law or the Planck distribution.

**Heat capacity** I do not expect you to remember the definition of heat capacity (although you probably will remember it).

\[
C_V = T \left( \frac{\partial S}{\partial T} \right)_{V,N} \tag{11.22}
\]

\[
= \left( \frac{\partial U}{\partial T} \right)_{V,N} \tag{11.23}
\]

\[
C_p = T \left( \frac{\partial S}{\partial T} \right)_{p,N} \tag{11.24}
\]

I do expect you to be able to make use of these equations when given. Similarly, you should be able to show that the two expressions for \(C_V\) are equal, using the thermodynamic identity.

**Enthalpy** If I give you the expression for enthalpy \((U + pV)\) you should be able to work with it, but since we didn’t touch it in class, I don’t expect you to remember what it is.

**Any property of an ideal gas** I don’t expect you to remember any property of an ideal gas, including its pressure (i.e. ideal gas law), free energy, entropy, internal energy, or chemical potential. You should be comfortable with these expressions, however, and if I provide them should be able to make use of them.

**Stefan-Boltzmann equation** You should be able to make use of

\[
I = \sigma B T^4 \tag{11.25}
\]

where \(I\) is the power radiated per area of surface, but need not remember this.

**Clausius-Clapeyron equation** You should be able to make use of

\[
\frac{dp}{dT} = \frac{s_g - s_l}{v_g - v_l} \tag{11.26}
\]

but I don’t expect you to remember this. You should also be able to convert between this expression and the one involving latent heat using your knowledge of heat and entropy.

**Carnot efficiency** You need not remember the Carnot efficiency

\[
\epsilon = 1 - \frac{T_C}{T_H} \tag{11.27}
\]

but you should remember what an efficiency is, and should be able to pretty quickly solve for the net work and high-temperature heat for a Carnot engine by looking at it in \(T/S\) space. (Or similarly for a Carnot refrigerator.)

**Density of states for particular systems** You need not remember any expression for the density of states e.g. for a gas. But given such an expression, you should be able to make use of it.

**Fermi energy** You need not remember any particular expression for the Fermi energy of a particular system, but should be able to make use of an expression for the Fermi energy of a system.
Chapter 12

Solutions

Here are the solutions for all the homework problems. Although these solutions are available even before homework is due, I recommend that you do your best to solve the homework problems without checking the solutions. I would encourage you to go so far as to not check the solutions until after you have turned in your homework. This will enable you to practice determining if your answer is correct without knowing what the correct answer is. This is what you will have to do after you have graduated (or on the exam)!

In any case, please include for each homework problem that you solve an explanation of what resources you made use of, whether it be help from other students, these solutions, or some other resource. Please explain in each case how you used the resource. e.g. did you look at the solutions to confirm that your answer was correct, or did you look at the solutions to see how to start the problem? Your grade on the homework will not be diminished, even if you essentially copied the solution.

I would also appreciate it if you let me know where you got stuck on a given problem. I may address your difficulty in class, or I may choose to change the homework problem for next year.

Please note that verbatim copying of any solution (whether it be these, or a homework from another student) is plagiarism, and is not permitted. If you wish to copy a solution, please use it as a guide for how to do the steps, but perform each step on your own, and ideally add some words of your own explaining what you are doing in each step.

Solution for week 1

PDF version of solutions

1. Energy, Entropy, and Probabilities

To begin, as the question prompts, we will stick the probabilities into our expressions for $U$ and $S$. If you knew how everything was going to work out, you could only stick them into the $\ln P_i$, but I’ll act as though I haven’t solved this $N \gg 1$ times before.

$$U = \sum_i E_i \frac{e^{-\beta E_i}}{Z} \quad (12.1)$$

$$S = -k_B \sum_i \frac{e^{-\beta E_i}}{Z} \ln \left( \frac{e^{-\beta E_i}}{Z} \right) \quad (12.2)$$

At this point, we can see that there is a chance to simplify the $\ln$. 

\[ S = -k_B \sum_i e^{-\beta E_i} \left( \ln(e^{-\beta E_i}) - \ln Z \right) \quad (12.3) \]

\[ = -k_B \sum_i e^{-\beta E_i} (-\beta E_i - \ln Z) \quad (12.4) \]

\[ = k_B \sum_i e^{-\beta E_i} (\beta E_i + \ln Z) \quad (12.5) \]

\[ = k_B \sum_i \frac{e^{-\beta E_i}}{Z} (\beta E_i) + k_B \sum_i \frac{e^{-\beta E_i}}{Z} \ln Z \quad (12.6) \]

\[ = k_B \beta U + k_B \ln Z \quad (12.7) \]

\[ U = \frac{S}{k_B \beta} - \frac{1}{\beta} \ln Z \quad (12.8) \]

I’ll note that I would normally not show so many steps above in my own work, but am being extra thorough in this solution.

We are now at the point where we can start thinking thermo, and make use of the thermodynamic identity. To do that, let us “zap with d” to see what \( dU \) is in terms of \( dS \) and \( d\beta \), etc.

\[ dU = \frac{dS}{k_B \beta} - \left( \frac{S}{k_B \beta} - \frac{\ln Z}{\beta} \right) \frac{d\beta}{\beta} - \frac{1}{\beta Z} dZ \quad (12.12) \]

Let’s begin by lumping together the two \( d\beta \) terms. They look suspiciously similar to our previous expression for \( U \), which is unshocking, since Eq. 12.9 showed that \( U \) was inversely proportional to \( \beta \).

\[ dU = \frac{dS}{k_B \beta} - \left( \frac{S}{k_B \beta} - \frac{\ln Z}{\beta} \right) \frac{d\beta}{\beta} - \frac{1}{\beta Z} dZ \quad (12.13) \]

Let’s start by unpacking this \( dZ \):

\[ dZ = \sum_i e^{-\beta E_i} (-E_i d\beta) \quad (12.14) \]

\[ = -d\beta \sum_i e^{-\beta E_i} E_i \quad (12.15) \]

\[ = -Z d\beta \sum_i e^{-\beta E_i} \frac{E_i}{Z} \quad (12.16) \]

\[ = -Z U d\beta \quad (12.17) \]

Yay for recognizing something we have computed before! Now let’s put this back in our \( dU \).

\[ dU = \frac{dS}{k_B \beta} - \frac{U}{\beta} d\beta - \frac{1}{\beta Z} (-Z U d\beta) \quad (12.18) \]

\[ = \frac{dS}{k_B \beta} \quad (12.19) \]

Whew! Everything cancelled (as it had to, but one algebra error would mess this all up...), and we are left with a simple expression that does not have a \( d\beta \) in sight! This is good, because we argued before that with volume held fixed

which is a nuisance we can live without for now.

I’ll note that I would normally not show so many steps above in my own work, but am being extra thorough in this solution.

We are now at the point where we can start thinking thermo, and make use of the thermodynamic identity. To do that, let us “zap with d” to see what \( dU \) is in terms of \( dS \) and \( d\beta \), etc.

\[ dU = T dS - p dV \quad (12.10) \]

\[ = \frac{dS}{k_B \beta} - \frac{S}{k_B \beta^2} d\beta + \frac{\ln Z}{\beta^2} d\beta - \frac{1}{\beta Z} dZ \quad (12.11) \]

So far, this may not look promising to you, but perseverance pays off!

Note I threw out the \( dV \) because our statistical formalism only includes states with a given volume. Including the volume dependence is not complicated, but it requires us to take derivatives of \( E_i \) with respect to volume,
\[ dU = TdS = \frac{1}{k_B} d\beta S \]  
(12.20)

\[ T = \frac{1}{k_B} \beta \]  
(12.21)

\[ \beta = \frac{1}{k_B T} \]  
(12.22)

So we have just proven what you all knew about the relationship between \( \beta \) and \( T \). This is valuable, because it establishes the connection between the theoretical Lagrange multiplier and the temperature defined in thermodynamics.

The text uses a different (microcanonical) approach to establishing the connection between the statistical approach and the temperature that we define in thermodynamics.

2. **Gibbs entropy is extensive**

a) To begin, we remember the relationship between probabilities given in the problem:

\[ P_{ij}^{AB} = P_i^A P_j^B \]  
(12.23)

This means that the probability of finding system \( A \) in state \( i \) while system \( B \) is in state \( j \) is just the product of the separate probabilities. Now the entropy is

\[ S_{AB} = \sum_{\alpha}^{\text{all states}} P_{\alpha} \ln P_{\alpha} \]  
(12.24)

states of \( A \) states of \( B \)

\[ \sum_{i}^{\text{states of } A} \sum_{j}^{\text{states of } B} P_i^A P_j^B \ln (P_i^A P_j^B) \]  
(12.25)

\[ = \sum_{i}^{\text{states of } A} \sum_{j}^{\text{states of } B} P_i^A P_j^B (\ln P_i^A + \ln P_j^B) \]  
(12.26)

\[ = \sum_{i}^{\text{states of } A} \sum_{j}^{\text{states of } B} P_i^A P_j^B \ln P_i^A + \sum_{i}^{\text{states of } A} \sum_{j}^{\text{states of } B} P_i^A P_j^B \ln P_j^B \]  
(12.27)

\[ = \sum_{i}^{\text{states of } A} P_i^A \ln P_i^A \sum_{j}^{\text{states of } B} P_j^B + \sum_{i}^{\text{states of } A} P_i^A \sum_{j}^{\text{states of } B} P_j^B \ln P_j^B \]  
(12.28)

\[ = \left( \sum_{i}^{\text{states of } A} P_i^A \ln P_i^A \right) \left( \sum_{j}^{\text{states of } B} P_j^B \right) + \left( \sum_{i}^{\text{states of } A} P_i^A \right) \left( \sum_{j}^{\text{states of } B} P_j^B \ln P_j^B \right) \]  
(12.29)

\[ = S_A + S_B \]  
(12.30)

b) At this stage, we can basically use just words to solve this. We consider the system of \( N \) identical subsystems as a combination of a single one and \( N - 1 \) subsystems, thus \( S_N = S_1 + S_{N-1} \) from what we showed above. Then we repeat \( N \) times, to show that \( S_N = NS_1 \). There are other ways to show this, e.g. by repeatedly dividing the system \( (S_N = S_{N/2} + S_{N/2}) \).

3. **Boltzmann probabilities**

a) At infinite temperature \( \beta = 0 \), which makes computing probabilities easy: they are all equal. Thus the probabilities are each 1/3.

b) At very low temperatures \( \beta \epsilon \gg 1 \). Remember that the probabilities are given by
\[ P_i = \frac{e^{-\beta E_i}}{Z} \quad (12.31) \]

\[ Z = e^{\beta \epsilon} + 1 + e^{-\beta \epsilon} \quad (12.32) \]

We can see that our “small quantity” for a power series should be \( e^{-\beta \epsilon} \), since that is the small thing in the partition function. We can start with the ground state, which we expect to be overwhelmingly occupied:

\[ P_0 = \frac{e^{\beta \epsilon}}{e^{\beta \epsilon} + 1 + e^{-\beta \epsilon}} \quad (12.33) \]

\[ = \frac{1}{1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}} \quad (12.34) \]

\[ \approx 1 - (e^{-\beta \epsilon} + e^{-2\beta \epsilon}) + (e^{-3\beta \epsilon} + e^{-2\beta \epsilon})^2 + \cdots \quad (12.35) \]

At the last step, we used a power series approximation for \( 1/(1-z) \). We now need to gather terms so that we keep all terms to the same order. In this case the best option is to keep all terms up to \( e^{-2\beta \epsilon} \), since that way we will be able to account for the occupation of the highest energy state. Keeping these terms gives

\[ P_0 \approx 1 - e^{-\beta \epsilon} + O(e^{-3\beta \epsilon}) \quad (12.36) \]

because the \( e^{-2\beta \epsilon} \) terms cancel each other out. Thus the ground state will be almost 100% occupied. When we look at the other two states we will get exponentially smaller probabilities:

\[ P_1 = \frac{1}{e^{\beta \epsilon} + 1 + e^{-\beta \epsilon}} \quad (12.37) \]

\[ = \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}} \quad (12.38) \]

\[ = e^{-\beta \epsilon} P_0 \quad (12.39) \]

\[ \approx e^{-\beta \epsilon} (1 - e^{-\beta \epsilon}) \quad (12.40) \]

\[ = e^{-\beta \epsilon} - e^{-2\beta \epsilon} \quad (12.41) \]

The middle state with zero energy is less occupied by precisely a factor of \( e^{-\beta \epsilon} \). We could have predicted this from the Boltzmann ratio.

\[ P_2 = \frac{e^{-\beta \epsilon}}{e^{\beta \epsilon} + 1 + e^{-\beta \epsilon}} \quad (12.42) \]

\[ = \frac{1}{1 + e^{-\beta \epsilon} + e^{-2\beta \epsilon}} \quad (12.43) \]

\[ \approx e^{-2\beta \epsilon} \quad (12.44) \]

And the high energy state is hardly occupied at all, the same factor smaller than the previous state.

This solution kept all terms that were at least order \( e^{-2\beta \epsilon} \) for each probability, which resulted in a set of probabilities that add up to one. It would also have been reasonable to answer that \( P_0 \approx 1 \) and \( P_1 \approx e^{-\beta \epsilon} \), and then discuss that actually the probability of being in the ground state is not precisely 1.

I could understand saying that \( P_2 \approx 0 \), but ideally you should give a nonzero answer for each probability when asked about very low temperatures, because none of them are exactly zero. If you have an experiment that measures \( P_2 \) (perhaps state 2 has a distinctive property you can observe), then you will not find it to be zero at any temperature (unless you have poor resolution), and it is best to show how it scales.

c) If we allow the temperature to be negative, then higher energy states will be more probable than lower energy states. If the energy
is small and negative (which was not specified in the question), then the system will almost always be in the $+\epsilon$ energy state.

Another behavior with negative temperatures for this system is that $U > 0$. For positive temperatures, the internal energy only approaches zero as the temperature gets very high. If the temperature becomes negative, the energy can exceed zero. For other systems, of course, this will not be the case, but this will be true for any system in which the energy states are symmetrically arranged around zero.

Solution for week 2

PDF version of solutions

1. Entropy and Temperature (K&K 2.1)

a) We begin by finding the entropy given the provided multiplicity.

\[
S(U, N) = k_B \log g(U, N) = k_B \log \left( C U^{3N/2} \right) = k_B \left( \log C + \log \left( U^{3N/2} \right) \right) = k_B \log C + \frac{3}{2} N k_B \log U
\]

(12.45)

(12.46)

(12.47)

(12.48)

(12.49)

In the last two steps there, we made use of properties of log. If these are not obvious to you, you absolutely must take the time to review the properties of logarithms. They are absolutely critical to this course!

\[
\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{V,N} = \frac{3}{2} N k_B \frac{1}{U} \quad \text{(12.50)}
\]

\[
U = \frac{3}{2} N k_B T \quad \text{(12.51)}
\]

Yay.

b) We just need to take one more derivative, since we already found $\left( \frac{\partial S}{\partial U} \right)_{V,N}$ in part (a).

\[
\left( \frac{\partial^2 S}{\partial U^2} \right)_{V,N} = -\frac{3}{2} N k_B \frac{1}{U^2} \quad \text{(12.52)}
\]

\[
< 0, \quad \text{(12.53)}
\]

where in the last step we only needed to assume that $N > 0$ (natural for the number of particles) and that the energy $U$ is real (which it always must be). Thus ends the solution.

Because the second derivative of the entropy is always negative, the first derivative is monotonic, which means that the temperature (which is positive) will always increase if you increase the energy of the system and vice versa.

2. Paramagnetism (K&K 2.2)

Okay, here we can understand the fractional magnetization if we think $N m$ as being the maximum possible magnetization (all spins are pointing the same way). The quantity $s$ is defined as the total value of the spin. Because each spin has a value of $\pm \frac{1}{2}$, twice $s$ per particle also tells us the fractional magnetization.

To convert from $S(s)$ to $S(U)$ we need to relate the energy to the excess spin $s$. This relies on the energy expression

\[
U = -B2sm \quad \text{(12.54)}
\]

which uses the equations given. At this point, it is a simple substitution of $s = -\frac{U}{2mB}$:
\[ S(U) = S_0 - k_B \frac{2}{N} \left( \frac{U}{2mB} \right)^2 \] (12.56)

\[ = S_0 - k_B \frac{U^2}{2m^2B^2N} \] (12.57)

To determine \(1/kT\), we just need to take a derivative:

\[ \frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_V \] (12.58)

\[ = -k_B \frac{U}{m^2B^2N} \] (12.59)

\[ \frac{1}{k_BT} = -\frac{U}{m^2B^2N} \] (12.60)

At this point we have finished the problem, with just a bit of algebra. It is helpful at this stage to do a bit of checking. The left hand side here is an inverse energy. On the right hand side, \(mB\) is an energy, so we have an energy over an energy squared, so all is good. \(N\), of course, is dimensionless. However, it is also extensive, as is \(U\). This is good, because the left hand side is intensive, so the right hand side should be also.

The equilibrium fractional magnetization is thus given by

\[ \frac{\mu_{\text{tot}}}{Nm} = \frac{U}{NmB} \] (12.61)

\[ = \frac{1}{NmB} \left( \frac{m^2B^2N}{kT} \right) \] (12.62)

\[ = \frac{mB}{kT} \] (12.63)

Thus the fractional magnetization is just equal to the ratio between \(mB\) (which is the energy of one spin in the magnetic field) to \(kT\) (which is a measure of the available energy).

Of interest This relationship is very different than the one we saw in the previous problem! Previously, we saw the temperature being proportional to the internal energy, and here we see it as inversely proportional, meaning that as the energy approaches zero the temperature becomes infinite.

We also previously had an energy that was positive. Here we have a negative sign, which suggests that the energy should be negative in order to maintain a positive temperature. This relates to the energy of a single spin always being either positive or negative, with equal and opposite options.

This problem illustrates a weird phenomenon: if the energy is positive, then we must conclude that the temperature is negative. Furthermore, the temperature discontinuously passes from \(\infty\) to \(-\infty\) as the energy passes through zero. There are different interpretations of these “negative temperature” states. You cannot reach them by heating a system (adding energy via heating), and they cannot be exist in equilibrium if the system has contact with any quantity of material that can have kinetic energy. So I consider these to be unphysical (or non-equilibrium) states. Since temperature is an equilibrium property, I would not say that a negative temperature is physically meaningful. That said, there is an analogy that can be made to population inversion in a laser, which is a highly non-equilibrium system that is pretty interesting.

3. Quantum harmonic oscillator (K&K 2.3)

a) Given the multiplicity, we just need to take a logarithm, and simplify.
You need not simplify your answer this far, but it is good to get practice simplifying answers, particularly involving logarithms. In particular, it is usually helpful at this point in a computation to verify that the entropy is indeed extensive. Both \(N\) (the number of oscillators) and \(n\) (the sum of all the quantum numbers of all the oscillators) are extensive quantities. Thus \(n/N\) and \(N/n\) are intensive, which is good because otherwise we could not add them to 1. Each term is now clearly extensive, and the entropy behaves as we expect.

b) Now we want to find \(U(T)\), which will require us to find \(S(U)\) (via simple substitution of \(n = U/\hbar\omega\)) and \(T\) from a derivative of that.

\[
S(U) = Nk \log \left( 1 + \frac{U}{N\hbar\omega} \right) + Nk \frac{U}{N\hbar\omega} \log \left( 1 + \frac{N\hbar\omega}{U} \right) \tag{12.71}
\]

Now we just have a derivative to take, and then a mess of algebra to simplify.

\[
\frac{1}{T} = \left( \frac{\partial S}{\partial U} \right)_{N,V} \tag{12.72}
\]

\[
\frac{1}{T} = \frac{Nk}{1 + \frac{U}{N\hbar\omega}} \frac{1}{N\hbar\omega} \tag{12.73}
\]

\[
\frac{1}{T} = \frac{Nk}{1 + \frac{U}{N\hbar\omega}} \log \left( 1 + \frac{N\hbar\omega}{U} \right) \tag{12.74}
\]

\[
\frac{1}{T} = \frac{Nk}{1 + \frac{U}{N\hbar\omega}} \log \left( 1 + \frac{N\hbar\omega}{U} \right) - \frac{N\hbar\omega}{1 + \frac{N\hbar\omega}{U}} \tag{12.75}
\]

And now to simplify...

\[
\frac{\hbar\omega}{kT} = \frac{1}{1 + \frac{U}{N\hbar\omega}} + \log \left( 1 + \frac{N\hbar\omega}{U} \right) - \frac{N\hbar\omega}{1 + \frac{N\hbar\omega}{U}} \tag{12.76}
\]

\[
\frac{\hbar\omega}{kT} = \frac{N\hbar\omega}{U} + \log \left( 1 + \frac{N\hbar\omega}{U} \right) - \frac{N\hbar\omega}{1 + \frac{N\hbar\omega}{U}} \tag{12.77}
\]

\[
\frac{\hbar\omega}{kT} = \log \left( 1 + \frac{N\hbar\omega}{U} \right) \tag{12.78}
\]

Well, didn’t that simplify down nicely? The key was to multiply the first term by \(N\hbar\omega/\hbar\omega\) so that it shared a denominator with the last term (and ended up being equal and opposite). Solving for \(U\) is not bad at all, now, we’ll just take an exponential of both sides:

\[
e^{\frac{N\hbar\omega}{U}} = 1 + \frac{N\hbar\omega}{U} \tag{12.79}
\]

\[
N\hbar\omega \frac{U}{1} = e^{\frac{N\hbar\omega}{U}} - 1 \tag{12.80}
\]

\[
U = \frac{N\hbar\omega}{e^{\frac{N\hbar\omega}{U}} - 1} \tag{12.81}
\]

Note As I mentioned in the homework, this is the hard way to solve this problem. That said, it wasn’t actually particularly hard, you just need to be comfortable doing algebra with logarithms, and simplifying annoying ratios.
Solution for week 3

PDF version of solutions

1. **Free energy of a two state system** (K&K 3.1, modified)

   a) The partition function of this two-state system is very simple:

   \[
   Z = \sum_{s} e^{-\beta E_s} \quad \text{(12.82)}
   \]

   \[
   = e^0 + e^{-\beta \epsilon} \quad \text{(12.83)}
   \]

   \[
   = 1 + e^{-\beta \epsilon} \quad \text{(12.84)}
   \]

   Now the free energy is just a log of this:

   \[
   F = -kT \log Z \quad \text{(12.85)}
   \]

   \[
   = -kT \log (1 + e^{-\beta \epsilon}) \quad \text{(12.86)}
   \]

   \[
   = -kT \log (1 + e^{-\frac{\epsilon}{kT}}) \quad \text{(12.87)}
   \]

   We can ask ourselves if this simplifies in any limits, and the easiest one is the low-temperature limit where \( e^{-\beta \epsilon} \ll 1 \). In this limit, the free energy is given by

   \[
   F \approx -kT e^{-\frac{\epsilon}{kT}} \quad \text{(12.88)}
   \]

   b) To solve for the internal energy and entropy we can make use of the definition of the free energy the thermodynamic identity:

   \[
   F = U - TS \quad \text{(12.89)}
   \]

   \[
   dF = dU - TdS - SdT \quad \text{(12.90)}
   \]

   \[
   = TdS - pdV - TdS - SdT \quad \text{(12.91)}
   \]

   \[
   = -SdT - pdV \quad \text{(12.92)}
   \]

   which tells us that we can find the entropy by taking a derivative:

   \[
   S = -\left( \frac{\partial F}{\partial T} \right)_V \quad \text{(12.93)}
   \]

   \[
   = k \log (1 + e^{-\frac{\epsilon}{kT}}) + \frac{kT}{1 + e^{-\frac{\epsilon}{kT}}} e^{-\frac{\epsilon}{kT}} \frac{\epsilon}{kT^2} \quad \text{(12.94)}
   \]

   \[
   = k \log (1 + e^{-\frac{\epsilon}{kT}}) + \frac{\epsilon}{T} \frac{1}{1 + e^{\frac{\epsilon}{kT}}} \quad \text{(12.95)}
   \]

   I note here that entropy has dimensions of energy per temperature, and so do both of my terms, so we’re looking good so far. It is also worth checking that our entropy is positive, which it should always be. In this case each term is always positive so we are good. **Interesting note: the first time I solved this I lost the minus sign, and things did not make sense!** Now to find \( U \) I just need to add \( TS \) to my free energy.

   \[
   U = F + TS \quad \text{(12.96)}
   \]

   \[
   = -kT \log (1 + e^{-\frac{\epsilon}{kT}}) \quad \text{(12.97)}
   \]

   \[
   + kT \log (1 + e^{-\frac{\epsilon}{kT}}) + \frac{\epsilon}{T} \frac{1}{1 + e^{\frac{\epsilon}{kT}}} \quad \text{(12.98)}
   \]

   I will point out that you could have solved for the internal energy using the “derivative trick” or some other memorized formula involving partition function, but in this class I want you to always go back to the physics.

   c) Here is a nice plot of the entropy versus temperature. As you can see, the entropy asymptotes to a maximum value of \( k \log 2 \) as the temperature increases (the dotted line is at that value). This is reasonable because there are only two microstates possible, so the maximum possible entropy is \( k \log 2 \). You can think of the Boltzmann formulation with its log of the number of microstates. At high temperatures the system
Figure 12.1: Plot of entropy vs. temperature

approaches this maximum entropy state, in which both states are equally probable.

Figure 12.2: Plot of entropy vs. energy

d) Now let us look at this plot of the entropy as a function of internal energy. The first thing you can note (and that the problem asks about) is that the internal energy only goes up to $\frac{1}{2}\epsilon$. This may be counterintuitive, since the maximum energy of the system is $\epsilon$. The reason the internal energy maxes out halfway there is because no matter how hot the system gets, it will never occupy the higher energy state with greater probability than the lower energy state, so we can never get it to have more than a 50% probability of being in that state with energy $\epsilon$.

If we had approached this problem from a microcanonical perspective, where we choose the energy and then solve for the entropy and temperature, we could have specified an internal energy greater than $\frac{1}{2}\epsilon$, and would have found that the entropy decreases for these energies, and that the temperature therefore is negative. This is discussed in Schroeder 3.3 and K&K Appendix E.

2. Magnetic susceptibility

a) Before anything else, I’ll define the energy of a single spin to be given by:

\[ E_{\pm} = \pm mB \]  
(12.99)  

\[ F = -NkT \ln Z \]  
(12.100)

where the $\pm$ refers to the direction of the spin. We just need to find the partition function (and thus free energy) for a single spin and then multiply that free energy by $N$ to find a total free energy.

\[ Z = e^{\beta mB} + e^{-\beta mB} \]  
(12.101)

\[ F = -NkT \ln \left( e^{\beta mB} + e^{-\beta mB} \right) \]  
(12.102)

This gives us the free energy, and clearly $\frac{F}{NkT}$ is only a function of $\beta mB$. This tells us that the once we know the behavior at one temperature and all magnetic fields we actually know the behavior at all temperatures.

b) To find the magnetization (which is a per volume quantity), we start by finding the average magnetization of a single spin:
\[ \langle m \rangle = mP_+ - mP_- \quad (12.104) \]

\[ = m \frac{e^{\beta E_+} - e^{\beta E_-}}{e^{\beta E_+} + e^{\beta E_-}} \quad (12.105) \]

\[ = m \frac{e^{\beta mB} - e^{\beta (-m)B}}{e^{\beta mB} + e^{\beta (-m)B}} \quad (12.106) \]

\[ = m \tanh (\beta mB) \quad (12.107) \]

To find the magnetization \( M \), we just need to know the total dipole moment per unit volume, which is just the mean dipole moment of a single spin times the number of spins per unit volume. Thus

\[ M = n \langle m \rangle = nm \tanh \left( \frac{mB}{kT} \right) \quad (12.108) \]

as given in the problem. To find the susceptibility, we now just need to take a derivative of this thing with respect to \( B \) while holding temperature fixed. I’ll assume you don’t know the derivative of a \( \tanh \), since I couldn’t remember it myself.

\[ \chi = nm \left( \frac{\partial}{\partial B} \right) \frac{e^{\beta mB} - e^{\beta (-m)B}}{e^{\beta mB} + e^{\beta (-m)B}} \]

\[ = nm \left( \frac{e^{\beta mB} + e^{-\beta mB} - (e^{\beta mB} - e^{-\beta mB})^2}{(e^{\beta mB} + e^{-\beta mB})^2} \right) \beta m \quad (12.109) \]

\[ = nm^2 \frac{1 - (e^{\beta mB} - e^{-\beta mB})^2}{(e^{\beta mB} + e^{-\beta mB})^2} \frac{\beta m}{kT} \quad (12.110) \]

\[ = \frac{nm^2}{kT} \frac{e^{\beta mB} + e^{-\beta mB}}{2} \left( \frac{e^{\beta mB} - e^{-\beta mB} + 1}{e^{\beta mB} + e^{-\beta mB}} \right)^2 \quad (12.111) \]

\[ = \frac{nm^2}{kT} \frac{4}{(e^{\beta mB} + e^{-\beta mB})^2} \quad (12.112) \]

It’s not necessary to fully simplify this answer, but it is helpful to practice making your answers as pretty as possible, as it tends to make it easier to understand and easier to reason about.

Looking at this solution, you can see that the susceptibility is always positive (as it must be), and that it is proportional to the density of spins as it must be (*interesting note: when I solved this at first I omitted the factor of \( n \) and only when doing this reasoning caught the error). You can see that at large \( B \) field (either positive or negative) the susceptibility vanishes (because everything is already pointing the right way). You can see that the susceptibility is an even function of \( B \), which reflects the symmetry of the system under a redefinition of the “up” direction.

\[ e^{\pm \beta mB} \approx 1 \pm \beta mB \quad (12.114) \]

\[ \chi \approx \frac{nm^2}{kT} \frac{4}{(1 + \beta mB + 1 - \beta mB)^2} \quad (12.115) \]

\[ = \frac{nm^2}{kT} \quad (12.116) \]

and we can see that this is accurate even to first order in \( B \). In fact the symmetry of the system prevents \( \chi \) from having any odd terms in its power series. You might wonder why \( m \) shows up squared. That is because one factor of \( m \) comes from the magnetic moment causing the spins to align with the magnetic field, while the other factor comes from the fact that the total dipole moment is also proportional to \( m \).

3. **Free energy of a harmonic oscillator**

a) We start as usual by writing down the partition function, from which finding the free energy is easy.
Here we need a little trick, which is how you do a harmonic sum. The trick involves multiplying by $e^{-\beta \hbar \omega}$ (with no $n$) on both sides of the above. This gives us

$$e^{-\beta \hbar \omega} Z = \sum_{n=0}^{\infty} e^{-\beta (n+1) \hbar \omega} \quad (12.118)$$

Now we can shift $n$ by 1 in this infinite sum:

$$e^{-\beta \hbar \omega} Z = \sum_{n=1}^{\infty} e^{-\beta n \hbar \omega} \quad (12.119)$$

Now we can observe that the right hand side is just the original expression for $Z$ missing the $n = 0$ term, after which the rest is algebra:

$$e^{-\beta \hbar \omega} Z = Z - 1 \quad (12.120)$$

$$\left(1 - e^{-\beta \hbar \omega}\right) Z = 1 \quad (12.121)$$

$$Z = \frac{1}{1 - e^{-\beta \hbar \omega}} \quad (12.122)$$

$$F = -kT \ln Z \quad (12.123)$$

$$F = kT \ln (1 - e^{-\beta \hbar \omega}) \quad (12.124)$$

where in the last step I used the properties of a logarithm to put the denominator on top.

b) To solve for the entropy, we just need to remember (or derive) the total differential of the free energy:

$$dF = -SdT - pdV + \mu dN \quad (12.125)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \quad (12.126)$$

So let’s start taking a derivative!
predicted if you remembered the equipartition theorem (or if I had taught it already?).

4. **Energy fluctuations** There are two ways to approach this problem: from the right or from the left. I will show how to approach it from the left, but you could alternatively start by taking a derivative of $U$ and work from there.

We begin by writing down an expression for the mean energy (or internal energy).

$$U = \langle \varepsilon \rangle = \sum_i E_i P_i \quad (12.130)$$

Now let’s look at the variation that we are looking for:

$$\langle (\varepsilon - U)^2 \rangle = \sum_i (E_i - U)^2 P_i$$

$$= \sum_i E_i^2 P_i - 2 \sum_i E_i U P_i + \sum_i U^2 P_i \quad (12.131)$$

$$= \sum_i E_i^2 P_i - 2U^2 + U^2 \quad (12.132)$$

$$= \sum_i E_i^2 P_i - U^2 \quad (12.133)$$

$$= \langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2 \quad (12.134)$$

At this point we can interpret a couple of the sums physically, and then cope with the derivative of the partition function (which you have probably seen before).

$$\left( \frac{\partial U}{\partial T} \right)_V = \frac{\langle \varepsilon^2 \rangle}{kT^2} - U \frac{1}{Z} \frac{\partial Z}{\partial T} \quad (12.140)$$

So let’s do that derivative of the partition function.

$$\frac{1}{Z} \frac{\partial Z}{\partial T} = \frac{1}{Z} \sum_i \frac{\partial e^{-\beta E_i}}{\partial T} \quad (12.141)$$

$$= \frac{1}{Z} \sum_i \frac{e^{-\beta E_i}}{kT^2} \quad (12.142)$$

$$= \frac{1}{kT^2} \sum_i E_i e^{-\beta E_i} \quad (12.143)$$

$$= \frac{U}{kT^2} \quad (12.144)$$

Thus we see that

$$\left( \frac{\partial U}{\partial T} \right)_V = \frac{\langle \varepsilon^2 \rangle}{kT^2} - \frac{U^2}{kT^2} \quad (12.145)$$

$$= \frac{\langle (\varepsilon - U)^2 \rangle}{kT^2} \quad (12.146)$$
And thus we have shown that the fluctuations in the energy are proportional to the heat capacity $C_V$ as we were told to show. One can find a similar relationship for the fluctuation of any thermal variable, e.g. the fluctuation-dissipation theorem (which we will not cover in class).

5. **Quantum concentration** (K&K 3.8) We need to start by finding the formula for the ground state energy of a particle in a box. It’s all right if you just remember this, but it also isn’t hard to figure out without doing any complicated math or boundary conditions. The particle needs to have a half-wavelength of $L$ in each direction in order to fit in the box, thus $\lambda = 2L$ for each direction. This means that that the wave vector is given by $k_x = k_y = k_z = \pm \frac{2\pi}{2L}$. Of course, the particle isn’t in a traveling wave, but rather in a superposition of the $\pm$ versions of these traveling waves (i.e. a standing wave). The kinetic energy is given by

$$KE = \frac{p^2}{2M} = \frac{\hbar^2 k^2}{2M} = \frac{\hbar^2 \pi^2}{2ML^2} \quad (12.147)$$

Now as instructed we set the kinetic energy to $kT$ and solve for the density, given by $n = \frac{1}{\pi^2}$.

$$kT = \frac{\hbar^2 \pi^2}{2ML^2} \quad (12.150)$$

$$n = \frac{(\frac{1}{\pi^2})^{\frac{3}{2}}}{(2MkT)^{\frac{3}{2}}} \quad (12.152)$$

As predicted, this differs from $n_Q$ by a factor of $(\frac{4}{\pi})^{\frac{3}{2}}$, which is of order unity. Its value is around 1.4.

Let’s remind ourselves: this is the density at which quantum stuff becomes really important at a given temperature. In this problem, we showed that the density $n_Q$ is basically the same as the density of a single particle that is confined enough that its kinetic energy is the same as the temperature.

6. **One-dimensional gas** (K&K 3.11) Consider an ideal gas of $N$ particles, each of mass $M$, confined to a one-dimensional line of length $L$. Find the entropy at temperature $T$. The particles have spin zero.

To find the entropy at temperature $T$ we need first to consider the energy eigenstates of this system. We could use either periodic boundary conditions or a particle-in-a-box potential to confine the particles. The kinetic energy of a plane wave is given by

$$E_k = \frac{\hbar^2 k^2}{2m} \quad (12.154)$$

For a particle in a box, a half-integer number of wavelengths must fit in the box:

$$L = \frac{n\lambda}{2} \quad (12.155)$$

$$k_n = \frac{\pi n}{L}. \quad (12.156)$$

Thus, the energy is given by

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2mL^2} \quad (12.158)$$

No, you don’t need to derive this, but in my opinion it is easier to derive than to remember.
If I were not writing up solutions, I would have done several of the steps above in my head.

Now that we have our energy, we can start thinking about how to find the partition function for a single particle. We can get away with this because the particles are non-interacting, so the total energy is just a sum of the energies of each individual particle.

\[
Z_1 = \sum_{n=1}^{\infty} e^{-\beta E_n} \tag{12.160}
\]

\[
= \sum_{n=1}^{\infty} e^{-\beta \frac{\mathbf{p}_n^2}{2mL^2}} \tag{12.161}
\]

This is the point where we typically step back and tell ourselves that \( k_B T \gg \frac{\pi^2 \hbar^2}{2mL^2} \) (because the distance \( L \) is macroscopic, and we aren’t looking at crazy-low temperatures), which means that we can turn the sum into an integral:

\[
Z_1 \approx \int_0^{\infty} e^{-\beta \frac{\mathbf{p}_n^2}{2mL^2}} \, dn \tag{12.162}
\]

The smart move here is to do a \( u \) substitution, to get all the ugly stuff out of our integral.

\[
u = \sqrt{\frac{\beta \pi \hbar}{2mL}} \quad du = \sqrt{\frac{\beta \pi \hbar}{2mL}} \, dn \tag{12.163}
\]

This gives us a simple gaussian integral:

\[
Z_1 \approx \sqrt{\frac{2mkT}{\pi \hbar}} \frac{L}{\pi \hbar} \int_0^{\infty} e^{-u^2} \, du \tag{12.164}
\]

The value of the gaussian integral here doesn’t have any particular physical impact, since it is just a dimensionless numerical constant. It does, of course, impact the numerical value.

**Gaussian integrals** You are welcome to look up the value of integrals like this, or memorize the answer (I always just remember that it’s got a \( \sqrt{\pi} \) in it, which doesn’t help much). I’ll show you here how to find the value of a gaussian integral, which is a nice trick to be aware of.

\[
I_G \equiv \int_0^{\infty} e^{-u^2} \, du \tag{12.165}
\]

\[
= \frac{1}{2} \int_{-\infty}^{\infty} e^{-u^2} \, du \tag{12.166}
\]

\[
(2I_G)^2 = \left( \int_{-\infty}^{\infty} e^{-u^2} \, du \right)^2 \tag{12.167}
\]

\[
= \left( \int_{-\infty}^{\infty} e^{-x^2} \, dx \right) \left( \int_{-\infty}^{\infty} e^{-y^2} \, dy \right) \tag{12.168}
\]

\[
= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} \, dx \, dy \tag{12.169}
\]

\[
= \int_0^{\infty} \int_0^{2\pi} e^{-r^2} r \, d\phi \, dr \tag{12.170}
\]

\[
= 2\pi \int_0^{\infty} e^{-r^2} \, r \, dr \tag{12.171}
\]

\[
= \pi \int_0^{\infty} e^{-\xi} \, d\xi \tag{12.172}
\]

\[
(2I_G)^2 = 2\pi \int_0^{\infty} e^{-\xi} \, d\xi \tag{12.173}
\]

\[
= \pi \tag{12.174}
\]

\[
I_G = \frac{\sqrt{\pi}}{2} \tag{12.175}
\]

The trick was simply to square the integral, and then move from Cartesian to polar co-ordinates. This only works because we are integrating to \( \infty \).

Back to our original task, we have now found that

\[
Z_1 \approx \sqrt{\frac{\pi mkT}{\pi \hbar}} \frac{L}{\pi \hbar} \tag{12.176}
\]
To find the entropy, we will want to construct the Helmholtz free energy. We will need the entire partition function, which will have the $N!$ in it to avoid double-counting states, since these are indistinguishable particles.

\[ Z = \frac{Z_1^N}{N!} \]  
\[ F = -k_B T \log Z \]  
\[ = -k_B T \log \left( \frac{Z_1^N}{N!} \right) \]  
\[ = -k_B T \left( N \log Z_1 - \log N! \right) \]  
\[ \approx -k_B T \left( N \log Z_1 - N \log N + N \right) \]  
\[ = -N k_B T \left( \log Z_1 - \log N + 1 \right) \]  
\[ = -N k_B T \left( \log \left( \sqrt{\frac{\pi m k_T}{2 \pi \hbar^2}} \frac{L}{\pi N} \right) + \log N + 1 \right) \]  
\[ = -N k_B T \left( \log \left( \sqrt{\frac{m k_T}{2 \pi \hbar^2}} \frac{L}{\pi N} \right) + 1 \right) \]  
\[ = -N k_B T \left( \log \left( \sqrt{\frac{m k_T}{2 \pi \hbar^2}} \frac{L}{\pi N} \right) + \frac{1}{2} \log \frac{L}{N} \right) \]  
\[ (12.182) \]

\[ (12.183) \]

Here we are at a good point to check whether our answer makes sense. Firstly, we can check that $F$ is indeed extensive. It is, since it is proportional to $N$, and the only other extensive quantities in it are the $L$ and $N$ in the logarithm, and they form a ratio, which is therefore intensive. We can also check dimensions.

We know that $\frac{\hbar^2 k^2}{2m}$ is an energy, which means that $\frac{\hbar^2}{m}$ has dimensions of energy times distance squared. The $kT$ cancels the energy, and the square root turns the resulting one over distance squared into an inverse distance, which happily cancels with the $L$, so the argument of our logarithm is dimensionless.

Now we will get to the answer pretty soon! Recall that:

\[ dF = -SdT - pdV \]  
\[ (12.186) \]

(although the second term should have a $dL$ for a 1D system) which means that

\[ -S = \left( \frac{\partial F}{\partial T} \right)_{L,V,N} \]  
\[ (12.187) \]

\[ S = -\left( \frac{\partial F}{\partial T} \right)_{L,V,N} \]  
\[ = N k_B \left( \log \left( \sqrt{\frac{m k_T}{2 \pi \hbar^2}} \frac{L}{\pi N} \right) + 1 \right) + N k_B T \frac{1}{2T} \]  
\[ = N k_B \left( \log \left( \sqrt{\frac{m k_T}{2 \pi \hbar^2}} \frac{L}{\pi N} \right) + \frac{3}{2} \right) \]  
\[ (12.189) \]

This is our final answer. It looks shockingly like the entropy of a 3D ideal gas, right down to the quantum length scale (which is no longer a quantum density), commonly called the “thermal de Broglie wavelength.”

**Nasty logs** In computing the derivative of a nasty logarithm (which I did in my head above), you can use the following shortcut, provided you remember the properties of logarithms:

\[ \log \left( \sqrt{\frac{m k_T}{32 \pi \hbar^2}} \frac{L}{N} \right) = \log \left( \sqrt{\frac{m k}{32 \pi \hbar^2}} \right) + \log \left( \frac{L}{N} \right) \]  
\[ (12.191) \]

\[ = \frac{1}{2} \log \left( \frac{m k}{32 \pi \hbar^2} \right) + \log \left( \frac{L}{N} \right) \]  
\[ (12.192) \]

\[ = \frac{1}{2} \log (T) + \frac{1}{2} \log \left( \frac{m k}{32 \pi \hbar^2} \right) + \log \left( \frac{L}{N} \right) \]  
\[ (12.193) \]

Now you can take a derivative of this, which is way easier than a derivative of the whole.
mess, and clearly must give you the same answer. There are other ways to do it, but I find this particularly simple, and it has the advantage that it’s the same kind of manipulation you’re doing all the time anyhow, just to simplify your results.

If you do this in your head (or on scratch paper), you can immediately discard any of the terms that will vanish when you take a derivative of them, which makes it much simpler than what I wrote down.

Solution for week 4

PDF version of solutions

1. Radiation in an empty box

a) To find the free energy, we’ll first want to find the partition function, so we can take a log of it. That will involve summing over all the possible microstates of the entire system. This can be a little confusing, and there are indeed several ways that you could approach this other than the one I show here. Please feel free to try something else, and talk with me about whether it is also correct.

Summing over microstates will be similar to what we did for the ideal gas, and you’ve seen things like this before, but I think it’s worth talking through again in detail. A microstate is defined by a single quantum number \( n_x, n_y, n_z \) (plus polarization, which I’ll ignore for now). The sum over all microstates then becomes

\[
Z = \sum_{n_{111}=0}^{\infty} \sum_{n_{112}=0}^{\infty} \sum_{n_{113}=0}^{\infty} \cdots \sum_{n_{\infty\infty}=0}^{\infty} e^{-\beta \hbar \omega_{111} n_{111}} e^{-\beta \hbar \omega_{112} n_{112}} e^{-\beta \hbar \omega_{113} n_{113}} \cdots e^{-\beta \hbar \omega_{\infty\infty} n_{\infty\infty}}
\]

(12.194)

So we’ve got an infinite number of nested sums (one sum for each mode), each going from \( 0 \rightarrow \infty \), and an exponential with an infinite number of \( n \)'s added together. The energy separates (the modes are independent, or the photons don’t interact with each other), which means that the sums separate.

\[
Z = \sum_{n_{111}=0}^{\infty} \sum_{n_{112}=0}^{\infty} e^{-\beta \hbar \omega_{111} n_{111}} \sum_{n_{113}=0}^{\infty} \cdots \sum_{n_{\infty\infty}=0}^{\infty} e^{-\beta \hbar \omega_{\infty\infty} n_{\infty\infty}}
\]

(12.195)

Each of these sums can now be done independently...

\[
Z = \left( \sum_{n_{111}=0}^{\infty} e^{-\beta \hbar \omega_{111} n_{111}} \right) \left( \sum_{n_{112}=0}^{\infty} e^{-\beta \hbar \omega_{112} n_{112}} \right) \cdots \left( \sum_{n_{\infty\infty}=0}^{\infty} e^{-\beta \hbar \omega_{\infty\infty} n_{\infty\infty}} \right)
\]

(12.196)

and this turns our nested sums into a product of sums. We can now write down explicitly this product in a simpler way, and we can plug in the expression for \( \omega_{n_x n_y n_z} \). Note also that for every \( \vec{k} \), there are two polarizations of photon, so we need to square it all. I left that out above, because I thought we had enough indices to worry about.

\[
Z = \left( \prod_{n_x=1}^{\infty} \prod_{n_y=1}^{\infty} \prod_{n_z=1}^{\infty} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega \sqrt{n_x^2 + n_y^2 + n_z^2}} \right)^2
\]

(12.197)

Fortunately, the inmost sum over \( n \) we have already solved in class (we recognize it as a geometric sum). Thus we get
\[ Z = \left( \prod_{n_x=1}^{\infty} \prod_{n_y=1}^{\infty} \prod_{n_z=1}^{\infty} \frac{1}{1 - e^{-\frac{\hbar c}{\kappa T} \sqrt{n_x^2 + n_y^2 + n_z^2}}} \right)^2. \]

This still probably doesn’t leave you dancing with joy. Fortunately, there are quite a few simplifications left. Before we start simplifying further, let’s go ahead and look at the Helmholtz free energy, which will turn our products into more familiar summations.

\[ F = -kT \ln Z \quad (12.199) \]

\[ F = -2kT \ln \left( \prod_{n_x=1}^{\infty} \prod_{n_y=1}^{\infty} \prod_{n_z=1}^{\infty} \frac{1}{1 - e^{-\frac{\hbar c}{\kappa T} \sqrt{n_x^2 + n_y^2 + n_z^2}}} \right) \quad (12.200) \]

\[ F \approx 2kT \sum_{n_x=1}^{\infty} \sum_{n_y} \sum_{n_z} \ln \left( 1 - e^{-\frac{\hbar c}{\kappa T} \sqrt{n_x^2 + n_y^2 + n_z^2}} \right) \quad (12.201) \]

This is starting to look more friendly. As usual (and as the problem instructs us), we’d like to take a large-volume approximation, which will mean that \( \frac{\hbar c}{\kappa T} \ll 1 \). In this limit, we can turn our summation into an integration.

\[ F \approx 2kT \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} \ln \left( 1 - e^{-\frac{\hbar c}{\kappa T} \sqrt{n_x^2 + n_y^2 + n_z^2}} \right) \, dn_x dn_y dn_z \quad (12.202) \]

\[ F \approx \frac{kT}{4} \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} \ln \left( 1 - e^{-\frac{\hbar c}{\kappa T} \sqrt{n_x^2 + n_y^2 + n_z^2}} \right) \, dn_x dn_y dn_z \quad (12.203) \]

This integral is begging to be done in spherical coordinates, and I’ll just define \( n \equiv \sqrt{n_x^2 + n_y^2 + n_z^2} \) for that integral. I’ll also divide by 8 and do the integral over all “n” space, instead of just the positive n space.

\[ F \approx \frac{kT}{4} \int_{0}^{\infty} \ln \left( 1 - e^{-\frac{\hbar c}{\kappa T} \sqrt{n_x^2 + n_y^2 + n_z^2}} \right) 4\pi n^2 \, dn \quad (12.204) \]

\[ = 8\pi kT \left( \frac{LkT}{\hbar c} \right)^3 \int_{0}^{\infty} \ln \left( 1 - e^{-\xi} \right) \xi^2 \, d\xi \quad (12.205) \]

\[ = 8\pi \frac{V(kT)^4}{\hbar^3 c^3} \int_{0}^{\infty} \ln \left( 1 - e^{-\xi} \right) \xi^2 \, d\xi \quad (12.206) \]

At this point we have pretty much solved for the free energy of a vacuum at temperature \( T \). We know it should scale as \( T^4 \), and that it should scale with volume. The latter should have been obvious, since it’s the only way that the free energy could be extensive. You might worry about the definite integral, but it is just a dimensionless number! Yes, it matters if we want to know precisely how much radiation to expect from a black body, but we could solve this integral numerically, or we could have just done an experimental measurement to see what this number is. Wolfram Alpha tells us that this number is -2.165. You could tell it should be negative because the thing in the \( \ln \) is always less than one, meaning the \( \ln \) is always negative. You might be weirded out that the free energy density is negative, but this just means it is dominated by entropy, since the entropy term is always negative.

**Extra fun:** Can any of you find an elegant solution to the above definite integral? If so, please share it with me, and I’ll share it with the class.

\[ \int_{0}^{\infty} \ln \left( 1 - e^{-\xi} \right) \xi^2 \, d\xi = \frac{\pi^4}{45} \quad (12.207) \]

but I don’t know how to prove this except numerically.

b) We can solve for the entropy straight off:
\[ S = -\left( \frac{\partial F}{\partial T} \right)_V \]  \hspace{1cm} (12.208)

\[ = -32\pi k V \left( \frac{kT}{hc} \right)^3 \int_0^\infty \ln (1 - e^{-\xi}) \xi^2 d\xi \]  \hspace{1cm} (12.209)

c) We also want to know the internal energy

\[ U = F + TS \]  \hspace{1cm} (12.210)

\[ = (8 - 32)\pi V \left( \frac{kT}{hc} \right)^4 \int_0^\infty \ln (1 - e^{-\xi}) \xi^2 d\xi \]  \hspace{1cm} (12.211)

\[ \frac{U}{V} = -24\pi \left( \frac{kT}{hc} \right)^4 \int_0^\infty \ln (1 - e^{-\xi}) \xi^2 d\xi \]  \hspace{1cm} (12.212)

So the internal energy scales the same as the free energy, but is positive, as we would expect.

2. Surface temperature of the earth

This problem comes down to balancing the radiation absorbed by the earth with the radiation emitted by the earth. Interestingly, the answer won’t change if we drop the assumption that the earth is a perfect black body, so long as its absorption is independent of frequency (which isn’t true). The assumption that it remains constant temperature over day and night is also a bit weak, but fractionally the variation of temperature is actually relatively small.

The total energy radiated by the sun is

\[ P_\odot = \sigma_B T_\odot^4 4\pi R_\odot^2 \]  \hspace{1cm} (12.213)

Now, the fraction \( f \) of that power that is absorbed by the Earth is given by

\[ f = \frac{\text{cross-sectional area of earth}}{\text{area of sphere with Earth’s orbit}} \]  \hspace{1cm} (12.214)

\[ = \frac{\pi R_E^2}{4\pi AU^2} \]  \hspace{1cm} (12.215)

Okay, now we just need the energy radiated by the earth:

\[ P_E = \sigma_B T_E^4 4\pi R_E^2 \]  \hspace{1cm} (12.216)

Setting the energy absorbed by the earth to the energy radiated by the earth gives

\[ \frac{\pi R_E^2}{4\pi AU^2} \sigma_B T_\odot^4 4\pi R_\odot^2 = \sigma_B T_E^4 4\pi R_E^2 \]  \hspace{1cm} (12.217)

\[ T_E^4 = \frac{R_\odot^2}{4AU^2} T_\odot^4 \]  \hspace{1cm} (12.218)

\[ = \frac{1}{4} T_\odot^4 \frac{R_\odot^2}{AU^2} \]  \hspace{1cm} (12.219)

\[ T_E = \sqrt{\frac{R_\odot}{2AU}} T_\odot \]  \hspace{1cm} (12.220)

\[ = \sqrt{\frac{7 \times 10^{10} \text{cm}}{3 \times 10^{15} \text{cm}} 5800 \text{K}} \]  \hspace{1cm} (12.221)

\[ \approx 280 \text{K} \]  \hspace{1cm} (12.222)

This is a bit cold, but when you consider the approximations isn’t a bad estimate of the Earth’s temperature. This neglects the power from radioactivity, and also the greenhouse effect (which is a violation of the assumption that the absorption and emission have the same proportion at all wavelengths).

3. Pressure of thermal radiation

Okay, let’s begin with the free energy from class:
\[ F = \frac{8\pi V}{\hbar^3 c^3} \int_0^\infty \ln \left( 1 - e^{-\xi} \right) \xi^2 d\xi \quad (12.223) \]

Since this is proportional to volume, its derivative with respect to volume is really easy.

\[ p = -8\pi \frac{(kT)^4}{\hbar^3 c^3} \int_0^\infty \ln \left( 1 - e^{-\xi} \right) \xi^2 d\xi \quad (12.224) \]

Unfortunately, we’ve already done our summation over all the modes, so this didn’t help us as much as we might have hoped for part (a). To get an expression in terms of the modes, we need to go back to the expression for free energy that had \( \sum_n \sum_y \sum_z \) and recognize that as a sum over modes.

\[ F = kT \sum_j \ln \left( 1 - e^{-\beta \omega_j} \right) \quad (12.225) \]

Now we can take our derivative and hope to get an expression involving photons in modes:

\[ p = -\left( \frac{\partial F}{\partial V} \right)_T \quad (12.226) \]

\[ = -kT \sum_j \frac{-e^{-\beta \omega_j}}{1 - e^{-\beta \omega_j}} \left( -\beta \hbar \frac{d\omega_j}{dV} \right) \quad (12.227) \]

\[ = -\sum_j \frac{-e^{\beta \omega_j}}{1 - e^{\beta \omega_j}} \hbar \frac{d\omega_j}{dV} \quad (12.228) \]

\[ = -\sum_j \langle n_j \rangle \hbar \frac{d\omega_j}{dV} \quad (12.229) \]

So yay. It worked out as we were told, which is also reasonably intuitive: the pressure is just the total pressure from all the photons.

Now we want to find the actual pressure, and relate it to the internal energy. We can do this two ways. One is to use the above expression for total pressure and compare with \( U \) from class. This is totally correct and fine. I’ll use a different approach here, since it may be less obvious, and may give insight.

We’ll take this expression we just found, and see how the mode frequencies change with volume. Recall from class that:

\[ \omega_{n_x n_y n_z} = \frac{2\pi c}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} \quad (12.230) \]

\[ = \frac{2\pi c}{\sqrt{V}} \sqrt{n_x^2 + n_y^2 + n_z^2} \quad (12.231) \]

Thus we have that

\[ \frac{d\omega_{n_x n_y n_z}}{dV} = -\frac{1}{3} \frac{\omega_{n_x n_y n_z}}{V} \quad (12.232) \]

Putting this into our pressure, we see that

\[ p = -\sum_j \langle n_j \rangle \hbar \frac{d\omega_j}{dV} \quad (12.233) \]

\[ = -\sum_j \langle n_j \rangle \hbar \left( -\frac{1}{3} \frac{\omega_j}{V} \right) \quad (12.234) \]

\[ = \frac{1}{3V} \sum_j \langle n_j \rangle \hbar \omega_j \quad (12.235) \]

\[ = \frac{U}{3V} \quad (12.236) \]

which tells us that the pressure is one third of the internal energy per volume. You might want a dimension check: work (which is an energy) is \( dW = pdV \) which will remind you that pressure is energy per volume. If you have doubts, you could remind yourself that pressure is force per area, but force is energy per distance (going back to work from classical mechanics).

The factor of \( \frac{1}{3} \) comes from the fact that we’re in three dimensions, and the linear dispersion relation for light.
4. Heat shields

The middle plane is going to absorb the same rate of energy from the hot side that it gives to the cold side. The net transfer from hot to middle (per area) will be

\[ J_h = \sigma_B (T_h^4 - T_m^4) \]  

while the transfer from middle to cold will be

\[ J_c = \sigma_B (T_m^4 - T_c^4) \]  

Setting these equal tells us that

\[ T_h^4 - T_m^4 = T_m^4 - T_c^4 \]  

\[ 2T_m^4 = T_h^4 + T_c^4 \]  

\[ T_m = \sqrt[4]{\frac{T_h^4 + T_c^4}{2}} \]

Now we can see that the power transferred per area is given by

\[ J_h = \sigma_B (T_h^4 - T_m^4) \]  

\[ = \sigma_B (T_h^4 - \frac{T_h^4 + T_c^4}{2}) \]  

\[ = \sigma_B \frac{T_h^4 - T_c^4}{2} \]

which is precisely \( \frac{1}{2} \) of the power that would have been transferred without the heat shield.

1. Centrifuge

The key concept here is to recognize that when working with a rotating system such as a centrifuge, there is classically a centrifugal potential energy. This energy serves as the external chemical potential, and allows us to solve for the properties of the gas by setting the total chemical potential equal everywhere, and solving for the internal chemical potential, which we can relate to the concentration.

![Centrifugal Force](https://xkcd.com/2248/)

First we need the centrifugal potential. You may remember this from Central Forces, but you can also solve for it if you remember how to derive the centripetal acceleration. This comes from the

Solution for week 5

PDF version of solutions
second derivative of the displacement of an object moving in a circle.

\[ \ddot{r}(t) = R \cos(\omega t) \dot{x} + R \sin(\omega t) \dot{y} \quad (12.245) \]

\[ \frac{d^2 \vec{r}}{dt^2} = -\omega^2 \vec{r} \quad (12.246) \]

\[ = \frac{1}{m} \ddot{F} \quad (12.247) \]

So the centrifugal force is \( m\omega^2 \vec{r} \) (which is outward, opposite the centripetal force). The centrifugal work is the integral of the centrifugal force, which gives us a **centrifugal potential energy** that is \( V = -\frac{1}{2}m\omega^2 r^2 \). The potential is negative because the force is outwards.

Now that we have a potential energy, we can find the internal chemical potential from the total:

\[ \mu_{\text{tot}} = \mu_{\text{int}} - \frac{1}{2}m\omega^2 r^2 \mu_{\text{int}} = \mu_{\text{tot}} + \frac{1}{2}m\omega^2 r^2 \quad (12.248) \]

Finally, we need to use the expression for the chemical potential of an ideal gas.

\[ \mu_{\text{int}} = k_B T \ln \left( \frac{n}{n_Q} \right) \quad (12.249) \]

or alternatively

\[ n = n_Q e^{\beta \mu_{\text{int}}} \quad (12.250) \]

Now we can just plug in our \( \mu_{\text{int}}(r) \) to find \( n(r) \):

\[ n(r) = n_Q e^{\beta (\mu_{\text{tot}} + \frac{1}{2}m\omega^2 r^2)} \quad (12.251) \]

We were asked to find the ratio between \( n(r) \) and \( n(0) \) in order to avoid having to solve for \( \mu_{\text{tot}} \) or to specify something banal like the total number of molecules.

\[ \frac{n(r)}{n(0)} = \frac{n_Q e^{\beta (\mu_{\text{tot}} - \frac{1}{2}m\omega^2 r^2)}}{n_Q e^{\beta \mu_{\text{tot}}}} = e^{\frac{1}{2}m\omega^2 r^2} \quad (12.252) \]

As you would expect, the density is higher at larger radii, since the centrifugal force compresses atoms near the edge.

2. **Potential energy of gas in gravitational field** We can begin by writing down (from class notes) the expression for the (internal) chemical potential of an ideal gas.

\[ n = n_Q e^{\beta \mu_{\text{int}}} \quad (12.254) \]

In this case the external potential is linear

\[ \mu_{\text{ext}} = Mgh \quad (12.255) \]

The internal chemical potential is the total minus the external, telling us that

\[ n(h) = n_Q e^{\beta (\mu_{\text{tot}} - Mgh)} = n(0) e^{-\beta Mgh} \quad (12.256) \]

We can find the average potential energy by finding the **total** potential energy and dividing by the number of atoms.
\[ \langle V \rangle = \frac{\int Mg h n(h) dh}{\int n(h) dh} \quad (12.258) \]
\[ = Mg \frac{\int_0^\infty h e^{-\beta Mgh} dh}{\int_0^\infty e^{-\beta Mgh} dh} \quad (12.259) \]
\[ = Mg \frac{\int_0^\infty \xi e^{-\xi d\xi}}{\int_0^\infty e^{-\xi d\xi}} \quad (12.260) \]
\[ = kT \frac{1}{0!} \quad (12.261) \]
\[ = kT \quad (12.262) \]

So that is interesting, our potential energy per atom is just \( kT \), as if we had two degrees of freedom according to equipartition (which we don’t). In this case, the equipartition theorem doesn’t apply, because the potential is not quadratic.

My favorite integral I’ll just mention that I used here (twice!) my very favorite definite integral:

\[ \int_0^\infty u^n e^{-u} du = n! \quad (12.263) \]

You can prove this using integration by parts a few times, if need be. But it’s really handy to remember this. It comes up very often when working on the hydrogen atom, for instance. And yes, I learned this from an integral table.

3. Active transport The question here is to find \( \Delta \mu_{\text{int}} \) across the cell membrane. This must be equal and opposite to \( \Delta \mu_{\text{ext}} \), where the external chemical potential will be the electrostatic potential across the cell wall. We are given that

\[ n_{\text{inside}} = 10^4 n_{\text{outside}} \quad (12.264) \]
\[ \frac{n_{\text{inside}}}{n_{\text{outside}}} = 10^4 \quad (12.265) \]
\[ = \frac{nQ e^{\beta \mu_{\text{int},\text{inside}}}}{nQ e^{\beta \mu_{\text{int},\text{outside}}}} \quad (12.266) \]
\[ = e^{\beta \Delta \mu_{\text{int}}} \quad (12.267) \]
\[ \Delta \mu_{\text{int}} = kT \ln (10^4) \quad (12.268) \]

At this point it is convenient to know that at room temperature \( kT \approx \frac{1}{40} \text{eV} \). Of course, you could do this in any unit system you are comfortable with.

\[ \Delta \mu_{\text{int}} = \frac{1}{40} \ln (10^4) \text{ eV} \approx 0.23 \text{eV} \quad (12.269) \]

Getting the sign right is a different story. What we found was \( \mu_{\text{int},\text{inside}} - \mu_{\text{int},\text{outside}} \). The voltage we are considering would be the external chemical potential, which would swap the sign, suggesting the outside should be at a higher electrostatic potential than the inside. More accurately, the cells are actively pumping K\textsuperscript{+} into the cell.

Geeky anecdote When I was an undergrad, I went through a phase in which I attempted to become familiar with everyday temperatures in electron volts. “It’s a balmy 25.8 millielectron volts today, but in the library it’s a chilly 24.9 millielectron volts.”

4. Gibbs sum for a two level system Okay, we have three microstates, which I’ll call 0, 1, and 2

\[ N_0 = 0 \quad (12.270) \]
\[ N_1 = N_2 = 1 \quad (12.271) \]
\[ E_0 = E_1 = 0 \quad (12.272) \]
\[ E_2 = \epsilon \quad (12.273) \]

Now we remind ourselves that the activity \( \lambda \) is defined by
\[ \lambda \equiv e^{\beta \mu} \]  

(12.274)

\textbf{a) The Gibbs sum is just}

\[ Z = \sum_i e^{-\beta (E_i - \mu N_i)} \]  

(12.275)

\[ = \sum_i e^{\beta (\mu N_i - E_i)} \]  

(12.276)

\[ = \sum_i \lambda^{N_i} e^{-\beta E_i} \]  

(12.277)

\[ = 1 + \lambda + \lambda e^{-\beta \epsilon} \]  

(12.278)

\[ \langle N \rangle = \sum_i P_i N_i \]  

(12.279)

\[ = \sum_i N_i \frac{\lambda^{N_i} e^{-\beta E_i}}{Z} \]  

(12.280)

\[ = \frac{\lambda + \lambda e^{-\beta \epsilon}}{1 + \lambda + \lambda e^{-\beta \epsilon}} \]  

(12.281)

\textbf{c) This is just the probability of the state being at energy \( \epsilon \), which is}

\[ P_i = e^{-\beta (E_i - \mu N_i)} \]  

(12.282)

\[ P_\epsilon = \frac{e^{-\beta \epsilon}}{Z} \]  

(12.283)

\[ \langle E \rangle = \frac{\lambda e^{-\beta \epsilon}}{Z} \epsilon \]  

(12.284)

\textbf{d) The thermal average energy is even easier, since the energies are zero and \( \epsilon \), the average is just probability of energy \( \epsilon \) times \( \epsilon \).}

\[ \langle E \rangle = \frac{\lambda e^{-\beta \epsilon}}{Z} \epsilon \]  

(12.284)

\textbf{e) Now we’re adding one more microstate to the system, which is a microstate with \( E = \epsilon \) and \( N = 2 \). Our Gibbs sum will just have this one additional term in it.}

\[ Z = \sum_i \lambda^{N_i} e^{-\beta E_i} \]  

(12.285)

\[ = 1 + \lambda + \lambda e^{-\beta \epsilon} + \lambda^2 e^{-\beta \epsilon} \]  

(12.286)

\[ = (1 + \lambda)(1 + \lambda e^{-\beta \epsilon}) \]  

(12.287)

\textbf{5. Carbon monoxide poisoning} The main idea here is that because the oxygen and carbon monoxide are in equilibrium with air, we can determine the activities (or equivalent chemical potential) of the molecules from the air.

\textbf{a) We are looking for probabilities of occupancy, so as usual let’s start with a Gibbs sum. Right now we only have oxygen, so}

\[ Z = 1 + \lambda_{O_2} e^{-\beta \epsilon_A} \]  

(12.288)

\[ P_{O_2} = \frac{\lambda_{O_2} e^{-\beta \epsilon_A}}{1 + \lambda_{O_2} e^{-\beta \epsilon_A}} \]  

(12.289)

\[ = \frac{1}{1 + e^{\beta \epsilon_A}/\lambda_{O_2}} \]  

(12.290)

We are working to solve for \( \epsilon_A \) here...

\[ \frac{1}{P_{O_2}} = 1 + e^{\beta \epsilon_A}/\lambda_{O_2} \]  

(12.291)

\[ e^{\beta \epsilon_A} = \lambda_{O_2} \left( \frac{1}{P_{O_2}} - 1 \right) \]  

(12.292)

\[ \epsilon_A = kT \ln \left( \lambda_{O_2} \left( \frac{1}{P_{O_2}} - 1 \right) \right) \]  

(12.293)

\[ = 26.7 \text{meV} \ln \left( 10^{-5} \left( \frac{1}{0.9} - 1 \right) \right) \]  

(12.294)

\[ = 26.7 \text{meV} \times -13.7 \]  

(12.295)

\[ = -366 \text{meV} \]  

(12.296)
where I used $k_B = 8.617 \times 10^{-2} \text{meV K}^{-1}$ and body temperature is $T = 310.15 \text{K}$ to find $kT$ in meV. This binding energy is quite high, more than a third of an eV! Covalent bonds tend to be a few eV in strength, but they don’t reverse without significant effort, whereas it’s really important for oxygen to spontaneously unbind from hemoglobin.

b) When we add in carbon monoxide, our hemoglobin will have three possible states, so it will look a heck of a lot like our last homework problem.

$$Z = 1 + \lambda_{O_2} e^{-\beta \varepsilon_A} + \lambda_{CO} e^{-\beta \varepsilon_B} \quad (12.297)$$

We are now asking how strongly carbon monoxide has to bind in order to allow only 10% of the hemoglobin to be occupied by oxygen. So we are again going to be looking at the probability of oxygen occupying the hemoglobin

$$P_{O_2} = \frac{\lambda_{O_2} e^{-\beta \varepsilon_A}}{1 + \lambda_{O_2} e^{-\beta \varepsilon_A} + \lambda_{CO} e^{-\beta \varepsilon_B}} \quad (12.298)$$

We are looking to isolate $\varepsilon_B$ now, since we are told everything else.

$$1 + \lambda_{O_2} e^{-\beta \varepsilon_A} + \lambda_{CO} e^{-\beta \varepsilon_B} = \frac{\lambda_{O_2}}{P_{O_2}} e^{-\beta \varepsilon_A} \quad (12.299)$$

And moving everything to one side gives

$$\lambda_{CO} e^{-\beta \varepsilon_B} = \lambda_{O_2} \left( \frac{1}{P_{O_2}} - 1 \right) e^{-\beta \varepsilon_A} - 1 \quad (12.300)$$

$$e^{-\beta \varepsilon_B} = \frac{\lambda_{O_2}}{\lambda_{CO}} \left( \frac{1}{P_{O_2}} - 1 \right) e^{-\beta \varepsilon_A} - \frac{1}{\lambda_{CO}} \quad (12.301)$$

and at long last

$$\varepsilon_B = -kT \ln \left( \frac{\lambda_{O_2}}{\lambda_{CO}} \left( \frac{1}{P_{O_2}} - 1 \right) e^{-\beta \varepsilon_A} - \frac{1}{\lambda_{CO}} \right) \quad (12.302)$$

$$= -26.7 \text{meV} \ln \left( 10^2 \times 9 e^{13.7} - 10^7 \right) \quad (12.303)$$

$$= -26.7 \text{meV} \ln 7.9 \times 10^8 \quad (12.304)$$

$$= -26.7 \text{meV} \times 20.5 \quad (12.305)$$

$$= -547 \text{meV} \quad (12.306)$$

So the carbon monoxide doesn’t need to be much favored over oxygen energetically (in terms of ratio) in order to crowd out almost all the oxygen, even though there is way less carbon monoxide available. Of course, it is not ratios of energies that matter here, so much as energy differences, ant that is about $7kT$, which is hardly a small difference.

**Solution for week 6**

PDF version of solutions

1. **Derivative of Fermi-Dirac function** This just comes down to math on the Fermi function. I’m going to use Newton’s notation for the derivative (which I rarely use) because it makes it a bit easier to specify at which value we are evaluating the derivative:

$$f(\varepsilon) = \frac{1}{1 + e^{-\beta (\varepsilon - \mu)}} \quad (12.307)$$

$$f'(\varepsilon) = -\frac{1}{(1 + e^{-\beta (\varepsilon - \mu)})^2} e^{-\beta (\varepsilon - \mu)} (\beta) \quad (12.308)$$

$$= \frac{1}{kT (1 + e^{-\beta (\varepsilon - \mu)})^2} \quad (12.309)$$

Now I will plug in to find $f'(\mu)$:
2. Symmetry of filled and vacant orbitals

We are interested in \( f(\mu \pm \delta) \), so I’ll start by just handling both versions at the same time.

\[
f'(\mu) = \frac{1}{kT} \frac{e^{-\beta(\mu-\mu)}}{(1 + e^{-\beta(\mu-\mu)})^2}
\]
(12.310)

\[
f(\mu) = \frac{1}{kT} \frac{1}{(1 + 1)^2}
\]
(12.311)

\[
f(\mu) = \frac{1}{4kT}
\]
(12.312)

\[
f(\mu \pm \delta) = \frac{1}{1 + e^{-\beta(\mu \pm \delta) - \mu}}
\]
(12.313)

\[
= \frac{1}{1 + e^{-\beta(\pm \delta)}}
\]
(12.314)

\[
= \frac{1}{1 + e^{\mp \beta \delta}}
\]
(12.315)

So we can see that these two things look pretty similar, but they don’t look like they should add to one. To show that, I’ll add the two together and then use the old multiply-top-and-bottom trick.

\[
f(\mu - \delta) + f(\mu + \delta) = \frac{1}{1 + e^{\beta \delta}} + \frac{1}{1 + e^{-\beta \delta}}
\]
(12.316)

\[
= \frac{1}{1 + e^{\beta \delta}} + \frac{1}{1 + e^{-\beta \delta} e^{\beta \delta}}
\]
(12.317)

\[
= \frac{1}{1 + e^{\beta \delta}} + \frac{e^{\beta \delta}}{e^{\beta \delta} + 1}
\]
(12.318)

\[
= \frac{1 + e^{\beta \delta}}{1 + e^{\beta \delta}}
\]
(12.319)

\[
= 1
\]
(12.320)

3. Distribution function for double occupancy statistics

a) This is much like we did in class for the fermions. We will solve for the Gibbs sum, and then for \( \langle N \rangle \).

\[
Z = 1 + e^{-\beta(\varepsilon - \mu)} + e^{-\beta(2\varepsilon - 2\mu)}
\]
(12.321)

\[
= 1 + e^{-\beta(\varepsilon - \mu)} + e^{-2\beta(\varepsilon - \mu)}
\]
(12.322)

The occupancy is given by

\[
\langle N \rangle = \frac{0 \times 1 + 1 \times e^{-\beta(\varepsilon - \mu)} + 2 \times e^{-2\beta(\varepsilon - \mu)}}{1 + e^{-\beta(\varepsilon - \mu)} + 2e^{-2\beta(\varepsilon - \mu)}}
\]
(12.323)

\[
= \frac{e^{-\beta(\varepsilon - \mu)} + 2e^{-2\beta(\varepsilon - \mu)}}{1 + e^{-\beta(\varepsilon - \mu)} + e^{-2\beta(\varepsilon - \mu)}}
\]
(12.324)

\[
= \frac{1 + 2e^{-\beta(\varepsilon - \mu)}}{e^{\beta(\varepsilon - \mu)} + 1 + e^{-\beta(\varepsilon - \mu)}}
\]
(12.325)

b) If we have two fermion energy levels with the same energy \( \varepsilon \), the total occupancy of the two will just be the sum of their individual occupancies.

\[
\langle N \rangle = f(\varepsilon) + f(\varepsilon)
\]
(12.326)

\[
= \frac{2}{1 + e^{\beta(\varepsilon - \mu)}}
\]
(12.327)

It’s kind of hard to say how it differs from (a), they are so dissimilar. The low energy \((\beta(\varepsilon - \mu) \ll -1)\) behavior has a different exponential scaling. At high temperatures (or equivalently, \( \varepsilon = \mu \)) both systems have a total occupancy of 1. At high energies, once again the “double-occupancy statistics” occupation has the same exponential behavior, but half as many occupants. This is because at high energies the “double occupied” state becomes irrelevant relative to the “single occupied” state. In the Fermi-Dirac statistics, since they are different orbitals, each orbital contributes the same amount to the occupancy.
4. Entropy of mixing

a) We are considering two sets of atoms with same temperature and volume. Initially they are separate, and in the end, they will be equally mixed (according to intuition: mixed gasses don’t unmix, and everything is equal). So we can just use the Sackur-Tetrode entropy for the two scenarios. The key idea that is not obvious here is that we can compute the entropy of each gas separately and add them together even when they are mixed! We will call the initial volume $V_0$, and the initial entropy $S_0$. I’ll define each gas to have a distinct $n_Q$, since they presumably have different masses. I’ll just use $N$ for the number of each gas type.

$$
\frac{S_0}{Nk} = \ln \left( \frac{n_Q A V_0}{N} \right) + \frac{5}{2} + \ln \left( \frac{n_Q B V_0}{N} \right) + \frac{5}{2}
$$

(12.328)

$$
= \ln (n_Q A n_Q B) + 2 \ln \left( \frac{V_0}{N} \right) + 5
$$

(12.329)

We can rewrite this to look like a single ideal gas with the geometric mean of the two $n_Q$s, with twice the volume and number:

$$
\frac{S_0}{2Nk} = \ln \left( \sqrt{n_Q A n_Q B} \frac{V_0}{N} \right) + \frac{5}{2}
$$

(12.330)

So the total initial entropy would be just twice the individual entropy if the two gasses had the same mass. We now seek the final, mixed entropy $S_f$. For this, each gas will have a volume of $2V_0$.

$$
\frac{S_0}{Nk} = \ln \left( n_Q A \frac{2V_0}{N} \right) + \frac{5}{2} + \ln \left( n_Q B \frac{2V_0}{N} \right) + \frac{5}{2}
$$

(12.331)

$$
= \ln \left( n_Q A n_Q B \frac{(2V_0)^2}{N} \right) + 5
$$

(12.332)

$$
= 2 \ln \left( \sqrt{n_Q A n_Q B} \frac{2V_0}{N} \right) + 5
$$

(12.333)

$$
= 2 \ln \left( \sqrt{n_Q A n_Q B} \frac{V_0}{N} \right) + 5 + 2 \ln 2
$$

(12.334)

$$
\frac{S_0}{2Nk} = \ln \left( \sqrt{n_Q A n_Q B} \frac{V_0}{N} \right) + \frac{5}{2} + \ln 2
$$

(12.335)

The challenging step here is to explain why we can just treat each gas individually when they are mixed. One reason is that the two gasses don’t interact, so we have separation of variables. Moreover, since they are different kinds of particles, they don’t occupy the same orbitals (or you could say the overall wavefunction is just a product of the two individual wave functions $A$ and $B$).

Another argument we could make would be a thought experiment. Suppose we had two boxes, one of which was entirely permeable to atoms $A$, but held $B$ in, and the other of which was entirely permeable to $B$ but held in $A$. With these boxes, without doing any work, we could separate the mixed gasses into unmixed gasses, each with the same volume of $2V_0$. Thus the mixed gasses must have the same free energy as two unmixed gasses with twice the volume. By this reasoning, what we are seeing is not the entropy of mixing, but rather the entropy of expansion. (But it is called entropy of mixing, so that is what we call it.)

b) Now we consider a different final entropy, when the particles are identical. From our thermodynamic perspective, this should have the same entropy as the two unmixed (but identical) gasses,
just by the extensivity reasoning we always use. But it’s worth seeing that happen mathematically. Note that we now have one gas with volume $2V_0$ and number $2N$.

\[
S_{AA} = \frac{1}{2Nk} \ln \left( nQ \frac{2V_0}{2N} \right) + \frac{5}{2} \quad (12.336)
\]

\[
= 2 \ln \left( nQ \frac{V_0}{N} \right) + 5 \quad (12.337)
\]

This is the same as $S_0$, provided the two $nQ$s are the same.

The “Gibbs paradox” here is just that if you view this scenario classically (with no wavefunctions), it is not obvious why the behavior of distinguishable and indistinguishable objects should differ. If I have a bunch of billiard balls, writing numbers on them shouldn’t affect the pressure they exert on the walls of a container, for instance. The resolution to the classical paradox is to note that as long as the numbers you draw on the balls do not impact their behavior in an experiment, you will predict the same outcome for your experiment whether or not you view the particles as indistinguishable. True, they have a different entropy, but without quantum mechanics (which makes explicit the difference between indistinguishable and distinguishable particles in terms of the wave function) there is no absolute definition of entropy, since there is no unique way to count microstates.

5. Ideal gas in two dimensions
   a) This requires us to use the eigenstates of the 2D box. We can go ahead and use non-periodic boundary conditions, which gives single-particle energy eigenvalues of

\[
\varepsilon_{n_xn_y} = \frac{\hbar^2}{2mL^2} (n_x^2 + n_y^2) \quad (12.338)
\]

where $n_x$ goes from 1 to $\infty$, since we have to fit a half-integer number of wavelengths in the box with side length $L$. We can assume this is a low-density system in the classical limit, since it is described as an ideal gas. Thus we can say that the occupancy of each orbital will be

\[
f(\varepsilon) = e^{-\beta(\varepsilon - \mu)} \quad (12.339)
\]

Thus we can add up to find $N$:

\[
N = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} e^{-\beta(\varepsilon_{n_xn_y} - \mu)} \quad (12.340)
\]

\[
= \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} e^{-\beta \left( \frac{\hbar^2}{2mL^2} (n_x^2 + n_y^2) \right) - \mu} \quad (12.341)
\]

\[
Ne^{-\beta\mu} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} e^{-\frac{\hbar^2}{2mL^2} \left( n_x^2 + n_y^2 \right)} \quad (12.342)
\]

\[
\approx \int_{0}^{\infty} \int_{0}^{\infty} e^{-\frac{\hbar^2}{2mL^2} \left( n_x^2 + n_y^2 \right)} dn_x dn_y \quad (12.343)
\]

Now let’s do a change of variables into a dimensionless argument, and let’s also change the limits to go down to $-\infty$ and divide by a factor of 2 (per integral).

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\[ Ne^{-\beta \mu} = \frac{1}{4} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{\beta h^2 \pi^2}{2mL^2} (x^2 + y^2)} \, dx \, dy \]  

(12.344)

At this point we want to do a substitution that turns our integral into a dimensionless one. It’s a little weird defining \( x \) and \( y \) as dimensionless coordinates, but it’s compact and will naturally transition us into polar.

\[ x = \sqrt{\frac{\beta h^2 \pi^2}{2mL^2}} n_x \quad y = \sqrt{\frac{\beta h^2 \pi^2}{2mL^2}} n_y \]

(12.345)

This gives us in cartesian coordinates

\[ Ne^{-\beta \mu} = \frac{1}{4} \frac{2mL^2}{\beta \hbar^2 \pi^2} \int\int e^{-\left(x^2 + y^2\right)} \, dx \, dy \]

(12.346)

\[ = \frac{mL^2}{2\pi^2 \beta \hbar^2} \int\int e^{-\left(x^2 + y^2\right)} \, dx \, dy \]

(12.347)

Now we could go into polar coordinates, or we could use the fact that we each of these two integrals gives \( \sqrt{\pi} \). I’ll use the latter approach.

\[ Ne^{-\beta \mu} = \frac{mL^2}{2\pi \beta \hbar^2} \]

(12.348)

Now we can go about solving for the chemical potential:

\[ -\beta \mu = \ln \left( \frac{A^2}{N} \right) \frac{m}{2\pi \beta \hbar^2} \]

(12.349)

\[ \mu = -kT \ln \left( \frac{A^2}{N} \right) \frac{m}{2\pi \beta \hbar^2} \]

(12.350)

\[ = kT \ln \left( \frac{N}{A} \right) \frac{2\pi \beta \hbar^2}{m} \]

(12.351)

b) There are a few ways we could solve for the internal energy of the 2D ideal gas. The one most suggested by this chapter would be to add up the probability of each orbital being occupied times the energy of that orbital.

\[ U = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \varepsilon_{n_x n_y} e^{-\beta \left( \varepsilon_{n_x n_y} - \mu \right)} \]

(12.352)

At this point we could recognize that there is a derivative trick we can do, since this sum looks so very similar to the sum for \( N \) we had earlier. (Note, this problem is also very much solvable by just doing the integral, which isn’t much harder than the previous portion). We can see that

\[ \left( \frac{\partial N}{\partial \beta} \right)_\mu = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} (\mu - \varepsilon_{n_x n_y}) e^{-\beta \left( \varepsilon_{n_x n_y} - \mu \right)} \]

(12.353)

\[ = \mu N - U \]

(12.354)

And thus that

\[ U = \mu N - \left( \frac{\partial N}{\partial \beta} \right)_\mu \]

(12.355)

Now we can use our expression for \( N \) from before to compute \( U \).

\[ N = \frac{mA}{2\pi \beta \hbar^2} e^{\beta \mu} \]

(12.356)

\[ \left( \frac{\partial N}{\partial \beta} \right)_\mu = -\frac{mA}{2\pi \beta \hbar^2} e^{\beta \mu} + \frac{A}{\pi} \frac{\beta \hbar^2}{2\pi m} e^{\beta \mu} \]

(12.357)

\[ = -NkT + N\mu \]

(12.358)

Thus the internal energy is

\[ U = \mu N - N(\mu - kT) \]

(12.359)

\[ = NkT \]

(12.360)
This matches with the equipartition expectation, which would be \( \frac{1}{2}kT \) per degree of freedom, which in this case is two degrees of freedom per atom.

c) The entropy of this system we can just add up the entropy of each orbital. This uses a perspective where we recognize each orbital as a separate non-interacting system, with only two eigenstates either occupied or unoccupied. The probability of being occupied is \( e^{-\beta(\varepsilon - \mu)} \), so the probability of not being occupied is \( 1 - e^{-\beta(\varepsilon - \mu)} \).

\[
S_{\text{orbital}} = -k \sum_{P_i} P_i \ln P_i
\]

\[
= -ke^{-\beta(\varepsilon - \mu)} \ln \left( e^{-\beta(\varepsilon - \mu)} \right)
- k \left( 1 - e^{-\beta(\varepsilon - \mu)} \right) \ln \left( 1 - e^{-\beta(\varepsilon - \mu)} \right)
\]

\[
= \frac{1}{T}(\varepsilon - \mu)e^{-\beta(\varepsilon - \mu)}
- k \left( 1 - e^{-\beta(\varepsilon - \mu)} \right) \ln \left( 1 - e^{-\beta(\varepsilon - \mu)} \right)
\]

Here we can use that in the classical limit the occupancy of every orbital is small. Thus the exponential is small, and we can approximate the log.

\[
S_{\text{orbital}} \approx \frac{\varepsilon - \mu}{T} e^{-\beta(\varepsilon - \mu)}
- k \left( 1 - e^{-\beta(\varepsilon - \mu)} \right) \left( -e^{-\beta(\varepsilon - \mu)} \right)
\]

\[
\approx \frac{\varepsilon - \mu}{T} e^{-\beta(\varepsilon - \mu)} + ke^{-\beta(\varepsilon - \mu)}
\]

\[
= \left( k + \frac{\varepsilon - \mu}{T} \right) e^{-\beta(\varepsilon - \mu)}
\]

In the second approximation, I dropped the term that was proportional to the occupancy squared, since it was much smaller than the other terms. Now to find the total entropy, we can add up the entropy of all the orbitals.

\[
S = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \left( k + \frac{e_n}{\varepsilon_{n_x} n_y - \mu} \right) e^{-\beta(\varepsilon_{n_x} n_y - \mu)}
\]

\[
= Nk + \frac{U}{T} - N\frac{\mu}{T}
\]

\[
= 2Nk - N\frac{\mu}{T}
\]

\[
= 2Nk - Nk \ln \left( \frac{N}{A} \frac{2\pi\hbar^2}{m} \right)
\]

\[
= Nk \left( \ln \left( \frac{A m kT}{2\pi\hbar^2} \right) + 2 \right)
\]

This looks vaguely like the Sackur-Tetrode equation, but an number-per-area density rather than a volume density, and a \( \frac{5}{2} \) where there would otherwise be a \( \frac{5}{2} \).

**Note** You can also solve for the entropy by finding the free energy as we did in class, and then taking its derivative. That is almost certainly an easier approach.

6. Ideal gas calculations

a) The easy one is the second process: \( Q_2 = 0 \), since the process is adiabatic. The first process, we could either use the change in entropy, the change in free energy, or we could integrate the work. In the latter two cases, we would also invoke the First Law, to argue that the work done to the system must equal the change in internal energy plus the energy added to it by heating. Let’s just go with the \( \Delta S \) approach.
\[ \bar{d}Q = TdS \quad (12.372) \]
\[ Q = \int TdS \quad (12.373) \]
\[ = T \int dS \quad (12.374) \]
\[ = T \Delta S \quad (12.375) \]
\[ = NkT \left( \ln \left( \frac{nQ}{n_f} \right) + \frac{5}{2} - \ln \left( \frac{nQ}{n_i} \right) - \frac{5}{2} \right) \quad (12.376) \]
\[ = NkT \ln \left( \frac{n_i}{n_f} \right) \quad (12.377) \]
\[ = NkT \ln 2 \quad (12.378) \]

where in the last step I used the fact the the final density was \( \frac{1}{2} \) of the initial density.

b) Finding the temperature at the end of the second process requires finding the state with four times the original volume that has the same entropy as twice the original volume. The text finds a relationship between \( p \) and \( V \) for an adiabatic expansion involving \( pV^\gamma \), but knowing that result is less useful than deriving that result. We have at least two ways to derive this relationship. One would be to use the ideal gas law combined with the internal energy \( \frac{3}{2}NkT \) and to make use of energy conservation. Since we have recently derived the Sackur-Tetrode equation for the entropy of an ideal gas, we may as well use that.

\[ S = Nk \left( \ln \left( \frac{nQ}{n} \right) + \frac{5}{2} \right) \quad (12.379) \]

We just need to set the two entropies to be equal before and after expansion, keeping in mind that \( N \) doesn’t change either.

\[ Nk \left( \ln \left( \frac{nQ_i}{n} \right) + \frac{5}{2} \right) = Nk \left( \ln \left( \frac{nQ_f}{n} \right) + \frac{5}{2} \right) \]
\[ \frac{nQ_iV_i}{N} = \frac{nQ_fV_f}{N} \quad (12.380) \]
\[ nQ_iV_i = nQ_fV_f \quad (12.381) \]
\[ T_i^3 V_i = T_f^3 V_f \quad (12.382) \]
\[ T_f = 2^{-\frac{3}{2}} T_i \quad (12.383) \]
\[ \approx 189 \text{ K} \quad (12.384) \]

I’ll note that you could have skipped a few steps in solving this. But once again, you really need to always keep in mind that \( n_Q \) depends on temperature!

c) The increase of entropy of a system in an irreversible process is the same as for a reversible process with the same starting and ending conditions. In this case, an irreversible expansion into vacuum will do no work (since it moves nothing other than the gas itself), which means that it will not change the internal energy (unless energy is transfered by heating). Since for a monatomic ideal gas \( U = \frac{3}{2}NkT \), keeping the internal energy fixed means the temperature also remains fixed, there won’t be any heating and the temperature will certainly stay fixed. Thus we can work out the change in entropy using the Sackur-Tetrode equation again.

\[ S_f - S_i = Nk \ln \left( \frac{nQ_f}{n} \right) - Nk \ln \left( \frac{nQ_i}{n} \right) \quad (12.385) \]
\[ = Nk \ln \left( \frac{n_i}{n_f} \right) \quad (12.386) \]
\[ = Nk \ln 2 \quad (12.387) \]
\[ = Nk \ln 2 \quad (12.388) \]

We could also have obtained this by integrating \( \Delta S = \int \frac{dQ}{T} \) for a reversible isothermal expansion, as I think you did in Energy and Entropy.
Solution for week 7

PDF version of solutions

1. **Energy of a relativistic Fermi gas** There are a couple of ways you could go through this problem. One would be to just integrate to find the Fermi energy, and then to integrate to find the internal energy. It's not bad done that way. The other way, which I'll demonstrate, is to first solve for the density of states, and then use that to find the Fermi energy and $U$.

$$D(\varepsilon) = 2 \left( \frac{L}{2\pi} \right)^3 \iiint_{-\infty}^{\infty} \delta(\varepsilon(k) - \varepsilon) d^3k$$

$$= 2 \left( \frac{L}{2\pi} \right)^3 \int_{0}^{\infty} \delta(hck - \varepsilon) 4\pi k^2 dk$$

Note that the factors of two above are for the spin degeneracy. Now changing variables to an energy:

$$\varepsilon = hck \quad d\varepsilon = hcdk$$

And we get

$$D(\varepsilon) = 8\pi \left( \frac{L}{2\pi} \right)^3 \left( \frac{1}{hc} \right)^3 \int_{0}^{\infty} \delta(\varepsilon - \varepsilon) \varepsilon^2 d\varepsilon$$

$$= 8\pi \left( \frac{L}{2\pi hc} \right)^3 \varepsilon^2$$

$$= \frac{V}{\pi^2 h^3 c^3} \varepsilon^2$$

a) Solving for the Fermi energy comes down to solving for $N$.

$$N = \int_{0}^{\varepsilon_F} D(\varepsilon) d\varepsilon$$

$$= \frac{V}{\pi^2 h^3 c^3} \int_{0}^{\varepsilon_F} \varepsilon^2 d\varepsilon$$

$$= \frac{V}{\pi^2 h^3 c^3} \frac{1}{3} \varepsilon_F^3$$

$$\varepsilon_F = \left( \frac{N}{V} \frac{3\pi^2 h^3 c^3}{3} \right)^{\frac{1}{3}}$$

$$= (3\pi^2 n)^{\frac{1}{3}} hc$$

just as the problem says. The dimensions are energy because $n^{\frac{1}{3}}$ is inverse length, which when multiplied by $c$ gives inverse time. $h$ is energy times time, so we get an energy as we expect.

b) The internal energy at zero temperature (which is the total energy of the ground state) just requires us to just integrate the density of states time energy.

$$U = \int_{0}^{\varepsilon_F} D(\varepsilon) \varepsilon d\varepsilon$$

$$= \frac{V}{\pi^2 h^3 c^3} \int_{0}^{\varepsilon_F} \varepsilon^3 d\varepsilon$$

$$= \frac{V}{\pi^2 h^3 c^3} \frac{1}{4} \varepsilon_F^4$$

$$= \left( \frac{V}{\pi^2 h^3 c^3} \frac{1}{3} \varepsilon_F \right)^{\frac{3}{4}} N \varepsilon_F$$

$$= \frac{3}{4} N \varepsilon_F$$

The trickiest step was looking back at our previous expression for $N$ to substitute.

2. **Pressure and entropy of a degenerate Fermi gas**

a) As we saw before (when working with the radiation pressure of a vacuum) the pressure is given by the thermal average value of the derivative of the energy eigenvalues.
\[
p = -\left( \frac{\partial U}{\partial V} \right)_{S,N} \quad \text{(12.405)}
\]
\[= \sum \text{all microstates} \quad P_i \left( -\frac{\partial E_i}{\partial V} \right) \quad \text{(12.406)}
\]

The usual challenge here is that fixed temperature is not the same thing as fixed entropy. In this case, when \( T = 0 \), we know that the probabilities are all predetermined (via the Fermi-Dirac distribution), and we can just take a simple derivative of the energy we derived in class.

\[
U = \frac{3}{5} N \varepsilon_F \quad \text{(12.407)}
\]
\[= \frac{3}{5} N \frac{\hbar^2}{2m} \left( 3\pi^2 \frac{N}{V} \right)^{2/3} \quad \text{(12.408)}
\]
\[
p = -\left( \frac{\partial U}{\partial V} \right)_{S,N} \quad \text{(12.409)}
\]
\[= \frac{3}{5} N \frac{\hbar^2}{2m} \left( 3\pi^2 \frac{N}{V} \right)^{2/3} \frac{2}{3} \frac{1}{V} \quad \text{(12.410)}
\]
\[= \frac{2}{5} N \frac{\varepsilon_F}{V} \quad \text{(12.411)}
\]
\[= \frac{1}{5} \frac{\hbar^2}{m} 3^{2/3} \pi^{1/3} \left( \frac{N}{V} \right)^{2/3} \quad \text{(12.412)}
\]

This agrees with the expression given in the problem itself, so yay.

b) The entropy is a Fermi gas, when \( kT \ll \varepsilon_F \). We can start with the general form of entropy:

\[
S = -k \sum \text{states} \quad P_i \ln P_i \quad \text{(12.413)}
\]

We will begin by first finding the entropy of a single orbital, and then adding up the entropy of all the orbitals. One orbital has only two microstates, occupied and unoccupied, which correspondingly have probabilities \( f(\varepsilon) \) and \( 1 - f(\varepsilon) \). Before we go any farther, it is worth simplifying the latter.

\[
1 - f = 1 - \frac{1}{\text{e}^{\beta(\varepsilon - \mu)} + 1} \quad \text{(12.414)}
\]
\[= \frac{\text{e}^{\beta(\varepsilon - \mu)} + 1}{e^{\beta(\varepsilon - \mu)} + 1} - \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \quad \text{(12.415)}
\]
\[= \frac{\text{e}^{\beta(\varepsilon - \mu)}}{e^{\beta(\varepsilon - \mu)} + 1} \quad \text{(12.416)}
\]
\[= \frac{1}{e^{-\beta(\varepsilon - \mu)} + 1} \quad \text{(12.417)}
\]

The entropy corresponding to a single orbital, thus is

\[
S_{\text{orbital}} = -k(f \ln f + (1 - f) \ln(1 - f)) \quad \text{(12.418)}
\]
\[= -k \left( \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \ln \left( \frac{1}{e^{\beta(\varepsilon - \mu)} + 1} \right) \right) \quad \text{(12.419)}
\]
\[= \frac{k}{e^{\beta(\varepsilon - \mu)} + 1} \ln \left( e^{\beta(\varepsilon - \mu)} + 1 \right) \quad \text{(12.420)}
\]

This is inherently symmetric as we change the sign of \( \varepsilon - \mu \), which makes sense given what we know about the Fermi-Dirac distribution. It is less obvious in this form that the entropy does the right thing when \( |\varepsilon - \mu| \gg kT \). We expect the entropy to go to zero in this case, and one term very obviously goes to zero, but the other requires a bit more thinking, which I’m not going to go into here.

Using this expression for the entropy of a single orbital, we can solve for the entropy of the whole gas.
\[ S = \int_0^\infty D(\varepsilon) S_{\text{orbital}}(\varepsilon) d\varepsilon \quad (12.421) \]
\[ \approx D(\varepsilon_F) \int_{-\infty}^\infty S_{\text{orbital}}(\varepsilon) d\varepsilon \quad (12.422) \]
\[ = D(\varepsilon_F) \int_{-\infty}^\infty \left( \frac{k}{e^{\beta(\varepsilon-\mu)} + 1} \ln \left( e^{\beta(\varepsilon-\mu)} + 1 \right) + \frac{k}{e^{-\beta(\varepsilon-\mu)} + 1} \ln \left( e^{-\beta(\varepsilon-\mu)} + 1 \right) \right) d\varepsilon \quad (12.423) \]

This looks nasty, but we can make it dimensionless, and it’ll just be a number!

\[ \xi = \beta(\varepsilon - \mu) \quad d\xi = \beta d\varepsilon \quad (12.424) \]

which gives us

\[ S = D(\varepsilon_F) k^2 T \int_{-\infty}^\infty \left( \ln \left( e^{\xi} + 1 \right) + \ln \left( e^{-\xi} + 1 \right) \right) d\xi \quad (12.425) \]

Now the last bit is just a number, which happens to be finite.

3. White dwarf

a) Showing that something is a given order of magnitude can be both tricky and confusing. The potential energy is exactly given by

\[ U = -\frac{1}{2} \int d^3r \int d^3r' \frac{G\rho(\vec{r})\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} \quad (12.426) \]
as you learned in static fields, where \( \rho(\vec{r}) \) is the mass density. Unfortunately, we don’t know what the mass density is as a function of position, or how that function depends on the mass of the white dwarf.

An adequate if not satisfying set of reasoning is to say that the integral above must scale as \( M^2 \), since increasing \( M \) will either increase \( \rho \) or increase the volume over which the mass is spread. The denominator \( |\vec{r} - \vec{r}'| \) is going to on average scale as the radius \( R \). Thus it makes sense that the potential energy would be about \( \sim -\frac{GM^2}{R} \). Another approach here would have been to use dimensional analysis to argue that the energy must be this. Alternatively, you could have assumed a uniform mass density, and then argued that the actual energy must be of a similar order of magnitude.

b) The kinetic energy of the electrons is the \( U \) of the Fermi gas, which in class we showed to be

\[ KE \sim N \varepsilon_F \]
\[ \sim N \frac{\hbar^2}{2m} \left( \frac{N}{V} \right)^{\frac{2}{3}} \]
\[ \sim \frac{\hbar^2 N \frac{2}{3}}{mR^2} \quad (12.429) \]

where \( m \) is the mass of the electron. Then we can reason that the number of electrons is equal to the number of protons, and if the star is made of hydrogen the total mass of the star is equal to the total mass of its protons.

\[ N \approx \frac{M}{M_H} \quad (12.430) \]
\[ KE \sim \frac{\hbar^2}{m} \frac{M_H \frac{2}{3}}{R^2} \quad (12.431) \]

c) At this stage is is worth motivating the virial theorem from mechanics, which basically says that the magnitude of the average potential energy of a bound system (which is bound by a power law force) is about the same as the average of its kinetic energy. This makes sense in that the thing that is
holding a bound state together is the potential energy, while the thing that is pulling it apart is the kinetic energy. If they aren’t in balance, then something weird must be going on. BTW, this virial theorem also applies quite well to the quantum mechanical hydrogen atom.

All right, so

\[
\frac{GM^2}{R} \sim \frac{\hbar^2 M^\frac{5}{3}}{m M^\frac{5}{3} R^2} \quad (12.432)
\]

\[
M^\frac{5}{3} R \sim \frac{\hbar^2}{m M^\frac{5}{3} G} \quad (12.433)
\]

At this point we just need to plug in numbers.

d) Again we need to plug in numbers.

\[
M^\frac{5}{3} R \sim \frac{\hbar^2}{m M^\frac{5}{3} G} \quad (12.434)
\]

\[
R^3 \sim \left( \frac{\hbar^2}{m M^\frac{5}{3} G} \right)^3 \frac{1}{M} \quad (12.435)
\]

\[
\rho = \frac{M}{4\pi R^3} \quad (12.436)
\]

\[
\sim M^2 \left( \frac{\hbar^2}{m M^\frac{5}{3} G} \right)^3 \quad (12.437)
\]

At this point we just need to plug in numbers.

d) Again we need to plug in numbers.

\[
\frac{GM^2}{R} \sim \frac{\hbar^2 M^\frac{5}{3}}{m M^\frac{5}{3} R^2} \quad (12.438)
\]

\[
M^\frac{5}{3} R \sim \frac{\hbar^2}{M^\frac{5}{3} G} \quad (12.439)
\]

\[
R \sim \frac{\hbar^2}{M^\frac{5}{3} M^\frac{5}{3} G} \quad (12.440)
\]

Plug in numbers to find the neutron star radius in kilometers when its mass is one solar mass.

\[
R \sim \frac{\left( 10^{-27} \text{ g cm}^2 \right)^2}{(10^{44} \text{g})^{\frac{1}{3}} (10^{-24} \text{g})^{\frac{2}{3}} \left( 10^{-3} \text{ cm}^3 \text{ g s}^{-2} \right)} \quad (12.441)
\]

\[
\sim 10^6 \text{cm} \sim 10 \text{km} \quad (12.442)
\]

That’s what I call a small-town star!

4. **Fluctuations in the Fermi gas** We are looking here at a single orbital, and asking what is the variance of the occupancy number.

\[
\langle (\Delta N)^2 \rangle = \langle (N - \langle N \rangle)^2 \rangle = \sum_i P_i (N_i - \langle N \rangle)^2 \quad (12.443)
\]

Now this single orbital has only two possible states: occupied and unoccupied! So we can write this down pretty quickly, using the probability of those two states, which are \( f \) and \( 1 - f \). We also note that \( \langle N \rangle = f \), so we’re going to have \( f \) all over the place.

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\[
\langle (\Delta N)^2 \rangle = P_1 (1 - f)^2 + P_0 (0 - f)^2 
= f (1 + f^2 - 2f) + (1 - f)^2 
= f - f^2 
= \langle N \rangle (1 - \langle N \rangle)
\]

(12.445)

(12.446)

(12.447)

This tells us that there is no variation in occupancy when the occupancy reaches 0 or 1. In retrospect that is obvious. If there is definitely an electron there, then we aren’t uncertain about whether there is an electron there.

5. **Einstein condensation temperature** I’m going to be sloppier on this solution, because this is done in the textbook, and I’m still quite sick. The idea is to set the chemical potential to 0, which is its maximum value and integrate to find the number of atoms not in the ground state, \( N_E \), which is normally essentially equal to the number of atoms total.

\[
N_E = \int_0^\infty D(\varepsilon) f(\varepsilon) d\varepsilon 
= \frac{V}{4\pi^2} \left( \frac{2M}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \varepsilon^{\frac{3}{2}} e^{\frac{\varepsilon}{kT}} d\varepsilon 
\]

(12.449)

(12.450)

Naturally at this stage we will want to use a change of variables to take the physics out of the integral as we typically do.

\[
N_E = \frac{V}{4\pi^2} \left( \frac{2M}{\hbar^2} \right)^{\frac{3}{2}} (kT)^{\frac{3}{2}} \int_0^\infty \varepsilon^{\frac{3}{2}} e^{\frac{\varepsilon}{kT}} d\varepsilon 
\]

(12.451)

Now we can simply solve for \( T_E \).

\[
T_E = \frac{1}{k_B} \frac{\hbar^2}{2M} \left( \frac{N}{V} \int_0^\infty \sqrt{\xi} e^{\frac{\sqrt{\xi}}{kT}} d\xi \right)^{\frac{2}{3}}
\]

(12.452)

**Solution for week 8**

**PDF version of solutions**

1. **Heat pump**

a) To approach this, I’ll essentially do a quick re-derivation of the Carnot efficiency, based around the idea that the process is reversible. Since it is a cycle, the state of the system doesn’t change, only that of the environment. The hot side in this case gets hotter, while the cool side gets cooler, and the entropy change of each must be equal and opposite.

\[
\Delta S_H = \frac{Q_H}{T_H} \quad (12.453)
\]

\[
\Delta S_C = -\frac{Q_C}{T_C} \quad (12.454)
\]

\[
\Delta S_H + \Delta S_C = 0 \quad (12.455)
\]

\[
\frac{Q_H}{T_H} = \frac{Q_C}{T_C} \quad (12.456)
\]

\[
\frac{T_C}{T_H} = \frac{Q_C}{Q_H} \quad (12.457)
\]

Note that I’m defining all heats and works to be positive, and taking their direction into account (which explains the minus sign in \( \Delta S_C \). Now to find the amount of work we had to do, we just need to use energy conservation (i.e. the First Law). The energy *inputs* to the heat pump are our work \( W \) and the heat from the cool side \( Q_C \). The energy output is just \( Q_H \).

\[
W + Q_C = Q_H \quad (12.458)
\]

\[
\frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H} \quad (12.459)
\]

\[
\frac{W}{Q_H} = 1 - \frac{T_C}{T_H} \quad (12.460)
\]

which is just the Carnot efficiency, as predicted. Note however, that in this case this
efficiency is not “what we get out divided by what we put in,” but rather the inverse of that. So in this case, when $T_C \ll T_H$, we have a very inefficient heat pump, since we hardly get any “free” energy.

If the heat pump is not reversible, as always, things look worse, we will need more work to get the same amount of heating. Note here that there are two possible interpretations of the word “reversible”. What is meant in the question is that the entropy of the pump and its surroundings doesn’t change. From a practical perspective a heat pump may be described as “reversible” when it can also function as an air conditioner in the summer (as most do).

b) Now we have an engine driving a heat pump. The work output from the engine must equal the work input of the pump. We can recall from class (or reproduce with reasoning like that above) that

$$\frac{W}{Q_{HH}} = 1 - \frac{T_C}{T_{HH}}$$

Now we just need to eliminate the work to find how much heat input at the very high temperature $Q_{HH}$ we need in order to get a given amount of heat in our home $Q_H$.

$$\frac{W}{Q_{HH}} = 1 - \frac{T_C}{T_{HH}}$$

For the three temperatures requested, this comes out to

$$Q_H = \frac{600 300 - 270}{300 600 - 270} = \frac{2}{330} = \frac{2}{11} \approx .18$$

So you save about a factor of five in fuel by not just burning it in your home to heat it, but instead using it to power a heat pump. Yay. And this is with it freezing outside, and uncomfortably warm inside!

c) Here is a pretty picture illustrating where the energy and entropy come and go. The heats all came from the above computations, while the entropies came from dividing each heat by its temperature. For the energy plot I made a distinction between the heat added or removed by the heat pump (left) and the engine (right). For the entropy plot I just lumped those together.

Figure 12.5: Sankey diagram of energy and entropy in the engine-heat-pump combination
a) The engine starts at $T_H$ and $V_1$ and first expands isothermally to $T_H$ and $V_2$. Then it expands adiabatically to $T_C$ and $V_3$. Next is is compressed at fixed temperature to $V_4$, from which it expands adiabatically to $V_1$. So we can identify $V_3$ and $V_4$ as the two volumes that have the same entropy at $T_C$ as $V_2$ and $V_1$ have at $T_H$.

\[ S_3 = S_2 \quad (12.468) \]

\[ 32\pi k V_3 \left( \frac{kT_C}{hc} \right)^3 \frac{\pi^4}{45} = 32\pi k V_2 \left( \frac{kT_H}{hc} \right)^3 \frac{\pi^4}{45} \quad (12.469) \]

\[ V_3 T_C^3 = V_2 T_H^3 \quad (12.470) \]

\[ V_3 = V_2 \left( \frac{T_H}{T_C} \right)^3 \quad (12.471) \]

\[ V_4 = V_1 \left( \frac{T_H}{T_C} \right)^3 \quad (12.472) \]

b) Now we could integrate to find the work, but the easy approach is to find the heat from $T_H \Delta S$, and then use the First Law to find the work.

\[ Q_H = \int T dS \quad (12.473) \]

\[ = T_H \Delta S \quad (12.474) \]

\[ = kT_H 32\pi (V_2 - V_1) \left( \frac{kT_H}{hc} \right)^3 \frac{\pi^4}{45} \quad (12.475) \]

\[ = 32\pi (V_2 - V_1) \left( \frac{kT_H}{hc} \right)^4 \frac{\pi^4}{45} \quad (12.476) \]

Now using the First Law...

$$\Delta U = Q_H + W_H$$

$$24\pi \left( \frac{kT_H}{hc} \right)^4 \frac{\pi^4}{45} (V_2 - V_1) = 32\pi (V_2 - V_1) \left( \frac{kT_H}{hc} \right)^4 \frac{\pi^4}{45} + W_H$$

$$W_H = -8\pi \left( \frac{kT_H}{hc} \right)^4 \frac{\pi^4}{45} (V_2 - V_1)$$

This tells us that the photon gas does work as it expands, like the ideal gas does, but unlike the ideal gas, the work done is considerably less than the heat absorbed by the gas, since its internal energy increases significantly.

c) To find the work on each adiabatic stage just requires finding $\Delta U$, since $Q = 0$ for any isentropic (or adiabatic) process. The first adiabatic stage goes from $V_2$ to $V_3$ while the temperature changes from $T_H$ to $T_C$. The internal energy change is thus

$$\Delta U_{32} = W_2$$

$$= 24\pi \left( \frac{kT_H}{hc} \right)^4 \frac{\pi^4}{45} (V_3 T_C^4 - V_2 T_H^4)$$

$$= 24\pi \left( \frac{kT_H}{hc} \right)^4 \frac{\pi^4}{45} \left( V_2 \left( \frac{T_H}{T_C} \right)^3 T_C^4 - V_2 T_H^4 \right)$$

$$= 24\pi \left( \frac{kT_H}{hc} \right)^4 \frac{\pi^4}{45} V_2 T_H^4 (T_C - T_H)$$

So the system is losing energy (thus doing work) as we adiabatically expand it down to lower temperature. At the other end, going from $V_4$ and $T_C$ to $V_1$ and $T_H$, we have
\[ \Delta U_{14} = W_4 \]  
\[ = 24\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} (V_1 T_H^4 - V_4 T_C^4) \]  
\[ = 24\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} (V_1 T_H^4 - V_2 \frac{T_H^3 T_C}{T_C}) \]  
\[ = 24\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} V_1 T_H^3 (T_H - T_C) \]  
\[ = 12.484 \]

\[ W_C = 8\pi \frac{(kT_C)^4}{h^3c^3} \frac{\pi^4}{45} (V_4 - V_3) \]  
\[ = 8\pi \frac{(kT_C)^4}{h^3c^3} \frac{\pi^4}{45} (V_1 - V_2) \frac{T_H^3}{T_C} \]  
\[ = 8\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} (V_1 - V_2) T_H^3 T_C \]  
\[ = 12.489 \]

Note also that the sign of the work was opposite because we were compressing rather than expanding. Plugging this in we can see that:

\[ W = W_H + W_2 + W_C + W_4 \]  
\[ = -8\pi \frac{(kT_H)^4}{h^3c^3} \frac{\pi^4}{45} (V_2 - V_1) + 24\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} V_2 T_H^3 (T_C - T_H) + 8\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} (V_1 - V_2) T_H^3 T_C + 24\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} V_1 T_H^3 (T_H - T_C) \]  
\[ = 12.492 \]

\[ = -8\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} (V_2 - V_1) T_H^4 + 24\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} V_2 T_H^3 (T_C - T_H) + 8\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} (V_1 - V_2) T_H^3 T_C + 24\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} V_1 T_H^3 (T_H - T_C) \]  
\[ = 12.493 \]

\[ = -8\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} T_H^3 (V_2 - V_1) (T_H - T_C) + 24\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} T_H^3 (V_1 - V_2) (T_H - T_C) \]  
\[ = 12.494 \]

\[ = -32\pi \frac{k^4}{h^3c^3} \frac{\pi^4}{45} T_H^3 (V_2 - V_1) (T_H - T_C) \]  
\[ = 12.495 \]
I’ll take the ratio that I want now. Almost everything will cancel.

\[
\frac{W}{Q_H} = \frac{-32\pi \frac{k^4 \pi^4}{45} T_H^4 (V_2 - V_1)(T_H - T_C)}{32\pi (V_2 - V_1) \left(\frac{kT_H \pi^4}{h^3 c^3 \pi^4} \right)^4}
\]  

(12.496)

\[
= -\frac{T_H - T_C}{T_H}
\]  

(12.497)

\[
= - \left(1 - \frac{T_C}{T_H}\right)
\]  

(12.498)

This is just the Carnot efficiency from class with a minus sign. This sign came from the convention that positive work means work added to a system, which I used in this solution (and is convenient when using the First Law), but differs from the standard convention when discussing engines, where all signs are taken to be positive.

3. **Light bulb in a refrigerator**

We have a 100W light bulb in a refrigerator that draws 100W power. This means the work done by the refrigerator per second is 100W. How we need to ask how efficient the refrigerator can be, to see how much it can cool its inside. The refrigerator operates between two temperatures the inside (which I’ll call \(T_C\)) and the room (which I’ll call \(T_H\)). Energy conservation tells us that

\[
Q_C + W = Q_H
\]  

(12.499)

where I’ve taken the usual convention (for this kind of problem) where all signs are positive, so \(Q_C\) is the magnitude of heat drawn from the inside, \(W\) is the work done, and \(Q_H\) is the amount of heat dumped in the room. If this is a reversible cycle, then the change in entropy of the room must be equal and opposite to the change in entropy of the inside of the fridge. That means that

\[
\frac{Q_C}{T_C} = \frac{Q_H}{T_H}
\]  

(12.500)

\[
Q_H = Q_C \frac{T_H}{T_C}
\]  

(12.501)

If we have an irreversible fridge, entropy of the room plus fridge can only go up, which would mean less cooling in the fridge (since the entropy of the inside is going down). Putting these equations together, we can see that

\[
Q_C + W = Q_C \frac{T_H}{T_C}
\]  

(12.502)

\[
W = Q_C \left(\frac{T_H}{T_C} - 1\right)
\]  

(12.503)

\[
Q_C = \frac{W}{\frac{T_H}{T_C} - 1}
\]  

(12.504)

\[
\frac{Q_C}{W} = \frac{1}{\frac{T_H}{T_C} - 1}
\]  

(12.505)

This tells us the efficiency of our refrigerator. As long as this efficiency is greater than 1, our fridge can out-cool the light bulb. So when is this equal to one?

\[
\frac{1}{\frac{T_H}{T_C} - 1} = 1
\]  

(12.506)

\[
1 = \frac{T_H}{T_C} - 1
\]  

(12.507)

\[
T_H = 2T_C
\]  

(12.508)

So our fridge can indeed cool the insides below room temperature even with the light bulb (who *ever* put a 100W light bulb in a fridge?!), and could in fact (in principle) cool it down to like 150K which would be crazy cold. Of course, the poor insulation would prevent that, as well as the capabilities of the pumps and refrigerant.

Is this the answer you were expecting for this problem? I can tell you that it was *not* the answer I was expecting. Kind of crazy.
Solution for week 9

PDF version of solutions

1. Vapor pressure equation

   a) To solve for \( \frac{dp}{dT} \) we will begin with the Clausius-Clapeyron equation derived in class.

   \[
   \frac{dp}{dT} = \frac{L}{T(V_g - V_l)} \quad (12.509)
   \]

   \[
   = \frac{L}{TV_g} \quad (12.510)
   \]

   \[
   = \frac{L}{TNkT} \quad (12.511)
   \]

   \[
   = \frac{LP}{NkT^2} \quad (12.512)
   \]

   b) Now we will assume \( L \) is a constant, and solve for the vapor pressure \( p(T) \). The key will be to put \( p \) and \( T \) on separate sides of the equation so we can integrate.

   \[
   \int_{p_0}^{p} \frac{dp}{dT} = \int_{T_0}^{T} L \frac{1}{TNkT^2} dT \quad (12.513)
   \]

   \[
   \int_{p_0}^{p} \frac{dp}{p} = \frac{L}{Nk} \int_{T_0}^{T} \frac{1}{T^2} dT \quad (12.514)
   \]

   \[
   \ln \left( \frac{p}{p_0} \right) = - \frac{L}{Nk} \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (12.515)
   \]

   Now we can solve for \( p! \)

   \[
   p = \left( p_0 e^{\frac{L}{NkT_0}} \right) e^{-\frac{L}{NkT}} \quad (12.516)
   \]

   We could clump all the stuff in parentheses into a big constant without any loss, but I kind of like making it explicit that if we know that \((p_0, T_0)\) is on the coexistence curve then we have a closed solution here. Note again that this makes an assumption about \( L \) being independent of temperature that is not entirely accurate.

2. Entropy, energy, and enthalpy of van der Waals gas

We will begin with the free energy of the van der Waals gas:

\[
F = -NkT \left( \ln \left( \frac{nQ(V - Nb)}{N} \right) + 1 \right) - \frac{N^2a}{V} \quad (12.517)
\]

a) We can find the entropy as usual by taking a derivative of the free energy.

\[
S = -\left( \frac{\partial F}{\partial T} \right)_V \quad (12.520)
\]

\[
= Nk \left( \ln \left( \frac{nQ(V - Nb)}{N} \right) + 1 \right) + \frac{NkT \frac{dnQ}{dT} - nQ}{nQ} \quad (12.521)
\]

\[
= Nk \left( \ln \left( \frac{nQ(V - Nb)}{N} \right) + 1 \right) + \frac{NkT \frac{dnQ}{dT}}{nQ} + \frac{NkT}{nQ} \quad (12.522)
\]

\[
= Nk \left\{ \ln \left( \frac{nQ(V - Nb)}{N} \right) + \frac{5}{2} \right\} \quad (12.523)
\]

In the penultimate (second-to-last) step, I used the fact that \( nQ \propto T^2 \).

b) We can find the internal energy from \( F = U - TS \) now that we know the entropy.
\[ U = F + TS \]  
\[ U = -NkT \left( \ln \left( \frac{n_O(V - Nb)}{N} \right) + 1 \right) - \frac{N^2a}{V} \]  
\[ + Nk \left( \ln \left( \frac{n_O(V - Nb)}{N} \right) + \frac{5}{2} \right) T \]  
\[ = \frac{3}{2} NkT - \frac{N^2a}{V} \]  
(12.526)

which looks like the monatomic ideal gas internal energy plus a correction term, which depends on the density of the fluid.

c) To find the enthalpy we just need the pressure. We could find it using a derivative of the free energy, but that was done in class and in the text, so we needn’t duplicate it.

\[ H = U + pV \]  
(12.527)

\[ p = \frac{NkT}{V - Nb} - \frac{N^2a}{V^2} \]  
(12.528)

\[ H = \frac{3}{2} NkT - \frac{N^2a}{V} + \frac{NkT}{V - Nb} - \frac{N^2a}{V^2} \]  
(12.529)

\[ = \frac{3}{2} NkT - 2 \frac{N^2a}{V} + \frac{NkT}{1 - \frac{Nb}{V}} \]  
(12.530)

\[ \approx \frac{3}{2} NkT - 2 \frac{N^2a}{V} + NkT \left( 1 + \frac{Nb}{V} \right) \]  
(12.531)

\[ = \frac{5}{2} NkT - 2 \frac{N^2a}{V} + \frac{N^2bkT}{V} \]  
(12.532)

\[ H(T, p) = \frac{5}{2} NkT + Nb \frac{p}{kT} - \frac{2Na}{kT} \]  
(12.533)

In the approximate step, we were just doing a power series expansion since \( Nb \ll 1 \). Now we just want to express the enthalpy in terms of pressure, since it is usually used at fixed pressure. That requires us to replace volume with pressure. Solving for volume in terms of pressure is a slight nuisance.

\[ \left( p + \frac{N^2}{V^2}a \right) (V - Nb) = NkT \]  
(12.534)

\[ pV - pNb + \frac{N^2}{V}a \approx NkT \]  
(12.535)

\[ pV - pNb + N^2a = NkTV \]  
(12.536)

\[ pV^2 - (pNb + NkT)V + N^2a = 0 \]  
(12.537)

Now we can use the quadratic equation.

\[ V = \frac{pNb + NkT \pm \sqrt{(pNb + NkT)^2 - 4pN^2a}}{2p} \]  
(12.538)

\[ \approx \frac{pNb + NkT \pm \sqrt{(NkT)^2 + 2pN^2bkT - 4pN^2a}}{2p} \]  
(12.539)

\[ = \frac{pNb + NkT + NkT \left( 1 + \frac{1}{2} \frac{2pN^2bkT - 4pNa}{kT} \right)}{2p} \]  
(12.540)

\[ \approx \frac{pNb + 2NkT + \frac{2pN^2bkT - 4pNa}{kT}}{2p} \]  
(12.541)

\[ \approx \frac{2pNb + 2NkT - 2pNa}{2p} \]  
(12.542)

\[ = \frac{NkT}{p} + Nb - \frac{Na}{kT} \]  
(12.543)

\[ = \frac{NkT}{p} + Nb - \frac{Na}{kT} \]  
(12.544)

What a nuisance. Each approximation I made eliminated a term that had two or more factors of \( a \) or \( b \), which are taken to be small quantities (albeit with dimensions).
Note that the first term is just what we get from the ideal gas law. The rest is the first-order correction to the volume. Now that we have an expression for $V$ in terms of $p$ and $T$

\[ H = \frac{5}{2} N k T + \frac{N^2 b k T - 2 N^2 a}{V} \]  

(12.545)

\[ = \frac{5}{2} N k T + \frac{N^2 b k T - 2 N^2 a}{N k T} + N b - \frac{N a}{k T} \]  

(12.546)

\[ = \frac{5}{2} N k T + \frac{p}{N k T} \left( N^2 b k T - 2 N^2 a \right) \frac{1}{1 + (N b - \frac{N a}{k T}) \frac{p}{N k T}} \]  

(12.547)

\[ \approx \frac{5}{2} N k T + \frac{p}{N k T} \left( N^2 b k T - 2 N^2 a \right) \left( 1 - \left( N b - \frac{N a}{k T} \right) \frac{p}{N k T} \right) \]  

(12.548)

Okay, this is admittedly looking a little hairy. But remember that we only need to keep terms that are linear in $a$ and $b$, so that actually just kills our correction term entirely. And after all that work!

\[ H \approx \frac{5}{2} N k T + \frac{p}{N k T} \left( N^2 b k T - 2 N^2 a \right) \]  

(12.549)

\[ = \frac{5}{2} N k T + N \frac{p}{k T} (b k T - 2 a) \]  

(12.550)

\[ = \frac{5}{2} N k T + N p \left( b - \frac{2 a}{k T} \right) \]  

(12.551)

which matches with the expected answer. So yay. In retrospect, we could have simplified the solving for the volume bit drastically, if I had noticed that $V$ only occurred in $H$ in a ratio to a small quantity, and thus we didn’t need to keep up to the first order terms, we only needed up to the zero order term, which would have eliminated most of the work. You are welcome to argue this in your solution, but should try to argue it well. Otherwise, you’d just want to do all the same tedium I did.

3. **Calculation of $\frac{dT}{dp}$ for water** (K&K 9.2)

We begin with the Clausius-Clapeyron equation. However, to do this we have to ensure that we get everything in the right units, and such that the volume we divide by corresponds to the same quantity of water as the latent heat on top. Let’s say we have one gram of water (which is nice up top), we need the volume of a gram of steam.

\[ \Delta V \approx V_g \]  

(12.552)

\[ = \frac{N k T}{p} \]  

(12.553)

\[ \Delta V \approx 3.35 \times 10^{22} \left( \frac{p}{N k T} \right) \]  

(12.554)

I’ll start by finding the number of molecules in a gram of water:

\[ N = \frac{1 g}{18 g \text{ mol}^{-1}} N_A \]  

(12.555)

\[ = \frac{1 g}{18 g \text{ mol}^{-1}} 6.0221 \times 10^{23} \]  

(12.556)

\[ \approx 3.35 \times 10^{22} \]  

(12.557)

Since one atmosphere is $\sim 10^5$ pascals, we have

\[ \Delta V \approx 3.35 \times 10^{22} (1.38 \times 10^{-23} \text{ J K}^{-1})(373 \text{K}) \]  

(12.558)

\[ \approx 1.7 \times 10^{-3} \text{ m}^3 \]  

(12.559)

Just as a check, we may as well verify that $V_g \gg V_l$. I know that liquid water has a density of about $1 g \text{ cm}^{-3}$. Which makes the vapor density about two thousand times higher, so we’re okay ignoring the liquid density, yay. Putting this together, we can find the slope we are asked for.
\[
\frac{dp}{dT} = \frac{L}{T \Delta V} \quad (12.559)
\]
\[
= \frac{2260 \text{ J g}^{-1}}{(373 \text{ K})(1.7 \times 10^{-3} \text{ m}^3 \text{ g}^{-1})} \quad (12.560)
\]
\[
= 3530 \frac{\text{ Pa}}{\text{ K}} \quad (12.561)
\]

Now we were asked for this in units of atmosphere per Kelvin, which gives us a change of five orders of magnitude.

\[
\frac{dp}{dT} = 3.5 \times 10^{-2} \text{ atm K}^{-1} \quad (12.562)
\]

Actually, we were asked for the inverse of this, presumably so we’d have a number greater than one.

\[
\frac{dT}{dp} = 28 \text{ K atm}^{-1} \quad (12.563)
\]

That tells us that if the liquid-vapor coexistence curve were a straight line, it would drop to zero vapor pressure at 72°C, which is emphasizes how much curvature there is to the coexistence curve.

4. **Heat of vaporization of ice** (K&K 9.3)

Okay, once again we’ll want to find the volume of gas, which gives us part of the answer. In addition, we’ll need to find \( \frac{dT}{dp} \) from the given pressures at a couple of temperatures. That leaves us with nothing but the latent heat to solve for. I’ll start with the volume of a gram of water. It’s like the last problem, but at a lower temperature. I’ll not copy the work that is identical. One mm Hg is 133 Pa, so

\[
\Delta V \approx \frac{3.35 \times 10^{22}(1.38 \times 10^{-23} \text{ J K}^{-1})(272 \text{ K})}{4.2 \times 133 \text{ J m}^{-3}} \quad (12.564)
\]
\[
\approx .225 \text{ m}^3 \quad (12.565)
\]

So the volume of the gram of chilly steam is dramatically higher, due to the vapor pressure being way lower at these frigid temperatures. Note that I used a pressure halfway between the two pressures give, since we know the derivative most accurately at this half-way point.

Now for the derivative itself:

\[
\frac{dp}{dT} = \frac{611 - 518}{2.01 \text{ K}} \frac{\text{ Pa}}{\text{ K}} \quad (12.566)
\]
\[
\approx 46 \frac{\text{ Pa}}{\text{ K}} \quad (12.567)
\]

Putting things together, we get:

\[
\frac{dp}{dT} = \frac{L}{T \Delta V} \quad (12.568)
\]
\[
L = T \Delta V \frac{dp}{dT} \quad (12.569)
\]
\[
= (272 \text{ K})(.225 \text{ m}^3 \text{ g}^{-1})(46 \frac{\text{ Pa}}{\text{ K}}) \quad (12.570)
\]
\[
\approx 2815 \frac{\text{ J}}{\text{ g}} \quad (12.571)
\]

And now I remember we want our final answer in J mol\(^{-1}\). I guess it would have been smart to compute the volume of a mole, rather than a gram. Oh well, it’s not a hard conversion.

\[
L = 2815 \frac{\text{ J}}{\text{ g}} (18 \text{ g mol}^{-1}) \quad (12.572)
\]
\[
\approx 51 \text{ kJ mol}^{-1} \quad (12.573)
\]

This isn’t all that accurate. The answer per gram can be compared with the latent heat of vaporization given in the last problem, and you can see that it’s higher for the ice, but only about twice as high, which reflects the fact that the liquid still has most of the same hydrogen bonds that hold the solid ice together.