Notes on Statistical Thermodynamics
to Accompany McQuarrie and Simon

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February 9, 2004
Credits

This material was created by Paul J. Gans as an adjunct to the material in the text *Physical Chemistry: A Molecular Approach* by Donald A. McQuarrie and John D. Simon for the course V25.0652, Physical Chemistry II given in the Chemistry Department at New York University in the Spring of 2004.

The current version was typeset using the \LaTeX\ typesetting system on a Linux-based computer using \TeX\ (Web2C 7.4.5) 3.14159 and \LaTeX2e\ Version 2001/06/01. Conversion to PostScript was done by dvips(k) 5.92b Copyright 2002 Radical Eye Software (www.radicaleyce.com)

The HTML version of this document was produced using \LaTeX2HTML, version 2002-2-1 (1.70) by Nikos Drakos; revised and extended by Marcus Hennecke, Ross Moore, Herb Swan and others producing markup for HTML version 3.2.

Version History:

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<td>January 14, 2004</td>
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1 Introduction

Thermodynamics, which will be studied a bit later in this course, is the field that describes energy relationships in macroscopic systems. It deals with the heat of reactions, heat capacities, equilibrium constants, etc., in systems large enough to be handled in a laboratory. In particular it is concerned with the laws that govern these things and the deductions that can be made from them. It is a macroscopic subject.

Quantum mechanics on the other hand, deals with the laws that govern the microscopic behavior of matter and energy. It gives detailed rules for the calculation of all sorts of properties of elements and molecules.

It is clear that these two fields must be related. Though we cannot usually observe the motion and behavior of individual atoms and molecules we understand that their behavior gives rise to what we observe in the macroscopic world. This must be so even though they describe the world in different terms.

Statistical thermodynamics is the field that connects quantum mechanics and thermodynamics. As a result it deals with both microscopic and macroscopic phenomena.

These notes will give an introduction to statistical thermodynamics. It will be a semi-rigorous treatment, though it will only scratch the surface of what is a complex and dynamic field.

Our basic idea is this: the equilibrium state of a single component macroscopic system (think of a gas as a simple example) can be described by three variables, say temperature, volume, and number of particles present. Or we might chose to use pressure, mass, and density as our variables. It does not matter which three we chose,1 we only ever need three.2

But a quantum mechanical description (even if we regard the system as made up of point particles) requires six coordinates per particle! Three specify the position of the particle and three more are needed to give the velocity of that particle. If we have a mole of particles, that’s six moles of coordinates. Compare that to the macroscopic description which requires only six variables! Why does the number of independent variables shrink so much when we go from microscopic to macroscopic?

The answer was first discerned by Ludwig Boltzmann back at the end of the 19th century. He pointed out that what was important was not the instantaneous properties of the molecules that made up the gas. What was important was the average properties of the gas. And only a few such properties actually mattered at all!

For instance, if we divide a system in half the properties of the system depend only on how many molecules are in each half, not which ones. In plain words, most of the 6 moles of quantum mechanical properties average down to three macroscopic ones!

Statistical thermodynamics deals with this averaging process. It takes microscopic information and produces macroscopic information.

1Actually, it does matter a little. At least one of them must allow us to determine the extent of the system. Mass or volume, for example, will do. And there are others. Such variables are called extensive variables and at least one is always needed. An extensive variable is one that doubles in value if the system is duplicated.

2The proof of this is contained in what is called the Gibbs Phase Rule.
2 Probability

Before we get involved in the details of statistical thermodynamics it is worthwhile to review a few simple ideas about probabilities.\(^3\) Let us have an experiment with \(N\) possible outcomes. We repeat the experiment \(n\) times and find that we get outcome \(j\) \(n_j\) times.

Then we can define the probability of outcome \(j\) as \(P_j\) given by:

\[
P_j = \lim_{n \to \infty} \frac{n_j}{n} \quad j = 1, 2, \ldots, N
\]  

(2.1)

That’s a somewhat formal definition. The idea is that the outcomes are governed by chance. So we have to do a large number of experiments to even out the fluctuations that chance can introduce.

If you want to test this yourself, get a six-sided die and roll it many times, keeping track of the outcomes. If you stop every 50 rolls and compute the estimated probabilities, you will find that they fluctuate a good bit. After a long while they will settle down, but in fact to avoid even the possibility of an unlikely series of outcomes (such as having 4 come up 300 times in a row) you need to roll the die an infinite number of times.

The probabilities \(P_j\) are normalized. That is, they always add up to 1 exactly:

\[
\sum_{j=1}^{N} P_j = 1
\]  

(2.2)

and, of course, each individual \(P_j\) must lie between 0 and 1, inclusive.

Let’s go one step further. Let us assume that there is some numerical value \(A_j\) associated with each possible outcome \(j\). Then the expected value of \(A\) is given by:\(^4\)

\[
<A> = \sum_{j=1}^{N} A_j P_j
\]  

(2.3)

This looks a bit odd at first glance, but it is exactly what you are used to for an average.

---

Example 2.1

A certain experiment has three possible outcomes. The first has a value of 3, the second a value of 5, and the third a value of 6. Each outcome is equally likely. What is the average value expected in this experiment?

Each probability is 1/3. Thus we have:

\[
<A> = (3 \times \frac{1}{3} + 5 \times \frac{1}{3} + 6 \times \frac{1}{3}) = \frac{14}{3}
\]  

(2.4)

---

\(^3\)I follow the text, MathChapter B, in this.

\(^4\)This expected value or expectation is commonly called the average value.
Example 2.2

A certain system can be in one of four different states, numbered from 1 to 4. These states have probabilities:

\[ p_1 = 0.35 \quad p_2 = 0.30 \quad p_3 = 0.20 \quad p_4 = 0.15 \]

Each state has a volume \( V_j \) associated with it. These volumes are:

\[ V_1 = 17 \quad V_2 = 21 \quad V_3 = 25 \quad V_4 = 32 \]

What is the expected value of the volume?

We use Equation 2.3:

\[ < V > = 17 \times 0.35 + 21 \times 0.30 + 25 \times 0.20 + 32 \times 0.15 = 22.05 \]  \hspace{1cm} (2.5)

See how simple it is?
3 Ensembles

Now that we have probability conquered we can return to statistical thermodynamics. When we last saw statistical thermodynamics we were wondering how to get macroscopic quantities (thermodynamics) from microscopic ones (quantum mechanics).

We are going to do this by averaging the properties of a system.

Instinctively what we want to do is to specify a system as being in a macroscopic state such as at definite values of temperature $T$, volume $V$, and number of particles $N$. We can clearly specify the volume and number of particles. It is just a matter of finding the right sized box and stuffing it with $N$ particles.

But how do we fix the temperature? The answer is that we stick our system into a constant temperature bath already at a temperature $T$. This will work if we assume that our box has heat-conducting walls.

Now with our system in place and at equilibrium, we are going to watch the atoms and molecules move around. Of course we can’t do this with our naked eyes, so we turn on our Super-Dooper MicroVision Video Camera and film the system as it evolves in time. Our film shows the position of each and every particle in the system at very rapid intervals and so we can sit down (at least in principle) and compute, for instance, the speed of each particle. And from the speed we can calculate the kinetic energy of each particle.

Further, if we knew the potential energy of interaction between the particles we could also compute the potential energy of each particle.

And knowing both the kinetic and potential energies of each particle we could determine the average energy all the particles.

We’d expect that energy to fluctuate over time as heat comes from the constant temperature bath or goes out to it. But as time goes on we’d expect the average to settle down to some constant value.7

We can go further. We can call the average energy of the particles in our system with the internal energy $U$ of our system. That’s what it is called in thermodynamics.8

And we could repeat this experiment for a temperature slightly different than the original. And then do it again for yet more temperatures. Soon we’d know the internal energy as a function of temperature.

Look at what we have done. We have used our “film” of the motion of all the particles in the system to determine the average energy of the system. The energies of the individual particles don’t matter much. One could be going abnormally fast, but then it is likely that another would be going abnormally slow. Our mole of individual energies gets averaged down to one single number, the average energy of the system.

7Actually, we don’t have a Super-Dooper MicroVision Video Camera, but it is the idea that is important here.
8Actually, we could determine that by observing how the motion of one particle changes as it gets near another.
9At least to some large number of decimal places.
10Because thermodynamics doesn’t care about the motion of the system as a whole, only the energies contained inside of it. That’s exactly the position we are in here.
But can we actually do this?

There are two problems to actually doing this. One is that we don’t really have a “film”, and even if we did a lifetime would not be enough to compute an average energy. To get around this we use a mathematical model of the system so that we can calculate all the “frames” in the file.

The other problem is more serious. Forget quantum mechanics for a moment. Consider a system with a large number of classical particles, ball bearings for instance. We could use Newton’s equations\(^9\) to predict the motions, but since we have to follow the particles in time, we have to do a lot of integrations. A whole lot. There is no good cure for this, even though today we have very fast computing equipment.

Is there another approach?

Of course there is or I wouldn’t be bringing this up.

To avoid having to follow the system in time, what if I get a huge number of macroscopically identical systems and just take a photograph of each at the same instant. If I do that I end up with a huge number of individual shots.

How different is that from taking a long film of one system evolving over time and then cutting it up so that I end up with the same huge number of photos?

In other words, is a huge number of photos of one system the same as one photo each of a huge number of systems?

The notion that they are the same is known as the **Ergodic Hypothesis**. The neat thing about the Ergodic hypothesis is that it is known NOT to be true, but it is also known to be ALMOST true!

That is, a very few of the huge number of systems might find their particles arranged in ways that the one system never does, and vice versa. So the hypothesis isn’t strictly true. But it turns out that those few situations make no practical difference in any “real” situation.\(^{10}\)

The huge number of systems is known as an **ensemble**. Technically, an ensemble of systems all at the same temperature, volume, and number of particles is called a **canonical ensemble**, but we won’t be too technical here.

One more point is worth noting. In our ensemble we prepare all systems so that they have *identical* values of \(T, V, \text{ and } N\). However, the do not have identical microscopic states. Each system will have its own arrangement of particles. And two particles near the same position in two different systems will not have the same velocities.

So while the systems are in the same *macroscopic state* they are in different *microscopic states*. That’s not a drawback, that’s an advantage. We want to be able to average over all microscopic configurations!

---

\(^9\)That’s \(F = ma\) to you.

\(^{10}\)It is very easy to construct systems that do not obey the Ergodic hypothesis. One is to imagine a system where all the particles move in parallel bouncing from one wall of their container to the other. They remain parallel forever. No huge collection of systems will all show this behavior. However, this would be a very strange system.
4 Relative State Probabilities

Let’s start with an assumption: let us assume that if we knew the probability that a system with fixed $V$, $T$, and $N$ was in any particular energy state $E_j$, we could figure out all the properties of the system.

Now that’s a big assumption, but it happens to be true (or almost true). Its truth was known to Boltzmann and Gibbs and many other early workers in this field.\(^\text{11}\)

Working out the actual energy of any one system is a quantum mechanical problem and to solve it we need to solve Schrödinger’s Equation for $N$ particles in a volume $V$. The result will of course depend on $N$ and $V$.

But we can avoid this step, at least for now. If we stick to the most general question: what is the probability that a system will be in state $j$ with energy $E_j(N, V)$?

We can solve that problem, at least formally,\(^\text{12}\) by making use of some of the properties we expect energies to have.

We start by forming (in our minds, at least) an ensemble of $A$ systems where $A$ is a huge huge number. In fact we want to have far more systems in our ensemble than there are different energy states.\(^\text{13}\) Let’s let the number of systems in state $j$ be $a_j$.

Now take two specific states, say state 1 and state 2. Though the actual state numbers are not important as long as they are fixed. Now the number of systems in state 1 depends on $E_1$ while the number of systems in state 2 depends on $E_2$. Then the ratio of the number of systems in each state must depend on both $E_1$ and $E_2$:

$$\frac{a_2}{a_1} = f(E_1, E_2) \quad (4.1)$$

where $f$ is some as yet unknown function of the energies.

However, there is no zero point for energy. Thus we can add a constant energy $C$ to each energy and change nothing:

$$\frac{a_2}{a_1} = f(E_1 + C, E_2 + C) = f(E_1, E_2) \quad (4.2)$$

and the only way this can be true is if the only thing that matters is the difference between the energies:

$$\frac{a_2}{a_1} = f(E_1, E_2) = f(E_1 - E_2) \quad (4.3)$$

because then the $C$’s cancel out.\(^\text{14}\) Let’s bring in a third energy state. The same relations must hold for it too. Thus

$$\frac{a_3}{a_2} = f(E_2 - E_3) \quad \frac{a_3}{a_1} = f(E_1 - E_3) \quad (4.4)$$

\(^\text{11}\)They knew this because both thermodynamics and physics had both been already invented. We know the physics, but we’ve not yet studied the thermodynamics, so we have to take this on faith at this point.

\(^\text{12}\)A formal solution to a problem is one that gives the answer in principle, though there is still a computation to be done. The quadratic formula is formal solution to the problem of finding the roots of a quadratic equation–but you still have to do the calculation.

\(^\text{13}\)Two comments: first, the number of energy states is finite since no real system can have infinite energy. Second, we can always imagining the number of systems to be larger than any chosen finite number.

\(^\text{14}\)See, we’ve already made use of one property of the energy!
But:
\[
\frac{a_3}{a_1} = \frac{a_2}{a_1} \frac{a_3}{a_2}
\]  
(4.5)

or, in terms of the energies:
\[
f(E_1 - E_3) = f(E_1 - E_2)f(E_2 - E_3)
\]  
(4.6)

Is there any such function \(f\)? The answer is yes, the exponential function which alone has the needed property:
\[
e^{x+y} = e^x e^y
\]  
(4.7)

which is exactly what we want. To show this I’ll replace \(x\) with \(E_1 - E_2\) and \(y\) with \(E_2 - E_3\). The result is
\[
e^{E_1 - E_3} = e^{(E_1 - E_2) + (E_2 - E_3)} = e^{E_1 - E_2}e^{E_2 - E_3}
\]  
(4.8)

One can also easily see that Equations 4.5 through 4.8 are satisfied by taking:
\[
a_j = Ce^{-\beta E_j}
\]  
(4.9)

where both \(\beta\) and \(C\) are constants

Remember now that there was nothing special about the states 1, 2, or 3. They could have been any state at all. Thus we conclude that Equation 4.9 is the solution we want.

We can easily evaluate \(C\). All we have to do is to sum Equation 4.9 realizing that the \(a_j\) must add up to the total number of systems in the ensemble, \(A\):
\[
\sum_j a_j = A = C \sum_j e^{-\beta E_j}
\]  
(4.10)

so that
\[
C = \frac{A}{\sum_j e^{-\beta E_j}}
\]  
(4.11)

If we put this back into Equation 4.10 we get:
\[
\frac{a_j}{A} = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}
\]  
(4.12)

or, in terms of probabilities:
\[
P_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}
\]  
(4.13)

It is good to introduce a shorthand here. The sum in the denominator of Equation 4.13 occurs very very often in what follows. So to make life a bit easier we write:
\[
Q(N, V, T) = \sum_j e^{-\beta E_j}
\]  
(4.14)

thus making Equation 4.13 read
\[
P_j = \frac{e^{-\beta E_j}}{Q(N, V, T)}
\]  
(4.15)

The quantity \(Q(N, V, T)\) is known as the **canonical partition function** because it (a) comes from the canonical ensemble and (b) tells how the systems are partitioned among the various possible energy levels.
One last item. The quantity $\beta$ is a bit more difficult to evaluate. It is done later in the text but it is useful to know now what it is:\footnote{As a general rule I’m against presenting stuff that “will be proven later” since, if you are going to do that I might as well simply write a bunch of equations on the board for you to memorize and tell you that they will all be “will be proved later”.}

$$\beta = \frac{1}{kT}$$

(4.16)

where $k$ is Boltzmann’s constant and $T$ is the absolute temperature. This assumes that all energies are per molecule. If they are given per mole then Equation 4.16 becomes

$$\beta = \frac{1}{RT}$$

(4.17)

where $R$ is the gas constant.

We have now succeeded in finding the probability $P_j$ that a system in the ensemble would be found in state $j$. From the Ergodic hypothesis we can take this same probability as being the probability that any single system can be found in state $j$ at any particular point in time.

It is important to understand how we found it. We did it from the fact that if you put two systems together, their energies add. That’s a consequence of the Law of Conservation of Energy, also known as the First Law of Thermodynamics.
5 The Canonical Ensemble

The quantity $Q$ found in the last section is our central quantity in statistical thermodynamics. Thus it pays to take a better look at it.

The most important fact about the canonical partition function is that it involves a sum over all the energy levels of the *system*. Often these are impossible or at least very difficult to calculate exactly. Dealing with such systems usually involves a number of approximations.

Nevertheless, there are a number of special situations where the partition function $Q$ can be decomposed into simpler parts. The reason for this is that sometimes the system energies have parts that are independent of each other. An ideal gas would be a typical example of this.

If there are no interaction energies between the subsystems of a system, then the system is said to be made up of independent subsystems.

Often these independent subsystems are molecules. In that case we are assuming that the molecules do not interact.

In other cases the system can be transformed in some way to a situation where the subsystems are independent.

But in most cases the subsystems are not independent. In that case we often have to resort to approximate methods, not because the theory doesn’t work, but because the math is too complex.

5.1 Systems of Independent Distinguishable Molecules

Some systems are made up of distinguishable subsystems. Or, in the most usual case, some systems are made up of distinguishable molecules.

Why aren’t all systems like that? Because molecules made up of the same atoms are really indistinguishable. We cannot paint signs on them. If we exchange two such identical molecules, nothing changes. The final state is totally and completely indistinguishable from the initial state.

But sometimes we can distinguish molecules. A crystal provides such an example. While the molecules are identical, they can be identified by their position. For instance if we had a cubic lattice with molecules at unit positions in it, we can tell the molecule at $(x=1, y=4, z=2)$ from the one at $(x=1, y=3, z=2)$.

But the molecules in a crystal are clearly not independent. There must be interaction energies between them, because if there were not, what is keeping the crystal together?

There are several ways to get around the non-independence of molecules in a crystal. One is to assume that each molecule is fixed in place by some infinitely strong bond. Then the

---

16 There are other partition functions as well as the canonical one, $Q$. They differ from it in having different independent variables.

17 But sometimes we can tag them with isotopes, but then the tagged molecules are not the same as the untagged ones, even chemically...
molecules vibrate independently about that bound position. Another way is to consider the molecules bound to each other by perfect springs. They then undergo collective vibrations with the motion of one affecting its neighbor. But if one focuses on the vibrations alone it can be shown that they are essentially independent of each other. This is akin to a string vibrating at two or more frequencies simultaneously.

But the details don’t matter for us now. All we need to know is that the “subsystems” (whatever they are) are independent of each other.

When the subsystems are independent, then the total energy of the system is just the sum of the energies of the individual subsystems. Does that mean that we can factor \( Q \) into a product of particle partition functions \( q \)？ In fact, it does.

The system energy in energy level \( j \) for independent subsystems is:

\[
E_j(N,V) = \epsilon_a(V) + \epsilon_b(V) + \epsilon_c(V) + \ldots
\]  

and \( Q \) is:

\[
Q(N,V,T) = \sum_j e^{-\beta E_j} = \sum_{i,j,k} e^{-\beta(\epsilon_a(V)+\epsilon_b(V)+\epsilon_c(V)+\ldots)}
\]

which is:

\[
Q(N,V,T) = \sum_i e^{-\beta \epsilon_i} \sum_j e^{-\beta \epsilon_j} \sum_k e^{-\beta \epsilon_k} \ldots
\]

or

\[
Q(N,V,T) = q_a(V,T)q_b(V,T)q_c(V,T)\ldots
\]

but since the subsystems are identical so are their energy levels. Thus:

\[
Q(N,V,T) = [q(V,T)]^N
\]

The bothersome step here is in going from Equation 5.2 to Equation 5.3. The best way to see that it is correct is through a demonstration.

Consider a system having three identical particles each of which has two energy levels: \( \epsilon_1 \) and \( \epsilon_2 \). What are the system energy levels?

We can be more explicit if we introduce a notation for the energy levels. I’ll use \( e^{i,j,k} \) to mean

\[
e^{-\beta(\epsilon_i+\epsilon_j+\epsilon_k)}
\]

so that my notation supresses both the \( \beta \) and the \( \epsilon \) but which should nevertheless be readable.

The possible system energy levels are (there are eight of them):

\[
e^{1+1+1}, \ e^{1+1+2}, \ e^{1+2+1}, \ e^{1+2+2}, \ e^{2+1+1}, \ e^{2+1+2}, \ e^{2+2+1}, \ e^{2+2+2}
\]

\[18\]This very simple model was proposed by Einstein back almost a hundred years ago now. It was the first successful thermodynamic model of a crystal ever proposed.

\[19\]This model was proposed by Peter Debye some years after Einstein’s model. It works even better than Einstein’s!

\[20\]I’m going to call these independent subsystems, whatever they are, particles because writing (and reading) that is much quicker than “independent subsystems whatever they are.”
Note that some have identical energy values, 112 has the same energy as 121 and 211. But that doesn’t matter. Since the particles are distinguishable, the three energy levels are distinguishable.

The sum over the system energy levels is then:

\[ Q = e^{1+1+1} + e^{1+1+2} + e^{1+2+1} + e^{2+1+1} + e^{2+1+2} + e^{2+2+1} + e^{2+2+2} \]  

(5.7)

I can factor this:

\[ Q = e^{1}[e^{1+1} + e^{1+2} + e^{2+1} + e^{2+2}] + e^{2}[e^{1+1} + e^{1+2} + e^{2+1} + e^{2+2}] \]

(5.8)

which is:

\[ Q = (e^{1+2})(e^{1+2}) \]

(5.9)

which can be factored further into

\[ Q = (e^{1+2})(e^{1+2}) = (e^{1+2})^3 \]

(5.10)

which is the form \( Q = q^3 \) we wanted.

So we’ve established Equation 5.5 as correct in the case of independent subsystems.

### 5.2 Systems of Independent Indistinguishable Molecules

If the subsystems of a system are indistinguishable (as they most often are if they are atoms or molecules) then we have a slightly different problem. If, for example, we have a system of 5 indistinguishable atoms each in a different atomic energy state, how many different system energy levels is that?

To see the answer let me change our notation slightly and use an integer to denote the energy state of an atom and the position of the number in a group to indicate which particle we are dealing with. Thus 13524 means particle 1 in energy level 1, particle 2 in energy level 3, etc. These energies, added together, make up one system energy level.

It is clear that system state 13524 and system state 43152 have exactly the same system energy. And there are not just two states. There are, in fact, 5! = 120 different combinations of the digits 12345.

But with the particles indistinguishable there are NOT 120 different states, there is only 1!.

That is because one cannot tell which atom is in which state. All we know is that each of the five atoms is in a different state.

So when we multiply our subsystem \( q \)'s together to get \( Q \), we are overcounting our states. There are far fewer of them. In fact, if there are \( N \) subsystems, we have overcounted by \( N! \). To fix this we must divide by \( N! \).

Thus for independent and indistinguishable subsystems

\[ Q(N, V, T) = \frac{1}{N!} [q(V, T)^N] \]

(5.11)

The quick among you have already seen a complication here. The above argument fails for some states. For instance, the ground state of our system is 11111 and there is only
one such state, not 120. And there are states such as 12222. There are only 5 such states because the 1 can be in only five different positions.

But we have assumed that all states are overcounted by $N!$.

It turns out (and, if you have the patience you can see this for yourself) that as $N$ increases, the number of such "special" states becomes a smaller and smaller faction of the total. Most subsystems are in a unique quantum state. So while the $N!$ is an approximation, it is a good approximation.

Actually, there is another complication. It turns out that the universe is made up of two kinds of particles, fermions and bosons. Fermions are particles with half-integer spins, bosons have full-integer spins. Electrons, protons, and neutrons are typical fermions. Photons are typical bosons.

More technically, the difference between the two types of particles is this: if you interchange two fermions in a system wave function, the wave function changes sign. That is, fermion wave functions are antisymmetric. This makes no difference in the properties of the system since those depend on the square of the wave function.

Interchange of bosons, on the other hand, produces a symmetric wave function. There is no sign change.

For us however fermions and bosons have another set of properties we need to know about. Fermions obey the Pauli Exclusion Principle. That is, no two fermions can be in the same quantum state in a given system. Thus states like 11111 and 12222 can not occur with fermions.

Bosons, on the other hand, do NOT obey the Pauli Exclusion Principle, so they can have states like 11111 and 12222.

As a result, the system partition function can not be a simple product of subsystem partition functions.

Interestingly, systems of independent fermions and bosons can be handled, but we will not do so here. We will stick with our slightly approximate statistics where we "fix" things by dividing by $N!$.

### 5.3 Independent Internal Degrees of Freedom

If the independent subsystems are molecules, we can make one more “simplification”. One of the interesting things about the energetics of independent molecules is that the various sorts of energies they have are more or less independent of each other. For example, the energy of a given molecule, $\epsilon$ can often be written as:

$$
\epsilon_r = \epsilon_{\text{trans},i} + \epsilon_{\text{rot},j} + \epsilon_{\text{vib},k} + \epsilon_{\text{elec},l}
$$

(5.12)

where the total energy is shown as a sum of the translational, rotational, vibrational, and electronic energies of a molecule.

Are these energies really independent? The translational energy certainly is. One can always separate out the center of mass of a molecule from the internal coordinates.\footnote{Internal coordinates are the relative positional coordinates of a molecule.} So its
motion is not affected by any other motion inside the molecule.

Rotation and vibration are, however, linked. At high rotational energies the bonds in
the molecule stretch which affects their vibrational properties. This usually requires high
temperatures though and so assuming that the two are independent is often a good approx-
imation.

The same thing can be said about the electronic energy. The problems that we normally
deal with almost always involve molecules in their electronic ground state. And while that
energy can be affected by high rotational and vibrational energy levels, we do not often
meet with that situation.\(^{22}\)

So for our purposes we will \textit{assume} that these are all independent energies.

In that case the subsystem partition function \(q[V, T]\) can be written:

\[
q = \sum_r e^{-\beta \epsilon_r} = \sum_{i,j,k,l} e^{-\beta(\epsilon_{\text{trans}},i + \epsilon_{\text{rot}},j + \epsilon_{\text{vib}},k + \epsilon_{\text{elec}},l)}
\]

which becomes:

\[
q = \left[ \sum_i e^{-\beta \epsilon_{\text{trans}},i} \right] \left[ \sum_j e^{-\beta \epsilon_{\text{rot}},j} \right] \left[ \sum_k e^{-\beta \epsilon_{\text{vib}},k} \right] \left[ \sum_l e^{-\beta \epsilon_{\text{elec}},l} \right]
\]

which immediately becomes

\[
q = q_{\text{trans}}q_{\text{rot}}q_{\text{vib}}q_{\text{elec}}
\]

This greatly simplifies our work since we can deal with each of these subsystem partition
functions separately.

\(^{22}\)You will recall from quantum mechanics that the actual energy of an electronic state depends on
the internuclear separations in the molecule. These change as the molecule vibrates. But the standard
assumption is that the electrons move much faster than the heavy nuclei and have no trouble staying in
“equilibrium” with the nuclei.
6 The Translational Partition Function

The translational partition function can always be separated from all the other energy forms of a system. This is because the translational energy, the energy of motion of the molecule, is associated with the center of mass of the molecule. And the center of mass coordinates can always be separated out from all the other coordinates of the molecule.

To see this in at least a general way, we know that there are three space coordinates associated with each atom in a molecule. That means that for an $n$-atom molecule there are $3n$ space coordinates.

These are usually given in terms of some origin somewhere in the system containing the molecule. But I can form new coordinates giving the position of the center of mass of the molecule and the positions of all the other atoms relative to that center. If, for instance, $x_{cm}$ is the $x$-coordinate of the center of mass, the $x$-coordinate of the $i$'th atom relative to that center of mass is simply $x_i - x_{cm}$.

As a result, the motion of the molecule can be resolved into two sets of coordinates, the motion of the center of mass and the motion of the molecule about the center of mass.

Now the total energy of the center of mass is both kinetic and potential. The kinetic energy is given quantum-mechanically by:

$$\epsilon_{u,v,w} = \frac{\hbar^2}{8ma^2} (u^2 + v^2 + w^2)$$

where $u$, $v$, and $w$ are quantum numbers ranging from 1 to infinity in integer steps, $\hbar$ is Planck's constant, $m$ the mass of the molecule, and $a$ the length of one side of the container, assumed to be a cube for simplicity. The resulting partition function looks messier than it is:

$$q_{\text{trans}} = \sum_{u,v,w=1}^{\infty} e^{-\beta \epsilon_{u,v,w}}$$

$$= \sum_{u=1}^{\infty} \exp \left( -\frac{\beta \hbar^2 u^2}{8ma^2} \right) \sum_{v=1}^{\infty} \exp \left( -\frac{\beta \hbar^2 v^2}{8ma^2} \right) \sum_{w=1}^{\infty} \exp \left( -\frac{\beta \hbar^2 w^2}{8ma^2} \right)$$

The three sums are really the same since the variable over which we sum makes no difference. So our basic problem is to evaluate:

$$q = \sum_{w=1}^{\infty} \exp \left( -\frac{\beta \hbar^2 w^2}{8ma^2} \right)$$

The sum is of the basic form

$$q = \sum_{w=1}^{\infty} e^{-cw^2}$$

where $c$ is a combination of constants. That sum cannot be done. So what are we to do?

---

23 I’m not going to go through the formal derivation of this. Life is too short.

24 Which includes things such as rotation and vibration.
The answer is really contained in Problems 18-14 and 18-15 in the text, which I’ll not elaborate on in this version of these notes. Suffice it to say that there is an equation, the Euler-Maclaurin Summation Formula, which provides a direct link between sums and integrals. Using it one can show that the sum in equation 6.4 can be replaced by an integral with very little error.

If we do that the result is:

\[ q = \sum_{w=1}^{\infty} e^{-cw^2} \approx \int_{0}^{\infty} e^{-cw^2} = \left( \frac{\pi}{4c} \right)^{1/2} \]

(6.5)

Since here \( c = \beta h^2/8ma^2 \), our result is, when we recall that we’ve got three identical integrals:

\[ q_{\text{trans}} = \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} V \]

(6.6)

where the \( V \) (volume) comes from the product of three factors of \( a \).

Equation 6.6 is not only important in itself (we will meet it many times in the future) but it shows that the partition function \( q_{\text{trans}} \) is both a function of \( V \) and of \( T \), since \( \beta \) is \( 1/k_B T \). As a result, the canonical partition function \( Q(N,V,T) \) is also clearly a function of \( V \), and \( T \) because it includes not only \( q_{\text{trans}} \), but \( q_{\text{trans}} \) raised to the \( N \)th power, showing the \( N \) dependence as well.

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25 Physical Chemistry by D.A. McQuarrie and J.D. Simon
7 The Properties of Monatomic Gases

Monatomic gases do not have many different kinds of energies. In fact, leaving out nuclear spin energies\textsuperscript{26} there are only two, the translational energy and the electronic energy. The electronic energies are a bit of a problem because, with the exception of hydrogen and the hydrogen molecule ion, no exact solutions of Schroedinger’s equation exist for atoms.

Luckily, most atoms have electronic energy levels that are separated by large energy differences. These are so large that in most cases only the ground state needs be taken into account. In other words\textsuperscript{27} for electronic energy levels $\epsilon_j$, where $j$ indexes the level,

$$ q_{\text{electronic}} = \sum_{j=1}^{\infty} e^{-\beta \epsilon_j} \approx e^{-\beta \epsilon_1} $$

(7.1)

where $\epsilon_1$ is the ground state electronic energy. The distance (in energy units) to $\epsilon_2$ is so great that, typically\textsuperscript{28} the second term in the series is typically only about $10^{-5}$ of the first term for most gases.

Some general observations can be made. The ground electronic state of the noble gases is $^1S_0$, so that state is non-degenerate. For the alkali metals though the ground state is $^2S_{1/2}$, and the ground state is degenerate with a degeneracy of 2. For those atoms in the gas state, equation 7.1 has to be written:

$$ q_{\text{electronic}} = \sum_{j=1}^{\infty} e^{-\beta \epsilon_j} \approx 2 e^{-\beta \epsilon_1} $$

(7.2)

The halogen atoms are a bit more complex; the ground state is $^2P_{3/2}$ with a $^2P_{1/2}$ state lying just above it\textsuperscript{29}. Thus for flourine atoms as a gas the electronic partition function is given by:

$$ q_{\text{electronic}} = \sum_{j=1}^{\infty} e^{-\beta \epsilon_j} \approx 4 e^{-\beta \epsilon_1} + 2 e^{-\beta \epsilon_2} $$

(7.3)

However, it is easy to make too much of this. The general rule holds, only the first electronic state counts, and if (as is usually the case) its energy is taken as defining the zero of energy for the atom, then

$$ q_{\text{electronic}} = 1 $$

(7.4)

unless the ground state is $g$-fold degenerate in which case the electronic partition function is $g$.

Putting all this together, we have as the complete partition function of a monatomic ideal gas subsystem:

$$ q = \left( \frac{2\pi m}{\beta \hbar^2} \right)^{3/2} V g $$

(7.5)

and since these particles are indistinguishable:

$$ Q(N, V, T) = \frac{1}{N!} \left[ \left( \frac{2\pi m}{\beta \hbar^2} \right)^{3/2} V g \right]^N $$

(7.6)

\textsuperscript{26}Which are important in some applications.

\textsuperscript{27}If we can call an equation words...

\textsuperscript{28}As the text points out on page 734.

\textsuperscript{29}In contradiction to the general rule that the first excited state is much higher than the ground state.
8 Properties of Polyatomic Gases

Polyatomic gases are more complicated than monatomic gases and hence their partition functions are more complex as well. In addition to translation and electronic energies, they also have both rotational and vibrational energies. We’ll take these one at a time.

8.1 Translational Energy

The only thing that changes for a polyatomic gas molecule when we consider translation is the mass. The mass is now the mass of the entire molecule, not just that of the single atom as in a monatomic gas. The translational partition function is then:

\[ q_{\text{translation}} = \left( \frac{2\pi M k_B T}{\hbar^2} \right)^{3/2} V \]  

(8.1)

where \( M \) is the total mass of the molecule.

8.2 The Electronic Partition Function

The electronic partition function for polyatomic molecules becomes a bit more complex than for atoms. The most convenient choice of an energy zero for a molecule is the energy of the separated atoms. We begin with the component atoms infinitely apart. That energy is taken as zero. The atoms are then brought to their actual positions in the molecule (mentally, of course) and the resultant energy measured. That’s the total binding energy of the molecule. It has to be negative, because if it weren’t, it wouldn’t be a binding energy!

So the energy of the ground electronic state of a stable molecule is less than zero. The standard notation for this energy is \(-D_e\), where \( D_e \) itself is a positive number.

If we denote the first excited molecular state as \( \epsilon_{e2} \), then the electronic partition function (ignoring all other electronic states) is:

\[ q_{\text{electronic}} = g_{e1}e^{\beta D_e} + g_{e2}e^{-\beta \epsilon_{e2}} \]  

(8.2)

where \( g_{e1} \) and \( g_{e2} \) are the degeneracies of the ground and first excited electronic states respectively.\(^{30}\)

8.3 Vibration

Unlike atoms, molecules can vibrate, and in more than one way too. One can imagine all sorts vibrations in a molecule from shakes to shimmies.

In fact, we are only interested in vibrations that leave the center of mass unchanged.\(^{31}\) Further, many vibrations can be taken to be combinations of other vibrations, so that we

\( ^{30} \)A table of \( D_e \)’s for various molecules can be found in the text on page 739.

\( ^{31} \)Why? Because we take care of motions of the center of mass in the translational partition function.
need to search for a set of independent vibrations. These can be found for any molecule. They are called the normal modes of the molecule.\footnote{And no, I’m not going to show you how to find them. It isn’t really hard. In the end one simply has to diagonalize a certain matrix, but let’s not go there here.}

The next question is: how many normal modes does a molecule have? The answer is simple. We count up the number of degrees of motional freedom of the molecule. There is one degree of motional freedom for every coordinate for every atom. Thus an atom has three motional degrees of freedom, a diatomic molecule six, and benzene 54.

Of these, three degrees of motional freedom are translational; motion in the \(x\)-, \(y\)-, and \(z\)-directions. For diatomic molecules two additional ones are rotational, one about the \(x\)-axis and one about the \(y\)-axis and none about the \(z\) (bond) axis.\footnote{That’s because if you rotate a diatomic molecule around its bond axis, nothing changes, and so there is no rotation!} So for a diatomic molecule there are six motional degrees of freedom, three translational, two rotational, and hence only one vibrational.\footnote{And that’s a symmetrical stretch along the bond axis that leaves the center of mass unchanged.} For any non-linear polyatomic molecule of \(n\) atoms, there are \(3n\) motional degrees of freedom. Three are translational and three are rotational (around each axis), and \(3n-6\) are vibrational. Thus benzene has 48 independent normal vibrational modes.\footnote{And you wonder why its vibrational spectrum is so complicated!}

The only exception to this is linear molecules, of which the common example is carbon dioxide. Being linear, there is no rotation around the bond axis, so there are only two rotational degrees of freedom and \(3n-5\) vibrational degrees of freedom. Thus carbon dioxide has four vibrational degrees of freedom while water has only three.

If a given vibration has a fundamental frequency of \(\nu\), we know that the vibrational energies are given by:

\[
e_n = \left(n + \frac{1}{2}\right) \hbar \nu
\]  

(8.3)

This assumes that the vibrations are harmonic. They aren’t. Why? Because the actual interparticle potential is not a parabola at all. It is much more like a Lennard-Jones potential (Equation 16.29 and Figure 16.14 in the text). But the actual potential can be approximated by a parabola for small vibrations.

If the vibrational energies become large, the formulas below do not work. But it turns out that most vibrations are in their ground state at room temperature, so this is not a major concern.

The vibrational partition function is given by the sum:

\[
q_{\text{vib}} = \sum_{n=0}^{\infty} e^{-\beta \epsilon_n} = \sum_{n=0}^{\infty} e^{-(n+1/2)\beta \hbar \nu} = e^{-\beta \hbar \nu/2} \sum_{n=0}^{\infty} e^{-n \beta \hbar \nu}
\]  

(8.4)

This sum is surprisingly easy to do. It is simply a geometric series! This can be seen if we let \(x = \exp -\beta \hbar \nu\). The sum is then:

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

(8.5)
Inserting this into equation 8.4 gives

\[ q_{\text{vib}} = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \]  

(8.6)

There is one simplification that can be made. The quantity \( h\nu/k_B \) depends only on the fundamental vibrational frequencies of the given molecules. So it is customary to abbreviate this:

\[ \Theta_v = \frac{h\nu}{k_B} \]  

(8.7)

and equation 8.6 becomes

\[ q_{\text{vib}} = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \]  

(8.8)

The advantage of this should be obvious. All vibrations are represented by the same formula, only the value of \( \Theta_v \) varies. So we only have to do our math once—which any student will admit is a Good Thing!

There is a table of \( \Theta_v \) both on page 739 and another on page 743. It is clear that the lighter the molecule, the larger \( \Theta_v \) is and the smaller the fraction of molecules in an excited vibrational state.

### 8.4 Rotation

Rotational motion is complicated by the fact that as the molecule rotates, bonds stretch. This affects not only the rotational energies but the vibrational ones as well.

Luckily, this effect is usually small unless the temperature is high or the molecule excessively “floppy”. So it is reasonable to assume that we are dealing with a rigid rotator.

The energy levels of a rigid rotor are given by

\[ \epsilon_J = \frac{\hbar J(J + 1)}{2I} \quad g_J = 2J + 1 \]  

(8.9)

where \( I \) is the moment of inertia about whatever axis the rotation is around,\(^3\) and \( g_J \) is the degeneracy of the \( J \)’th level. As usual all we need do is sum these:

\[ q_{\text{rotation}} = \sum_{J=0}^{\infty} (2J + 1)e^{-\beta \hbar J(J+1)/2I} \]  

(8.10)

and we are done!

Of course, also as usual, the sum cannot be done. So we will convert it to an integral. First we will simplify equation 8.10 by using:

\[ \Theta_r = \frac{\hbar^2}{2Ik_B} = \frac{hB}{k_B} \]  

(8.11)

\(^3\) Be wary. \( I \) will usually be different for different rotational axes in the same molecule.
where \( B \) is defined in Chapter 5 of the text in text Equation 5.62. We then write the sum as an integral:

\[
q_{\text{rot}} = \int_{0}^{\infty} (2J + 1)e^{-\Theta_{r}(J+1)/T} dJ
\]  

(8.12)

which still looks quite formidable. It can be tamed by substituting \( x = J(J + 1) \) so that \( dx = (2J + 1)dJ \), then we get rather simply:

\[
q_{\text{rot}} = \int_{0}^{\infty} e^{-\Theta_{r}x/T} dx = \frac{T}{\Theta_{r}}
\]  

(8.13)

which is valid\(^{37}\) whenever \( \Theta_{r} << T \).

There is one catch when dealing with rotation. For us, a circle contains 360° degrees or \( 2\pi \) radians. That’s true for most molecules too. But some are a bit strange.\(^{38}\) For them, a circle may be only 180° degrees or just \( \pi \) radians around!

Think of an oxygen molecule. When it has turned 180° degrees the two oxygen atoms have changed places. This brings the molecule back to its starting position because we can’t tell that configuration from no rotation at all.

And for some rotations such as benzene around an axis perpendicular to the plane of the molecule, a full circle is only 60° degrees!

Thus when rotation about an axis involves a short circle, we have to fix up the partition function to account for this. The rule is simple. We invent a symmetry number \( \sigma \) which is normally 1. For a short circle we divide 360° degrees by the size of the short circle and call that \( \sigma \).

Thus for oxygen we’d have 360° degrees divided by 180° degrees and \( \sigma \) would be 2 and for benzene with the short circle equal to 60° degrees, \( \sigma \) would be six.

We stick \( \sigma \) into equation 8.13 to get:

\[
q_{\text{rot}} = \frac{T}{\sigma\Theta_{r}}
\]

(8.14)

which is our final result.

### 8.5 The Overall Picture

We’ve now developed partition functions for rotation, vibration, translation, and electronic energies. Here we put them all together.

\(^{37}\)Because we are approximating a sum by an integral. When the temperature is too low, all one need do is sum the first few terms of the actual series in equation 8.10 instead.

\(^{38}\)It comes from having to live in a quantum mechanical universe.
I’ll do this first for a general diatomic molecule. We have:

\[ q_{\text{translation}} = \left( \frac{2\pi M k_B T}{\hbar^2} \right)^{3/2} V \]

\[ q_{\text{electronic}} = g_{e1} e^{\beta D_e} + g_{e2} e^{-\beta \epsilon_e} \]

\[ q_{\text{vibration}} = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \]

\[ q_{\text{rotation}} = \frac{T}{\sigma \Theta_r} \]  

or, all together:

\[ Q(N, V, T) = \]  

\[ \frac{1}{N!} \left\{ \left( \frac{2\pi M k_B T}{\hbar^2} \right)^{3/2} V \left[ g_{e1} e^{\beta D_e} + g_{e2} e^{-\beta \epsilon_e} \right] \left[ \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \right] \left[ \frac{T}{\sigma_1 \Theta_r 1} \right] \left[ \frac{T}{\sigma_2 \Theta_r 2} \right] \right\}^N \]

The expression for a polyatomic molecule would only be slightly more complex. It would contain one vibrational term for each different normal vibrational mode (there are in general \(3n - 6\) of these), each with a different \(\Theta_v\), and three rotational terms, each with a separate \(\Theta_r\) instead of the two shown above.

However, what we’ve got is an amazing intellectual accomplishment.\(^{39}\) We have a complete theory for all the thermodynamics of an ideal gas\(^{40}\) no matter how many atoms it contains. From equation 8.16 (or the corresponding polyatomic equation) we can compute the molecule’s energy, heat capacity, entropy,\(^{41}\) and Gibbs and Helmholtz free energies!

\(^{39}\)I know it has seemed tedious at times, but there it is.

\(^{40}\)I’ve not proven it yet, but all these molecules obey the ideal gas law. We ensured that when we assumed that there were no intermolecular interactions.

\(^{41}\)Even if we don’t know what that is yet...
9 Thermodynamic Properties

Now it is time to do something with all of those partition functions we’ve accumulated.

I’ve lumped this material together because we’ve not yet studied any thermodynamics, so we don’t have a clear idea of what properties of systems we want to know about. So a bit of what follows has to be taken on faith.

What I’m going to do now is develop a bit of formal machinery\textsuperscript{42} the most important component of which is equation 4.15 which gives the probability of finding a system in a particular energy level. To keep you from rummaging through these notes to find that equation, here it is again:

\[ P_j = \frac{e^{-\beta E_j}}{Q(N,V,T)} \]

To use this we need to know the energy levels \( E_j \). And we need to know \( Q(N,V,T) \). We need actual values for these before we can know \( P_j \).

Once we know the \( P_j \)’s, we are all set. From those we can find all of the system properties that we need.

It turns out (as I’ve said) that knowing just \( Q(N,V,T) \) is enough, since we have to know all the \( E_j \)’s in order to calculate it.

But enough talking. It is time to develop a set of formal equations showing how we can find various system properties from \( Q(N,V,T) \).

9.1 The Internal Energy

First I will show that the average energy \( \langle E \rangle \) of a system can be obtained from \( Q \). This, like many other things in mathematics, is best done backwards.\textsuperscript{43} The formula is:

\[ \langle E \rangle = - \left( \frac{\partial \ln Q}{\partial \beta} \right) \] (9.1)

To see this we first write \( Q \)

\[ Q = \sum_j e^{-\beta E_j} \] (9.2)

and then differentiate with respect to \( \beta \):

\[ \left( \frac{\partial \ln Q}{\partial \beta} \right) = \frac{1}{Q} \frac{\partial}{\partial \beta} \sum_j e^{-\beta E_j} \] (9.3)

\[ = - \frac{1}{Q} \sum_j E_j e^{-\beta E_j} \] (9.4)

\[ = - \langle E \rangle \] (9.5)

\textsuperscript{42}Formal machinery is a mechanism for doing something, but which needs actual numbers (or something similar) in order to function. The famous quadratic formula is an example. It will give you the two roots of a quadratic equation, but not until you give it some numbers.

\textsuperscript{43}I don’t want to think about what this says about mathematics...
where the last comes from the definition of an average if we remember that

\[ P_j = \frac{1}{Q} e^{-\beta E_j} \]

From this you can see why I’ve kept using \( \beta \) rather than replacing it with \( 1/k_B T \). Try rewriting equation 9.2 using \( 1/k_B T \) instead of \( \beta \) and then differentiate the result with respect to \( T \). Wasn’t that fun!

We’ve already noted that the average energy of a system is the thermodynamic internal energy \( U \).\(^{44}\) While physics tells us that there is no absolute energy scale, there is an implied zero point for the energy here. It is the zero point from which we measure the system energies \( E_j \). If we call that \( U_o \), then we have:

\[ < E > = \Delta U = (U - U_o) \]  

(9.6)

where we have quite reasonably chosen \( U_o \) to be 0.

### 9.1.1 The Translational Energy

As an example, let us look at the internal energy of a gas having only translational energy. The appropriate partition function is:

\[ Q(N, V, T) = \frac{1}{N!} q^N = \frac{1}{N!} \left( \frac{2\pi m}{\beta h^2} \right)^{3N/2} V^N \]  

(9.7)

The natural logarithm of this is:

\[ \ln Q(N, V, T) = -\ln N! + \frac{3N}{2} \ln \left( \frac{2\pi m}{\beta h^2} \right) + N \ln V \]  

(9.8)

and differentiating with respect to \( \beta \) gets rid of all the terms except the one containing \( \beta \).\(^{45}\)

We end up with:

\[ \left( \frac{\partial \ln Q}{\partial \beta} \right)_{V,N} = \frac{3N}{2} \frac{\partial}{\partial \beta} \ln \left( \frac{2\pi m}{\beta h^2} \right) = -\frac{3N}{2} \frac{\partial}{\partial \beta} \ln \beta = -\frac{3N}{2\beta} = -\frac{3Nk_B T}{2} \]  

(9.9)

Comparison to equation 9.1 gives us the result:

\[ U = \frac{3Nk_B T}{2} \]  

(9.10)

Other examples, such as the vibrational energy of a diatomic molecule, are as easily done.

---

\(^{44}\)It is called the internal energy rather than simply the energy because it is meant to include only the energy of the stuff inside the system and not any energy, kinetic or potential, of the box holding the system. In other words, if we pick up the system and throw it, the internal energy does not change, though the total energy of the system plus container certainly does.

\(^{45}\)Yes, I know that you are not used to differentiating factorials, but we don’t have to do that here–except to note that \( \ln N! \) is simply a constant and disappears on differentiation.
9.1.2 The Heat Capacity at Constant Volume

The heat capacity of a system depends on its energy, and in the case of a monatomic gas, on equation 9.10. While it will not be shown until thermodynamics is discussed, the heat capacity of a system kept at a fixed volume (like a gas in a box) is given by:

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

(9.11)

which for our gas is

\[ C_V = \frac{3Nk_B}{2} \]  

(9.12)

which is a familiar result.

9.2 The Pressure

The pressure in a system is also related to the canonical partition function \( Q \). The derivation of the appropriate formulas however, needs an understanding of both the total derivative and work. The former is discussed on page 686 of the text and in the math notes for this course (available on the web site for this course.)

I’ll say a bit about the latter when it is needed.

What is more or less this derivation is given in Section 19-6 of the text.

We stated that the internal energy \( U \) is the average energy \( E \) of the ensemble. It is given by:

\[ U = \sum_j E_j P_j \]  

(9.13)

where the probabilities \( P_j \) are functions of \( N, V \), and \( \beta \) and the system energy levels \( E_j \) are, as we know from quantum mechanics, functions of just \( N \) and \( V \).

If we differentiate equation 9.13 and use the product rule we get:

\[ dU = \sum_j P_j dE_j + \sum_j E_j dP_j \]  

(9.14)

Let’s look at the first term in equation 9.14. A small change in the energy levels can be caused either by changing the number of particles (remember it is the system energy levels we are talking about), or by changing the volume. Since we are holding the number of particles constant it can’t be that, so we are dealing with a small change in volume.

\[ dE_j = \left( \frac{\partial E_j}{\partial N} \right)_V dN + \left( \frac{\partial E_j}{\partial V} \right)_N dV \]  

(9.15)

46Don’t you just hate it when the author says that. Who does he think he is, anyway?
47If \( z = xy \), then \( dz = ydx + xdy \).
48Recall that the particle in a box energy levels depend on the volume.
but since we are holding $N$ constant the first term goes away and we end up with:

$$dE_j = \left( \frac{\partial E_j}{\partial V} \right)_N dV$$  \hspace{1cm} (9.16)

Substituting this into Equation 9.14 gives

$$dU = \sum_j P_j \left( \frac{\partial E_j}{\partial V} \right)_N dV + \sum_j E_j dP_j$$  \hspace{1cm} (9.17)

Now the first term in Equation 9.17 is the change in the system energy caused by a small change in the volume. This is the mechanical work done by the system.

To see this think of an amount of gas trapped in a cylinder and held in place by a piston. Let the volume of the gas be $V$ and the pressure $p$. Now assume that there is a weight on top of the piston that exerts an infinitesimally smaller pressure $down$ on the piston\(^\text{49}\) so that the piston can, due to the pressure below, rise very very slightly. Since pressure is force per unit area or $p = f/A$, then the upward force is given by

$$f = pA$$

in response to this slight imbalance, the piston moves up a distance $dh$. Since force times distance is energy (work) we have

$$fdh = pAdh$$

Writing $w$ for $fh$ and $dV$ for $Adh$, we get:

$$dw = pdV = dU$$

and this is the change in energy of the system when the volume is allowed to change slightly. I’ve written this as equal to $dU$ since if there is no thermal energy involved, the work is the change in energy.

If the change is made slowly enough and no thermal energy allowed to enter or leave the system, the probabilities of finding a system in a given state will not change. Thus $dP_j$ in equation 9.17 is zero\(^\text{50}\) and we have:

$$dU = \sum_j P_j \left( \frac{\partial E_j}{\partial V} \right)_N dV$$  \hspace{1cm} (9.18)

Setting this equal to $pdV$:

$$pdV = \sum_j P_j \left( \frac{\partial E_j}{\partial V} \right)_N dV$$  \hspace{1cm} (9.19)

and we can identify the pressure as

$$p = \sum_j P_j \left( \frac{\partial E_j}{\partial V} \right)_N$$  \hspace{1cm} (9.20)

\(^\text{49}\)Assumed weightless, frictionless, and thus totally unreal, but this is school where you learn five totally unreal things each day.

\(^\text{50}\)You might be asking how the energy can change if the occupations of the various energy states does not change? The answer is that the energy changes because the energy levels themselves change energy and not because systems change which energy level they are in.
So all we need to do is evaluate the right-hand side of equation 9.20.
Once again, let’s start with the answer and work backwards. The answer is:

$$p = \langle p \rangle = \frac{1}{\beta} \left( \frac{\partial \ln Q}{\partial V} \right)_N$$

(9.21)

Once again we have:

$$Q = \sum_j e^{-\beta E_j}$$

(9.22)

and so

$$\left( \frac{\partial \ln Q}{\partial V} \right)_N = -\frac{\beta}{Q} \sum_j \left( \frac{\partial E_j}{\partial V} \right)_N e^{-\beta E_j} = \beta \sum_j P_j \left( \frac{\partial E_j}{\partial V} \right)_N = \beta p$$

(9.23)

which gives the desired result.

### 9.3 The Ideal Gas Law

We’ve already noted that the canonical partition function $Q$ can be written as:

$$Q(N, V, \beta) = \frac{[q(V, \beta)]^N}{N!}$$

(9.24)

The only thing that depends on the volume is the translational partition function $q^{\text{trans}}$. This can be written as written as:

$$q(V, \beta) = \left( \frac{2\pi m}{\hbar^2 \beta} \right)^{3/2} V$$

(9.25)

Let us calculate the pressure in this gas. Since we are going to take a logarithm and then differentiate with respect to $V$ it pays to expand $Q$ first as:

$$\ln Q = N \ln q - \ln N! = \frac{3N}{2} \ln \left( \frac{2\pi m}{\hbar^2 \beta} \right) + N \ln V - \ln N!$$

(9.26)

$$\ln Q = N \ln V + \text{terms not involving } V$$

(9.27)

so we simply get:

$$\left( \frac{\partial \ln Q}{\partial V} \right)_{N, \beta} = \frac{N}{V}$$

(9.28)

from which we get the *amazing* result:

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

(9.29)

If you followed this closely you can see yet another amazing result. The subsystem partition function $q$ can be written as:

$$q = C_1 V$$

(9.30)

where $C_1$ is a term *not* involving the volume. So $Q$ is:

$$Q = C_2 V^N$$

(9.31)
where $C_2$ is another term not involving the volume. Then when the pressure is calculated the only quantity that enters is $N \ln V$ and we get the ideal gas law every time! In other words all systems made up of independent subsystems obey the ideal gas law!

That’s a good thing to remember.\textsuperscript{51}

### 9.4 Polyatomic Gases

It is interesting to look at the properties (such as we have them) for a diatomic molecule. Extension to polyatomics is simple. It should be recalled that the full partition function for a diatomic molecule was given in equation 8.16:

$$Q(N, V, T) = \frac{1}{N!} \left\{ \left[ \frac{2\pi M k_B T}{\hbar^2} \right]^{3/2} V \left[ g_{e_1} e^{\beta D_e} + g_{e_2} e^{-\beta e_2} \right] \left[ \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \right] \left[ \frac{T}{\sigma_1 \Theta_r} \right] \left[ \frac{T}{\sigma_2 \Theta_r^2} \right] \right\}^N$$

(9.32)

It is useful to break this down into separate contributions to $Q$, as long as we recall that

$$Q(N, V, T) = \frac{1}{N!} [q_{\text{translation}} q_{\text{electronic}} q_{\text{vibration}} q_{\text{rotation}}]^N$$

(9.33)

Then with

$$q_{\text{translation}} = \left[ \frac{2\pi M k_B T}{\hbar^2} \right]^{3/2} V$$

$$q_{\text{electronic}} = g_{e_1} e^{\beta D_e} + g_{e_2} e^{-\beta e_2}$$

$$q_{\text{vibration}} = \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}}$$

$$q_{\text{rotation}} = \frac{T}{\sigma \Theta_r}$$

(9.34)

(where there are really two rotational functions of exactly the same form), we take logs to get:

$$\ln q_{\text{translation}} = -\ln N! + \frac{3N}{2} \ln \left[ \frac{2\pi M k_B T}{\hbar^2} \right]^{3/2} + \ln V$$

$$\ln q_{\text{electronic}} = \ln \left[ g_{e_1} e^{\beta D_e} + g_{e_2} e^{-\beta e_2} \right]$$

$$\ln q_{\text{vibration}} = N \ln \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}}$$

$$\ln q_{\text{rotation}} = N \ln \frac{T}{\sigma \Theta_r}$$

\textsuperscript{51}And that’s probably the strangest derivation of the Ideal Gas Law you’ve ever seen! See the advantages of an education?
We’ve already done the translational energy. It turned out to be:

\[ U_{\text{translation}} = \frac{3Nk_B T}{2} \] (9.36)

which looks as if it is zero at absolute zero, but this is misleading. We left the zero-point energy out of the quantum mechanical expression for a particle in a box. But it is so very small (for any macroscopic box) that we can ignore it. The translational energy increases \textit{linearly} with temperature. Thus the translational heat capacity \( C_V \) is:

\[ C_{V,\text{translation}} = \frac{3Nk_B}{2} \] (9.37)

which is \textit{independent} of temperature. This isn’t correct as it is known that \( C + V \) goes to zero as \( T \) goes to zero, but that happens long after the gas has liquified.\(^{52}\)

The electronic energy is simple to calculate. It works out to be:

\[ U_{\text{electronic}} = -g_1D_e e^{\beta D_e} - g_2 e^{\beta \epsilon_2} e^{-\beta \epsilon_2} + g_1 e^{\beta D_e} e^{-\beta \epsilon_2} \] (9.38)

What is going on here is best seen by dropping the second term for a moment. We then have

\[ U^*_{\text{electronic}} = -\frac{g_1D_e e^{\beta D_e}}{g_1 e^{\beta D_e} + g_2 e^{-\beta \epsilon_2}} = -D_e \] (9.39)

in other words, the electronic energy would be a constant equal to the binding energy and independent of temperature. Of course this is a result of having \textit{no} excited level to go to. The real expression, equation 9.38 does have some temperature dependence. But it is hard to see in the equation itself. A bit of numerical exploration shows that the electronic energy is \textit{almost} constant with the contribution from increasing temperature small until \( k_B T \) gets to be about the same order of magnitude as \( \epsilon_2 \).

For this reason the electronic heat capacity is usually taken as zero unless one is either very careful or a rocket scientist.\(^{53}\)

The vibrational energy is a bit tedious to find but not difficult to evaluate as long as one uses a single trick. That depends on the fact that it is far easier to find the energy by differentiating with respect to \( \beta \) than with respect to \( T \). But equation 9.35 gives \( q_{\text{vibration}} \) in terms of \( T \), not \( \beta \). But it is easy enough to fix that. In doing so we get:

\[ \ln q_{\text{vibration}} = \ln \left[ \frac{e^{-\Theta_v/2T}}{1 - e^{-\Theta_v/T}} \right] = \ln \left[ \frac{e^{-\beta k_B \Theta_v/2}}{1 - e^{-\beta k_B \Theta_v}} \right] \] (9.40)

The vibrational energy is then:

\[ U_{\text{vibrational}} = \frac{Nk_B \Theta_v}{2} + \frac{Nk_B \Theta_v}{e^{\beta k_B \Theta_v} - 1} \] (9.41)

The first term is the zero-point energy and is usually not significant. The behavior of the second term depends on \( \beta \). As the temperature goes up, \( \beta \) gets smaller and the exponent

\(^{52}\)Except in the case of helium which is sufficiently odd as to merit its own discussion. Sadly, it won’t get it here...

\(^{53}\)No joke here. When working at the temperatures of typical exhaust gases from rockets, one must take electronic excitation into account.

\(^{54}\)And thus is left as an exercise for the reader.
approaches 0. Thus the denominator also gets closer and closer to zero with the result that the vibrational energy increases indefinitely.

This is all right, since in our model the bond never breaks and all that happens at high temperature is that more and more energy goes into vibration.

To see how this energy increases we can approximate the exponential at high temperatures (small $\beta$) by the first two terms of the series approximation for the exponential:

$$e^{\beta k_B \Theta_v} \approx 1 + \beta k_B \Theta_v = 1 + \frac{\Theta_v}{T}$$

so that the expression for the energy at high temperatures then becomes:

$$U_{\text{vibration, high}T} \approx N k_B T$$

(9.42)

Now we know that at high temperatures the vibrational energy is proportional to $T$.

But this is not the case at low temperatures. There $\beta$ is large and so the 1 can be neglected in comparison to the exponential in the denominator. And the zero point energy cannot be neglected. So at low temperatures we end up with:

$$U_{\text{vibration, low}T} \approx \frac{N k_B \Theta_v}{2} + e^{-\Theta_v/T}$$

(9.43)

so the second term disappears exponentially until only the zero point energy is left.

The vibrational heat capacity is not too hard to find. Here one does want to differentiate with respect to $T$, so equation 9.41 should be converted to $T$ notation:

$$U_{\text{vibrational}} = \frac{N k_B \Theta_v}{2} + \frac{N k_B \Theta_v}{e^{\Theta_v/T} - 1}$$

(9.44)

Now differentiating with respect to $T$ gives:

$$C_{V,\text{vibration}} = N k_B \left( \frac{\Theta_v}{T} \right)^2 \frac{e^{-\Theta_v/T}}{(1 - e^{-\Theta_v/T})^2}$$

(9.45)

As is shown in the text, at high temperatures this becomes:

$$C_{V,\text{vibration, high}T} \approx N k_B$$

(9.46)

which is constant.

At low temperatures things are a bit different. Here $\Theta/T$ is very large and the constant 1 in the denominator of equation 9.45 can be neglected. We then end up with the low-temperature heat capacity

$$C_{V,\text{vibration, low}T} = N k_B \left( \frac{\Theta_v}{T} \right)^2 e^{-\Theta_v/T}$$

(9.47)

which goes to zero exponentially.

Last we have the rotational energy. This is quite simple. The rotational energy is given by:

$$U_{\text{rotation}} = \frac{N k_B T}{2}$$

(9.48)
for each rotational degree of freedom. The heat capacity is then very simple:

$$C_{V,\text{rotation}} = \frac{Nk_B}{2}$$ (9.49)

In summary then the energy of a diatomic molecule with two rotations and one vibration is:

$$U = \frac{3Nk_B}{2} + Nk_B \left( \frac{\Theta_v}{T} \right)^2 e^{-\Theta_v/T} + \frac{2Nk_BT}{2}$$ (9.50)

where the terms are in the order translation, vibration, and rotation and the electronic contribution has been left out.

At high temperatures we end up with:

$$U_{\text{high}T} \approx \frac{3Nk_B}{2} + Nk_BT + \frac{2Nk_BT}{2} = \frac{7Nk_B}{2}$$ (9.51)

while at low one we get:

$$U_{\text{low}T} \approx \frac{3Nk_B}{2} + Nk_B \left( \frac{\Theta_v}{T} \right)^2 e^{-\Theta_v/T} + \frac{2Nk_BT}{2}$$ (9.52)

which is approximately

$$U_{\text{low}T} \approx \frac{5Nk_B}{2}$$ (9.53)

So the energy of a diatomic molecule goes (roughly) from $5RT/2$ per mole to $7RT/2$ per mole as the temperature rises.

Heat capacities follow the same scheme. The total heat capacity of a diatomic molecule is:

$$C_V = \frac{3Nk_B}{2} + Nk_B \left( \frac{\Theta_v}{T} \right)^2 \frac{e^{-\Theta_v/T}}{(1 - e^{-\Theta_v/T})^2} + Nk_B$$ (9.54)

These are also in the order translation, vibration, and rotation. At high temperatures we have:

$$C_{V,\text{high}T} \approx \frac{3Nk_B}{2} + Nk_B + Nk_B = \frac{7Nk_B}{2}$$ (9.55)

and at low temperatures:

$$C_{V,\text{low}T} \approx \frac{3Nk_B}{2} + Nk_B \left( \frac{\Theta_v}{T} \right)^2 e^{-\Theta_v/T} + Nk_B$$ (9.56)