

Chapter 33

33 Speeds and Systems

2.2.4, 2.3.1

We found in our last lecture that v_{rms} is a nice average kind of speed that tells us in bulk how our molecules are moving. But surely if we have an average speed, some molecules are moving more slowly and some are moving more quickly. Can we say how many molecules have a particular speed? We will take on this problem in this lecture.

We will also consider energy conservation in thermodynamic processes. In thermodynamics, conservation of energy is known as the first law of thermodynamics.

Fundamental Concepts

- The number of molecules that have a specific speed in an ideal gas is given by the Maxwell-Boltzman distribution $N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}}$
- We characterize a gas by giving the v_{rms} , the average speed \bar{v} , and the most probable speed v_{mp}
- Thermodynamic systems are just the part where we want to know state it's variables P , V , n , and T . All the material and space around the system is called the surroundings.
- We think of quasi-static processes in thermodynamics and would prefer reversible processes.

33.1 Speed of molecules

The internal energy of a system might consist of nuclear internal energy, or chemical internal energy, but let's reserve those internal energies for our Prin-

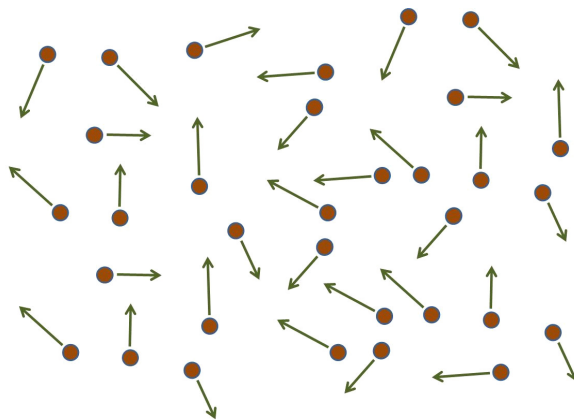
ciples of Physics IV course. For us, internal energy is mostly due to the motion of the molecules in the system. That motion has kinetic energy associated with it. But not a kinetic energy of the whole system moving together. It is a kinetic energy of the parts of the system, the molecules. Think of driving a car. We could describe the kinetic energy of the whole car. That is the kinetic energy we learned about in PH121. But we could also talk about the kinetic energy of one of the pistons in the engine. These two kinetic energies would be different! Just like this, the kinetic energy of the molecules will be different than the kinetic energy of the system as a whole.



To find this kinetic energy of the molecules, we would need to know how fast the molecules are going in an ideal gas at a particular temperature and pressure in a particular volume. Let's review a bit from our last lecture.

The average velocity is not helpful, because with our ideal gas model, the molecules move randomly. So we would guess that on the whole their velocities would cancel. If this is not true, we call the situation wind. But if there is no over-all movement, the average velocity, $\bar{\mathbf{v}} = 0$. But we know there must be movement because the molecules have some internal energy. The kinetic energy depends on the speed of the molecules. But not all molecules have the same velocity. So when we say "speed of the molecules" we have to be specific, what speed? The average? The speed the most particles have?

The average velocity won't do.



The molecule motions have random directions. So the average velocity is zero. Some velocities are in negative directions and some are in positive directions, so the velocities cancel out. But if we square the velocities they are all positive. Then we could find the average of the squared velocities and that would be better. But a velocity squared is not a velocity. So to get back to velocity, let's take a square root.

$$v_{rms} = \sqrt{v^2}$$

This quantity is like an average, and gives a representative value that is near the most probable speeds. We have seen this quantity before, it is the rms speed.

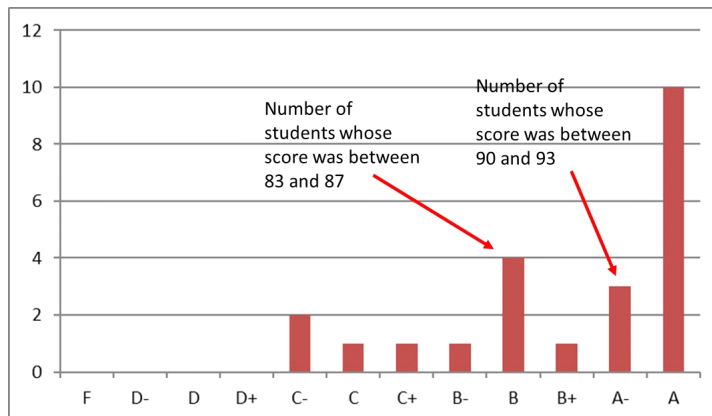
Using this, we can get an expression that relates the temperature of our gas to the speed of the molecules. But it we need to know something about how many molecules have what speed. To find the *distribution* of speeds, let's remember the idea of number density

$$n_V = \frac{\# \text{ of molecules}}{V}$$

We can express the number of molecules this way assuming we know the volume. But we want the speed of the molecules, and we have learned that concept of energy usually can get us a speed if we don't care to know the direction. Knowing the direction for every air molecule in a room would not be helpful in most cases, so we can be content with just knowing the speed. So let's find a sort of "energy density," that is, the density of molecules that have energy between two amounts of energy, say, E_1 and E_2 . We want E_1 and E_2 to be quite close together. So let's let $E_1 = E$ and $E_2 = E + \Delta E$ where ΔE is a small amount of energy. If you take quantum mechanics, or statistical mechanics, you will likely see this quantity quite a lot. Then the number of molecules with a particular energy between E_1 and E_2 could be written as

$$n_V(E) dE = \frac{\# \text{ of molecules with energy between } E \text{ and } E + \Delta E}{V} \quad (33.1)$$

This is called a *distribution function*. We find distribution functions in statistics. They are associated with probabilities. The standard “bell curve” used sometimes in grading is a distribution function. It tells the total number of students that got a particular number of points in a class. Think of grades on a test. If we plot the grades, the height of the bar for a “B” grade is the number of students that scored between 83% and 87%.



This graph is a distribution of grades and it tells us for each score segment, say S and $S + \Delta S$ (think 83% and $83\% + 4\% = 87\%$) how many students had scores in that range. We are doing the same for our molecules and their energy. We will make a graph that shows for each energy segment from E to $E + \Delta E$ how many molecules have that energy. This gives us the probability that the molecules will have a particular energy (or speed, since this is kinetic energy). A function that gives the amount of molecules that have a particular amount of energy also is called a *distribution function* just like it was for grades. The distribution function that we will use is written symbolically in this cryptic fashion, $n_V(E)dE$. It is the number of molecules with a particular energy (because our ΔE is so small it is a dE) divided by the total number of molecules. That make is like a percent.

We won't derive an equation for this quantity, instead we will borrow a result from our junior level thermal physics class.

$$n_V(E) = n_E e^{-\frac{E}{k_B T}} \quad (33.2)$$

where $n_E dE$ is the number of molecules per unit volume having energy between $E = 0$ and $E = dE$. This distribution function is called the *Boltzmann distribution law*. It tells us that the probability of finding the molecules in a particular energy state varies exponentially as the negative of the energy divided by $k_B T$.

33.2 Distribution of Molecular Speeds

Since there is a distribution of energies, we expect our gas molecules to have a distribution of velocities. That is the same as saying the molecules in the gas

do not all go the same speed. Again we won't derive this (at least not in this class!), but the distribution should depend on temperature, T , since we know the internal energy is tied to temperature. The distribution is as follows:

$$N_v(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}} \quad (33.3)$$

where m is the mass of the molecule. The kinetic energy of the molecules is hiding in the exponent, so we could write this as

$$N_v = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{K}{k_B T}} \quad (33.4)$$

Note that this is of the form for our distribution function because for an ideal gas the only internal energy we have is kinetic energy, $E = K$ so we have $E/(k_B T)$ as the exponent. So we used this to turn our energy distribution function into a speed distribution function.

If there are dN molecules with speeds between v and $v + dv$ then

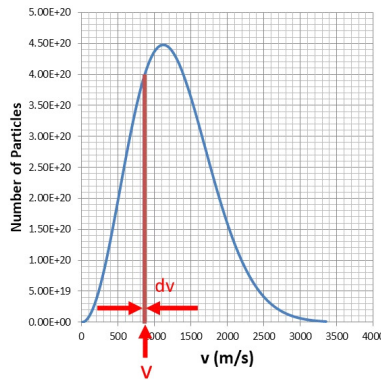
$$dN = N_v dv \quad (33.5)$$

so there should be

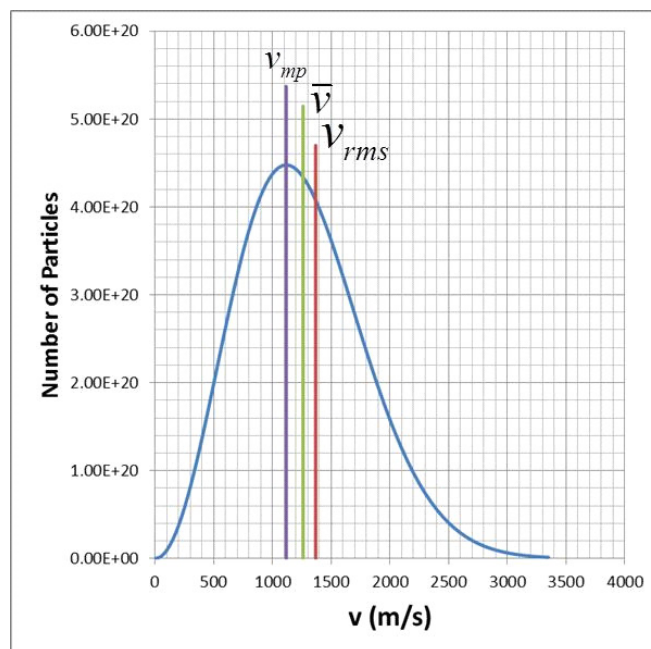
$$N = \int_0^\infty N_v dv \quad (33.6)$$

total molecules. This tells us that the $4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}}$ is a *normalization constant* that makes sure our integral of $N_v dv$ gives us N , the total number of particles.

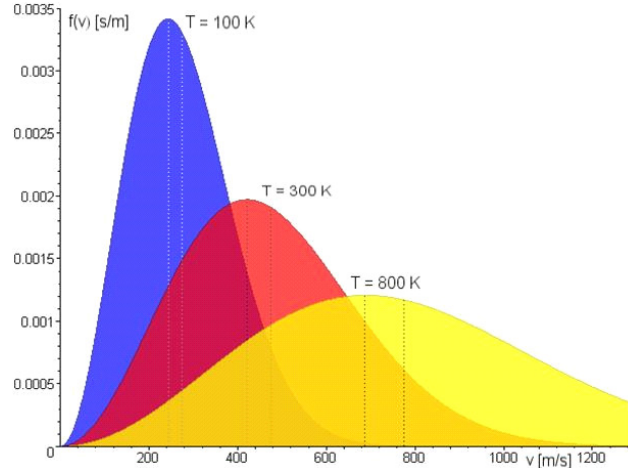
If we plot N_v vs. v we get the figure below. We get a plot that is a little like our grade distribution plot, only for molecular speeds. The number of molecules with speeds between v and $v + dv$ is the area under the blue curve at v . It would be the area of the thin red rectangle right at v with width dv shown in the next figure.



The peak of the curve tells us the most probable speed, that is, the speed the most molecules have, v_{mp} (like in our grade example, the most students got an “A” because that bar was the tallest). The curve is not symmetric, so the most probable speed is not the average speed, \bar{v} . There is also our new speed estimate marked v_{rms} .



If we plot N_v for different temperatures, we observe that the peak shifts, and the curve broadens



Temperature dependence of the Maxwell-Boltzmann distribution (Image in the Public Domain courtesy Fred Stoer)

A motivated student could now find the most probable speed by finding the maximum of N_v . We know from our calculus experience how to find a maximum. We take a derivative

$$\begin{aligned}
 \frac{dN_v}{dv} &= \frac{d}{dv} \left(4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}} \right) \\
 &= 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \frac{d}{dv} \left(v^2 e^{-\frac{mv^2}{2k_B T}} \right) \\
 &= 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \frac{d}{dv} \left(v^2 \frac{d}{dv} e^{-\frac{mv^2}{2k_B T}} + e^{-\frac{mv^2}{2k_B T}} \frac{d}{dv} v^2 \right) \\
 &= 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \left(-2 \frac{m}{2k_B T} v^3 e^{-\frac{mv^2}{2k_B T}} + 2v e^{-\frac{mv^2}{2k_B T}} \right) \\
 &= -2v e^{-\frac{mv^2}{2k_B T}} \left(4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \right) \left(\frac{mv^2}{2k_B T} - 1 \right)
 \end{aligned}$$

and set it equal to zero. I didn't spend a lot of time simplifying, because all the factors out front will go away when we set it equal to zero:

$$\begin{aligned}
 0 &= -2v e^{-\frac{mv^2}{2k_B T}} \left(4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \right) \left(\frac{mv^2}{2k_B T} - 1 \right) \\
 \frac{mv^2}{2k_B T} &= 1 \\
 v_{mp} &= \sqrt{\frac{2k_B T}{m}}
 \end{aligned}$$

$$v_{mp} = \sqrt{\frac{2k_B T}{m}} \quad (33.7)$$

and this is great! We have related the temperature, T , to the most probable speed of the molecules. But it is more convenient to use v_{rms} , so let's see if we can modify this expression to be in terms of v_{rms} . And it gives us some insight into using a distribution function.

The average value of v^n is given by

$$\overline{v^n} = \frac{1}{N} \int_0^\infty v^n N_v dv$$

Think of this as summing up v^n but using the fact that we already know that for each v there are $N_v dv$ molecules with speed v . So our distribution function makes the integral easier. That motivated student could also use this to find the average speed (not the average velocity, which is zero). He or she will want the average value of v^1

$$\begin{aligned} \overline{v^1} &= \frac{1}{N} \int_0^\infty v^1 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}} dv \\ &= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv \end{aligned}$$

You might be thinking that this integral looks a little hard to do. You would be right. You could use a symbolic math program to do this. Or you can dust off your second semester calculus knowledge. I prefer the symbolic math program, but let's do it the calc II way here. Looking just at the integral

$$\int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv = \int_0^\infty v^2 e^{-\frac{mv^2}{2k_B T}} v dv$$

Let's do a substitution. let $x = v^2$, $dx = 2v dv$ and $a = -\frac{m}{2k_B T}$ then we have

$$\int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv = \int_0^\infty x e^{ax} dx$$

and now we have one of those many integration identities that you memorized (and now have forgotten) from Calc II. So we look in an integral table and find

$$\int_0^\infty x e^{ax} dx = \frac{e^{ax}}{a^2} (ax - 1)$$

This matches our integral that we need. We now know the answer. We just have to undo our substitution.

$$\begin{aligned}
\int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv &= \frac{e^{-\frac{m}{2k_B T} v^2}}{\left(\frac{m}{2k_B T}\right)^2} \left(\left(-\frac{m}{2k_B T}\right) v^2 - 1 \right) \Bigg|_0^\infty \\
&= \left[\frac{e^{-\frac{m}{2k_B T} (\infty)^2}}{\left(\frac{m}{2k_B T}\right)^2} \left(\left(-\frac{m}{2k_B T}\right) (\infty)^2 - 1 \right) \right] - \left[\frac{e^{-\frac{m}{2k_B T} (0)^2}}{\left(\frac{m}{2k_B T}\right)^2} \left(\left(-\frac{m}{2k_B T}\right) (0)^2 - 1 \right) \right] \\
&= 0 - \left[\frac{1}{\left(\frac{m}{2k_B T}\right)^2} \left(\left(-\frac{m}{2k_B T}\right) (0)^2 - 1 \right) \right] \\
&= \frac{1}{\left(\frac{m}{2k_B T}\right)^2}
\end{aligned}$$

And we can put our result back in our equation for $\overline{v^1}$

$$\begin{aligned}
\overline{v^1} &= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty v^3 e^{-\frac{mv^2}{2k_B T}} dv \\
&= 2\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \left(\frac{1}{\left(\frac{\pi m}{2\pi k_B T}\right)^2} \right) \\
&= 2\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \left(\left(\frac{m}{2\pi k_B T}\right)^{-\frac{4}{2}} \pi^{-2} \right) \\
&= 2\pi \left(\frac{m}{2\pi k_B T} \right)^{-\frac{1}{2}} (\pi^{-2}) \\
&= 2 \left(\frac{2\pi k_B T}{m} \right)^{\frac{1}{2}} (\pi^{-1}) \\
&= \sqrt{\frac{8k_B T}{\pi m}}
\end{aligned}$$

so

$$\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$$

which is also great, but not what we wanted. But it is close. This time let's find the average value of v^2 . We hinted that the root mean squared value would be useful. that is, $\overline{v^2} = v_{rms}$. We can find this like we found the average velocity

$$\begin{aligned}
\overline{v^2} &= \frac{1}{N} \int_0^\infty v^2 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}} dv \\
&= 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty v^4 e^{-\frac{mv^2}{2k_B T}} dv
\end{aligned}$$

But the math is a bit more cumbersome. Let

$$a = \frac{m}{2k_B T}$$

Then we have

$$\overline{v^2} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty v^4 e^{-av^2} dv$$

It is time to look up our integral in a table of integrals. My table tells me that

$$\begin{aligned}
\int x^4 e^{-ax^2} dx &= -\frac{1}{8a^{\frac{5}{2}}} \left(6\sqrt{a} x e^{-ax^2} - 3\sqrt{\pi} \operatorname{erf}(\sqrt{a}x) + 4a^{\frac{3}{2}} x^3 e^{-ax^2} \right) \Big|_0^\infty \\
&= -\frac{1}{8a^{\frac{5}{2}}} (-3\sqrt{\pi})
\end{aligned}$$

The quantity $\operatorname{erf}(\sqrt{a}x)$ is called the “error function.” If you study this function in a good mathematical book on integration you will find that

$$\operatorname{erf}(\sqrt{a}\infty) = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-t^2} dt = 1$$

so

$$\overline{v^2} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \left(-\frac{1}{8 \left(\frac{m}{2k_B T} \right)^{\frac{5}{2}}} (-3\sqrt{\pi}) \right)$$

or

$$\overline{v^2} = 3 \frac{T}{m} k_B$$

now recognize that $v_{rms} = \sqrt{\overline{v^2}}$ so

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} \quad (33.8)$$

and this is what we wanted. We have an expression that relates the temperature of the gas to the *rms* speed of the molecules of the gas. And you might object that we have already seen this form for v_{rms} and it was much easier to find last time! But it is worth seeing that our distribution of molecular speeds produces this result. It gives us confidence in our distribution function. Notice that, indeed, v_{rms} is close to the average and most probable speeds.

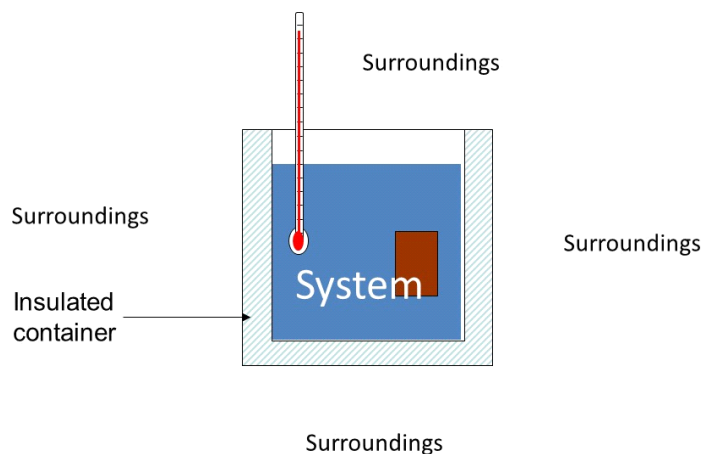
That we have some speeds higher than others explains why things do not evaporate or all boil away at once.

A few rms Speeds for Gasses		
Gas	Molar Mass (kg/ mol)	v_{rms} at 20 °C (m/ s)
H ₂	2.02×10^{-3}	1902
He	4.0×10^{-3}	1352
H ₂ O	18×10^{-3}	637
N ₂	28×10^{-3}	511
O ₂	28×10^{-3}	478
CO ₂	44×10^{-3}	408

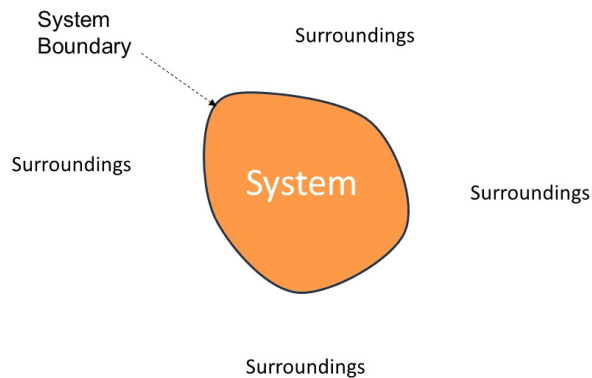
Armed with a molecular model for gasses, let's return to our state variables for a system and see how to find the state variables for different thermodynamic processes. Let's start this by looking at some special ways to change thermodynamic systems.

33.3 Thermodynamic systems

We are going to talk a lot about thermodynamic systems. But what is a thermodynamic system? It is just the group of material that we care about, that we want to know the state variables of in our problem or experiment. In our calorimetry problems we had an insulated container. The stuff in the container was our thermodynamic system and the container and air and table and room and everything else around the container is what we call the surroundings.



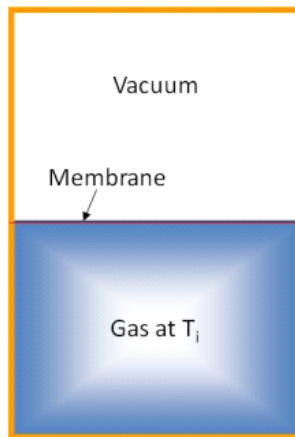
We could draw a more general picture of a thermodynamic system



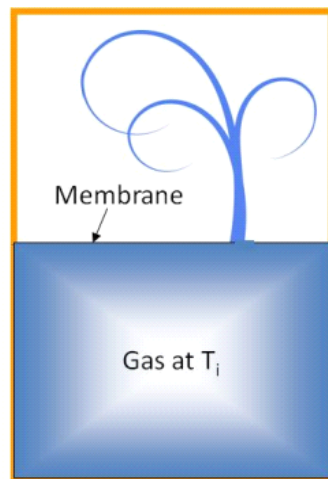
In our first system example we had an insulated container. That insulation prevents energy transfer by heat, and if it is ridged it prevents energy transfer by work. But this is a special case. We call such a system a *closed system*. But most thermodynamic systems do exchange energy with their surroundings. We call them *open systems*.

In our problems, we generally think of the material inside of our system as being in thermodynamic equilibrium. This is not always the case.

Consider the situation shown below



We have a gas in one side of a sealed container and a vacuum on the other side. A membrane separates the two. We have a very definite temperature in the gas, and also a definite temperature in the vacuum. But if I puncture the membrane,



gas goes swirling into the vacuum. The density will not be constant as the gas swirls. Where there is gas, we would say we have a temperature closer to T_i . But where there is no gas, we have a temperature nearer 0 K. It takes a while for the gas to come to equilibrium. During this process we can't say that we have a definite temperature, or definite pressure for the system. Higher physics classes (and engineering classes) deal with the difficult situation that exists before equilibrium is achieved. For now, we will only look at situations that have reached an equilibrium, or are not too far from equilibrium. We call states that change slowly so they are never far from equilibrium, *quasi-static*. The situation we have just described is called a *free expansion* because the gas is allowed to expand with no outside influences. A free expansion is *not* a quasi-static process. Let's think of how we might make a quasi-static process happen.

33.4 Reversible and Irreversible Processes

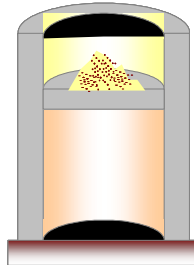
A reversible process is one in which every point along some path is an equilibrium state and one for which the system can be returned to its initial state along the same path.

All natural processes are known to be irreversible. Reversible processes are an idealization, like frictionless surfaces or massless strings. But some real processes are good approximations to reversible processes.

Our free expansion, of course, is not a reversible process. Imagine trying to get all the gas atoms back through the hole in the membrane!

We could try to put the gas back into a smaller volume by putting a piston in the system and applying a force. We would be transferring energy by work. This would increase the temperature, so we would have to let energy transfer out of the system (by heat) to keep the temperature the same. This would allow the system to return to its final state, but the surroundings will have changed.

We will have heated up the surroundings. This is not a reversible process!
But suppose we apply our force on our piston in a quasi-static way.



Imagine dropping sand on a frictionless piston to compress a gas. Then slowly removing the sand. The system stays almost in equilibrium as it changes, so that it returns to a new equilibrium right away. After all, you only moved one grain of sand at a time. This process is almost reversible. Of course, you still have to do work in moving the sand, so the outside environment is changed, so even this process is not truly reversible. But it is a good mental model for the sort of processes we will study in this class; slow, almost in equilibrium all the time.

For our quasi-static process we can say we stay in thermodynamic equilibrium. Recall that we have one “law” of thermodynamics. The zeroth law. It tells us that if two objects are in thermodynamic equilibrium they have the same temperature. From what we have done in this and the last lecture we now see this zeroth law is telling us about forces and collisions between molecules. When the molecules of the two objects have the same average kinetic energy, no net energy is transferred between them and this is thermodynamic equilibrium.