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5.112 Principles of Chemical Science, Fall 2005
Transcript – Lecture 13

Good afternoon.

I hope you had a nice weekend. Did you have a nice weekend? Good.

Today we are going to start talking about the motion of molecules. We are first going to talk about the translational motion of molecules today and Friday.

And then we are going to talk about the internal motion, in particular the vibrational motion of molecules and their rotational motion. That will be early next week. First translational motion.

Certainly, the quintessential equation that represents the behavior of gases is, of course, the ideal gas law $P = n/V \times RT$.

This equation accurately represents the behavior of gases at low pressures. It is an empirical law, of course. It is a law that Boyle and Charles discovered by doing experiments.

They noted that as the temperature is raised the pressure went up.

They noted as the amount of gas or the number of moles of gas added goes up, the pressure goes up. They noted as the volume of their gaseous container goes up, the pressure goes down. Literally, this is an equation established by experiment and just bearing one variable at a time.

And since it looked like the pressure was directly proportional to the temperature they wrote an equation where it was directly proportion to the temperature, etc.

And the proportionality constant here was always this one constant R no matter what gas you had. But this ideal gas law describes the macroscopic properties of a gas.

And what I mean by macroscopic properties are properties that describe a collection of molecules.

For example, to really talk about a pressure you have to have a collection of molecules. We are going to talk about the pressure due to one molecule, but that is really just a model. If you want to talk about pressure you need to have a collection of molecules.

If you talk about temperature, it really only has meaning when you have a collection of molecules.

But what we want to understand is what are the underlying microscopic phenomenon that gives rise to this macroscopic equation or these macroscopic properties. We want to know what is going on in terms of the behavior of the individual particles, the individual molecules that make up this gas.

Inquiring minds want to know what the temperature means when we talk about individual molecules.

And that is also what Maxwell and Boltzmann wanted to know. They wanted a microscopic explanation for $Pv = nRT$. And, to do so, they put forth a theory called the Kinetic Theory, or the kinetic theory for the behavior of gases.

And that is exactly what we are going to take a look at here, this kinetic theory.

We are going to do what they did. Basically, this kinetic theory allowed properties of gases at low pressures to be predicted, and it allowed an understanding of why some of the properties of real gases at higher pressures deviated from this ideal gas law.

But, more importantly, what it did was allowed the quantity, pressure times the volume, to be understood in terms of the motions of the molecules.

And it provided a means to understand this concept of a temperature in terms of the motions of the molecules. And that is what we are going to look at today. We are going to see how we can describe pressure and volume in terms of the motion of the molecules and temperature in terms of the motion of the molecules.

That is our goal.

In order to do that, the first thing we have to do is to understand what we mean by pressure. For example, if you have some gas here in a container and you are measuring the pressure of this gas in that container --

What you are really measuring is the force that the gas exerts on one of the walls of this container.

That is pressure is the force exerted by the gas on one of these walls. It is the force per unit area that is exerted on the walls of that container. That is what pressure is. But what Maxwell did --

And this is 1850, 1855.

What Maxwell did was recognize that he could understand this macroscopic pressure in terms of the individual forces of the molecules when they hit the container. In other words, he proposed that this gas was composed of these molecules and that these molecules were moving.

That was his proposal.

And that when they moved and hit the walls of the container, well, that was the force that was exerted by the gas. In other words, the force was really the individual forces, $f_{sub\ i}$ here of the individual molecules.

That total force was the individual force of the molecules hitting the walls of the container. That is what led to this macroscopic concept, the macroscopic quantity of pressure. That was his idea.

Well, if that was his idea, he carried it through now to a prediction. The idea is this force arises from the individual forces of these individual molecules hitting the walls of the container.

Let's look at what theory he wrote down.

His goal here was to calculate these individual forces $f_{sub\ i}$.

And, of course, go back to classical mechanics.

Force is the mass times the acceleration, the mass of the particle, the molecule times its acceleration. And acceleration we can write just in

terms of Δv over Δt . That is just the mass times Δv over the change in time.

And if the mass is constant here, this numerator, that is the change in momentum per unit change in time.

That is what this force is. What we have to do here is calculate the change in the momentum of the wall when the molecule hits the wall.

That will be the force of the individual molecule in the wall, that over the time between the collisions of the molecule with the wall. That is the individual forces.

That is what we are trying to calculate right here.

Let's do that and calculate ΔP , the change in the wall's momentum. Let's do it in one-dimension first. Here is our box. This is just a cross-sectional view of that box I drew over here. And this is going to be the wall that we are going to be interested in.

The box has a length l .

And we have this molecule with some mass m . It is coming into the wall and is going to collide with it, and it has some velocity vector v . But let's do it in one-dimension because it is simpler to do.

And then we are going to extend it to three-dimensions in a few minutes. We are just going to do it in one-dimension now.

We are only going to be interested in then the x component of the velocity of this molecule coming into the wall, and we want to know what is the force exerted by this molecule when it collides with this wall.

First we have to get the change in the momentum. This molecule comes in and hits the wall, and we are going to consider it to be an elastic collision.

If the component of the velocity in the x direction before the collision is v_x then after the collision it is $-v_x$.

We have just changed the direction of our velocity vector, not the magnitude. The change in the atom's momentum then is just the

momentum after minus the moment before. The momentum after was m times minus v sub x .

The momentum before m sub v sub x .

Delta, in the change in the atom's momentum, is minus $2mv$ sub x . However, we have to conserve momentum. The momentum change in the atom, plus the momentum change in the wall has to equal zero. And what we want to know is the momentum change in the wall because we are after this macroscopic quantity pressure.

And so, if the change in the momentum of the atom is minus $2mv$ sub x then the change in the momentum of the wall is $2mv$ sub x .

We have one quantity here. We have delta p . But now we have to calculate how often that momentum in the wall changes due to this molecule's collisions.

We need the delta t . And so, what happens here? The molecule comes in, collides and then reflects.

And the molecule is now going in this direction where it hits the back wall and reflects. And then ultimately it comes back and hits the front wall. And what we want to know is what is the time here between the collisions.

The time between when that molecule makes the momentum in the wall change.

What is this time delta t ? Well, if we know the length of the box and we know the value of v sub x , we can calculate that time. That time is just two times the length of the box because that molecule is traveling back and then forth.

That is $2l$ divided by the velocity component in the x direction, v sub x .

That is delta t . Now we have delta p and delta t , and we can plug that in and make it simple a little bit. And so, here is the force exerted by the collision of one molecule on that one wall of the container, mv sub x squared over l .

But we said that Maxwell's idea was that the macroscopic total force was the sum of these individual forces.

What we have to do is take the force of each individual molecule and add them up over all the molecules. There is that force for molecule one, molecule two, molecule three, all the way up to molecule n .

I am going to pull out an m over l out of this.

I just pull out an m over l , and I have left the sum of the squares of the velocities in the x direction for each one of the molecules. Notice here, in this treatment, we have identical m 's. The particles are the same, but, and this is important, the velocities of the molecules are not the same.

That is going to be important.

Now, this expression here, I want to simplify a little bit. In particular, I want to simplify the sum of the squares of the velocity components in the x direction for each one of the molecules. To do that simplification, I am going to introduce this quantity.

This quantity is the average of the square of the velocity in the x direction.

What this means is I take the velocity in the x direction, square it and then I take the average. This is not the square of the average velocity in the x direction. That is different. This is the average of the square of the velocity in the x direction.

How am I going to evaluate that quantity? Well, I am going to take the velocity in the x direction for molecule one and square it and add to that the square of the velocity in the x direction for molecule two and add to that the square of the velocity in the x direction for molecule three all the way up to molecule n .

And then, if I want the average, I am going to divide by n , the number of molecules there are. I am just going to bring n here over to the other side. I have n times the average of the velocity in the x direction squared as this sum, and this is exactly the sum that I had in my expression for the total force.

I can simplify that now.

There is that same expression. Here is my total force. What I am going to do is substitute n times the average of the velocity in the x direction

squared in for this whole sum, and I have now something that is much tidier.

That is the total force exerted by all the collisions of the molecules in the container on that front wall.

But now I want the pressure. And the pressure is just force per unit area. And so, I am going to take my expression for the force and divide it by the unit area.

The area is the area of this wall here in my initial example. I am going to call that area a .

And if this is a q , and I am going to make it a q because it is easier to do it that way, the area times the length then of this box is just the volume.

Here is the volume. There is my expression for the pressure due to all of the molecule colliding with the front wall of that box. However, this is an expression for the pressure in one dimension only, the x dimension.

And we know, in real life, we have three dimensions.

We have to take care of that. Let's do that now. Let's extend this problem to three dimensions. To do so, I am just going to realize right here that the square of the velocity is the sum of the squares of the components.

That you understand.

That is OK. What is not so obvious is this. The average of the square of the velocity is the sum of the average of the squares of each one of the components. That is true. You can prove that.

We are not going to prove that. I won't hold you responsible for proving that, but it is true.

That is correct, but now here comes a critical assumption in Boltzmann's treatment. The critical assumption is that the motion of the molecules in this gas here is random in the sense that the molecules don't have a preferred direction.

They are going in the x direction as often as they are going in the y direction as often as they are going in the x direction, so the motion is random.

If that motion is random then the average of the velocity squared in the x direction is going to be equal to that in the y direction.

It is going to be equal to that in the x direction if that motion is random. And that is great because it is going to make things a little simpler for us up here. If that is right then the average of the velocity squared is three times the average of the velocity squared in any one of the dimensions.

That is going to make it easy to extrapolate this to three dimensions because now I am going to be able to substitute, which had the average of the velocity squared only in the x direction, in an expression for the average velocity in three dimensions.

That is just going to be one-third that.

This is going to be one-third the average of the velocity squared. That is great. Now I am going to do that substitution way up into there. And when I do that look at this.

I have a result. This is the kinetic theory result.

We just did exactly what Maxwell did. We have an expression for the pressure times the volume, which is written here in terms of the average of the velocity squared of the molecules. It is written in terms of the motion of the molecules.

For the first time there is an understanding here of what gives rise to pressure, and that is the velocity or the motion of these molecules hitting the wall.

That is great. That is the kinetic theory result. But now Boltzmann also knew from experiment that p times v is equal to nrt . That is the experimental result which had been known already for over a hundred year.

That is the experiment.

If his theory is correct, if p times v is equal to n times m average velocity squared over three, it better be equal to nrt . That will give us here a prediction

for what the velocity of the molecules ought to be in terms of something experimentally controllable.

We can see if this kinetic theory model is correct.

We can solve this for the average of the velocity squared. It is equal to $3nrt$ over m . We can go in the laboratory, vary t and see if, in fact, the average of the velocity squared of the molecules is equal to this expression here.

That is great.

We have a way to experimentally check this theory. And you also see here now a relationship between the velocity of the molecules and this macroscopic quantity temperature. Temperature is related to the motion of these molecules.

But, before we go on, this is kind of a messy expression here.

It has too many n 's and m 's in it. Let me simplify that a little bit for you. I am going to simplify this so that this is $3rt$ over capital M where the following is true.

Over here n is the number of moles in the gas.

That is little n . Big N was the number of molecules in the gas. Little m was the mass per molecule. All of this is equivalent to one over big M where big M was kilograms per mole. You can convince yourselves of this equality.

I am taking all these n 's and m 's and making one big M .

That is my expression here. I have the average of the velocity squared equal to $3rt$ over m . But this quantity is the average of the velocity squared.

It is more convenient for us to talk about a quantity proportional to the velocity and not the velocity squared.

What I am going to do is take the square root of it. That is simple. I now have the square root of the average of the velocity squared.

That is the square root of $3rt$ over m . I am going to call that the root mean square velocity. I am going to put an rms here as a subscript for

the velocity. It is the root mean square velocity. I wanted to talk about a quantity proportional to the velocity instead of the velocity squared.

That is all I did there.

That is the root mean square velocity. But the other big thing about it here is you can see, for the first time, now we have, and Maxwell had, an understand of what temperature was. Temperature is related to the motions of the molecules.

Temperature is related, in this way, to the speed of the molecules.

Those are the two important results. And this kinetic theory makes a prediction for what those velocities ought to be.

In addition, the temperature is a measure of the kinetic energy of the molecules.

How is that? Well, it is for this reason. Here is the expression we derived from the kinetic theory. And then here is an expression that I just wrote down that says the average kinetic energy of a molecule is $\frac{1}{2}m\overline{v^2}$ where m is kilograms per mole times the average of the velocity squared.

If I substitute the average of the velocity squared into here, I get three-half rt .

This is telling us right here that the temperature is also a measure of the kinetic energy of these molecules. We are getting a microscopic view here of what temperature is.

It is related to the motions of these molecules.

Now, before I go on talking about this, let me make one big point. That is, this expression here, for the average energy, notice that it is one-half m times the average of the velocity squared. It is not one-half m times the square of the average velocity.

This is important.

The average energy is not the square of the average velocity. Rather, the average energy is the average of the velocity squared. There is a big distinction. This is because the average energy is the second moment of the velocity distribution function.

Variables don't always correspond in a one-to-one manner.

You don't have to understand that, if this is foreign to you, but I do want you to know this is correct. Now let me pick up back here. What I want you to notice is that the root mean square velocity has a mass dependence in it.

What does that mean? Well, it means the following.

For some constant temperature, say we pick 300 degrees kelvin, the velocity of the molecule is going to depend on its mass. And it is inversely proportional to the mass, so heavier molecules move more slowly, lighter molecules move more quickly.

For example, helium at 300 degrees kelvin, it is cruising along at 3060 mph at room temperature.

Xenon, on the other hand, which is much more massive, is moving at a measly 534 mph. There is a mass dependence here.

However, there is no mass dependence to the kinetic energy. The kinetic energy we saw was three-half RT . You don't see a mass dependence in here, do you?

The kinetic energy is only dependent on the temperature.

Whether or not you have helium or xenon, the kinetic energy of those atoms is 3.74 kilojoules per mole at 300 degrees kelvin. It does not matter that helium is moving six times as fast as xenon. They both have the same kinetic energy.

There is no mass dependence in kinetic energy.

Now you say, oh, but look at this, here is a mass, there is a mass dependence. No, because you have to remember that you substitute in here. If you square this, there is an m here and that cancels.

There is no mass dependence in the kinetic energy, but the velocity is dependent on the mass.

That is important. Well, I told you that this was the kinetic theory result. That is, that the root mean square velocity of these molecules was represented by this equation.

And, from this equation, if you calculate at 300 degrees kelvin these are, in fact, the velocities of those atoms.

But how do we know this is right? How do we go and measure the velocities or the speeds of molecules or atoms? Well, this is the way we do it.

It is called the time-of-flight technique. Are we all onboard here? Questions? OK. How are we going to do this time-of-flight technique? What we are going to do is have a little pinhole here that we can open and shut really quickly.

We are going to let out a little pulse of gas.

To measure the velocity of the molecules, we are literally going to measure the time it takes the molecules to fly from where we let them out to some detector. And since we know the distance, we are going to be able to calculate the velocity from that.

The idea is at time $t=0$ we let out a little pulse of gas, and then we start a clock running.

Then we just measure how long it takes the molecules to fly from this origin here to this detector. And since we built the apparatus and know what l is, we can calculate the velocity. Time of flight, that is what is done.

However, when we let this little pulse of gas out and now we let the molecules fly to that detector over here, what happens as a function of time? What will happen is that pulse of gas will spread out because not all of the molecules or atoms in that pulse of gas have the same velocity.

Some of those atoms are moving faster than the other atoms.

And so, what is going to happen is that the molecules or atoms that are moving faster are going to hit the detector first. The molecules or atoms that are moving more slowly are going to hit the detector at a later time.

And that is what we also want to know, this distribution of velocities. But in the measurement, what we are going to measure is a distribution of times.

Out of our detector we are going to have a plot that looks like this.

This is going to be f of t , essentially the number of molecules hitting the detector at a certain time t versus the time. When we first let our pulse of gas out, that is time $t=0$. Then for a while there are no molecules hitting the detector because it takes a while for them to get over here to this detector.

But then all of a sudden they start reaching the detector.

And this is essentially just a number of molecules that hit the detector as a function of time. That number of molecules increases and becomes a maximum here at some time, and then it exponentially decays here.

So, this is what we measure. This is a distribution here of flight times of the molecules in this pulse of gas.

Well, that is nice, but this is a distribution of flight time. It is not a distribution of velocities, and we wanted a distribution of velocities.

We want to know the velocity here of these molecules. You know how to convert time given the path length to velocity, but it is not so straightforward because we have a distribution function.

We have a distribution in time, and we want to convert that to a distribution in velocity.

We have to change the variable here in a distribution function. How do we do that? Well, we want this f of t to be an f of v . We recognize here that this distribution in time, the probability of finding a molecule between t and t plus dt has got to be equivalent to the probability of finding a molecule with a velocity between v and v plus dv .

But to get from one distribution function to another, for example, if we want f of v , what we have to know is how one variable changes with respect to another.

We have this distribution function f of t , but we need to know how t changes with v .

We need vt by dv , and I will tell you why in a moment. We know how v changes with t . We are going to take the derivative of v with respect

to t and turn things around. So, dt/dv is proportional to minus t squared over l .

This is telling us essentially how the variable t changes with v .

To every point in our time-of-flight distribution, we are going to multiply this by what is called the Jacobean. We need this because the time and the velocity do not correlate in a one-to-one manner.

That often happens with two distribution functions.

If you do not understand what I just said, it is OK. This was just some extra. I do not hold you responsible for it. I just changed my variable in the distribution function.

Yes? I think in the notes, I might have had as a proportionality. Up here I actually have the equal sign.

That actually won't matter in this transformation. Pardon? I understand that. That is fine.

I don't have the equal sign there. That is why I left it out there, I think. Anyway, this is the velocity distribution. You don't have to understand how I got there. This is what the velocity distribution looks like.

It is what is called the Maxwell-Boltzmann velocity distribution.

And the bottom line is that Maxwell and Boltzmann predicted this about 1855. They actually predicted this distribution function. We did not predict it. We did not go through that part of kinetic theory, but they predicted it.

However, it was only until 1955 that the technology existed, fast enough timing and electronics existed to actually measure this experimentally.

This took a hundred years or so in order for this distribution function to actually be measured, but here it is, f of v .

First of all, there is all of this stuff which is proportionality constants. We will talk about that in a moment. But the variable here is v squared times an exponentially decaying function with a v squared in there.

What does that mean? Well, if you look at the form of f of v , this v squared is what gives rise to this increase in f of v .

Right here at low velocities that is a quadratic v squared. But you are multiplying it by an exponentially decaying function with this v squared in the argument. And so that is what gives you this tail.

If you are multiplying a function that is going up and one decreasing, you are going to get a maximum at some value of v .

That is where the shape of the Maxwell-Boltzmann distribution function comes from.

And what this is telling you is the probability here of finding a molecule in a gas with a speed between v and v plus dv . That is what it is telling you.

We often characterize these distribution functions by some quantities, and one of those quantities is what we call the most probable speed.

Here is the distribution function, and I have the most probable speed labeled. The most probable speed, v_{mp} , is simply the value of v at which the probability is the largest. That was like our most probable value of r in the radial distribution functions.

That is what the most probable speed is.

If you wanted to get that mathematically, what you would do is take this distribution function, take the derivative, set it equal to zero and then solve for v . That makes that derivative equal to zero.

The derivative is zero at maxima or minima. And then you would find that the value of the most probable speed is the square root of $2kT$ over m .

You are not responsible for taking this derivative and setting it equal to zero.

You are responsible for knowing physically what the most probable speed is. The fact that it is this value here where the probability is the largest. It is the most probable value of v . And you are responsible for recognizing this.

I don't ask you to memorize it or write it down.

But, if you see it, you should know what it is. That is one quantity that we use to characterize this distribution function. Another quantity that we use is the average speed, \bar{v} , average speed.

And the first thing that you see is that the average speed is a little bit higher than the most probable speed.

It is a little bit larger. Why is that? Well, it is a little bit larger because on these Maxwell-Boltzmann distribution functions there are molecules way out here that have very high speeds.

There are not a lot of molecules that have very high speeds, but there are molecules with very high speeds. And so, when you average over this distribution function, because there is such a long Boltzmann tail here, is what it is called, the average velocity is going to be a little higher than the most probable velocity.

That is physically why the average velocity is a little bit larger than the most probable velocity.

That is important. If I wanted to calculate what the average velocity is, I would take the distribution function, multiply it by v and then integrate over the range of v , which is zero to infinity.

You don't have to do that, but the quantity that you would get, if you had done that, is the square root of 8π over πm .

It is larger than the most probable value. And then, finally, the other way we characterize the distribution function is by this root mean square speed that we have already talked about a lot. That root mean square speed here is even a larger value than the average velocity or the average speed.

And the reason for that is, again, because of this Maxwell-Boltzmann tail.

We have molecules here that have very high speeds. We don't have a lot of molecules with high speeds, but we have very high speeds. When we take that speed and square it, and then take the average, they make a big contribution and they push this root mean square speed even higher than the average speed.

Again, if you wanted to calculate what that is, you would take v squared, multiply it by the distribution function, integrate it over all values of e and you would get what we got before, the square root of $3kT$ over m .

Bottom line here, for argon at 300 degrees kelvin, the most probable speed is 353 meters per second.

For argon at 300 degrees kelvin, the average speed is 399 meters per second. And the root mean square speed is 433 meters per second.

Here you can see how these three quantities increase as you go from most probable to the root mean square speed.

And, in fact, no surprise, if you actually go and measure the argon speed distribution function and then evaluate these characteristics, you find that indeed those measurements agree with what Mr.

Maxwell and Mr. Boltzmann predicted in 1850, 1855. No surprise.

Back to this distribution function. We saw how to characterize it, but I want to talk about a couple of other parameters that it has in it.

It has in it the mass and it has it in the temperature. Let's talk about what this distribution function looks like for different masses and different temperatures. That is the general form but different masses and different temperatures.

Let's start by keeping the temperature constant, 300 degrees kelvin.

And now we are going to look at the distribution functions for three different masses, and I am going to plot that. Here it is for xenon. What you can see is xenon, very narrow distribution. Here it is for argon, lighter mass, broader distribution.

Here it is for helium, really broad distribution. Well, first of all, you can see that the average speed of helium is much greater than it is for argon than it is for xenon.

Because we already saw that it was inversely proportional to the square root of the mass.

But the other thing to note is how broad the distribution is for helium compared to xenon. And that is the general case. The lighter masses have broader distributions.

Helium is so broad, meaning that there are helium atoms here that are so fast that this is the reason why there is relatively little helium and hydrogen in our atmosphere.

That is because, at our temperatures, there are enough molecules with high enough velocities to escape the earth's gravitational pull because they are here at the tail end.

And so, the helium and the hydrogen leave our atmosphere.

Unlike Jupiter which is 300 times more massive than the earth where the gravitational pull is greater. And, in that case, those helium atoms don't have enough velocity to escape the earth's gravitational pull.

So, that is mass. What about temperature?

Now we are going to keep the mass constant and are going to look at temperature. Here is the distribution function at 100 degrees kelvin, pretty narrow. Here is the distribution function for argon at 300 degrees kelvin, broader.

Here is the distribution function at 1000 degrees kelvin, broader again. You see that as we increase the temperature the average speed increases. As we increase the temperature the width of that distribution function increases.

Now, one thing to note here is this is a probability.

The areas under these curves have to all add up to one. If this distribution function is going to move to higher velocities as we increase the temperature, well, of course this maximum probability is going to have to go down because we cannot lose any molecules.

All the area under this curve at 100 degrees kelvin has to equal the area under this curve at 1000 degrees kelvin because this is a probability that we are plotting here. That is our description of the Maxwell-Boltzmann distribution.

See you on Friday.