LECTURE 9 (2004-02-04)

Adiabatic expansions and compressions

Lots of subtle concepts today. First a review the last lecture. We are heading for $pV^\gamma = \text{const}$ using a simple model of a one-dimensional gas. A wall compresses the gas and we are trying to relate $\Delta p/p$ to $\Delta V/V$. Since $p \sim n\epsilon$, where n is number density and ϵ is the energy per molecule, we need first to know $\Delta\epsilon$. We'll do it in steps.

Step 1: One gas molecule collides with the wall

A gas molecule, moving to the left with speed v_x, collides with the wall moving to the right with speed v_{wall}. After the collision, the molecule is moving to the right with speed $v_x + 2v_{\text{wall}}$.

How much did its energy change? Its energy is

$$\epsilon = \frac{1}{2}mv_x^2 + \cdots,$$

where the $\cdots$ includes all other contributions to the energy such as rotational and vibrational (or if the motion is in two or three dimensions, the other kinetic energy terms). For a molecule hitting the wall, the fractional change in energy is

$$\frac{\Delta\epsilon}{\epsilon} = 2\,\frac{\Delta v_x}{v_x} \times \frac{1}{d}.$$

Why the factor of 2 rather than an exponent of 2?

This question came up in the previous lecture (see the example of the square). It is worth understanding the answer backwards and forwards.

Why the factor of $1/d$*?*

It arises because there are d terms in the energy. The collision increases only the x-direction kinetic energy. This extra energy redistributes among all the other modes, until they all have equal average energy: *equipartition.* So the extra blob of energy in just that one mode now becomes d blobs of energy, each $1/d$ of the size. The fractional change in energy is easy to compute once you know that all the modes have the same energy: It's just the fractional change in any one of them.

According to equipartition, energy is equally distributed among all the modes. However, if you have more modes: Do you get more energy per molecule or is the same energy shared among the now larger number of modes?

A damn fine question. It relates to the definition of temperature. You asked, 'What exactly is temperature?' It has many definitions. The standard one involves entropy, energy, and derivatives, and I dislike that one because it is not intuitive. A theme of this course is to connect physics to intuition. The definition I like (which works classically) is that temperature is proportional to the kinetic energy in one translational mode, for example in the x direction. The constant of proportionality depends on the units of temperature (Fahrenheit versus Celsius for example) and of energy, and even then we could throw in a dimensionless constant. By convention it is $k/2$, where k is Boltzmann's constant, and the energy in one mode is then $kT/2$.

But that assertion does not explain *why* the energy is $kT/2$ per mode rather than $kT/2$ for all the modes put together. To sort out this tricky question, consider a gas (still moving in one dimension) with two kinds of molecules. One kind is made of simple atoms. The other kind is made of ‘atoms’ containing a rattle (a spring and mass). The wall is at some temperature T, so its atoms are bouncing back and forth. We all agree that a simple atom will have energy $kT/2$, which is also its kinetic energy (it has only 1 mode). What about the complex atom? Will it have centre-of-mass kinetic energy $kT/2$, and then have additional kinetic and potential energies for the rattle, each also $kT/2$. Or will those three modes have to share one $kT/2$?

To gain insight into this question, first think how the simple atom gets to have kinetic energy $kT/2$. Suppose first that it has less. When it collides with the wall, it will hit hotter molecules (those molecules have kinetic energy $kT/2$), so on average it will gain energy and the wall molecules will lose energy. The wall is being maintained at a temperature T, so someone will supply the wall with the energy it gave to the simple atom (if not, the wall would cool).

On the other hand, imagine the simple atom with an energy larger than $kT/2$. In a collision it will on average give some energy to the wall and eventually the wall will give that to the surroundings. Both wall atoms and the simple atom will converge to have average kinetic energy $kT/2$.

Once that physics is clear, I can explain what happens to the atoms with a rattle. Imagine one such atom, moving with centre-of-mass (CM) kinetic energy $kT/2$ but with a quiet rattle. So it has $kT/2$ total energy in all the modes. When it hits the wall, the rattle will get a shaking. The energy for that shaking will come from the wall atoms (and eventually from the surroundings) and from the CM kinetic energy. If energy comes from the CM kinetic energy, then it will drop below $kT/2$, and on the next collision with the wall, CM kinetic energy will get a boost (on average). So collisions redistribute energy among the modes. You need a collision to redistribute. The rattle energy could not otherwise become CM energy: Conservation of momentum means that in free space the CM momentum (and therefore energy) is constant. So the energy redistributes due to collisions and CM energy is fed in until it hovers around $kT/2$. So the total energy in this complex atom will increase, and it turns out that it keeps increasing until the energy in each mode is $kT/2$.

What about the Boltzmann factor?

Yeah, I am sloppy. The molecules do not all have the same speed, given by $E_x = kT/2$. Rather the speeds are distributed according to the Maxwell distribution, which is another form of the Boltzmann distribution. But for this simple model, I ignore the spread in velocities.

Back to the $1/d$ *factor*

Since each mode has the same energy, and the collision with the wall gives energy to only one mode (the x kinetic energy), the fractional change in the molecule's energy is

$$\frac{\Delta\epsilon}{\epsilon} = 2\,\frac{\Delta v_x}{v_x} \times \frac{1}{d}.$$

Only some of the molecules hit the wall while it is moving. These molecules get that fractional change and then share it with the rest. So the fractional change in molecular energy, once the wall's donations are shared around, is

$$\left(\frac{\Delta\epsilon}{\epsilon}\right)_{\text{all}} = \frac{\Delta\epsilon}{\epsilon} \times \text{fraction hitting wall.}$$

Step 2: What fraction hits the wall?

Let's say the wall moves for a short time Δt. In that time, the wall sweeps out a distance $v_{\text{wall}}\Delta t$. So the fraction of the gas that the wall sweeps out is $v_{\text{wall}}\Delta t/x$, where x is the length of the container. Should that fraction be the fraction of gas molecules hitting the wall?

At first I thought it was, but as you pointed out in lecture, it cannot be. Imagine an extreme case where $v_{\text{wall}} = 0$. It sweeps out no volume, but molecules still hit it (which causes the pressure). So something went wrong. The problem is that $v_x \gg v_{\text{wall}}$. What decides how many gas molecules hit the wall is basically the velocity of the gas molecules. So maybe

$$\text{fraction hitting wall} = \frac{v_x\Delta t}{x}?$$

This result is almost right, except imagine another extreme case where all the molecules decided to move right at the same time. Then none would hit the wall! Only one-half move right, so I need a factor of one-half:

$$\text{fraction hitting wall} = \frac{1}{2}\frac{v_x\Delta t}{x}.$$

Then

$$\left(\frac{\Delta\epsilon}{\epsilon}\right)_{\text{all}} = 2\frac{\Delta v_x}{v_x} \times \frac{1}{d} \times \frac{1}{2}\frac{v_x\Delta t}{x}.$$

The factor of 2 is because fractional energy changes are twice fractional velocity changes; the factor of one-half is because only one-half of the molecules move to the left. Using $\Delta v_x/v_x = 2v_{\text{wall}}/v_x$,

$$\left(\frac{\Delta\epsilon}{\epsilon}\right)_{\text{all}} = 2 \times \frac{2v_{\text{wall}}}{v_x} \times \frac{1}{d} \times \frac{1}{2}\frac{v_x\Delta t}{x}.$$

The pair of v_x's cancel and the combination $v_{\text{wall}}\Delta t/v_x$ is

$$\frac{v_{\text{wall}}\Delta t}{v_x} = \frac{\text{distance wall moves}}{\text{length of box}} = \text{fractional change in volume} = \frac{\Delta V}{V}.$$

So

$$\left(\frac{\Delta\epsilon}{\epsilon}\right)_{\text{all}} = -\frac{2}{d}\frac{\Delta V}{V}.$$

The minus sign is because I was careless in defining positive and negative distance: really the length of the box is negative if I am careful, but that just introduces minus signs to chase down. Much easier to put it in now, when it's easy to keep the sign straight: As the volume drops, the energy increases, so I need a minus sign.

What else do I need to work out?

Given that $p \sim n\epsilon$, what is $\Delta p/p$? If n is fixed, then

$$\frac{\Delta p}{p} = \frac{\Delta\epsilon}{\epsilon}.$$

But n is the *number density*, not the total number of molecules, and the density increases as the volume decreases. If ϵ were fixed, then

$$\frac{\Delta p}{p} = \frac{\Delta n}{n}.$$

Neither ϵ nor n is fixed, and the fractional changes add:

$$\frac{\Delta p}{p} = \frac{\Delta n}{n} + \frac{\Delta \epsilon}{\epsilon}.$$

That equation is most of the theory of error analysis that you used last year in the IA practicals.

But we also learnt equation where those terms were squared.

True. It depends whether the factors in the product are correlated. For example, if $A = x^2$, then a 5% uncertainty in x will produce a 10% uncertainty in A. Now imagine that $A = xy$, where x and y are independent (maybe we're measuring a rectangle). Then the errors in x and y will be uncorrelated. So we might measure x too high, but get lucky and measure y too low. So have a better chance of cancelling mistakes in the independent-factor case. Here it turns out that the *squared* fractional uncertainties add – for the same reason that in a random walk the squared distance grows linearly with number of steps (think of each factor's error contribution as a step in a random walk).

Working out $\Delta n/n$

We worked out $\Delta\epsilon/\epsilon$ above; now we work out $\Delta n/n$. Start with $n \propto V^{-1}$. Is

$$\frac{\Delta n}{n} = \left(\frac{\Delta V}{V}\right)^{-1}$$

or is

$$\frac{\Delta n}{n} = -1 \times \left(\frac{\Delta V}{V}\right)?$$

The first choice is so tempting. But the *extreme case* of no volume change ($\Delta V = 0$) produces an infinite Δn! That can't be right. With the second choice, Δn is zero, as it should be. The second choice is right.

Here is an example of its use in calculating 1/13:

$$\frac{1}{13} = \frac{1}{13} \times \frac{8}{8} = \frac{8}{104} \approx \frac{8}{100}.$$

In the last step I decreased the denominator by roughly 4%, so I should decrease 8/100 by roughly that amount:

$$\frac{1}{13} \approx \frac{8}{100} - 4\% = \frac{8 - 0.32}{100} = 0.0768.$$

Combining the fractional changes

Thus

$$\frac{\Delta p}{p} = -\frac{\Delta V}{V} - \frac{2}{d}\frac{\Delta V}{V} = -\left(1 + \frac{2}{d}\right)\frac{\Delta V}{V}.$$

Almost there!

What is that $1 + 2/d$?

If a molecule has d degrees of freedom, then its internal energy is $d \times (kT/2)$ and its specific heat (per molecule) at constant volume is $d \times k/2$. The specific heat at constant pressure contains an additional contribution of k, because as the gas heats up it will expand (pressure, not volume is now constant), and one must do work to create the new space. See Adkins, p. 42 for this point (he does it per mole instead of per molecule, so $R = N_{\mathrm{A}}k$ shows up). So for an ideal gas

$$c_{\mathrm{v}} = d \times \frac{k}{2},$$

and

$$c_{\mathrm{p}} = c_{\mathrm{v}} + k = (d + 2) \times \frac{k}{2}.$$

Then $1 + 2/d = (d + 2)/d$ has a simple expression as $c_{\mathrm{p}}/c_{\mathrm{v}}$, which is defined as γ:

$$\frac{\Delta p}{p} = -\gamma \frac{\Delta V}{V}.$$

Science and weapons

Here are some statements to think about for Friday:

- Research is essential so that we know what threatening weapons are possible.
- I only work on defensive, not offensive weapons.
- By being involved in the weapons program I can be an effective influence on the government.
- I am just a scientist doing my job; I stay out of politics.
- I work on currency trading for a merchant bank; I don't work on weapons.
- I do only pure research. Whether it leads to weapons or not is out of my control.
- I am fooling the MoD by taking their money for my basic research, which they would otherwise spend on weapons.
- I don't use MoD money; EPSRC fund my research.
- I don't have any government research funds; I am just a physics teacher.