

IB Classical Thermodynamics (Lent 2004)

This large handout is (almost) all the course materials for you to take home for the vac. Let me know of any errors; I'll fix them in the electronic copy and make an errata page on the website. Also let me know of any suggestions for improving the explanations or of any questions you have. If there are enough errors or new explanations, or if I add a bunch of diagrams, I'll make a revised version to hand out at the beginning of next term. Easter term we'll have a **revision session** to discuss all your questions: **Tuesday 20 April, 5.00–6.30, Corpus Christi College, Room I4** (that's Tuesday of 0th week).

–*Sanjoy Mahajan* <sm324@cam.ac.uk>

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Here are quantities worth knowing. Estimate them before looking them up (some you may just have to memorise, such as Avogadro's number).

- sound speed in water, air, steel
- density of water, air, rock, iron
- typical molecular spacing in solid or liquid
- specific heat of water
- orbital radius of earth
- radius of earth
- Avogadro's number
- angular size of sun
- Converting eV to Joules
- typical bond energies (in eV)
- wavelength of visible light
- mechanical power a person can generate
- mean free path of air molecules
- chemical energy in a jelly donut

Here are equations to understand. What do the quantities mean? Where does the equation come from, where does it apply? For each one, construct an example using it.

- $pV^\gamma = \text{const}$.
- $R = N_A k$.
- $n\sigma\ell \sim 1$ (where ℓ is mean free path)
- $\rho = mn$ where n is number density.
- $p = nkT$.
- $p_{\text{vap}} \propto e^{-L_{\text{vap}}/RT}$.
- $F = \sigma T^4$.
- $F = K\Delta T/\Delta x$.
- In gases, $c_v = (d/2)k$ per molecule.
- $c_p = c_v + k$ for an ideal gas (per molecule).
- $c_p = 3k$ for a solid (per atom).

Here are problems to help you revise important ideas. Also study the example sheets and solutions, as well as the examples done in lectures.

1 *Sound waves*

Do sound waves produce adiabatic or isothermal compressions? Hint: Imagine a sound wave of frequency f and consider the time for heat to diffuse between a compressed and rarefied area.

2 *Breath*

Why can you see your breath on a cold day?

3 *Freezing locks*

High-pressure carbon dioxide comes out of a cannister at, say, 5 atm. What temperature does it reach when it has expanded and reached atmospheric pressure?

4 *Turkey*

What is cooking? A small turkey takes 3 hours to cook. How long does it take to cook a geometrically similar turkey with twice the mass?

5 *Tungsten*

Here is vapour pressure data for tungsten:

$T(^{\circ}\text{C})$	$p(\text{Pa})$
2550	10^{-3}
3205	10^0

Find its heat of vaporisation.

6 *Pluto*

What is the blackbody temperature of Pluto?

7 *Iron*

Estimate the specific heat of iron.

8 *Gases*

Estimate the specific heat of helium and nitrogen gases.

9 *Thermal diffusivity*

Discuss why thermal diffusivity is given by

$$\kappa \sim \text{mean free path} \times \text{speed},$$

including how heat transport in a solid or liquid different from that in a gas. Estimate κ for ice and for air.

10 *Thermal conductivity*

Discuss why thermal conductivity is given by $K = \rho c_p \kappa$. Estimate K for air.

11 *Conduction*

What is heat flux? Discuss

$$F = K \frac{\Delta T}{\Delta x},$$

including the reason for Δx in the denominator.

12 *Lakes*

In problem C2 from sheet 2 (ice on lakes), sketch the temperature profile within the ice. Make several sketches on one graph showing the profile at different times (i.e. as the ice thickens).

13 *Vaporisation*

Estimate heat of vaporisation of water using any reasonable method.

14 *Sun's surface*

Estimate the temperature of the sun's surface.

15 *Size of molecules*

Estimate size of air molecules given that the mean free path is 10^{-7} m.

16 *Rain shadows*

Pick a mountain you like. What fraction of water gets dumped as air rises up the mountain?

17 *Fogged windows*

Why do windows fog on a cold day? Why on the inside?

18 *Blanket*

How does a blanket keep you warm? Be as quantitative as you can.

19 *Random walks*

Explain why time is proportional to distance squared.

20 *Gravity*

Explain gravity slingshots.

EXAMPLES 1

1 *Energy in a jelly donut*

To the nearest power of ten, how much energy is in a jelly donut (in J)? A jelly donut is a moderate-sized torus of dough filled with sweet, sticky stawberry jam.

2 *Energy scales*

Draw a long, *logarithmic* energy scale spanning, say, 30 orders of magnitude and fill it with lots of physical phenomena, estimating their energies as you need. Don't forget to specify the unit! Here are a few energies to get you started: energy in a 9V battery, energy in a jelly donut (from problem 1), energy a lightbulb consumes in its lifetime, typical chemical bond energy, energy of a Radio 4 (MW) photon, . . .

Email me (sm324@cam.ac.uk) your favorites and I'll put them on the course website, giving you credit of course (unless you want your contribution anonymous).

3 *Power scales*

Same as problem 2 but for *power*. Again, email me (sm324@cam.ac.uk) your favorites for the course website.

4 *Water*

In as many ways as you can think of, estimate the heat of vaporization of water, L_{vap} , in dimensions of energy/mass. Compare the estimates. Again, email me your favorites for the course website.

5 *How old is the sun?*

In the 19th century, the leading biologists argued that the earth must be billions of years old to allow evolution enough time. The leading physicists, in particular Helmholtz and Kelvin, used thermodynamics to argue that the earth is much younger. One episode in the debate involved the age of the sun. What powered the sun? One theory was gravity: The sun slowly contracted and turned the gravitational energy released into radiation.

First check the sign in this explanation! Is energy released or absorbed as the sun contracts?

If the sun were once significantly larger than now, estimate how long it could have been shining at its present luminosity. Which side of the debate does your estimate support?

EXAMPLES 2

As you can now read on the Frequently Asked Questions on the course website, the thermodynamics part of the exam paper will have 4 short questions (like section A), 2 longer questions (à la section C last year), and 1 essay/notes question (in section D). This problem sheet follows that schedule with questions of roughly the right level.

Questions A1 and A5 are not going to show up on a thermodynamics paper, but they are important to your education as a physicist – another example of how exams are separate from learning. A skilled physicist has lengths, energies, speeds, and powers at her fingertips, and has fun expanding her repertoire of scales (A1). A skilled physicist also makes friends with numbers and is fluent in approximations (A5).

A1 *Useful lengths*

Useful lengths to know and have at your fingertips: light-year, sheet of A4 (length), a bacterium, a car, human hair (thickness), sheet of A4 (thickness), Cambridge, distance to the sun (astronomical unit), radius of sun, distance to the moon, diameter of hydrogen, radius of earth, football pitch (length), height of atmosphere, mean free path of air molecules, average depth of the oceans, height of Mt Everest, Don't feel restricted to this list; include your favorite lengths.

A2 *Age of sun by a different mechanism*

Another theory for the sun's power, which also came up in the debate over the age of the earth: that the sun uses chemical energy. So imagine the sun as a giant petrol tank. If almost all the petrol has by now been converted to energy, how old is the sun?

A3 *Air everywhere*

How does thermal diffusivity of air (κ) depend on temperature, T ? How does $\rho\kappa$ depend on temperature? The product $\rho\kappa$ is the (dynamic) viscosity.

A4 *Air conditioning on the cheap*

One summer I lived in a small flat in Manhattan, about 30 m^2 . At least it was larger than the London 'flat' reported in the *Independent* (20 January): $11\text{ ft} \times 6\text{ ft}$ on sale for £125,000!

Summers are already hot in New York; the beautiful people flee for cooler beach areas. Thanks to lousy electrical wiring in the building (too old to use an air conditioning) and to global warming, it became 30°C in the flat even at night. A friend who grew up before air conditioning said, 'Oh, we used to take a wet sheet and use a fan to blow air past it.' How does this system cool the flat? Estimate the temperature change.

A5 *Number sense*

Useful facts: $2^{10} = e^7 = 10^3$. Estimate without a calculator: $1/0.98$, 1.1^{10} , 0.9^{70} , $\sqrt{1.05}$, $\sqrt{50}$, $\ln 2000$, $\ln 3$, and $\sin 7$ (radians).

C1 *Light bulb*

The resistivity of tungsten (at light-bulb temperatures, roughly 3000 K) is $10^{-6}\ \Omega\text{ m}$. Estimate the length and diameter of a light-bulb filament.

C2 *Ice on lakes*

In winter in cold climates, lakes freeze: for example in New England and high in the mountains. First, guess how thick a layer of ice forms during the winter. Don't calculate anything right now. Use your experience, direct or indirect, and choose the nearest power of ten: Is it $1\ \mu\text{m}$, 1 mm , 1 cm , 10 cm , 1 m , 10 m , ...?

Now work it out using physics. The water below the layer of ice is at 0°C (why?). For the water to freeze, the air above the ice must be colder than the water and ice, say at $-T_{\text{diff}}$. A temperature gradient! So as heat flows through the ice into the air, ice freezes.

Formalize this analysis into (god forbid) a differential equation and solve it; it will be easy to solve. Thereby find the thickness of the ice formed in a winter. Use symbols until the end, then put in estimates for the constants, such as T_{diff} and how long the winter lasts. A useful rule of thumb for most substances:

$$L_{\text{fusion}} \sim \frac{L_{\text{vap}}}{10}.$$

The rule arises from a logarithm appearing through entropy and the further rule (due to Fermi) that all logs are 10.

How close was your initial guess for the thickness?

For fun: Why is it important for life in lakes that water is more dense than ice? What would happen during a winter if it were the reverse?

D1 *Random walks*

Explain random walks to yourself. Imagine an earlier self, one before you came to the brilliant lecture on random walks. How would *you* explain random walks to that earlier self? Consider how they work and why they are important, as well as any other points that help *you* understand them.

EXAMPLES 3

A1 *Cooking a turkey*

Estimate how long it takes to cook a turkey given that it takes 10 min to cook an egg.

A2 *Diamond*

At room temperature the thermal conductivity of diamond is $K \sim 2000 \text{ W m}^{-1} \text{ K}^{-1}$, much higher even than copper or silver. Should diamond's thermal conductivity increase or decrease as it is cooled?

Given the above K , estimate the mean free path of the lattice vibrations (*phonons*), as an absolute length and in units of the interatomic spacing. How does this distance compare with the mean free path of phonons in water, and what accounts for the difference?

A3 *Speeds*

Speeds worth knowing (don't estimate all of them, just make friends with them, see why the values are reasonable, and give estimates for a few): speed of sound in air, speed of sound in rock, walking speed, train speed, orbital velocity of the earth, velocity of the sun relative to the cosmic microwave background radiation, speed of light, speed an ant walks, speed of a plane, flow speed of the Cam, speed of packets on the Internet, speed continents move, speed bacteria swim, [and a few more added later: electron drift speed in a lightbulb circuit, escape velocity from earth, escape velocity from solar system (once escaped from earth), ...]

A4 *Temperature of Venus*

The atmosphere of Venus is full of carbon dioxide and water vapor (evaporated ocean!), the cause and result of a runaway greenhouse effect. If Venus had no greenhouse effect, what would be its average surface temperature given that (1) the Earth's no-greenhouse temperature is 255 K, as worked out in the first lecture, and (2) Venus's orbital radius is 0.72 AU?

Thanks to the greenhouse effect, the surface temperature is instead 727 K. How does the greenhouse effect increase the surface temperature? By roughly what factor does the greenhouse effect reduce the outgoing flux (compared to the flux at the same high surface temperature but with no greenhouse gases)?

B1 *Temperature in the atmosphere*

Imagine a parcel of air rising to a height z , where presumably the pressure is lower. As it rises, it expands adiabatically. Why is the expansion adiabatic? As it expands, its temperature drops to, say, T_{new} . In an *adiabatic* atmosphere, the surrounding temperature at that height, $T(z)$, is equal to T_{new} and no heat flows in or out of the parcel.

(a) Imagine an isothermal atmosphere. How does it become an adiabatic atmosphere? Hint: What happens to the atmosphere's temperature profile (temperature at a given height) as parcels rise and fall?

(b) What are $p(z)$ and $T(z)$ for the adiabatic atmosphere? In an exam, I would have phrased it modularly: Show that $p(z)$ and $T(z)$ are given by ..., but for here I'll leave that information in the hints and solutions.

(c) What is the temperature drop as one ascends Snowdon in Wales (elevation 1000 m)? Is your answer reasonable?

EXAMPLES 4

A1 *Isothermal atmosphere*

Last week you showed that in an adiabatic atmosphere:

$$T = T_0 \left(1 - \beta \frac{z}{H}\right),$$

and

$$T \propto p^\beta,$$

where T_0 is the sea-level temperature and β and H are constants defined by

$$\beta \equiv 1 - \frac{1}{\gamma},$$

and

$$H \equiv \frac{kT_0}{mg}.$$

Show that as $\gamma \rightarrow 1$ these results become the isothermal atmosphere that you studied last year. (Note: In the original solutions for sheet 3, I mistakenly left out β in the relation between T and z .)

A2 *Ice skating*

In ice skating the blade must slide on wet ice or else the friction would be too high. One idea for how the ice gets wet is ‘pressure melting’ due to the high pressure of the ice skate lowering the freezing point. Let’s test this idea.

How much does the freezing point drop? The theory is complicated but as a rough guess for the result:

$$\left(\frac{\text{fractional change}}{\text{in pressure}}\right) \sim \left(\frac{\text{fractional change}}{\text{in } T_{\text{freeze}}}\right)$$

or

$$\frac{\Delta p}{p} \sim \frac{\Delta T_{\text{freeze}}}{T_{\text{freeze}}},$$

where the missing constant is hopefully of order 1. Fractional changes are your friend! For water, what p should you use? It has dimensions of energy per volume so construct a reasonable quantity of those dimensions, and estimate the drop in T_{freeze} while ice skating. Is it large enough to melt ice? Whether or not it is, what other effects could melt the ice? Which effects do you think most important?

A3 *Fog*

Fog is tiny water droplets. Why does it form?

How large are the droplets? *Hint:* The mean free path of a light ray is roughly how far you can see on a foggy day.

B1 *Vapor pressure*

Here is vapor pressure data for water:

T (°C)	p (Pa)
-10	286.6
0	610.6
10	1227.9
20	2338.5
25	3167.7
30	4239.7
37	6275.5
40	7372.7
60	19918.4
80	47342.8
95	84526.4
100	101325.0
101	105058.0
200	1554405.5

You’ll find a more complete version of the data at the course website, so you don’t need to type in all the numbers. The purpose of this problem is to explore the relation between vapor pressure and temperature. Perhaps using a spreadsheet and the online data:

(a) First graph p vs T (in Celsius).

(b) The units of temperature and pressure are not natural, so the data is hard to make sense of in this form. Use Kelvin temperature and measure pressures against atmospheric pressure ($p_{\text{atm}} = 101325.0 \text{ Pa}$) by plotting p/p_{atm} vs T (in Kelvin). Notice that $p = p_{\text{atm}}$ at $T = 100^\circ\text{C}$. Coincidence?

(c) Notice how widely p/p_{atm} varies, which suggests using a logarithmic scale. Plot $\ln(p/p_{\text{atm}})$ vs T (in Kelvin). Notice that $\ln p$ itself would be a nonsense because you cannot take the logarithm of a Pascal (or any dimension). You need to use a reference pressure, which you have done by using p/p_{atm} .

(d) The graph is still not too straight. As $T \rightarrow \infty$, the pressure may asymptote to a constant, although it’s hard to tell. One possible solution is to use $1/T$ on the x axis. Plot $\ln(p/p_{\text{atm}})$ vs $1/T$ (in K^{-1}).

(e) Therefore show that

$$p = p_0 e^{-T_0/T},$$

where T_0 is a temperature and p_0 is a pressure (it’s not atmospheric pressure). Find the temperature and convert it to an energy per mole, an energy per mass, and an energy (in eV) per molecule. These values should look familiar!

Examples 4

(f) Explain this result using the Boltzmann factor. As part of your explanation, discuss the behavior as $T \rightarrow \infty$.

(g) Using the results from sheet 3 (repeated in question A2 this week), what is the temperature drop going up the Rocky Mountains ($h = 3 \text{ km}$)? By what factor does going up the mountain change the vapor pressure of water? What are the consequences of this change for the climate?

D1 *Carnot cycle*

Explain, with suitable diagrams, the four steps of a Carnot cycle. Evaluate the heat flows in each step, and therefore the mechanical work done, and show that a full cycle leaves the entropy unchanged.

SOME SOLUTIONS FOR SHEET 1

1 *Energy in a jelly donut*

A typical person eats 2500 Cal (1 Cal = 1 kcal) per day. Since 1 cal = 4 J, the daily consumption is 10 MJ. Two jelly donuts alone would give me enough food for breakfast (if I wanted to eat so much sugar), which is my smallest meal. Lunch might require three donuts, and dinner perhaps four donuts. So one day's food is about 10 donuts, and each donut contains 10^6 J (so I will often call 1 MJ a 'jelly donut').

Note for non-Americans. I thought that English donuts, like American ones, are topological toruses but a few of you explained that they are spheres. In American jelly donuts, the jelly is a torus inside the dough torus. In America, you can also get cream-filled donuts. It is the land of the free, at least if you are hungry for topologically correct donuts.

2 *Energy scales*

A few energy calculations.

Energy in a 9V battery. Maybe most batteries store the same energy per weight? It's a reasonable guess anyway. My laptop battery, which is about five 9V batteries in weight or volume, lasts about 3 hours when the network card is shut down and the drive is quiet. The LCD screen is not as bright as a regular light bulb (60 W), and it is much more efficient, so maybe it uses a few Watts, say 3 W, and the processor perhaps another 3 W. The energy stored in the laptop battery is then

$$E \sim 3 \text{ hr} \times 3600 \text{ s hr}^{-1} \times 6 \text{ W} \sim 60 \text{ kJ}.$$

So a 9V battery stores about one-fifth of that energy, or 10^4 J.

Energy of a radio 4 (FM) photon. Photon energy is $E = hf$ and medium-wave broadcasts are roughly at 10^8 Hz, so

$$E \sim 7 \times 10^{-34} \text{ J s} \times 10^8 \text{ Hz} \sim 10^{-25} \text{ J}.$$

Note: Sorry! I got confused translating American names (FM and AM) into British, and thought MW was FM while LW was AM. Half right anyway. So I just calculated it for the FM frequency. The AM frequency of Radio 4 is 198 kHz (LW).

The 'Tuner Guide at Superfi Online' <<http://www.superfi.co.uk/index.cfm/>> says:

In the UK, domestic AM broadcasts are divided into LW (Long Wave) which occupies the frequency range between 150 and 285 kHz and MW (Medium Wave) which occupies the frequency range between 531 and 1620 kHz. Usually tuners which claim AM coverage just cover the MW band, whereas those that cover both MW and LW bands state this specifically.

In America, AM uses only the medium-wave band. At least, I've never seen an American AM dial that goes below 500 kHz

Typical chemical bond energy. To ionize hydrogen requires roughly 10 eV, and chemical bonds are created by similar physics (electron-proton attraction), over a slightly longer distance, which makes it somewhat weaker. So perhaps $E \sim 5 \text{ eV}$ or

$$E \sim 5 \text{ eV} \times 1.6 \times 10^{-19} \text{ J eV}^{-1} \sim 10^{-18} \text{ J}.$$

Energy a lightbulb consumes in its lifetime. I change my most used lightbulb once every six months and use it say 4 hours a day, for a lifetime of 1000 hr. At 60 W, the energy consumed is

$$E \sim 60 \text{ W} \times 10^3 \text{ hr} \times 3.6 \times 10^3 \text{ s hr}^{-1} \sim 2 \times 10^8 \text{ J}.$$

Energy consumed by 1 person flying across the Atlantic. Perhaps planes get the same fuel efficiency, per person, as a car does: roughly $10 \text{ km } \ell^{-1}$. The trip is 5000 km, so you use 500 ℓ . The energy density of petrol is roughly the same as that of fat, 10 kcal g^{-1} or 40 MJ kg^{-1} . A litre of petrol is roughly 1 kg, so

$$E \sim 500 \ell \times 1 \text{ kg } \ell^{-1} \times 40 \text{ MJ kg}^{-1} \sim 2 \times 10^{10} \text{ J}.$$

3 *Power scales*

Power used by a typical lightbulb. Looking at one, it says 60 W.

Power generated by a nuclear power plant. A nuclear power plant can probably power a medium (Western) city, say 10^5 people. Each person uses maybe the equivalent of say 20 lightbulbs (includes lighting plus washing machines, dishwashers, computers, equipment at work, etc), so

$$P \sim 60 \text{ W} \times 20 \text{ lightbulbs person}^{-1} \times 10^5 \text{ people} \sim 10^9 \text{ W}.$$

Power a person can generate. I ran up the stairs in my building as fast as I could. It took me about $t = 3 \text{ s}$, so

$$P = E/t \sim \frac{mgh}{t} \sim \frac{60 \text{ kg} \times 10 \text{ m s}^{-2} \times 3 \text{ m}}{3 \text{ s}} \sim 600 \text{ W}.$$

Power radiated by the sun. From lecture, the solar flux at the earth's orbit is $F = 1.3 \times 10^3 \text{ W m}^{-2}$, so integrated over a spherical shell at the earth's orbit,

$$P = 4\pi R_{\text{orbit}}^2 F \sim 4 \times 3 \times (1.5 \times 10^{11} \text{ m})^2 \times 1.3 \times 10^3 \text{ W m}^{-2} \sim 4 \times 10^{26} \text{ W}.$$

4 *Water*

After a rain, a hard-surface tennis court has puddles on the ground. After the sun comes out, the shallowest puddles evaporate in perhaps 15 minutes. The puddles are a lot less than 1 cm thick – such a deep puddle stays for a long time. So I'll guess that the puddles are $h = 1 \text{ mm}$ thick.

Imagine such a puddle with area A (which I hope will cancel out). Its volume is Ah and the energy required to evaporate it is

$$\text{volume} \times \text{density} \times L_{\text{vap}} = \rho Ah L_{\text{vap}}.$$

In time t the sun provides an energy

$$\text{flux} \times \text{time} \times \text{area} = FAt,$$

where F is the solar flux. I equate the energies to find L_{vap} :

$$\rho Ah L_{\text{vap}} \sim FAt,$$

or

$$L_{\text{vap}} \sim \frac{FAt}{\rho Ah} = \frac{Ft}{\rho h}.$$

In the lecture we used $F \sim 1.3 \text{ kW m}^{-2}$, so

$$L_{\text{vap}} \sim \frac{1.3 \times 10^3 \text{ W m}^{-2} \times 15 \text{ min} \times 60 \text{ s min}^{-1}}{10^3 \text{ kg m}^{-3} \times 10^{-3} \text{ m}} \sim 10^6 \text{ J kg}^{-1}.$$

5 How old is the sun?

Is energy released by the contraction? As the sun contracts, mass falls into the centre. Similarly, as an object falls towards the earth, it gains speed (kinetic energy), which could be converted into radiation. So the sign is okay.

For the energy available from gravitational collapse, it is the starting gravitational energy minus the current gravitational energy. Gravitational *potential* is

$$U = -\frac{GM}{R},$$

so the gravitational potential energy is roughly $-GMM/R$. If the sun were much more spread out long ago, then the starting energy is close to zero, and the energy available for conversion is roughly

$$E \sim GMM/R.$$

The power radiated is the luminosity of the sun, which is also the flux at the earth's orbit times the area of the spherical shell at the earth's orbit:

$$P \sim 4\pi R_{\text{orbit}}^2 F,$$

where F is the solar flux, 1.3 kW m^{-2} . So the time that the sun could have been shining is

$$t \sim E/P \sim \frac{GMM/R}{4\pi R_{\text{orbit}}^2 F}.$$

Rather than immediately feeding in all the constants with their giant exponents, I'll use a useful trick to avoid a few such constants. In a circular orbit driven by gravitation, the gravitational acceleration, GM/R_{orbit}^2 , provides the acceleration, v^2/R_{orbit} , where v is the orbital velocity of the earth. So

$$t \sim \frac{Mv^2}{4\pi RR_{\text{orbit}}F}.$$

Another simplification happens because $v = 2\pi R_{\text{orbit}}/T$, where $T = 1 \text{ yr}$. So

$$t \sim \frac{M \times 4\pi^2 R_{\text{orbit}}^2}{4\pi RR_{\text{orbit}}FT^2} = \frac{M\pi}{FT^2} \frac{R_{\text{orbit}}}{R}.$$

The sun's *diameter* subtends 0.5 degree or 10^{-2} rad , so $R_{\text{orbit}}/R \sim 200$, and $T \sim \pi \times 10^7 \text{ s}$. Therefore

$$t \sim \frac{2 \times 10^{30} \text{ kg} \times 3}{10^3 \text{ W m}^{-2} \times 10^{15} \text{ s}^2} \times 200 \sim 10^{15} \text{ s} \sim 3 \times 10^7 \text{ yr}.$$

30 million years! Hardly enough time for evolution, the physicists argued. What could biologists at the time say?

SOME SOLUTIONS FOR SHEET 2

A1 Useful lengths

I don't expect you to find ways to estimate all of these quantities. Just take a guess, look them up, and make friends with them; see how they connect to other quantities. Figure out a few that grab your interest and that you want to discuss in supervision. For your enjoyment I give methods for most of them.

Light year

Using the useful approximation that $1 \text{ yr} \sim \pi \times 10^7 \text{ s}$,

$$1 \text{ ly} = c \times 1 \text{ yr} \sim 3 \times 10^8 \text{ m s}^{-1} \times \pi \times 10^7 \text{ s} \sim 10^{16} \text{ m}.$$

A4 sheet (length)

My foot, at least with a shoe on, is almost the same length as a sheet of A4, and my foot is, surprise, about *one foot* long. A foot is one-third of a yard, or roughly 0.3 m. An alternative method for Americans, who instead of A4 use 'eight and a half by eleven' paper (in inches of course), so a sheet is again about as long as one foot (12 inches). You can also figure it out from the A_n system. All sizes have length/width = $1/\sqrt{2}$ – what's the use of that? A sheet of A0 has area 1 m^2 , a sheet of A1 has area $1/2 \text{ m}^2$, etc. So sheet of A4 has area $1/16 \text{ m}^2$, or if it were square, $1/4 \text{ m} \times 1/4 \text{ m}$. It's unsquare by a factor of $\sqrt{2}$ so it is a bit longer than $1/4 \text{ m}$.

Bacterium

A bacterium is probably the size of a rod or cone cell in the retina. Light arrives through the pupil and spreads out due to diffraction over an angle $\theta \sim \lambda/d$, where λ is the wavelength of light and d is the diameter of the pupil. There is not much point making pixels more closely spaced than the resolution of the lens, and the cones in the eye fit this pattern. So their size is roughly θl , where l is the length of the eyeball, maybe 3 cm. The wavelength of light is roughly $0.5 \mu\text{m}$ (a useful length to know), and a pupil may have a diameter around 1 cm or a bit less (look at someone nearby to find out). So

$$\text{cone size} \sim \frac{\lambda}{d} l \sim \frac{0.5 \times 10^{-6} \text{ m}}{10^{-2} \text{ m}} \times 3 \times 10^{-2} \text{ m} \sim 1.5 \times 10^{-6} \text{ m}.$$

So cells are roughly $1 \mu\text{m}$.

Car

One can almost lie down in the back seat of a car, so a car is perhaps 2 m wide. Perhaps the car culture is not as widespread in Britain as in America, where many students in high school, through diverse nocturnal activities, learn this approximation – and why it is a bit on the low side. A car looks about twice as long as wide, so 4 m is a reasonable length. A useful experiment is to pace it off, and one pace is typically 1 m.

Human hair (thickness)

Grabbing a handy eyelash, it looks a lot smaller than 1 mm but is easily visible, so maybe 0.3 mm.

A4 sheet (thickness)

A ream of copier paper is about 2 in thick or 5 cm and contains 500 sheets, so 10^{-2} cm or 10^{-4} m .

Cambridge

It takes me about 30 minutes to cycle across Cambridge, say from the boundary with Girton on Huntingdon Road to past the railway station. I cycle maybe 10 or 15 miles per hour, so Cambridge is about 6 miles long or 10 km.

Distance to the sun (1 AU)

Very hard to estimate just from data you can see around you; so memorize it: $1.5 \times 10^{11} \text{ m}$. The ancient Greeks spent a long time trying to work it out (Aristarchus in particular) and estimated that it was about 20 times the distance to the moon. It is more like 400 times.

Radius of the sun

Its diameter subtends about 0.5° , which is 10^{-2} rad , so

$$d \sim 1 \text{ AU} \times 10^{-2} \sim 1.5 \times 10^9 \text{ m}.$$

The radius is therefore $7 \times 10^8 \text{ m}$.

Distance to the moon

It orbits the earth once a month, from which I can find its orbital angular velocity. Its inward acceleration is $a = \omega^2 r$. This acceleration is due to the earth's gravity, so

$$a = \frac{GM}{r^2},$$

where M is the earth's mass and r is the distance to the moon. Oh, no, I have to estimate the earth's mass! But there's a trick, again using *scaling*. This GM/r^2 is an acceleration. Is it large or small? Never mind that question, it was just a way to remind you of the moral from 28 January's lecture: Nothing with dimensions is small or large in itself, it needs to be compared to another quantity of the same type. I want another acceleration; the only one that springs to mind is the acceleration due to gravity at the earth's surface:

$$g = \frac{GM}{R^2},$$

where R is the radius of the earth. Then

$$\omega^2 r = \frac{GM}{r^2} = \frac{GM}{R^2} \frac{R^2}{r^2} = \frac{gR^2}{r^2}.$$

So

$$r = \left(\frac{gR^2}{\omega^2} \right)^{1/3}.$$

The radius of the earth is on the list a bit later and is 6×10^6 m. The angular velocity is

$$\omega = \frac{2\pi}{1 \text{ month}} \sim \frac{6}{(1/12) \times \pi \times 10^7 \text{ s}} \sim 2.4 \times 10^{-6} \text{ rad s}^{-1}.$$

Putting in all the numbers,

$$r \sim \left(\frac{10 \text{ m s}^{-2} \times 36 \times 10^{12} \text{ m}^2}{5 \times 10^{-12} \text{ s}^{-2}} \right)^{1/3} \sim 70^{1/3} \times 10^8 \text{ m}.$$

The cube root of 70 is roughly 4, so

$$r \sim 4 \times 10^8 \text{ m}.$$

Diameter of hydrogen

Dimensional analysis to the rescue. I'll work out the radius r . It depends on quantum mechanics (without QM, the electron would radiate and spiral into the nucleus) so I include \hbar . Did I hear someone say electron? So it should depend on the electron charge q and that nasty constant ϵ_0 . Because all forces and energies depend on the combination $q^2/4\pi\epsilon_0$, the electron charge and ϵ_0 travel together in that form. The electron mass says how effectively electrostatics can accelerate it, so I better put m in. The dimensions:

<i>Symbol</i>	<i>Dimensions</i>
r	L
m	M
\hbar	ML ² T ⁻¹
$q^2/4\pi\epsilon_0$	ML ³ T ⁻²

The tricky one is the dimensions of $q^2/4\pi\epsilon_0$, but

$$\frac{q^2}{4\pi\epsilon_0 r^2}$$

is a force so the dimensions of $q^2/4\pi\epsilon_0$ are those of force times length squared. Only one combination of m , \hbar , and $q^2/4\pi\epsilon_0$ has dimensions of length, so

$$r \sim \frac{\hbar^2}{mq^2/4\pi\epsilon_0}.$$

That result turns out to be exact (the missing constant is 1) as you'll learn in the quantum mechanics course. You can just put in the constants from a table, or you can use the trick

$$\hbar c \sim 2000 \text{ eV } \text{\AA},$$

which is good to 1 percent. (I remember it as '200 MeV fermis' and shift powers of ten between the energy and length units). But the expression for r has no c in it, so what use is the value for $\hbar c$? Ah, but I can insert c^2 and take it out:

$$r \sim \frac{\hbar^2 c^2}{mc^2 q^2 / 4\pi\epsilon_0}.$$

Look how mc^2 shows up – I don't have to even look up the electron mass as long as I remember its rest energy. A related useful value is the proton rest energy, roughly 1 GeV, and a proton is about 2000 times as massive as an electron (no one knows why but so it is) so an electron rest energy is 0.5 MeV. What about the $q^2/4\pi\epsilon_0$? Another useful combination is the famous *fine-structure constant* α :

$$\alpha \equiv \frac{q^2/4\pi\epsilon_0}{\hbar c} \approx \frac{1}{137}.$$

This constant is fundamental to quantum electrodynamics and is the dimensionless, and therefore *only* measure of how strong the electric charge is.

So

$$r \sim \frac{\hbar c}{q^2/4\pi\epsilon_0} \frac{\hbar c}{mc^2} = 137 \times \frac{2000 \text{ eV } \text{\AA}}{500 \text{ keV}} \sim 0.5 \text{ \AA}$$

and the diameter is roughly 1 Å.

Radius of the earth

America is roughly three time zones wide and is about 3000 miles wide, so 24 time zones would be 24,000 miles. How do I know America is 3000 miles wide? It takes about 5 hours to fly across and planes go roughly the speed of sound, which is about 600 miles per hour. Since $\pi = 3$ the radius is 4,000 miles or 6×10^6 m. Sorry for sinning by using miles. Feel free to rewrite the solution in kilometers; but the numbers come out so easily at first in miles (1 time zone = 1000 miles).

An alternative method is that a nautical mile is one minute of arc on the globe, so the earth's circumference is

$$1 \text{ nautical mile} \times \frac{60 \text{ minutes}}{\text{degree}} \times \frac{360 \text{ degrees}}{\text{full circle}} \sim 20000 \text{ mi}.$$

And nautical miles are nearly the same size as regular miles.

Football pitch (length)

Perhaps a UK football pitch is like an American football field, which is standard at 100 yards, so roughly 100 m is reasonable.

Height of atmosphere

The atmosphere doesn't have a well-defined height since it just gets thinner and thinner, but a reasonable definition is how high before it gets 'significantly' thinner, say

by a factor of e . From the isothermal atmosphere model from last year, which produces the magic Boltzmann factor,

$$\rho = \rho_0 e^{-mgh/kT},$$

where ρ_0 is the sea-level density and m is the mass of a molecule of air, and k is Boltzmann's constant. So the height H at which the density has dropped by a factor of e is when $mgh/kT = 1$ or

$$H = \frac{kT}{mg} = \frac{RT}{m_{\text{molar}}g},$$

where I multiplied by Avogadro's number on top and bottom in the last step. Then, with the molar mass of air roughly 28 g (it's mostly diatomic nitrogen),

$$H \sim \frac{8 \text{ J mol}^{-1} \text{ K} \times 300 \text{ K}}{2.8 \times 10^{-2} \text{ kg mol}^{-1} \times 10 \text{ m s}^{-2}} \sim 10 \text{ km}.$$

A bogus method – or rather a fine method that works for subtle reasons – is to estimate how high a molecule could go unimpeded if launched with the thermal velocity. From physics you studied long ago, $H \sim v^2/g$, where $v \sim 300 \text{ m s}^{-1}$ is a crude estimate of the thermal velocity (made by using the sound speed). So

$$H \sim \frac{10^5 \text{ m}^2 \text{ s}^{-2}}{10 \text{ m s}^{-2}} \sim 10 \text{ km}.$$

Hey, not bad. The error in the thermal speed cancelled the missing factor of 2 in $H \sim v^2/g$.

As an alternative method, the pressure at sea level is $p_0 \sim 10^5 \text{ Pa}$ and

$$p = \rho gh.$$

This formula works only if the density is constant, which it is not in the atmosphere, but if we assume that the atmosphere has constant density up to the height H then stops abruptly:

$$H \sim \frac{p_0}{\rho g} \sim \frac{10^5 \text{ Pa}}{1.3 \text{ kg m}^{-3} \times 10 \text{ m s}^{-2}} \sim 10 \text{ km}.$$

Mean free path of air molecules

The method in lecture used $n\sigma l \sim 1$ where n is number density, σ is the cross-section, and l is the mean free path. The number density follows from the molar volume of 22 litres. With $\sigma = \pi d^2$ and $d \sim 3.5 \text{ \AA}$ for air, the mean free path is

$$l \sim \frac{1}{n\sigma} \sim \frac{2.2 \times 10^{-2} \text{ m}^3}{6 \times 10^{23}} \times \frac{1}{3 \times 12 \times 10^{-20} \text{ m}^2} \sim 10^{-7} \text{ m}.$$

Average depth of oceans

Hard to say. I'd guess somewhere between 1 and 10 miles or 1 and 10 km. It turns out to be about 4 km. If you find a way to figure it out from more obvious numbers, let me know.

Height of Mt Everest

Planes have trouble flying over the Himalayas, and planes fly at 10 km or so (they often display their cruising altitude now on those computer monitors), so roughly 10 km for the height of Everest seems reasonable.

A2 Age of sun by a different mechanism

Chemical energy causes very little change in mass (use $E = mc^2$ to check) so the sun won't disappear just because its alleged chemical energy has been mostly used up. Chemical energies are roughly 5 or 10 kcal g⁻¹ or 20–40 MJ kg⁻¹ (check a packet of crisps) with petrol toward the higher end. So the energy available is

$$E \sim 4 \times 10^7 \text{ J kg}^{-1} \times 2 \times 10^{30} \text{ kg} \sim 10^{38} \text{ J}.$$

The power output of the sun (its luminosity) is on the last solution sheet. Here it is again. The solar flux at the earth's orbit is $F = 1.3 \times 10^3 \text{ W m}^{-2}$, so integrated over a spherical shell at the earth's orbit,

$$P = 4\pi R_{\text{orbit}}^2 F \sim 4 \times 3 \times (1.5 \times 10^{11} \text{ m})^2 \times 1.3 \times 10^3 \text{ W m}^{-2} \sim 4 \times 10^{26} \text{ W}.$$

This the time the sun could burn is

$$\tau \sim \frac{E}{P} \sim \frac{10^{38} \text{ J}}{4 \times 10^{26} \text{ W}} \sim 2 \times 10^{11} \text{ s} \sim 10^4 \text{ yr}.$$

Not very long! That's when the first cities were founded, so this theory for the sun's power is really bogus. It was a great mystery for a long, long time how the sun got its power.

A3 Air everywhere

From lecture:

$$\kappa \sim l v_{\text{thermal}},$$

where l is the mean free path and v_{thermal} is the thermal speed of the molecules. The thermal velocity is from the thermal energy, which is $\propto T$, and velocity is the square root of energy so

$$v_{\text{thermal}} \propto T^{1/2}.$$

The mean free path is trickier. It depends on number density n and cross section σ :

$$l \sim \frac{1}{n\sigma}.$$

The cross section depends only on the molecule, not how hot it is, so it remains fixed. But the number density depends on temperature by the ideal-gas law:

$$P = nkT.$$

The number density, if the pressure is held constant, is therefore $\propto T^{-1}$. The mean free path is therefore:

$$l \propto \frac{1}{n} \propto T,$$

and

$$\kappa \propto T \times T^{1/2} = T^{3/2}.$$

A4 Air conditioning on the cheap

As heat from the room air evaporates the water in the sheet, the room air cools (as if the room were sweating). When I wash a double sheet it feels pretty heavy even after having lots of the water spin out of it (which also means it won't drip much), maybe $m \sim 1$ kg, most of it water. The energy to evaporate it is $E = mL_{\text{vap}}$. To cool the room by ΔT takes energy

$$E \sim \rho V c_p \Delta T,$$

where ρV is the mass of room air and c_p is its specific heat. The room may be 3 m high, so

$$V \sim 30 \text{ m}^2 \times 3 \text{ m} \sim 100 \text{ m}^3.$$

The specific heat of air is $7R/2$ or, since one mole of air has a mass of roughly 30 g:

$$c_p = \frac{7}{2} \times \frac{8 \text{ J}}{\text{mol K}} \times \frac{\text{mol}}{3 \times 10^{-2} \text{ kg}} \sim 10^3 \text{ J kg}^{-1} \text{ K}^{-1}.$$

Putting in all the numbers:

$$\Delta T \sim \frac{mL_{\text{vap}}}{\rho V c_p} \sim \frac{1 \text{ kg} \times 2 \times 10^6 \text{ J kg}^{-1}}{1 \text{ kg m}^{-3} \times 100 \text{ m}^3 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}} \sim 20 \text{ K}.$$

Hey, not bad. It makes the 30°C room into a reasonable 10°C , if the cooling is 100% efficient. Some heat comes from the walls, new heat comes in the window (and from the fan motor), so it won't work quite that well, but the calculation shows that this form of air conditioning is plausible. An evaporative cooler uses this principle. It's a fancy box that you pour water into and then use a fan to blow dry outside air past it. David MacKay used one to cool his room when he was a postgraduate in Pasadena, California (hot summers).

A5 Number sense

$$\boxed{1/0.98}$$

$$\frac{1}{0.98} = \frac{1}{1 - 0.02} \approx 1 + 0.02$$

because $(1+x)(1-x) \approx 1$.

$$\boxed{1.1^{10}}$$

The binomial theorem, cut off after one term, gives

$$(1+x)^{10} \approx 1 + 10x,$$

or 2 in this case. But the other terms are large enough to matter. So instead take the logarithm:

$$\ln 1.1^{10} = 10 \ln 1.1 = 10 \ln(1 + 0.1) \approx 10 \times 0.1 = 1.$$

So

$$1.1^{10} = e \approx 2.718.$$

$$\boxed{0.9^{70}}$$

From the first number-sense problem, $0.9 \approx 1/1.1$ so

$$0.9^{70} \approx 1.1^{-70} = (1.1^{10})^{-7}.$$

Using the result for 1.1^{10} and the *useful fact* given in the problem, that $2^7 = 10^3 = e^7$:

$$0.9^{70} \approx e^{-7} = 0.001.$$

$$\boxed{\sqrt{1.05}}$$

$(1+x)^2 \approx 1 + 2x$, so if $2x = 0.05$ then $x = 0.05/2$ and

$$\sqrt{1.05} \approx 1.025.$$

In other words, if you increase the area of a square by 5%, you increased its sides by 2.5%. In general, if $f = x^n$, then taking logarithms,

$$\ln f = n \ln x,$$

and then differentiating:

$$\frac{df}{f} = n \frac{dx}{x}.$$

In easy-to-remember English:

fractional change in $f = n \times$ fractional change in x .

$$\boxed{\sqrt{50}}$$

I take out the big part that I can do easily: $\sqrt{49}$. So

$$\sqrt{50} = 7\sqrt{1 + \frac{1}{49}} \approx 7 \times (1 + 1/98) = 7 + \frac{1}{14} \approx 7.07.$$

Or using the easy-to-remember English above: To go from 49 to 50 is an increase of 2%, so to go from $\sqrt{49}$ to $\sqrt{50}$ is an increase of 1%:

$$\sqrt{50} \approx 7 + 1\% = 7.07.$$

$$\boxed{\ln 2000}$$

$$\ln 2000 = \ln 1000 + \ln 2 = 7 + \frac{7}{10} = 7.7$$

since $\ln 1000 \approx 7$ (the *useful fact*) and $2^{10} = 1000$ implies that $\ln 2 = 0.1 \ln 1000$.

$\ln 3$

$$3 \approx e + 0.3 \approx e(1 + 0.1) \text{ so}$$

$$\ln 3 \approx \ln e + \ln(1 + 0.1) \approx 1.1.$$

 $\sin 7$

I take away the $2\pi \approx 6.3$ first and get

$$\sin 7 = \sin(7 - 2\pi) \approx \sin 0.7 \approx 0.7$$

and $\sin x \approx x$ for even moderately large x . The next correction is $x^3/6$, which is tiny even when $x = 0.7$.

C1 Light bulb

I have two unknowns, length l and diameter d . So I need two equations. The first comes from the resistance of the filament, since I know the power and voltage. The second comes from the power radiated by a 3000 K source (using the Stefan–Boltzmann law).

The *resistivity* ρ is a property of the material and is independent of how much there is. The *resistance* R depends on the length and thickness. If I double the length of a wire, I have put two resistors in series and so doubled the resistance. So $R \propto l\rho$. Furthermore, if I run two wires in parallel, I double the cross-sectional area A and halve the resistance, so $R \propto \rho/A$. Putting the two together:

$$R \propto \rho l/A.$$

Look at the dimensions of ρ : resistance times length. And R is just resistance. So the left and right sides above have the same dimensions, and

$$R \sim \rho l/A,$$

where the \sim means that the two sides have the same dimensions but maybe are off by a (dimensionless) constant. This constant turns out to be 1 because resistivity is defined to make it 1:

$$R = \rho l/A.$$

The only time such ‘constants by definition’ are not 1 is when a competing equation has a slightly different structure and prevents both constants from being 1 at the same time (the $1/3$ in the equation for thermal diffusivity is an example of this situation).

The resistance itself I do not know, but the light-bulb power $P = V^2/R$ where V is the mains voltage, so

$$P = \frac{V^2}{\rho l/A} = \frac{V^2 A}{\rho l}.$$

Both P and V are known quantities, and $A \sim d^2$, so I now get one equation for l and d :

$$\frac{l}{d^2} = \frac{V^2}{\rho P}.$$

The second equation comes from Stefan–Boltzmann:

$$P = \text{area} \times \text{flux} \sim \pi l d \times \sigma T^4,$$

where σ is the Stefan–Boltzmann constant. The temperature is known: $T \sim 3000$ K. Remember that the sun, which burns hotter than a lightbulb and therefore gives off bluer light, has $T_{\text{sun}} \approx 6000$ K, so 3000 K is reasonable. The second equation is then

$$P \sim \pi l d \times \sigma T^4$$

or

$$l d \sim \frac{P}{\pi \sigma T^4}.$$

Squaring this equation and multiplying by first one:

$$l \sim \left(\frac{P}{\pi^2 \sigma^2 T^8} \frac{V^2}{\rho} \right)^{1/3}$$

You should check that the units work! Putting in numbers:

$$l \sim \left(\frac{6 \times 10^1 \text{ W}}{10^1 \times 3.6 \times 10^{-15} \text{ W}^2 \text{ m}^{-4} \text{ K}^{-8} \times 6.4 \times 10^{27} \text{ K}^4} \times \frac{5 \times 10^4 \text{ V}^2}{10^{-6} \Omega^2 \text{ m}^2} \right)^{1/3}$$

I wrote everything with exponents, even $\pi^2 = 10 = 10^1$, to make them easy to track for the next step. First count the powers of 10 inside the cube root: 5 on top and 7 on the bottom, so they give 10^{-2} . The other factors are a 6×5 on top and 3.6×6.4 on the bottom, making roughly 1. So

$$l \sim 10^{-2/3} \text{ m} \sim 0.2 \text{ m}.$$

For fun figure out that last step without a calculator. How reasonable is this value? If I look in a lightbulb the filament is only 1 or 2 cm. But it’s a coil of a coil, so maybe unwound it is 20 cm.

Now I can get d from the second equation:

$$d = \frac{P}{\pi l \sigma T^4}$$

so

$$d \sim \frac{60 \text{ W}}{3 \times 0.2 \text{ m} \times 6 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4} \times 0.8 \times 10^{14} \text{ K}^4} \sim 20 \mu\text{m}.$$

Hmm, that seems very small. We’ll break a lightbulb and look at the filament under a microscope and see whether it’s right or not.

C2 Ice on lakes

I grew up near a lake frozen in winter so I have an idea of the thickness. If you did not, your children may. See ‘Global warming will plunge Britain into new ice age within decades’, (*Independent*, 25 January 2004, <<http://news.independent.co.uk/uk/environment/story.jsp?story=484490>>). The article quotes a study warning that global warming may disrupt the Gulf Stream, in which case England will have the weather of Labrador:

Robert Gagosian, the director of Woods Hole, considered one of the world’s leading oceanographic institutes, said: ‘We may be approaching a threshold that would shut down [the Gulf Stream] and cause abrupt climate changes.’

Without waiting that long for direct experience, you can guess the thickness by knowing that people, especially Canadians playing ice hockey, skate on frozen lakes. You can break a thin crust of ice on a puddle with a gentle tap of the finger. Maybe that layer is a few mm thick. So to *walk* on a frozen lake it better be a lot thicker than that, maybe a few cm. Skates exert a much higher pressure than you do when walking, because skates have such a thin blade (much smaller than your shoe), so the ice on the lake should be a fair amount thicker for skating than for walking, especially to allow a margin of safety, so at least 10–15 cm and it may get even thicker in a long or cold winter.

Now for a calculation. First I explain what is going on in words, then formalize it into an equation. Heat flows out of the warm lake (at 0 °C!) into the cold air. The barrier is the ice. As heat leaves, the water just below the ice freezes (so I’ll use heat of fusion later). As the ice thickens, the heat flows more slowly, so the rate of freezing falls too. A differential equation lurks in here!

Fluxes are power per area, but if I reason about fluxes instead of power itself, then I end up thinking about a unit area of ice and get confused. So I imagine a slab of ice of area A and set up the equations knowing that A will cancel (if it does not, it helps catch a mistake in reasoning). Similarly, the power per area is energy per time, and I imagine the energy transferred in a concrete time Δt . Let $z(t)$ be the thickness of the ice. Then the energy that flows out of an area A in time Δt is

$$E = \text{flux} \times \text{area} \times \text{time} = K \frac{\Delta T}{z} A \Delta t,$$

where K is the thermal conductivity of ice and ΔT is the temperature difference between the air and water. That energy loss freezes a mass of ice E/L_{fusion} , where L_{fusion} is the heat of fusion (energy per mass of ice). The volume is mass over density and the thickness is volume over area, so the extra thickness is

$$\Delta z \sim \frac{E}{L_{\text{fusion}} \rho A},$$

so

$$\Delta z \sim \frac{K \Delta T A \Delta t / z}{L_{\text{fusion}} \rho A}.$$

Hey the areas cancel, great, and

$$\Delta z \sim \frac{K \Delta T}{\rho L_{\text{fusion}}} \frac{\Delta t}{z}.$$

In the limit that $\Delta t \rightarrow 0$, the differential equation appears:

$$\frac{dz}{dt} \sim \frac{1}{z} \frac{K \Delta T}{\rho L_{\text{fusion}}},$$

whose solution is (leaving aside dimensionless constants)

$$z(t) = \sqrt{\frac{K \Delta T}{\rho L_{\text{fusion}}}} t.$$

Now put in numbers and see whether something reasonable comes out. New Hampshire has been much in the British news lately because the American presidential election holds an early hurdle election (a ‘primary’) there, and most of the news reports mention how frozen New Hampshire is, with temperatures of -20°C being typical and -30°C not uncommon. So I’ll use $\Delta T \sim 25^\circ\text{C}$. The thermal conductivity we did in lecture: $K \sim 2 \text{ W m}^{-1} \text{ K}^{-1}$. And the heat of fusion is roughly

$$L_{\text{fusion}} \sim \frac{L_{\text{vap}}}{10} \sim 0.2 \text{ MJ kg}^{-1}.$$

A cold winter lasts a few months, say 3 months or one-fourth of a year:

$$t \sim \frac{1 \text{ yr}}{4} \sim \frac{\pi \times 10^7 \text{ s}}{4} \sim 10^7 \text{ s}.$$

Putting in all the numbers:

$$z \sim \left(\frac{2 \text{ W m}^{-1} \text{ K}^{-1} \times 25 \text{ K}}{10^3 \text{ kg m}^{-3} \times 0.2 \times 10^6 \text{ J kg}^{-1}} \times 10^7 \text{ s} \right)^{1/2} \sim 1.5 \text{ m}$$

That’s deep ice!

D1 Random walks

This I’ll leave you to put together from the lecture material (see the notes for lecture 4) and whatever else you find interesting and useful to you.

SOME SOLUTIONS FOR SHEET 3

A1 *Cooking a turkey*

The cooking time, being dependent on diffusion, is proportional to size *squared*. Instead of calculating it from scratch using the diffusion constant for turkey (which I'll assume is the same as for egg or for water), I can use the squared dependence and the egg information to estimate the cooking time for a turkey. Always use *scaling*, never compute from scratch unless you have no choice whatsoever.

How much bigger is a turkey than an egg? An egg is roughly 5 cm in diameter, so the heat needs to diffuse about 2 cm to cook the center. A moderate turkey is perhaps 10 cm at its thickest. The meat makes roughly a shell around the bones, so heat comes in from only one side and therefore needs to diffuse the whole 10 cm (unlike in the egg, where it comes in from both sides). The cooking time is given by

$$\text{cooking time} \propto (\text{distance})^2,$$

and the turkey distance is about 5 times the egg distance, so the cooking time is 25 times as long, or $10 \text{ min} \times 25 \sim 4 \text{ hrs}$, which is reasonable.

A2 *Diamond*

As diamond is cooled, its atoms vibrate less: 'all matter is made of atoms' and 'heat is a form of motion', two great principles of physics. So the lattice becomes more perfect, and phonons travel farther before colliding with a lattice imperfection. So the conductivity will increase due to this effect. The specific heat will decrease because of quantum effects, though not by as much as the conductivity increases – until the temperature gets very low.

The thermal conductivity is $K = \rho c_p \kappa$. The mean free path lives in

$$\kappa \sim \frac{1}{3} v \ell,$$

where v is the speed at which heat travels and ℓ is the mean free path of that travel. In a gas, heat travels by molecules moving to a new location, so v is the thermal speed and ℓ is the molecular mean free path. In a liquid or solid, the molecules are jammed as near as possible to each other – which is why solids and liquids are so incompressible – so heat travels not by moving a molecule from a hot location to a cold location. Rather, vibrations move from one molecule to the next (phonons). Phonons are mini sound waves so the v in a liquid or gas is v_{sound} and the ℓ is the phonon mean free path (what I am trying to estimate). Thus

$$\ell \sim \frac{K}{\rho c_p v_{\text{sound}}/3}.$$

I can estimate $v = v_{\text{sound}}$ in several ways. In a typical rock, $v_{\text{sound}} \sim 5 \text{ km s}^{-1}$. Always compare with what you know! Will diamond have a lower or higher speed of sound than rock? Diamond is carbon atoms, and carbon has a higher bond energy than larger atoms (say silicon, a component of a lot of rock) so diamond will be stiffer than rock. More stiffness means higher v_{sound} . Carbon atoms are also lighter than rock

atoms, so sound moves faster because the atoms vibrate more quickly. This argument even makes dimensional sense:

$$(\text{speed})^2 \sim \frac{\text{bond energy}}{\text{atomic mass}}.$$

The two effects significantly increase v_{sound} to perhaps 10 km s^{-1} .

I can check that with the relation above from dimensions. A typical strong bond is 4 eV. Why? Chemical bonds, e.g. the bonds between carbon, oxygen, and hydrogen in your skin, withstand visible light (1–3 eV) but not ultraviolet: that's how sunburn causes cancer. So a reasonable guess is that the bond energy is a bit higher than 3 eV. Another argument is that the ground state of hydrogen is –14 eV, but hydrogen is very tiny so the electrostatic forces are larger than in bigger atoms; furthermore the electron in a carbon–carbon bond is not going to infinity, merely an angstrom or so, to be nearer the neighboring carbon. So again something like 5 eV (or 4 or 6 or even 8) is reasonable. Using that value to get a speed:

$$v_{\text{sound}}^2 \sim \frac{8 \text{ eV}}{12 \text{ amu}} \times \frac{1.6 \times 10^{-19} \text{ J}}{1 \text{ eV}} \times \frac{6 \times 10^{23} \text{ amu}}{10^{-3} \text{ kg}} \sim 10^8 \text{ m}^2 \text{ s}^{-2},$$

so $v_{\text{sound}} \sim 10 \text{ km s}^{-1}$.

I still need the density and specific heat. In density diamond is like a moderate rock, so perhaps $\rho \sim 3 \times 10^3 \text{ kg m}^{-3}$. The specific heat comes from three kinetic-energy degrees of freedom (the carbon atoms can move) and three potential-energy degrees of freedom (the carbon atoms live in a three-dimensional spring potential), so by equipartition

$$c_p \sim 3R \sim 3 \times \frac{8 \text{ J}}{\text{mol K}^{-1}} \times \frac{1 \text{ mol}}{1.2 \times 10^{-2} \text{ kg}} \sim 2 \times 10^3 \text{ J kg}^{-1}.$$

This value, the Dulong and Petit value (see Adkins, p. 51), turns out to be a factor of 4 too large because diamond's immense stiffness means that at room temperature the lattice vibrations are quantized. Only at high temperatures does the classical approximation (equipartition) become accurate. But I'll pretend I did not know that and will use the estimated value.

Once I put all the numbers together, the mean free path is

$$\ell \sim \frac{3 \times 2000 \text{ W m}^{-1} \text{ K}^{-1}}{3 \times 10^3 \text{ kg m}^{-3} \times 2 \times 10^3 \text{ J kg}^{-1} \times 10^4 \text{ m s}^{-1}} \sim 10^{-7} \text{ m}.$$

That's about 300 lattice spacings! (If I had used the correct c_p , the mean free path would have been a factor of 4 larger or 1000 lattice spacings.)

The mean free path in water is much smaller, roughly one lattice spacing or 3 Å, because water does not have the regular ordering of a solid (in ice the mean free path is longer, about 7 spacings). In a liquid, the molecules pack tightly but their lack of order means that every lattice point is an imperfection and phonons scatter in a short distance.

The thermal conductivity of diamond contains lots of interesting physics. If you lower the temperature enough, the thermal vibrations reduce and the lattice becomes

more ordered. At low enough temperatures, the main scattering is no longer from thermally displaced atoms but rather from imperfections due to carbon-13 atoms in the lattice.

Normal diamond has about 1% carbon-13. In sly experiments, Wei et. al.¹ vary diamond's isotopic composition and then measure its specific heat. For 99.9%-pure diamond, they measure $4 \times 10^4 \text{ W m}^{-1} \text{ K}^{-1}$ (at 104 K). For 99.999%-pure diamond, their fitted theory predicts $2 \times 10^5 \text{ W m}^{-1} \text{ K}^{-1}$ (at 80 K). Let's see if I can understand where the factor of 5 increase comes from. The diamond has been made (in one's thoughts) a factor of 100 more pure, so the number density of carbon-13 atoms is the same factor lower. The distance between carbon-13 atoms is then a factor of $100^{1/3} \sim 5$ greater, and phonons will travel five times farther before scattering. This longer mean free path increases κ and K by a factor of 5. Hey, good luck! A solid state physicist who reads this should check whether this argument is bogus!

A3 Speeds

Speed of sound in air

The speed of sound is roughly the thermal speed (not much else it could be, except for a dimensionless factor) and $v_{\text{thermal}} \sim \sqrt{3RT/M}$, where M is the molar mass of air. Putting in numbers:

$$v_{\text{thermal}} \sim \frac{3 \times 8 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{3 \times 10^{-2} \text{ kg}} \sim 500 \text{ m s}^{-1}.$$

The sound speed turns out to be roughly $v_{\text{thermal}}/\sqrt{3}$ so about 300 m s^{-1} , but either is in the ballpark (an American expression).

An alternative is to use dimensions: $v \sim \sqrt{P/\rho}$, where P is the pressure and ρ is the density. This formula turns out to be off by a γ because of adiabatic versus isothermal, but that may become a problem on the next sheet so I'll forget about the γ here. Putting in numbers:

$$v \sim \left(\frac{10^5 \text{ Pa}}{1 \text{ kg m}^{-3}} \right)^{1/2} \sim 300 \text{ m s}^{-1}.$$

Speed of sound in rock

The speed is a lot higher than in air but how much is hard to say. In solution A2 I worked out the speed in diamond as 10 km s^{-1} (in two ways), so perhaps 5 km s^{-1} for a typical rock.

¹ 'Thermal conductivity of isotopically modified single crystal diamond', *Physical Review Letters* 70(24):3764; online at http://prola.aps.org/abstract/PRL/v70/i24/p3764_1

Walking speed

I just walked across the room and timed how many paces I took per second: a bit less than two paces per second. Each pace is about 1 m so $v \sim 1.5 \text{ m s}^{-1}$ or maybe 2 m s^{-1} . An alternative method uses dimensions. Tall people walk faster, so the speed should depend on height or leg length l (which is also the center-of-mass height). Gravity keeps your feet on the ground, so it should also depend on g . Therefore by dimensions, $v \sim \sqrt{gl}$. Putting in numbers:

$$v \sim \sqrt{10 \text{ m s}^{-2} \times \text{m}} \sim 3 \text{ m s}^{-1}.$$

This speed turns out to be the fastest walking speed – any faster and your feet leave the ground (you're running or jogging).

Train speed

It depends whether there is snow on the lines ($v = 0$) and whether it is the right kind of snow. But assuming that the weather gods are kind and that Railtrack is repairing the tracks instead of paying Jarvis and Balfour Beatty shareholders and executives, the train to London takes about one hour to go the 50 or 60 miles, so

$$v \sim 100 \text{ kph}.$$

Orbital velocity of the earth

In terms of the orbital radius r ,

$$v \sim \frac{2\pi r}{1 \text{ yr}} \sim \frac{2 \times \pi \times 1.5 \times 10^{11} \text{ m}}{\pi \times 10^7 \text{ s}} \sim 30 \text{ km s}^{-1}.$$

Notice how nicely the π 's cancel using the approximation that $1 \text{ yr} \sim \pi \times 10^7 \text{ s}$.

Velocity of the sun relative to the microwave background

I have no idea how to estimate this! But the value is about 600 km s^{-1} .

Speed of light

$$c \sim 3 \times 10^8 \text{ m s}^{-1}.$$

Speed an ant walks

The last ant I saw took about 30 s to walk across one window in my room (about 1 m), so $v \sim 3 \text{ cm s}^{-1}$.

Speed of a plane

Planes fly nearly the speed of sound, so $v \sim 300 \text{ m s}^{-1}$. They also take about 5 or 6 hours to cross America, which is 3000 mi, so 600 mph (which is 300 m s^{-1}).

Flow speed of the Cam

A punt probably floats along at the flow speed, and the last time I walked to Granchester I saw a punt drifting somewhat slower than my walking speed. So $v \sim 1 \text{ m s}^{-1}$.

Speed of packets on the Internet

I ‘pinged’ a machine at Caltech in Pasadena, California and the round-trip time was 0.16 s. Caltech is 8 time zones away, so about 8000 mi along the equator but less up at these latitudes, so how about 8000 km. The round-trip distance is twice that, and the speed is

$$v \sim \frac{16000 \text{ km}}{0.16 \text{ s}} \sim 10^5 \text{ km s}^{-1},$$

or about one-third the speed of light!

Speed continents move

Earthquakes, for example the San Andreas fault, result from continental motion. I’ll guess that when the mismatch reaches 1 m, an earthquake happens, and a big earthquake happens maybe every 10 years, so $v \sim 10 \text{ cm yr}^{-1}$.

Speed bacteria swim

Lots of guesswork needed here. I’ll do it by estimating how much power *E. coli* can generate and how much power they need to swim. They are swimming in a viscous environment, like moving through honey, for which the drag force is Stokes drag:

$$F \sim 6\pi\rho\nu rv,$$

where ρ is the density of water, ν the viscosity of water (which turns out to be 6κ), r is the radius of the bacterium, and v is its speed. Except for the 6π , you can derive this result using dimensions and the requirement that the force be proportional to viscosity. So I’ll pretend I didn’t know the 6π . Then the power is

$$P \sim Fv \sim \rho\nu rv^2.$$

For the power it can generate, I’ll assume it has the same baseline power per mass as a person. A person generates 100 W from 100 kg, for 1 W kg^{-1} . An *E. coli* has a size of 10^{-6} m (see last week’s sheet) so its mass is roughly 10^{-15} kg if it is mostly water. So

$$P_{\text{generate}} \sim 10^{-15} \text{ kg} \times 1 \text{ W kg}^{-1} = 10^{-15} \text{ W}.$$

Hey an equals sign; they happen once in a while. Equating powers gives

$$v \sim \left(\frac{P_{\text{generate}}}{\rho\nu r} \right)^{1/2} \sim \left(\frac{10^{-15} \text{ W}}{10^3 \text{ kg m}^{-3} \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \times 10^{-6} \text{ m}} \right)^{1/2} \sim 10^{-3} \text{ m s}^{-1}.$$

A quick check on the web says this value is a factor of 30 or 40 too high, so the method is not great (approximation loses sometimes) probably because I approximated away too much of the mechanics of swimming.

Electron drift speed in a lightbulb

The current is given by

$$I = nqvA,$$

where n is the number density of free electrons, q is the electron charge, v is their drift speed (what I want), and A is the area of the wire. A 60-W lightbulb draws a current of $I = 0.25 \text{ A}$ through a wire of diameter of say $d \sim 3 \text{ mm}$. Copper has maybe 2 electrons (I’m an order-of-magnitude chemist) per atom, and atoms are spaced every 3 \AA , so

$$n \sim \frac{2}{(3 \times 10^{-10} \text{ m})^3} \sim 10^{29} \text{ m}^{-3}.$$

The drift speed is then

$$v = \frac{I}{nqA} \sim \frac{0.25 \text{ A}}{10^{29} \text{ m}^{-3} \times 1.6 \times 10^{-19} \text{ C} \times 10^{-5} \text{ m}^2} \sim 10^{-6} \text{ m s}^{-1}.$$

Very slow!

Escape velocity from earth

A low-earth-orbit satellite has a period of 90 min. I don’t know why I remember this. So

$$v_{\text{orbit}} \sim \frac{2 \times \pi \times 6 \times 10^6 \text{ m}}{90 \text{ min} \times 60 \text{ s min}^{-1}} \sim 7 \text{ km s}^{-1}.$$

The escape velocity is $\sqrt{2}v_{\text{orbit}}$, so 10 km s^{-1} .

Escape velocity from the solar system

The earth’s orbital velocity is 30 km s^{-1} so the escape velocity is 42 km s^{-1} .

A4 Temperature of Venus

Scaling again! Solar flux F at a distance r from the sun is proportional to r^{-2} , and blackbody temperature is proportional to $F^{1/4}$, so

$$T \propto r^{-1/2}.$$

So reducing the distance by a factor of 0.72 increase the temperature by a factor of $\sqrt{1/0.72}$. No need for a calculator:

$$\sqrt{1/0.72} \approx \sqrt{1.4} \approx 1.2,$$

so Venus would have a temperature of $1.2 \times 255 \text{ K} \sim 305 \text{ K}$. Hey, not bad, that’s a balmy summer day.

Instead the temperature is 727 K. Since flux is proportional to T^4 , going from 305 K to 727 K increases the flux by a factor of $(727/305)^4$ or 30. But the actual outgoing flux is what it would be for a no-greenhouse surface temperature of 305 K. Therefore the greenhouse gases reduce the outgoing flux by the same factor of 30. What if all that carbon dioxide and water vapor were on Mars? Maybe Mars would become cozy.

B1 *Temperature in the atmosphere*

Let's say a parcel of air is 1 m in size (the size of small gusts of air). The time for heat to diffuse within that parcel is

$$\tau \sim \frac{l^2}{\kappa} \sim 10^5 \text{ s} \sim 30 \text{ hr},$$

since $\kappa \sim 10^{-5} \text{ m}^2 \text{ s}^{-1}$. That's plenty of time for even a slow parcel (say moving with a slow wind of 5 m s^{-1}) to climb the whole atmosphere. So the parcel rises too fast for heat to flow, and the expansion is therefore adiabatic.

(a) Let's say the temperature starts out constant. The pressure drops with height (the Boltzmann factor argument from IA physics), so as a parcel rises, it expands. As it expands, it cools and will be cooler than the surrounding air. When it and the surrounding air come to equilibrium, the temperature at that height will have dropped slightly. This process will continue until the temperature is what it would be in an adiabatic change as the parcel rises.

(b) I have two unknowns, p and T , so I need two equations. One comes from the ideal gas law, which always applies:

$$p = nkT.$$

The other comes from the adiabatic law:

$$pV^\gamma = \text{const.}$$

Damn, now I have a third unknown, the volume. I can get rid of it by rewriting the ideal gas law as

$$pV = NkT,$$

where $N = nV$ is the number of molecules rather than the number density. Now I rewrite the adiabatic law to have pV in it. The first step is to take the γ 'th root of both sides,

$$p^{1/\gamma} V = \text{const.},$$

and then extract a pV :

$$p^{-1+1/\gamma} pV = \text{const.}$$

Now I use the ideal gas law to replace pV :

$$p^{-1+1/\gamma} T = \text{const.},$$

where the constants N and k have been sucked into the right hand side. Ah, so

$$T \propto p^{1-1/\gamma}.$$

Do everything in fractional changes:

$$\frac{\Delta T}{T} = \left(1 - \frac{1}{\gamma}\right) \frac{\Delta p}{p}.$$

For simplicity I'll define

$$\beta \equiv 1 - \frac{1}{\gamma},$$

so

$$\frac{\Delta T}{T} = \beta \frac{\Delta p}{p}.$$

I chose $\beta = 1 - 1/\gamma$ rather than its negative because I want β to be positive. Explicit minus signs are clearer than using variables that are definitely negative (i.e. that hide a minus sign within them).

To get rid of the Δp and get Δz instead, I need to balance gravity against pressure. Imagine a slab of air at height z with area A and thickness Δz . The pressure difference Δp produces an upwards force $A\Delta p$. Gravity provides a downwards force $mg = \rho g A \Delta z$. The two balance (unless the atmosphere is accelerating towards earth or into space), so $A\Delta p = \rho g A \Delta z$. The area cancels, which is a useful check, and

$$\Delta p = \rho g \Delta z.$$

Putting this into the fractional change:

$$\frac{\Delta T}{T} = -\beta \frac{\rho g}{p} \Delta z.$$

Substituting $p = nkT = \rho kT/m$, where m is the molecular mass:

$$\Delta T = -\beta \frac{mg}{k} \Delta z.$$

Dividing by T_0 , the sea-level temperature to go back to fractional changes:

$$\frac{\Delta T}{T_0} = -\beta \frac{mg}{kT_0} \Delta z.$$

The right side does not look like a fractional change, but it is one. The ratio kT_0/mg is the atmosphere scale height:

$$H = \frac{kT_0}{mg}.$$

So

$$\frac{\Delta T}{T_0} = -\beta \frac{\Delta z}{H}.$$

Thus the temperature changes *linearly* with height:

$$T = T_0 \left(1 - \beta \frac{z}{H}\right),$$

where $T_0 \sim 300 \text{ K}$ and $H \sim 10 \text{ km}$.

The pressure is given using the relation derived earlier:

$$T \propto p^\beta.$$

(c) For dry air (try finding that in Wales), $\gamma = 1.4$ so $\beta \approx 0.3$. Thus from part b, for $z = 1000 \text{ m}$,

$$\Delta T \sim \beta T_0 \frac{\Delta z}{H} \sim 0.3 \times 300 \text{ K} \times \frac{1000 \text{ m}}{10 \text{ km}} \sim 10^\circ \text{C}.$$

Which is quite reasonable. A check on the Internet showed a graph of Snowdon's year-round temperature and it values from 4 to 14°C , about 10°C colder than sea level.

SOME SOLUTIONS FOR SHEET 4

A1 *Isothermal atmosphere*

Given that

$$\beta \equiv 1 - \frac{1}{\gamma},$$

when $\gamma \rightarrow 1$ then $\beta \rightarrow 0$. So

$$T = T_0 \left(1 - \beta \frac{z}{H}\right)$$

becomes $T = \text{const}$: an isothermal atmosphere. Great! The pressure, however, is tricky because $T \propto p^\beta$ or

$$p \propto T^{1/\beta},$$

which becomes unpleasant as $\beta \rightarrow 0$.

Instead imagine γ very close to 1: $\gamma = 1 + \epsilon$. Then

$$\beta = 1 - \frac{1}{1 + \epsilon} \approx 1 - (1 - \epsilon) = \epsilon.$$

So

$$\frac{T}{T_0} \approx 1 - \epsilon \frac{z}{H}$$

and

$$p \propto T^{1/\epsilon}.$$

The combination of these two results is

$$\frac{p}{p_0} \propto \left(1 - \epsilon \frac{z}{H}\right)^{1/\epsilon}.$$

This equation may not look so familiar, but look at these:

$$\begin{aligned} 1.01^{100} &\approx e, \\ 1.001^{1000} &\approx e, \\ 1.0001^{10000} &\approx e. \end{aligned}$$

The pattern for large n is:

$$\left(1 + \frac{1}{n}\right)^n \rightarrow e,$$

which gives

$$\left(1 + \frac{x}{n}\right)^n \rightarrow e^x.$$

Why?! Thus

$$\left(1 - \epsilon \frac{z}{H}\right)^{1/\epsilon} \approx e^{-z/H}.$$

Since $H = mg/kT_0$ the pressure is

$$\frac{p}{p_0} \propto e^{-mgz/kT_0}.$$

Ah, the Boltzmann factor has returned with mgz as the potential energy of a gas molecule at height z and T_0 as the temperature of the isothermal atmosphere.

A2 *Ice skating*

For the magic pressure p I'll try

$$p \sim \frac{L_{\text{vap}} \text{ for one molecule}}{\text{molecular volume}}.$$

This quantity is also the volume heat of vaporization, ρL_{vap} so

$$p \sim \rho L_{\text{vap}} \sim 10^3 \text{ kg m}^{-3} \times 2 \times 10^6 \text{ J kg}^{-1} \sim 2 \times 10^9 \text{ J m}^{-3}$$

or about 20000 atm. An ice skate blade has area

$$A \sim 20 \text{ cm} \times 0.2 \text{ cm} = 4 \times 10^{-4} \text{ m}^2$$

so the pressure exerted by the ice skate blade is

$$\Delta p \sim \frac{\text{weight}}{\text{area}} \sim \frac{60 \text{ kg} \times 10 \text{ m s}^{-2}}{4 \times 10^{-4} \text{ m}^2} \sim 10^6 \text{ Pa}$$

or about 10 atm.

Thus the change in freezing temperature is

$$\Delta T_{\text{freeze}} \sim T_{\text{freeze}} \times \frac{10 \text{ atm}}{20000 \text{ atm}} \sim 0.1^\circ \text{C}.$$

That's not enough to allow ice skating through pressure melting when the air temperature is even 1 degree below freezing. Oh, well! You can also check the pressure-melting theory by skating and then picking up one skate and looking at the blade. If pressure were keeping the water around the blade melted, as soon as you lift the blade, the water would freeze back into ice crystals. But I haven't seen that happen.

Another effect is friction. As the skate slides along, the friction means energy dissipated into the ice. This energy will melt some thickness of ice below the blade no matter how low the friction.

A3 *Fog*

As night falls, moist daytime air cools, which reduces the the vapor pressure of water. The excess water vapor condenses into tiny water droplets. From the vapor pressures at the daytime temperature and nighttime temperatures, I can work out the density of water vapor condensed out (ρ_c). That's not enough however. The water could live as one giant drop or it could be trillions of nanometer-sized droplets. To decide, I need one more equation, which comes from the other piece of information: the mean free path of a light ray. I'll guess that a light ray that hits a droplet gets well scattered. From kinetic theory, $n\sigma\ell \sim 1$, where n is the number density of droplets, σ is the cross-sectional area of a droplet, and ℓ is the mean free path.

Imagine that the droplets are cubes of side d (for diameter) separated by a distance x . Then each has mass ρd^3 and the density of condensed-out water is

$$\rho_c \sim \rho \frac{d^3}{x^3}.$$

That's the first equation for the three unknowns, ρ_c , d , and x . Another equation comes from the mean free path, since $n = 1/x^3$ and $\sigma \sim d^2$:

$$\frac{1}{x^3} \sim \frac{1}{d^2 \ell}.$$

Combining these two equations:

$$\frac{\rho_c}{\rho} \sim \frac{d}{\ell}.$$

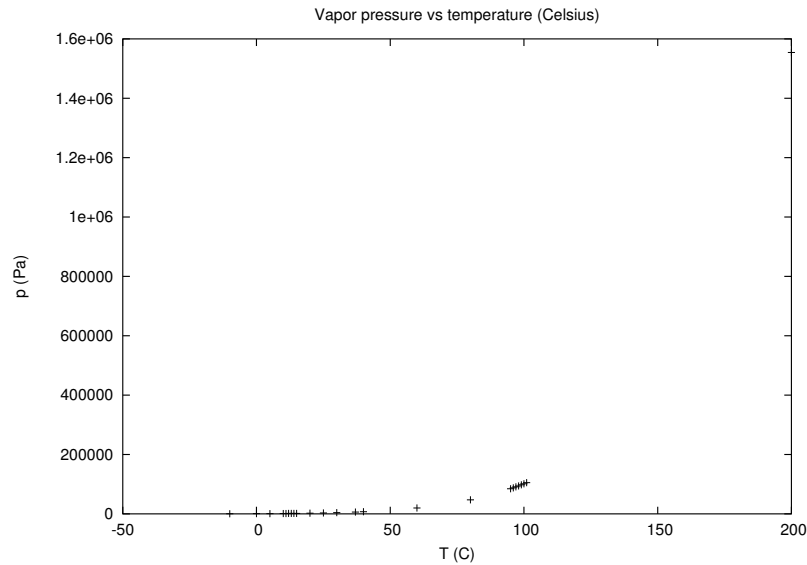
Let's say the temperature goes from a daytime 20°C to a nighttime 10°C . The table in question B1 says that $\Delta p_{\text{vap}} \sim 10^3 \text{ Pa}$ or about 10^{-2} atm . If water were air (in molar mass) then ρ_c would be 10^{-2} times the density of air. This approximation is not horrible, so I'll use it. Maybe it cancels another sloppiness in the derivation. Since ρ is 1000 times the density of air, $\rho_c/\rho \sim 10^{-5}$. In a moderate fog one can see maybe $\ell \sim 100 \text{ m}$, so

$$d \sim 100 \text{ m} \times 10^{-5} = 1 \text{ mm}.$$

That's way too big (real fog droplets are about 20 to 50 times smaller), so an assumption of the analysis is badly broken. Oh, well, not every problem works out nicely.

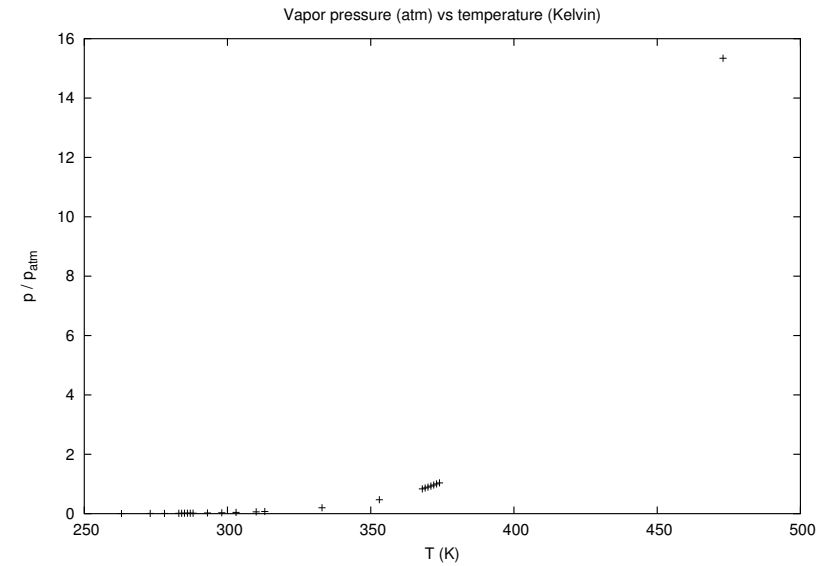
B1 Vapor pressure

(a)



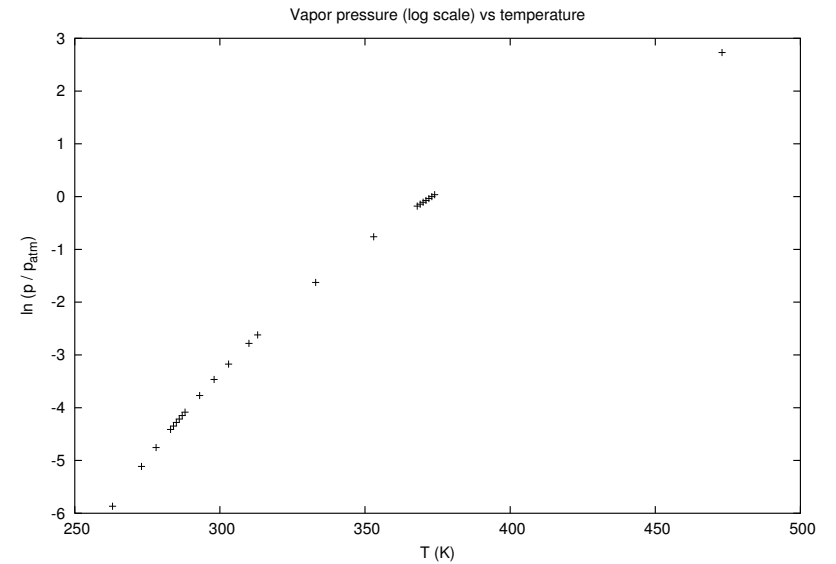
These axes are still useless! I can hardly see the points at low temperature because the high pressure at $T = 200^\circ\text{C}$ makes the y axis span a huge range.

(b)



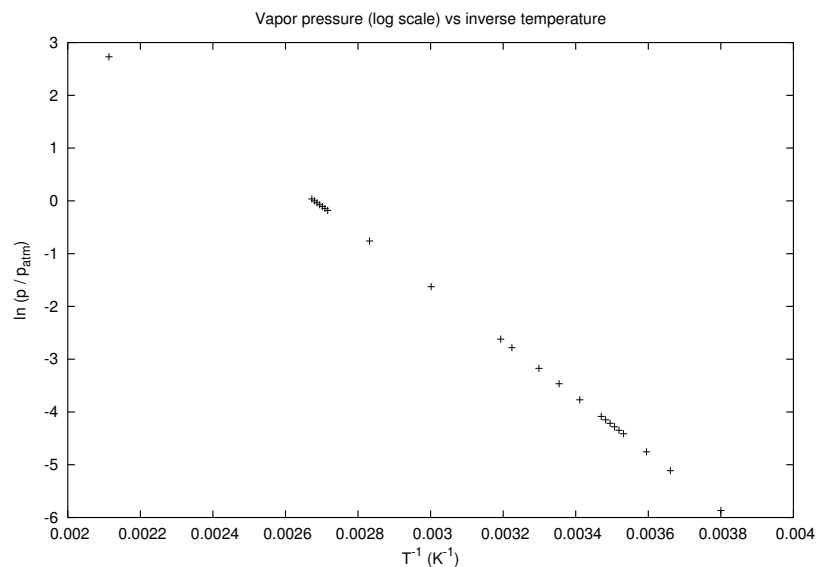
Slightly better in principle, but I still can't see anything useful.

(c)



Much better in that all the points are easy to distinguish.

(d)



And now the line is straight. Great!

(e) Since the line is straight,

$$\ln \frac{p}{p_{\text{atm}}} = -\frac{A}{T} + B,$$

where A and B are constants. The dimensions of A are temperature, so I'll use T_0 for it. B is dimensionless but its value isn't that important. Eyeballing the slope by taking the first point on the left and the penultimate point on the right:

$$\text{slope} = \frac{\text{rise}}{\text{run}} \sim \frac{-5.2 - 2.8}{(0.0036 - 0.0021) \text{ K}^{-1}} = -\frac{8}{15} \times 1000 \text{ K} \sim -5000 \text{ K}$$

So $T_0 \sim 5000 \text{ K}$. To convert it to more familiar units, I use $1 \text{ eV} \sim 10^4 \text{ K}$, so

$$\text{energy per molecule} = kT_0 \sim 0.5 \text{ eV},$$

$$\text{energy per mole} = RT_0 \sim 8 \text{ J mol}^{-1} \text{ K}^{-1} \times 5000 \text{ K} \sim 4 \times 10^4 \text{ J mol}^{-1},$$

and

$$\text{energy per mass} = 4 \times 10^4 \text{ J mol}^{-1} \times \frac{1 \text{ mol}}{1.8 \times 10^{-2} \text{ kg}} \sim 2 \times 10^6 \text{ J kg}^{-1}.$$

Especially the last value looks familiar. It's the *heat of vaporization of water*, L_{vap} .

(f) The Boltzmann factor gives the probability of finding a molecule in its different energy states. Here the states are liquid (low energy) or gas (much higher energy because all the bonds are gone). So the probabilities are:

$$P(\text{liquid}) \propto e^{-E_{\text{liquid}}/kT},$$

and

$$P(\text{vapor}) \propto e^{-E_{\text{vapor}}/kT}.$$

These probabilities are unnormalized. But their ratio is easy to compute without normalizing:

$$\frac{P(\text{vapor})}{P(\text{liquid})} = e^{-\Delta E/kT},$$

where $\Delta E = E_{\text{vapor}} - E_{\text{liquid}}$. This energy is L_{vap} . The amount of liquid is roughly constant since liquid is so much denser vapor. Then $P(\text{liquid})$ is roughly constant, and

$$P(\text{vapor}) \propto e^{-L_{\text{vap}}/kT}.$$

Since probability is proportional to density and density (by the ideal gas law) is proportional to pressure,

$$p \propto e^{-L_{\text{vap}}/kT}$$

or

$$p = p_0 e^{-L_{\text{vap}}/kT},$$

for some pressure p_0 . This pressure is not atmospheric pressure as you can see by putting in $T = 373 \text{ K}$ (boiling point of water) and $p = 1 \text{ atm}$ to solve for p_0 .

As T goes to infinity, this vapor pressure equation predicts that the pressure asymptotes to p_0 . The result seems strange. But think about the world at infinite temperature. Then everything gets huge amount of energy for free (from the heat bath), so the energy difference between liquid and gas becomes miniscule. The molecule no longer cares whether it is in the liquid or the gas. At temperatures almost as high, it cares almost as little. So as $T \rightarrow \infty$, the temperature becomes irrelevant and the vapor pressure becomes independent of temperature.

D1 Carnot cycle

The notes for 6 Feb have everything except the diagrams.

Estimate the temperature of the earth

Questions from the real world come messy. They don't come with labelled formulae saying 'Use me' or 'Apply me'. So the first step is to get yourself familiar with the physical system.

Why is the earth hot at all?

Why, for example, isn't the earth as cold as space, whatever that means? One meaning is the temperature of the microwave background radiation, which is 2.7 K. You suggested several reasons that the earth is much warmer:

- Radioactivity in the crust.
- Trapping of heat by the atmosphere.
- Sunlight!

The first one we'll talk about later in the course. The second, well, keep it in mind. The main effect is from sunlight. To see how it heats the earth, imagine a cold earth (0 K) and now the sun starts shining on it. The earth's surface will slowly warm up, and as it warms up it'll radiate energy. Eventually the radiated energy will match the received energy. This steady state sets the earth's surface temperature.

So how much does the earth radiate at a given temperature, T ? First, what sort of quantity are we looking for? Is it an energy? Is it a force? No, it's a power: energy/time. The sun feeds energy in at a particular rate and the earth sends it to space at the same rate.

Radiated power versus temperature

How does the radiated energy/time (the power) depend on T ? The honest derivation of the *blackbody-radiation* formula is a complicated affair and not possible within classical thermodynamics. You can read about it any textbook on statistical mechanics. We use a simpler approach, one that works for finding many formulae: *dimensional analysis*. You can read a lot about dimensional analysis in my textbook at <www.inference.phy.cam.ac.uk/sanjoy/> but I just use a cheap version of it here. In Part II ('Order of magnitude physics') I'll tell you the whole story about dimensional analysis.

You suggested the quantities on which P depends:

<i>Symbol</i>	<i>What it is</i>	<i>Why include it</i>
T	Temperature	We want to find it
c	Speed of light	We're talking about radiation
k	Boltzmann's constant	Only way to convert temperature to energy
A	Area of surface	More surface means more radiation

The radiated power is proportional to the surface area, so a more useful quantity is P/A , which is the *flux* or F .

We stir these quantities to make a flux. So here are their dimensions, including the F , where θ means dimensions of temperature (most often given in units of Kelvin

degrees):

<i>Symbol</i>	<i>Dimensions</i>
F	MT^{-3}
T	θ
c	LT^{-1}
k	$\text{ML}^2\text{T}^{-2}\theta^{-1}$

So k and T must appear together or nowhere, since they are the only two quantities with temperature units θ . And kT and F are the only two quantities with a mass; since each has power of mass:

$$F \propto kT.$$

The constant of proportionality has dimensions of T^{-1} , to convert an energy into a power, but the only quantity left is c , which has a time but also a length. So there's no way to make the dimensions match. Alas!

We must have forgotten a quantity. This law cannot be derived from classical thermodynamics. Light comes in photons, and photon energies depend on \hbar . Including this quantity, the list is (after combining k and T):

<i>Symbol</i>	<i>Dimensions</i>
F	MT^{-3}
c	LT^{-1}
kT	ML^2T^{-2}
\hbar	ML^2T^{-1}

A cheap trick is to rewrite the list in terms of E , the dimensions of energy (i.e. ML^2T^{-2}), and use c^2 instead of c :

<i>Symbol</i>	<i>Dimensions</i>
F	$\text{EL}^{-2}\text{T}^{-1}$
c^2	EM^{-1}
kT	E
\hbar	ET

By playing around you can find that

$$\frac{(kT)^4}{c^2\hbar^3}$$

has dimensions of flux, so

$$F \sim \frac{k^4}{c^2\hbar^3} T^4.$$

The missing dimensionless constant, which comes from integrating over phase space so throws in factors of 2π , turns out to be $\pi^2/60$, and

$$F = \frac{\pi^2}{60} \frac{k^4}{c^2\hbar^3} T^4.$$

The gaggle of constants

$$\frac{\pi^2}{60} \frac{k^4}{c^2 \hbar^3}$$

is called the Stefan–Boltzmann constant, σ , and the Stefan–Boltzmann law is written

$$F = \sigma T^4,$$

where $\sigma \approx 6 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$.

Calculating the earth's surface temperature: First attempt

How much energy from the sun hits the earth's surface? That flux is $F_{\text{sun}} \sim 1.3 \text{ kW m}^{-2}$, a quantity worth memorising. That's how much comes in. What comes in must go out, so $\sigma T^4 \sim F_{\text{sun}}$, or

$$T \sim \left(\frac{F_{\text{sun}}}{\sigma} \right)^{1/4} \sim \left(\frac{1.3 \times 10^3 \text{ W m}^{-2}}{6 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}} \right)^{1/4}$$

Check the units: The right side will end up with just a temperature, so all is well. Then do the arithmetic:

$$T \sim (0.2 \times 10^{11})^{1/4} = \left(\frac{1}{50} \times 10^{12} \right)^{1/4}$$

The fourth-root of 50 is roughly $\sqrt[4]{50}$, or 2.65, so the temperature is about $1000/2.65 \text{ K}$ or 380 K . In familiar units that is about 100°C . Hot, hot, hot! A quick note on how to evaluate $1000/2.65$ without a calculator:

$$\frac{1000}{2.6} = \frac{1000}{2.5 + 5\%} \approx \frac{1000}{2.5} - 5\% = 400 - 5\% \approx 380.$$

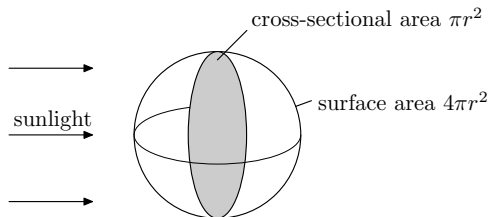


Figure 1. Flux hitting earth. The effective flux is one-fourth F_{sun} because only an area πr^2 intercepts the solar flux.

What went wrong so that the temperature is so high? The flux F_{sun} is for *perpendicular incidence*. But one-half of the earth is in darkness, and over the other half the angle of incidence varies; leaving aside the tilt of the earth's axis, only at the equator is the incidence perpendicular. The perpendicular area of the earth is πr^2 , where r is the radius of the earth, and the power intercepted is spread over a surface area of $4\pi r^2$ (Figure 1). The effective flux is therefore $F_{\text{sun}}/4$. This factor is further reduced

because some radiation bounces from or is absorbed in the atmosphere before reaching the ground. Roughly,

$$F_{\text{effective}} \sim F_{\text{sun}}/5.$$

So the surface temperature is reduced by a factor of $5^{1/4}$ – no need to recalculate T from scratch using σ because we instead can *scale* the previous result. A cheap trick for the fourth root of 5:

$$5 = \frac{80}{16} \approx \frac{81}{16} = \frac{3^4}{2^4}$$

so

$$5^{1/4} \approx \frac{3}{2}.$$

The new temperature estimate is then

$$\frac{380 \text{ K}}{3/2} \approx 255 \text{ K}.$$

In familiar units, it is -18°C . Cold, cold, cold!

What went wrong? We neglected the trapping of heat by the atmosphere: the *greenhouse effect*. The ground absorbs sunlight and radiates it as infrared. The atmosphere contains CO_2 and water vapour, which are particular good at blocking infrared. So the infrared radiation has a hard time leaving. It's as if it goes slower than c . Of course it moves at the speed of light but the bouncing back and forth slows its effective speed. Thus the radiated power is less than σT^4 , it turns out by a factor of 1.5, and the surface temperature goes up to compensate for this greenhouse reduction.

References and further reading

Blackbody radiation.

Adkins, pp. 94–97; Baierlein, pp. 123–125.

Stefan–Boltzmann law.

Adkins, pp. 97–99; Baierlein, pp. 123–125.

Dimensional analysis.

Textbook on *Order of magnitude physics* at www.inference.phy.cam.ac.uk/sanjoy/.

Estimate the surface temperature of the sun

You came up with many methods to estimate this temperature:

- Look at broadening of the spectral lines.
- Look at the wavelengths emitted and figure out the temperature using *Wien's displacement law*.
- Run the analysis from the first lecture backwards: We know the energy flux (power/area/time) on the earth's surface, so use that value to work out the flux at the sun's surface.
- Estimate the temperature required for thermonuclear fusion.
- Given that a few molecules are stable on the Sun's surface, get an upper bound by knowing at what temperature they dissociate.

Broadening of spectral lines

What is a spectral line? Electrons in an atom move from one energy level to another as they absorb and radiate energy. The radiation has a particular frequency that depends on the energy. It turns into a *spectral line* when you look at the entire spectrum through a diffraction grating (a spectrometer). Each frequency is diffracted by an angle depending on the frequency and the spacing of lines in the grating, so each frequency turns into a line on the wall.

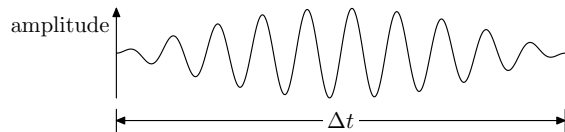


Figure 1. Wave train. An almost pure sinusoid: It lasts for a time Δt rather than being infinitely long as a pure sinusoid would be.

Line broadening means that the lines have width: They are not infinitely thin. To see why they have non-zero width, imagine an electron dropping from an excited energy level to the ground state and radiating energy. The radiated wave lasts for, say, a time Δt (Figure 1). Then it cannot be a pure sinusoid because a pure sinusoid lasts forever. So this finite wave train contains a band of frequencies. The width of the band is given by

$$\Delta\omega\Delta t \sim 1.$$

So every spectral line has a frequency width determined by the Δt , the lifetime of the excited state. If I multiply the relation between frequency and lifetime by \hbar and use $E = \hbar\omega$, then it looks more familiar:

$$\Delta E\Delta t \sim \hbar.$$

It is the *uncertainty principle*!

But lines in the sun are much broader than this intrinsic width. A typical transition in hydrogen is from the 2p to the 1s state, and the lifetime of the electron in the 2p state is roughly 10^{-8} s. So $\Delta\omega \sim 10^8 \text{ s}^{-1}$. That may seem large, but no quantity with dimensions can be large or small intrinsically. I must compare it to another quantity

with the same dimensions. A likely candidate is the line's frequency, ω . The frequency of the resulting ultraviolet light is roughly 10^{16} s^{-1} , so $\Delta\omega/\omega \sim 10^{-8}$. The fractional width of a line is tiny.

Many effects broaden this tiny width. One is the Doppler shift. Hot atoms move fast! Atoms moving towards us radiate bluer (higher frequency) light; atoms moving away from us radiate redder (lower frequency) light. Or at least that is how we see it. When an ambulance blaring its siren drives by, the frequency you hear changes because of the Doppler shift. How large is the Doppler shift? A cheap analysis – and the cheaper the method, the better – begins by saying, ‘Hmm, what can the frequency change depend on?’ It must depend on v , the velocity of the atom or ambulance; and on c , the speed of sound or light. Perhaps it also depends on the original frequency, ω (or f where $f = \omega/2\pi$). We are interested in the frequency change, $\Delta\omega$. So there are two dimensionless objects:

$$\frac{\Delta\omega}{\omega} \quad \text{and} \quad \frac{v}{c}.$$

A likely story is that these two objects are related as simply as possible:

$$\frac{\Delta\omega}{\omega} = \frac{v}{c}.$$

Maybe we've lost a dimensionless constant but it's a good guess. It also is nearly correct. From relativity last year you remembered that

$$\frac{\omega_{\text{new}}}{\omega_{\text{old}}} = \sqrt{\frac{c+v}{c-v}} = \sqrt{\frac{1+v/c}{1-v/c}}.$$

That expression looks quite different from v/c ! But for $v \ll c$ it behaves simply because $\sqrt{1+x} \approx 1 + x/2$ for small x . So

$$\sqrt{\frac{1+v/c}{1-v/c}} \approx \frac{1+v/2c}{1-v/2c}.$$

Since $1/(1-v/2c) \approx 1 + v/2c$,

$$\frac{1+v/2c}{1-v/2c} \approx (1+v/2c)^2 \approx 1 + v/c.$$

So $\omega_{\text{new}}/\omega_{\text{old}} = 1 + v/c$ and

$$\frac{\Delta\omega}{\omega} \approx \frac{v}{c}.$$

A *puzzle*: The exact relativity formula with the square root applies to light but not to sound even though both are waves. What is the relevant difference between light and sound?

How large is v/c for atoms on the surface of the sun? As we'll see later, the temperature is $T \sim 10^4$ K. The thermal energy per atom is roughly kT , so the thermal speed is $v \sim \sqrt{kT/m}$, where m is the mass of a hydrogen atom. We could calculate this speed from scratch by plugging in the values of k , T , and m . But it's always better

to find the value relative to a value you already know. Here that value could be the thermal speed of air molecules at room temperature. Air is mostly N_2 , which is roughly 30 times the mass of hydrogen. Room temperature is $T \sim 300$ K, or roughly 30 times lower than 10^4 K. So

$$\frac{\text{thermal speed on sun's surface}}{\text{thermal speed of room-temperature air molecules}} \sim \sqrt{\frac{30}{1/30}} \sim 30.$$

The thermal speed of room-temperature air molecules is roughly the same as the speed of sound (what else could it be?!), which is 300 m s^{-1} . Then on the sun

$$v_{\text{thermal}} \sim 30 \times 300 \text{ m s}^{-1} \sim 10^4 \text{ m s}^{-1}.$$

The fractional line width caused by Doppler broadening is

$$\frac{v}{c} \sim \frac{10^4 \text{ m s}^{-1}}{3 \times 10^8 \text{ m s}^{-1}} \sim 3 \times 10^{-5}.$$

It is much larger than the intrinsic width, and easily detectable with a good spectrometer.

In the lecture we have no spectrometer, although for next year I will try to make a demonstration of Doppler broadening in sunlight. So we cannot use this method here to determine the temperature on the sun's surface. The method is important anyway: It is used to do measure tiny velocities, for example of the wobble of stars caused by planets in orbit, and it illustrates lots of interesting physics.

Wien's displacement law

If we know the wavelength of sunlight, we can also figure out the temperature. Temperature is a bizarre concept, but it is basically energy: Boltzmann's constant, k , converts between temperature and energy units. How can we convert wavelength to energy? First convert the wavelength to frequency: $f = c/\lambda$. Then convert the frequency to energy: $E = hf$. And energy to temperature: $E \sim kT$. In the last relation I use a \sim instead of an $=$ because I don't know exactly how kinetic energy of thermal motion (roughly kT) relates to the energy of radiated light. Combining all the steps:

$$T \sim \frac{E}{k} = \frac{hf}{k} = \frac{hc}{\lambda k}.$$

Sunlight is visible light so its wavelength is say 700 nm (red light) or 350 nm (blue light). The wavelength of red light is easier to remember than that of blue light because helium-neon lasers produce red light and you may have run across their wavelength a few times (680 nm). You can remember the 350 nm by remembering the ratio: $700/350 = 2$ so visible light spans one *octave*. By comparison, audible sound ranges from 20 Hz to 20 kHz, which is a factor of 1000 or 10 octaves.

Let's first put in numbers to find the energy of visible light photons:

$$E = \frac{hc}{\lambda} \sim \frac{2\pi\hbar c}{\lambda}.$$

I use $2\pi\hbar$ because $\hbar c$ has a handy value accurate to 1 per cent:

$$\hbar c \sim 200 \text{ eV nm}$$

The State of Illinois (in the midwestern United States) once tried to decree by legislative fiat that $\pi = 3$. Ridiculous perhaps but it does simplify arithmetic:

$$E \sim \frac{2 \times 3 \times 200 \text{ eV nm}}{500 \text{ nm}} \sim 2.4 \text{ eV},$$

where I slid the wavelength from 700 nm to 500 nm because sunlight does not look red, so the peak wavelength is more blue than 700 nm.

Bond energies are determined by hydrogen's binding energy (14 eV). Most bonds are longer than hydrogen's radius (0.05 nm), so the energy is lower. A typical bond energy turns out to be 4 eV. So 2 or 3 eV for visible light is reasonable. It means that visible light does not usually break bonds whereas ultraviolet light does: sunburn and skin cancer are the result.

Now let's convert the energy to a temperature by converting 1 eV to Kelvin:

$$1 \text{ eV} \times \frac{1.6 \times 10^{-19} \text{ J}}{1 \text{ eV}} \times \frac{1 \text{ K}}{1.4 \times 10^{-23} \text{ J}},$$

where the last factor is Boltzmann's constant. So

$$1 \text{ eV} \sim 10^4 \text{ K},$$

which is a very useful approximation, and $2.4 \text{ eV} \sim 24,000 \text{ K}$. That temperature is much higher than the surface temperature of the sun because our formula for converting the peak wavelength to a temperature is off by a dimensionless factor, 4.965. So

$$T_{\text{surface}} \sim \frac{hc}{4.965\lambda_{\text{peak}}k}.$$

This result is the *Wien displacement law*.

Don't ask where the magic number comes from! Actually you can ask. It is the root of a transcendental equation resulting from Planck's radiation law. The important points are simple to remember. First:

$$T_{\text{surface}} \sim \frac{hc}{\lambda_{\text{peak}}k},$$

which you can derive any time either using dimensions or from your knowledge of basic quantum theory ($E = hf$). Second, the above formula requires a correction factor of 5. So

$$T_{\text{surface}} \sim \frac{24000}{5} \text{ K} \sim 5000 \text{ K}.$$

If we do the arithmetic more accurately, we find $T \sim 6000 \text{ K}$ is slightly more accurate and is the value that I remember.

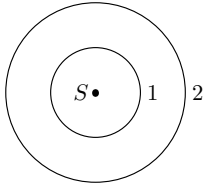


Figure 2. Flux decreasing with distance. The source S shines away. The power crossing sphere 1 is the same as the power crossing the larger sphere 2. So at a distance r from the source, the power per area, or flux, is proportional to r^{-2} .

Using Stefan–Boltzmann backwards

In lecture 1 we estimated the surface temperature of the earth using the solar flux. We can use that method backwards to find the solar temperature. As a function of distance from the source, flux, which is power per area, is given by

$$F \propto r^{-2} \text{ (Figure 2).}$$

From the Stefan–Boltzmann law,

$$F \propto T^4.$$

So

$$T \propto r^{-1/2}.$$

If we know the temperature at a particular distance from the centre of the sun, we can find the temperature at any other distance using this proportionality. Before doing that, let's check its sanity. It says that distant planets have a lower surface temperature. And indeed Mars is cool, Saturn is damn cold, and Pluto is even colder.

In the first attempt to find the earth's surface temperature, we found that the solar energy from the sun should bring it to 380 K. This attempt forgot that the solar energy intersects a circle of area πr^2 , where r is the earth's radius, but is smeared over a surface of area $4\pi r^2$. But in calculating the sun's temperature, we want to forget that factor of 4. The 380 K is the temperature of a black sphere with radius 1 AU (the radius of the earth's orbit), so what is the temperature of a sphere with radius r_{sun} ?

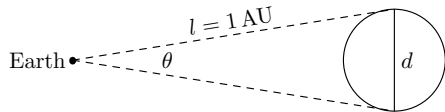


Figure 3. Angle sun subtends. Seen from earth, the diameter of the sun (d) subtends an angle d/l , where $l = 1 \text{ AU}$.

From the proportionality above,

$$\frac{T_{\text{sun}}}{380 \text{ K}} = \left(\frac{r_{\text{sun}}}{r_{\text{orbit}}} \right)^{-1/2}.$$

The ratio of radii is related to the angle that the sun's diameter subtends (Figure 3):

$$\theta = \frac{d_{\text{sun}}}{r_{\text{orbit}}}.$$

By looking at the sun (carefully!) and covering it with your finger at arm's length, you'll find that the sun subtends 0.5° , or 10^{-2} rad. So $r_{\text{sun}}/r_{\text{orbit}} \sim 1/200$ and

$$\frac{T_{\text{sun}}}{380 \text{ K}} = \sqrt{200} \sim 14.$$

So $T_{\text{sun}} \sim 6000 \text{ K}$!

Estimate the temperature required for thermonuclear fusion.

If we can calculate this temperature, and it's not easy, it tells us a useful temperature. However, it's not the surface temperature: Fusion happens in the core of the sun, where it is *much* hotter than at the surface. It is so much hotter because the pressure is higher. To estimate the pressure, imagine a simple model of a cylinder sitting over your head (Figure 4). The pressure from the cylinder is its weight (not mass!) divided by its cross-sectional area.

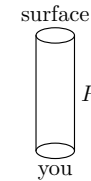


Figure 4. Cylinder on your head. You sit at the centre of the sun and a cylinder of length R and radius r sits over your head and extends to the surface.

To find the cylinder's mass, give symbols to its dimensions. Let's say its radius is r . Its length is R , the radius of the sun. Then its volume is, except for constants, Rr^2 . Assume further that the sun has uniform density. This assumption is lousy, but many wrongs make a right, so I will correct this wrong with other lousy assumptions. Then the cylinder's mass is

$$m \sim M \times \frac{\text{volume of cylinder}}{\text{volume of sun}},$$

where M is the mass of the sun. The volume of the sun is, except for constants, R^3 , so

$$m \sim M \frac{Rr^2}{R^3} \sim M \frac{r^2}{R^2}.$$

The gravitational acceleration varies a lot over the cylinder, but a typical value is

$$a \sim \frac{GM}{R^2},$$

give or take a dimensionless constant. So the cylinder's weight is

$$W \sim ma \sim M \frac{r^2}{R^2} \times \frac{GM}{R^2} \sim \frac{GM^2 r^2}{R^4}.$$

The pressure is weight per area:

$$p \sim \frac{W}{r^2} \sim \frac{GM^2}{R^4}.$$

Putting in $M \sim 2 \times 10^{30}$ kg and $R \sim 0.7 \times 10^9$ m:

$$p \sim \frac{7 \times 10^{-11} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2} \times 4 \times 10^{60} \text{ kg}^2}{0.25 \times 10^{36} \text{ m}^4} \sim 10^{15} \text{ Pa}.$$

The ideal-gas law, $p = nkT$, will convert the pressure to a temperature:

$$T = \frac{p}{nk} = \frac{m_1 p}{\rho k},$$

where m_1 is the mass of one hydrogen atom, n is the number density, and $\rho = m_1 n$. Except for constants the density is $\rho \sim M/R^3$, so

$$T \sim \underbrace{\frac{m_1}{k} \frac{GM^2}{R^4}}_{m_1 p/k} \bigg/ \underbrace{\frac{M}{R^3}}_{\rho} = \frac{m_1}{k} \frac{GM}{R}.$$

The factor m_1/k is also

$$\frac{N_A m_1}{N_A k},$$

and $N_A k = R \approx 8 \text{ J mol}^{-1} \text{ K}^{-1}$. Since $m_1 N_A = 1 \text{ g} = 10^{-3} \text{ kg}$ (the atoms are hydrogen),

$$T \sim \underbrace{\frac{10^{-3} \text{ kg}}{10^1 \text{ J mol}^{-1} \text{ K}^{-1}}}_{N_A m_1 / N_A k} \times \underbrace{\frac{0.7 \times 10^{-10} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-2} \times 2 \times 10^{30} \text{ kg}}{0.7 \times 10^9 \text{ m}}}_{GM/R} \sim 2 \times 10^7 \text{ K}.$$

And lo and behold, Google tells me that the core temperature is roughly $1.5 \times 10^7 \text{ K}$. To those who wondered about making so many dubious approximations, I say 'Ye of little faith'!

Hmm, the result is accurate even though it does not include the (complicated) physics of fusion. That's because I took the radius as a given, and the radius is determined by fusion. If the sun shrinks then the core heats up (the expression for T has R in the denominator), so fusion reactions happen more rapidly. The increase in fusion liberates extra heat and the increased pressure pushes the radius back to its larger value. This negative feedback keeps the sun stable until it starts to run out of its fuel (hydrogen).

Colour temperature

Another method to estimate the surface temperature is by going to your computer monitor and adjusting the so-called colour temperature. When the temperature is towards the high end, say 8000 K, then the monitor looks bluer than daylight. So daylight temperature is somewhat lower than 7000 K. At the other extreme, a light bulb glows at 3000 K (roughly) and it looks more yellow than daylight. Your eye compensates for this change, so it is hard to notice the difference unless you use a stupid eye such as a camera. If you use daylight film and photograph a room lit by light bulbs, it will look washed out and yellow. So the temperature of daylight is somewhat higher than 3000 K.

Molecules surviving on the sun's surface

And one final sly method that you suggested: Water molecules survive on the surface of the sun. How do you know? Because people have observed in sunlight the spectral lines of water (the spectrometer again). If the temperature is very high, then water molecules dissociate into hydrogen and oxygen atoms. So you can do an experiment on earth: Find the temperature at which water molecules dissociate, and then you know the maximum temperature of the sun's surface.

References and further reading

Wien displacement law.

Adkins, p. 99; Baierlein, pp. 122, 141 (problem 3).

Your comments and questions

What are we learning in this course?

I hope you will learn to speak physics. The area of knowledge I learnt most thoroughly is my native language. I know it more intuitively than I know any other language, than I know how to ride a cycle, or than I know how to do physics. It is probably the same for you. How did you learn your native language? Probably not by going to lectures where a teacher described the rules for making correct sentences. I learnt English by speaking it: as a baby, by desperately wanting to communicate and trying anything that worked. In the lectures I hope to introduce enough interesting uses of thermodynamics that you will want to speak physics, and thereby learn physics.

Many interesting uses involve applying physics to understand the world around you. For that purpose, approximate answers are usually more useful than exact answers. Approximate answers are mathematically simple, so mathematics does not obscure physics. The world is messy, and if you want to apply physics to the world around you, you need to approximate. Every example sheet and every lecture will give you practice.

Will we have to catch up later?

If you understand physical ideas, then you can figure out almost every result. If you learn without understanding, the concepts and equations soon vanish. I could teach you a bunch of equations, if I don't fall asleep myself doing it. Perhaps those equations would be just what you need for the next course. But by next year they would vanish from your understanding, and you would have to relearn much of the material. How much do you still understand from last year? Understanding the ideas from the start is not only more fun but is more efficient.

The Feynman lectures are (rightly) considered a model of brilliant physics teaching. A colleague of Feynman's told me how they were created. When Feynman was revising for his Generals – the very difficult PhD qualifying exams at Princeton – he went back to his old fraternity at MIT to hide for several weeks. He put together all of physics in his mind as he reviewed. By the end Feynman had index cards for his way of thinking about the important ideas. Twenty years later, when he taught the Caltech first-year course on which the lectures are based, he used those index cards as his lecture notes. The Feynman lectures are still the most useful preparation for PhD qualifying exams (I used them myself at Caltech), because if you understand 'first-year' material clearly and deeply, you can understand PhD-level material.

I hope after this course that you will gain long-lasting understanding of a few essential ideas.

Will the exam questions reflect the old style of course?

The examiners have already written to me asking for my questions and they are very friendly. Although final responsibility for the exam rests with the examiners, I have made the thermodynamics problems on the exam reflect what you learn from lectures and the example sheets. The examiners will refine the questions to make sure they are clear and fairly structured.

Once upon a time, the examiners created the questions and model answers by reading the syllabus and looking at the course handouts. This year, for the first time, the lecturers provide the questions and model answers. So, *don't worry*.

What does the inference group do?

Lots I said about this, but for here I'll refer you to the website at <http://www.inference.phy.cam.ac.uk>.

Can we do some physics?

Sure.

How much water do you drink running for an hour?

Before trying a theoretical method, take a guess or use your experience. What I learnt from one of the Part II students is that experience is also a scientific method. Basically, you are drawing upon past experimental data. In this case, based on drinking a glass of water after running a few minutes, probably I'd drink 10 glasses of water in an hour, so maybe 3 ℓ .

To estimate this value theoretically, we need first to understand why you sweat (or lose water in other ways). While exercising, you generate a lots of heat. This heat overwhelms how much you can lose just by conduction away from your skin, so your body temperature would rise if you don't find another way to get rid of the heat. So your body uses it to evaporate water and you get thirsty. To estimate how much water you lose, we need two pieces of information: how much power (including heat) you generate while exercising, and how much energy it takes to evaporate a unit mass of water (the heat of vaporisation).

Meanwhile, a *puzzle*: Dogs do not sweat, so how do they stay cool?

Estimate the heat of vaporisation of water

You suggested several methods to estimate L_{vap} :

- boiling kettle: From the power input and how long it takes to boil a kettle dry.
- annual rainfall. Oceans evaporate because of solar energy (the solar flux again). We also need the annual rainfall.
- electrostatic energy. Just guess it by comparing it to other bond energies
- puddle evaporation. Puddles, like oceans, evaporate because of solar energy (the solar flux again).

Boiling kettle

Careful: Here it matters whether you bring the kettle to a boil or whether you boil it dry. If you merely bring it to a boil, then you are calculating the specific heat of water rather than the heat of vaporisation. To boil 1 ℓ dry may take 15 minutes (10^3 s). If you cannot convince your kettle to stay on once it comes to a boil, you can use a stove and boil dry a saucepan of water. A kettle consumes say $P \sim 2$ kW. So

$$L_{\text{vap}} \sim \frac{Pt}{m} \sim \frac{2 \times 10^3 \text{ W} \times 10^3 \text{ s}}{1 \text{ kg}} \sim 2 \text{ MJ kg}^{-1}.$$

Electrostatic energy

To evaporate a water molecule, you supply energy to break its bonds with its neighbours. These bonds are *hydrogen bonds*, which are much weaker than the proper chemical bonds that link the two hydrogens and an oxygen together in one molecule. A

proper chemical bond has energy roughly 4 eV (lecture 2). But hydrogen bonds result because the water molecule is *polar* (Figure 1). The oxygen is hungry for electrons, and steals a bit of charge from the hydrogens. So the slightly negative oxygen end in one water molecule is attracted to the slightly positive hydrogen end of another water molecule. As a guess, perhaps each end has one-quarter the charge of a full bond. Since electrostatic energies are proportional to $q_1 q_2$, the energy should be 1/16th of a proper bond energy (Figure 2). Then each hydrogen bond is 0.25 eV. Each water molecule has perhaps two hydrogen bonds in each coordinate direction, for a total of six. Each bond is shared between two molecules, so each the total hydrogen-bond energy per molecule is roughly 3×0.25 eV or 0.75 eV. Converting this energy into macroscopic units:

$$L_{\text{vap}} \sim \frac{0.75 \text{ eV}}{\text{molecule}} \times \frac{1.6 \times 10^{-19} \text{ J}}{1 \text{ eV}} \times \frac{6 \times 10^{23} \text{ molecules}}{1 \text{ mol}} \times \frac{1 \text{ mol}}{1.8 \times 10^{-2} \text{ kg}} \sim 4 \text{ MJ kg}^{-1}.$$

I don't have a huge confidence in this value because estimating the energy of a hydrogen bond was quite rough, but the value is not far from the kettle method's.

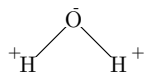


Figure 1. Polar molecule. The oxygen in water is electron-greedy and grabs a bit of the charge from the hydrogens.



(a)



(b)

Figure 2. Simple model of a hydrogen bond. A proper chemical bond, for example O–H in ethanol, has a proper charge, q , at each end as shown in (a). Its energy is typically 4 eV. A hydrogen bond has perhaps $q/4$ at each end, as shown in (b), so its energy is $(4 \text{ eV})/16 = 0.25 \text{ eV}$.

Annual rainfall

Imagine a 1 m^2 patch of ocean from which sunlight evaporates water (Figure 3). The vapour rises, cools, condenses, and falls back as rain. In a year perhaps 1 m of rain falls. So a year's worth of solar flux evaporates a cube of water with volume 1 m^3 or of mass 10^3 kg . The solar flux averaged over the earth's surface (which includes averaging over night and day) is 200 W m^{-2} (lecture 1). So the solar power hitting the patch of ocean is 200 W and

$$L_{\text{vap}} \sim \frac{200 \text{ W} \times 3 \times 10^7 \text{ s}}{10^3 \text{ kg}} \sim 6 \text{ MJ kg}^{-1},$$

where I used $1 \text{ yr} \approx \pi \times 10^7 \text{ s}$. This estimate of L_{vap} probably a bit high since it assumes that all the solar energy goes to creating water vapour, whereas some goes to heating oceans, some goes to powering the ascent of vapour against gravity, and some is reflected off the oceans without evaporating any water. Another source of error is

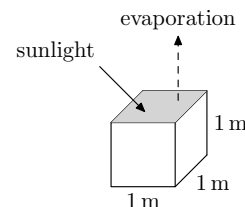


Figure 3. Sunlight evaporating water from a 1 m^2 patch of ocean (shaded area). In one year, roughly 1 m of rain falls over the earth, so a year's worth of solar energy evaporates the patch down to a depth of 1 m.

the guess for annual rainfall. I could easily imagine it being a factor of 2 higher or lower.

Actual value

The actual value is $L_{\text{vap}} \sim 2 \text{ MJ kg}^{-1}$, which is closest to the value from the method that feels the most reliable (using a kettle).

Power to dispose of through evaporation

You can figure out the waste power (i.e. not going to useful mechanical work) by first working out the useful power you can produce. Working out the power from running on flat ground is difficult, because it's not obvious what you are doing work against. Air resistance? Inelastic collisions of your foot with the ground? But in running uphill, most of the power goes to fighting gravity, whose physics we understand. Take a random staircase ascending from the ground to the first floor. I take 3 s to run up it (skipping every other stair or more). Each floor is roughly 3 m, so the power is

$$P = Fv \sim mg \frac{h}{t} \sim 60 \text{ kg} \times 10 \text{ m s}^{-2} \times \frac{3 \text{ m}}{3 \text{ s}} \sim 600 \text{ W}.$$

That's at a sprint. Let's say 500 W for ease of calculation.

If all the energy I consume goes to useful work, then I have no need to sweat. But my 'engine' is not 100% efficient. As a rough rule of thumb, petrol engines are 25% efficient, and a person is roughly a petrol engine. So I generate 1.5 kW of waste heat and 500 W of useful power. In one hour, I therefore evaporate

$$m \sim \frac{1.5 \times 10^3 \text{ W} \times 3.6 \times 10^3 \text{ s}}{2 \times 10^6 \text{ J kg}^{-1}} \sim 2 \text{ kg},$$

or 2 ℓ of water. Which seems reasonable, so the physical process underlying the method (evaporative cooling) is probably the one responsible.

I asked whether you wanted solutions with the problem sheets (give or take a day or two) or wanted them at the end of the course. The vote was 135–2 in favour of contemporaneous solutions.

I also wondered whether you comment more about this course than others. You told me that you do. So I asked why. Several answers:

- I listen to your comments.
- You are more awake in these lectures than most.
- You are obedient, and since I ask for comments you give them.
- Change is scary and this course is different from the others.
- There isn't a formal syllabus or plan of what we'll do, so the course seems rough around the edges, hence people worry.

I am glad that you give me feedback, good and bad. Keep it coming. I will try to make more explicit whatever organisation the course has. But you are right, it is less organised than most courses – I have lots of material prepared, from many angles, but I never know what is going to happen in lecture (one of the 'dangers' of teaching through discussion) until lecture happens.

How much heat do you lose on a cold winter's day in a T-shirt?

The real world doesn't serve up questions neatly labelled with equations and tell us which to use.

What does it mean to lose heat? What dimensions should this quantity have?

Power? Power per area? Energy? All good suggestions. You are constantly generating heat at some rate (how much?). Ah, rate, that means energy per time, or power. When you are outside in the cold, heat flows from you to the air. If much more heat flows from you than you generate, your body temperature drops, thereby reducing the outgoing flux until it matches what you generate. When your body temperature drops, especially your core temperature, you feel cold.

How do you stay warm in the cold?

You jog, you jump up and down, or as a last resort, you shiver involuntarily. All these methods generate extra heat per time, i.e. power.

How does fabric keep you warm?

Without the fabric (so if you are naked), the air near your skin that you warmed so considerably would rapidly leave, taking your heat with it. Cold air would replace it, you would donate your heat to it, and it too would soon leave. The fabric traps air between the fibres, so it keeps you from having to reheat air near you over and over again. This method works because still air is lousy at transmitting heat, as we will calculate.

Guess the power loss

100 W or maybe 1 kW? To get an idea of what is reasonable we can compare it with the power (heat per time) you generate while doing nothing. In one day, you could eat 10 jelly donuts (see problem 1 on sheet 1), and each jelly donut is 1 MJ (a useful unit to remember). So the power is

$$P \sim \frac{10 \text{ MJ}}{1 \text{ day}} \sim \frac{10 \text{ MJ}}{10^5 \text{ s}} = 100 \text{ W}.$$

Another useful number to remember (or derivation to remember). It sets the scale for biological power (at least for animals about our size). To feel cold, one must be losing a lot more than this baseline rate of 100 W; maybe closer to 1 kW.

How good an insulator is air?

To understand insulation we need to understand how heat is transferred. The process is easier to understand in a gas than in a solid or liquid. In a gas, heat is the motion of the molecules. 'Hot' (fast-moving) molecules, like all molecules, speed off to other sections of the container, collide with other molecules, give them extra energy, and then fly off in a random direction. Heat travels by a *random walk*.

How does a random walk work?

I'm glad you asked. Let's look at a simple random walk. Imagine a particle that moves on a number line. Each tick it moves either one step right or one step left, with equal probability. Suppose after n ticks it has got to $x = 7$. At the next tick it will be at either $x = 6$ or $x = 8$. Its expected position is still 7. But its expected squared position (different from the squared expected position!) has gone from 49 to

$$\langle x^2 \rangle = \frac{1}{2} (6^2 + 8^2) = 50.$$

That pattern looks nice. Let's check it for another case. Suppose the particle is at $x = 10$, so $\langle x^2 \rangle = 100$. After one tick,

$$\langle x^2 \rangle = \frac{1}{2} (9^2 + 11^2) = 101.$$

Yet again $\langle x^2 \rangle$ has increased by 1. So

$$\langle x_{n+1}^2 \rangle = \langle x_n^2 \rangle + 1.$$

A useful exercise is for you to show this result (I hate to say *prove*).

The pattern that $\langle x^2 \rangle$ is proportional to time worked for a one-dimensional random walk. It also works for any dimension, as a Pythagorean argument shows (or sort of shows, depending on how convinced you are). In one dimension, the particle can move only along the line of diffusion (either farther away or near to the origin). With a second dimension, the particle has an option to move perpendicular to the vector to the origin (Figure 1). Fortunately this new option also gives

$$\langle x_{n+1}^2 \rangle = \langle x_n^2 \rangle + 1.$$

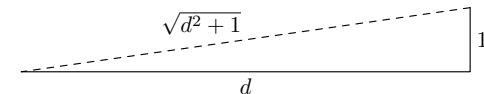


Figure 1. Two-dimensional random walk. The particle exercises its extra choice available in two dimensions and makes a perpendicular step relative to its current position. Before, it was a distance d from the origin, so $\langle x^2 \rangle = d^2$. After, it is a distance $\sqrt{d^2 + 1}$ so $\langle x^2 \rangle = d^2 + 1$. As in one dimension, the mean squared displacement grows by 1 unit.

How is a random walk different from a regular walk?

In a standard walk in a straight line, $\langle x \rangle \propto \text{time}$. Note the single power of x . There the interesting quantity is not x or t itself, since those can grow without limit, but their ratio x/t , or the speed. In a random walk, where $\langle x^2 \rangle \propto t$, the interesting quantity is $\langle x^2 \rangle / t$. It is the *diffusion constant* and has dimensions of $\text{L}^2 \text{T}^{-1}$.

The consequence for heat transfer

If a random walk of 5 steps take 1 tick (for an effective speed of 5) then a random walk of 10 steps takes 4 ticks, for an effective speed of $5/2$. Therein lies the essential difference from regular walking: In a random walk, the effective speed is *inversely proportional to the distance*.

Thus the heat flux (power per area) from your body to the air (through the shirt) will depend on the temperature difference between you and the air (colder air means more flux!) and on the thickness of your shirt. Already we have an idea why wearing a thick fleece is a hot idea: The thick air layers captured by the fleece slow down diffusion. Symbolically:

$$\text{flux} \propto \frac{\text{temperature difference}}{\text{thickness}}.$$

In fancier symbols,

$$F = K \frac{\Delta T}{\Delta x},$$

where K is the *thermal conductivity* and the $\Delta T / \Delta x$ is the *temperature gradient*.

What is that K ?

We don't know yet. But it must depend on the thermal diffusivity (the diffusion constant) since the faster heat can move around, the bigger K must be. So let's go back to κ , the thermal diffusivity, and then come back to how to make κ into K .

In a gas, what can the diffusion constant depend on?

It can depend the density, the molecular mass, the temperature, the pressure, and much else. To sort out exactly how from this variable soup, think how the random walk worked on the number line. A particle moved left or right one unit of space every unit of time. All we have to know is the unit of space and the unit of time and we know everything about the random walk; the nature of the particle doesn't matter beyond those two facts.

In a gas, molecules move for a distance, then collide with another molecule, and move randomly. The step size, also known as the *mean free path*, is crucial. It is determined by the molecular diameter d and by the number density n :

$$n\sigma\ell \sim 1, \text{ (Figure 2)}$$

where ℓ is the mean free path and σ is the scattering cross section πd^2 . Why is it πd^2 rather than the more intuitive πr^2 ? Have a look at your IA notes if you are stuck on this point (or ask me). You can recreate the $n\sigma\ell \sim 1$ relation by making sure the dimensions match: n has dimensions of $1/\text{volume}$, σ is an area, and ℓ is a length, so the left side has no dimensions. Great! Neither does the right side.

The diffusion constant depends also on the time to move a step (one tick in the line model). So the molecular velocity (the thermal velocity) will also be important, and it in turn depends on the pressure, temperature, and maybe density. But if we know the mean free path and the molecular velocity, we don't need anything else.

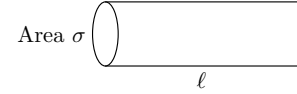


Figure 2. Mean free path. A molecule has scattering area σ , which is πd^2 . Once it sweeps out a volume containing one molecule, then it is likely to collide. The distance ℓ that makes the cylinder contain one molecule is then the mean free path. Its volume is $\sigma\ell$, so the number of molecules it contains is $n\sigma\ell$. Hence $n\sigma\ell \sim 1$.

How can we combine length and velocity into a quantity with dimensions of length squared per time?

Multiply them. It's the only way (check that). So, with κ as the diffusion constant:

$$\kappa \sim v_{\text{thermal}} \times \ell.$$

Another way of deriving this relation is to remember the model of a particle on a line. After n ticks,

$$\langle x^2 \rangle = n \times (\text{step size})^2.$$

Why $(\text{step size})^2$? Because we are asking about the squared distance, not the distance itself. In a gas, the step size is ℓ and each tick takes a time $\tau = \ell / v_{\text{thermal}}$. So

$$\frac{\langle x^2 \rangle}{t} \sim \frac{n\ell^2}{n\ell / v_{\text{thermal}}} = \ell v_{\text{thermal}}.$$

The thermal diffusivity itself is not simply this ratio $\langle x^2 \rangle / t$, but also includes a dimensionless constant. The constant turns out to be

$$\frac{1}{\text{number of dimensions.}}$$

So what is the thermal conductivity of air?

Putting it all together,

$$\kappa \sim \frac{1}{3} \ell v_{\text{thermal}}.$$

To compute ℓ , we need to know the molecular diameter of air. Air is N_2 , which is tightly bound and most lower-numbered atoms are a bit less than twice the size of hydrogen (so $1.7 \text{ \AA} = 1.7 \times 10^{-10} \text{ m}$), so it turns out that $d \sim 3.5 \text{ \AA}$. Then, with $\sigma = \pi d^2$,

$$\ell \sim \frac{1}{n\sigma} \sim \frac{2.2 \times 10^{-2} \text{ m}^3}{6 \times 10^{23}} \times \frac{1}{3 \times 12 \times 10^{-20} \text{ m}^2} \sim 10^{-7} \text{ m}.$$

What about the thermal velocity? There's only one macroscopic velocity in a gas, the speed of sound, so the thermal velocity must be related by a some dimensionless factor, with luck close to 1. It turns out to be $\sqrt{3}$, give or take a 15 per cent, so

$$v_{\text{thermal}} \sim 1.7 \times 300 \text{ m s}^{-1} \sim 500 \text{ m s}^{-1}.$$

So

$$\kappa \sim \frac{1}{3} \times 10^{-7} \text{ m} \times 500 \text{ m s}^{-1} \sim 1.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}.$$

And there we left it for the next lecture.

References and further reading

Thermal conductivity.

Adkins, pp. 31ff; or Baierlein, pp. 367–369

Heat capacities (specific heat).

Adkins, pp. 23–26; Baierlein, pp. 11–13.

Random walks.

Baierlein, pp. 360–362.

Heat flux

From the last lecture, thermal conductivity is

$$K = \rho c_p \kappa,$$

where ρ is the density, c_p the specific heat, and κ the thermal diffusivity. We created this formula by looking at the dimensions of all the quantities. Does it make sense physically? Thermal conductivity helps calculate how much heat flows, as part of

$$F = K \frac{\Delta T}{\Delta x}.$$

The amount flowing depends on how fast heat travels and on how much heat moves at a time. The speed is the diffusivity κ , and the quantity of heat is ρc_p . Why ρc_p rather than c_p ? Because κ is purely about length and time. It describes how long heat takes to move to a new region. So the heat (the energy) transported will be proportional to the energy stored in a region, in other words, to the energy per volume rather than the energy per mass. The specific heat c_p is heat per unit mass per unit temperature change, so ρc_p is heat per unit volume per unit temperature change. The product $\rho c_p \kappa$ contains a ‘per unit temperature change’, hence to get the flux we need to multiply somewhere by a temperature (the ΔT in the flux equation).

Thermal conductivity of air

Now let’s estimate K for air, as part of working out how much heat you lose outside on a cold winter day. In lecture 4, we estimated

$$\kappa \sim 1.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}.$$

Density of air

If you forget the density, you can easily recalculate it from the ideal-gas law: $p = nkT$ or $p = n_{\text{moles}}RT$, where n is number density and n_{moles} moles per unit volume. Then from R and T you can find n_{moles} :

$$n_{\text{moles}} \sim \frac{p}{RT} \sim \frac{10^5 \text{ Pa}}{8 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}.$$

The units look suspicious since the right side contains Pa/J where the left side contains inverse volume. But all is well, since pressure is force per area or, and this interpretation is surprising, energy per volume. So

$$n_{\text{moles}} \sim 40 \text{ mol m}^{-3}.$$

Or 1 mol has a volume of $0.025 \text{ m}^3 = 25 \ell$. Air is mostly N_2 , so its molar mass is 28 g and its density becomes

$$\rho \sim \frac{28 \text{ g}}{25 \ell} \sim 1 \text{ g } \ell^{-1} = 1 \text{ kg m}^{-3}.$$

Specific heat of air

Specific heat is energy required per mass per temperature change. A molecule with d degrees of freedom has an average energy $(d/2)kT$, from equipartition. So the energy required to change the temperature by ΔT is

$$\frac{d}{2} k \Delta T,$$

and the specific heat is

$$c_v = \frac{(d/2)k\Delta T}{m\Delta T} = \frac{d}{2} \frac{k}{m},$$

where m is the mass of one molecule. This specific heat is for putting in energy while keeping the volume constant, hence the subscript v. The mass of one molecule is difficult to remember, but I can multiply top and bottom by Avogadro’s number to convert the molecular mass to a molar mass:

$$c_v = \frac{d}{2} \frac{N_A k}{N_A m} = \frac{d}{2} \frac{R}{m_{\text{molar}}}$$

because $R \equiv N_A k$. Then

$$c_v \sim \frac{d}{2} \times \frac{8 \text{ J mol}^{-1} \text{ K}^{-1}}{28 \times 10^{-3} \text{ kg mol}^{-1}}.$$

I carefully included all the units, otherwise specific heats turn into a horrible unit porridge. The gas constant R has ‘per mole’, as does the molar mass (it is mass per mole). So the per mole on top and on bottom cancel, as they should if we want specific heat as energy per temperature per unit mass. Air is diatomic, so $d = 5$: three translation modes and two rotation modes (the nitrogen triple bond is very stiff and hence the vibrations are frozen out). So

$$c_v \sim \frac{2}{3} \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}.$$

The specific heat at constant pressure is slightly higher. If the pressure is constant, then as the temperature rises the volume increases: $pV = NkT$, where N is the (constant) number of molecules. To increase the volume requires doing work on the surroundings: You have to supply that energy as well as the energy required by equipartition. How much is that extra energy? For one molecule, $pV = kT$. At constant pressure, the work done in increasing the volume is $p\Delta V$, which is $k\Delta T$. Thus the total energy required to raise the temperature by ΔT is the sum of the equipartition contribution, which we calculated when working out c_v , and of this expansion contribution:

$$\Delta E = \frac{d}{2} k \Delta T + k \Delta T = \left(\frac{d}{2} + 1 \right) k \Delta T.$$

The specific heat for one molecule is the energy change per temperature or $(1 + d/2)k$. Thus, for an ideal gas,

$$\frac{c_p}{c_v} = \frac{d+2}{d} = 1 + \frac{2}{d}.$$

For air $d = 5$ so c_p/c_v , which is called γ , is 1.4 and then in the usual units,

$$c_p = 1.4 c_v \sim 10^3 \text{ J kg}^{-1} \text{ K}^{-1},$$

using the value for c_v computed above.

Putting it all together: the heat loss

Time to put all the pieces together for air:

$$\begin{aligned}\rho &\sim 1 \text{ kg m}^{-3}, \\ c_p &\sim 10^3 \text{ J kg}^{-1} \text{ K}^{-1}, \\ \kappa &\sim 1.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}.\end{aligned}$$

So

$$K = \rho c_p \kappa \sim 0.02 \text{ W m}^{-1} \text{ K}^{-1}.$$

Now we can estimate the heat loss outside on a cold day. Let's say that your skin is at 30°C and the air outside is 0°C , so $\Delta T = 30 \text{ K}$. A thin T-shirt may have thickness 2 mm , so

$$F = K \frac{\Delta T}{\Delta x} \sim 0.02 \text{ W m}^{-1} \text{ K}^{-1} \times \frac{30 \text{ K}}{2 \times 10^{-3} \text{ m}} \sim 300 \text{ W m}^{-2}.$$

Damn, I wanted a power not a power per area. Oh, flux is power per area, so all is well. I just need to multiply by my surface area. I'm roughly 2 m tall (approximately!) and 0.5 m wide, so my front and back each have area 1 m^2 . Then

$$P \sim FA = 300 \text{ W m}^{-2} \times 2 \text{ m}^2 = 600 \text{ W}.$$

No wonder it feels so cold! Just sitting around, your body generates 100 W (lecture 4). So you are losing a lot more than you generate, which would eventually drop your core body temperature. Then chemical reactions in your body slow down – partly because all reactions go slower at lower temperature, partly because enzymes would lose their optimised shape (see lecture 7). Eventually you die.

One solution is to jog and generate the extra heat. Again our number of 600 W is plausible. Cycling hard, which generates several hundred watts of waste heat, is probably enough exercise to stay warm even on a winter day in a T-shirt.

Another simple solution, as parents never tire of telling their children: Dress warmly by putting on thick layers. Let's recalculate the power loss if you put on a fleece, say 2 cm thick. You could redo the whole calculation from scratch, but simpler is to notice that the thickness has gone up by a factor of 10. Since $F \propto 1/\Delta x$, the power drops by a factor of 10:

$$P \sim 60 \text{ W}.$$

That heat loss is quite bearable, since you generate 100 W baseline. Indeed, when wearing a thick fleece, you feel most cold in your hands and face. Those regions are exposed to the air, so only a thin layer of still air protects them from heat loss, and a small Δx means a large heat flux. Bundle up!

How does diffusivity depend on mean free path?

Back to the thermal diffusivity, which everyone finds confusing. Heat diffuses by a random walk, which is described by its step size and step time (or the speed while making a step). So:

If the mean free path increases, what happens to diffusivity?

Here are some choices:

- a. Increases
- b. Decreases
- c. Remains constant
- d. I have no idea!

You offered many excellent arguments for and against. First, κ might increase because each step is longer. On the other hand, it might decrease because each step lasts longer (as long as the speed remains constant). Or the two effects may fight to a draw, in which case κ remains constant. So, which effect wins, if either?

One way to decide is to think about *extreme cases*. Imagine a physical situation where you increase the mean free path. For example, a gas made ever more dilute. As you remove gas, each gas molecule can travel farther. But will the molecular speed change? That depends on how you make the gas more dilute. One way is to let a bag of gas expand quickly. As it expands, it does work on the world: It loses energy and therefore its temperature drops because the energy has to come from the kinetic energy of the molecules (see lecture 7 for more details of such *adiabatic* expansions). If the molecules lose energy, then their speed drops. So if we want to keep the molecular speed constant while increasing the mean free path, we need another method. We could let it expand and then wait a while for the temperature to rise back to the surrounding temperature. Or we can use a pump and remove gas molecules, while leaving the remaining ones at the same temperature.

Okay, so by diluting the gas we can increase the mean free path while leaving the molecular speed alone. Keep diluting until you have a vacuum. A vacuum does not conduct any heat – that's how a thermos flask insulates the tea inside from the cooler air outside. So, the diffusivity decreased to zero, and probably decreases in general as the mean free path increases.

You offered another extreme: Make the gas more and more dense until it becomes a liquid. The mean free path has decreased but liquids conduct heat better than gases. So decreasing the mean free path increases the diffusivity, consistent with the result of the dilution thought experiment.

In response to the first thought experiment, you argued that it was too extreme to allow no molecules to remain. No 'vacuum' is perfect, and the few remaining molecules will zoom across a gap without hitting any other molecules. They travel quite rapidly (in air, a few hundred metres per second), so heat might travel quite rapidly in near-vacuum conditions, perhaps even more rapidly than at normal pressures (and with the usual mean free path). Hmmm.

In response to the second experiment (dense gas becoming a liquid), you wondered whether we are comparing like with like. Does diffusivity measure heat flux (which is almost certainly higher in a liquid than in a gas)? Or does it measure only how rapidly heat moves, with the amount moving being a separate question? To answer that question, go back to the discussion of thermal conductivity:

$$K = \rho c_p \kappa.$$

The first two factors, ρc_p , accounts for the amount of heat stored in a unit volume. The diffusivity κ accounts for how rapidly the heat moves. Our intuition is correct that

a liquid conducts heat much more rapidly than a gas, but the cause may be the much higher density rather than a higher κ . Hmmm, again.

So let's go back to first principles: κ describes a random walk. Does the walk make more progress with an increased step size? Imagine a gap of 10 m and a random walk with a step size of 1 m, made every 1 s. In a random walk, the mean squared distance grows linearly with the number of steps (lecture 4):

$$\langle x^2 \rangle \sim N\ell^2,$$

where N is the number of steps and ℓ is the step length. So it takes roughly 100 steps, or 100 s, for the random walk to cross the 10-step gap. If the step size increases to 2 m but the speed stays the same, then each new step takes 2 s. The gap is now only 5 new steps long, so crossing it takes 25 new ticks, or 50 s. The walk has got twice as rapid by doubling the step size! So κ , which measures the rapidity of the random walk, satisfies

$$\kappa \propto \ell.$$

Similarly, if the step size remains constant but the speed doubles, then all times drop by a factor of 2. So,

$$\kappa \propto v.$$

The dimensions of κ are L^2T^{-1} , and the simplest combination of v and ℓ with those dimensions is

$$\kappa \sim v\ell.$$

This formula turns out to be lacking only a factor of one-third (in three dimensions).

References and further reading

c_p and c_v .

Adkins, pp. 49–51; Baierlein, pp. 11–13.

What is the thermal conductivity of water?

We could work it out as we did the thermal conductivity of air (lecture 5) using $K = \rho c_p \kappa$. However, you learn more by *scaling*, or comparing, K_{water} against K_{air} . So let's work out

$$\frac{K_{\text{water}}}{K_{\text{air}}} = \frac{\rho_{\text{water}}}{\rho_{\text{air}}} \frac{c_p^{\text{water}}}{c_p^{\text{air}}} \frac{\kappa_{\text{water}}}{\kappa_{\text{air}}}.$$

Take the factors in turn. The density ratio is

$$\frac{\rho_{\text{water}}}{\rho_{\text{air}}} \sim 1000.$$

The ratio of specific heats takes a bit of work. We already have $c_p^{\text{air}} \sim 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ (lecture 5). What about c_p^{water} ? The specific heat of water is easy to remember, in ancient units. By definition, one calorie raises 1 g of water by 1 °C. Now you have to remember the conversion: 1 cal \sim 4 J. So

$$c_p^{\text{water}} \sim 4 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1},$$

and

$$\frac{c_p^{\text{water}}}{c_p^{\text{air}}} \sim 4.$$

The value of c_p^{water} bears further study. In monoatomic solids (and the few monoatomic liquids), each atom has 6 degrees of freedom: 3 translational and 3 vibrational (because it lives in a three-dimensional spring potential created by its neighbours). So the specific heat, by the same arguments as in lecture 5, is $3k$ per molecule. For solids and liquids, the difference between c_p and c_v is negligible because the volume hardly changes even if it is not held constant. So $c_p \sim 3k$ per atom or $3R$ (using moles instead of atoms). This result is the law of *Dulong and Petit*. Let's convert water's specific heat based on mass to one based on moles. The molar mass of water is 18 g, so

$$c_p^{\text{water}} \sim 4 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1} \times \frac{18 \times 10^{-3} \text{ kg}}{1 \text{ mol}} \sim 72 \text{ J mol}^{-1} \text{ K}^{-1}.$$

In terms of $R \sim 8 \text{ J mol}^{-1} \text{ K}^{-1}$, the specific heat is $9R$. Wow, three times larger than the monoatomic, Dulong and Petit value! Ah, each water molecule has three atoms. So in water the specific heat is $3k$ per atom, which is the Dulong and Petit value. Since the molecule has the sum of the atomic specific heat contributions, it means that all molecular motions are excited (i.e. not frozen out) and that each atom lives in a three-dimensional spring potential. This high specific heat has many useful consequences for life. It means that the oceans change temperature slowly due to changing weather (day or night, changing seasons). As a result, cities near seacoasts have more moderate weather than far-inland cities, such as in midwestern North America (Chicago).

Ratio of diffusivities

This step takes the most work. From lectures 4 and 5,

$$\kappa \sim v\ell,$$

where v is a speed and ℓ is a mean free path. The correct formula has a factor of $1/3$, but since we will take ratios, the missing factor will cancel anyway. Then

$$\frac{\kappa_{\text{water}}}{\kappa_{\text{air}}} \sim \frac{v_{\text{water}}}{v_{\text{air}}} \frac{\ell_{\text{water}}}{\ell_{\text{air}}}.$$

Take the factors in turn. In a gas we know the mechanism of heat travel: Molecules move and redistribute heat. So in air the relevant speed is the thermal speed, which is roughly the speed of sound, but it is higher by a factor of $\sqrt{3}$:

$$v_{\text{air}} \sim \sqrt{3} \times 300 \text{ m s}^{-1} \sim 500 \text{ m s}^{-1}.$$

The relevant ℓ is the mean free path for molecular collisions. From lecture 4, $\ell \sim 10^{-7} \text{ m}$.

In water, or in most liquids, the mechanism of heat transfer is different than in a gas. Water molecules are packed right next to each other, so molecules diffuse with great difficulty because there's no room to sneak about. Heat moves not by molecules moving to a new location, but by one molecule vibrating a lot and convincing its neighbour to do the same, and so on. So heat still moves by a random walk, but the step size (the mean free path) is some multiple of the intermolecular spacing, which is roughly 0.3 nm. [You can calculate the spacing from the density, the molar mass, and Avogadro's number should you ever need it.] What multiple? It depends how ordered the lattice is. These vibration signals are little sound waves, or phonons. They move until they get scattered by irregularities in the lattice. Water has no lattice at all, so they get scattered after one molecular spacing.

The relevant speed is then speed at which signals travel in water, which is the speed of sound. The speed of sound is related to the stiffness of the bonds between water molecules, which is related to the bond energies and therefore to the heat of vaporisation. It has dimensions of energy per mass or of velocity squared. So a likely guess is

$$c_{\text{sound}} \sim \sqrt{L_{\text{vap}}}.$$

From lecture 3, $L_{\text{vap}} \sim 2 \text{ MJ kg}^{-1}$, so

$$c_{\text{sound}} \sim 1.5 \times 10^3 \text{ m s}^{-1}.$$

Which turns out to be much more exact than we have a right to expect. Then

$$\frac{v_{\text{water}}}{v_{\text{air}}} \sim \frac{1500 \text{ m s}^{-1}}{500 \text{ m s}^{-1}} \sim 3.$$

The ratio of mean free paths is

$$\frac{\ell_{\text{water}}}{\ell_{\text{air}}} \sim \frac{3 \times 10^{-10} \text{ m}}{10^{-7} \text{ m}} \sim \frac{1}{300}.$$

Thus

$$\frac{\kappa_{\text{water}}}{\kappa_{\text{air}}} \sim 3 \times \frac{1}{300} = 10^{-2}.$$

This ratio gives us the value of κ_{water} :

$$\kappa_{\text{water}} \sim 10^{-2} \times 1.5 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} = 1.5 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}.$$

Putting it all together

Combining all the factors,

$$\frac{K_{\text{water}}}{K_{\text{air}}} \sim 1000 \times 4 \times 10^{-2} \sim 40.$$

So

$$K_{\text{water}} \sim 40 \times 0.02 \text{ W m}^{-1} \text{ K}^{-1} \sim 1 \text{ W m}^{-1} \text{ K}^{-1}.$$

The true value is $0.6 \text{ W m}^{-1} \text{ K}^{-1}$, so our estimate is reasonably close. One slight error is in the density ratio (it is a little less than 1000). Another is in the ratio of diffusivities (it is a little smaller than 0.01). However, these corrections are not important. In this course I hope you learn not to worry about exactness (you have plenty of practice with exact calculations in other courses). The main point is that water is a factor of 30 or 40 more conductive than air. Hence air at 15°C feels comfortable, but a swimming pool with the same water temperature feels very cold.

What is the thermal conductivity of ice?

We've worked out the thermal conductivity of a gas (air) and a liquid (water). By estimating the thermal conductivity of ice, we'll cover the third state of matter. Let's compare $K_{\text{ice}}/K_{\text{water}}$ instead of $K_{\text{ice}}/K_{\text{air}}$, because ice and water are more similar than ice and air. As in the previous section,

$$\frac{K_{\text{ice}}}{K_{\text{water}}} = \frac{\rho_{\text{ice}}}{\rho_{\text{water}}} \frac{c_{\text{p}}^{\text{ice}}}{c_{\text{p}}^{\text{water}}} \frac{\kappa_{\text{ice}}}{\kappa_{\text{water}}}.$$

The density ratio is 1. Take the other factors in turn.

Ratio of specific heats

The ratio of specific heats requires a bit of thought. Water had the maximum specific heat (per molecule) of $9k$, because each atom within a water molecule contributed the full Dulong and Petit value ($3k$). The Dulong and Petit value comes from an atom having 6 degrees of freedom: 3 kinetic and 3 potential. So a water molecule has 9 kinetic and 9 potential degrees of freedom. What about ice? The molecules are no longer as free as in water because they now live in a lattice (which is why ice is a solid). In water the molecules move around as the hydrogen bonds break and re-form themselves (which is why water is a liquid). So ice has fewer degrees of freedom than water. For example, molecular rotations are no longer possible. The bending of the hydrogen bonds between water molecules also goes away in ice. Each difference costs a few degrees of freedom. The result is that the specific heat of ice is one-half that of water:

$$\frac{c_{\text{p}}^{\text{ice}}}{c_{\text{p}}^{\text{water}}} \sim 0.5.$$

Ratio of diffusivities

As in the comparison of water and air, the diffusivity ratio is given by

$$\frac{\kappa_{\text{ice}}}{\kappa_{\text{water}}} \sim \frac{v_{\text{ice}}}{v_{\text{water}}} \frac{\ell_{\text{ice}}}{\ell_{\text{water}}}.$$

In water and ice, heat travels by phonons, unlike in air where it travels by molecules moving to new locations. Phonons are little sound waves, so here we need the ratio of sound speeds. The stiffness of the intermolecular bonds is roughly the same in water and ice (hydrogen bonds in both cases), so the sound speeds are roughly the same.

The mean free paths in water and ice are different. Here we are interested in how far a phonon can travel before it is scattered by irregularities in the lattice. Water has no lattice. The molecules are arranged randomly, so a phonon is scattered after one molecular spacing. Ice has a semi-decent lattice. It is not nearly as ordered as diamond (see problem A2 on example sheet 3). It has air bubbles and other defects in the crystal structure. A reasonable guess is that phonons travel 10 molecular spacings before scattering. Thus

$$\frac{\kappa_{\text{ice}}}{\kappa_{\text{water}}} \sim 1 \times 10 = 10.$$

Combining the pieces

$$\frac{K_{\text{ice}}}{K_{\text{water}}} = \frac{\rho_{\text{ice}}}{\rho_{\text{water}}} \frac{c_{\text{p}}^{\text{ice}}}{c_{\text{p}}^{\text{water}}} \frac{\kappa_{\text{ice}}}{\kappa_{\text{water}}} \sim 1 \times 0.5 \times 10 = 5.$$

So $K_{\text{ice}} \sim 3 \text{ W m}^{-1} \text{ K}^{-1}$. The true value is $2.2 \text{ W m}^{-1} \text{ K}^{-1}$, which again is reasonably close. The most unreliable piece of the ratio calculation is the mean free path in ice. The estimate of 10 molecular spacings is slightly high (7 is more accurate). But again the main point is not the exact value but the approximate ratio: ice is a somewhat better conductor than water.

Which leaves a small *puzzle* for you. In problem C2 on sheet 2, you saw how the growing layer of ice insulated a lake from the cold air above it. If water is a better thermal insulator than ice, how is ice insulating the lake?

References and further reading

Law of Dulong and Petit.

Adkins, p. 51; Baierlein, p. 137.

Which of K (thermal conductivity) or κ (diffusivity) determine the time to cook an egg?

Many points came into in the discussion. You need to get heat into the centre of the egg, and the higher the conductivity, the faster heat travels there.

from K and κ you can compute almost everything, so surely the answer is 'both'?

True, but one or the other may not be needed in the calculation. Since $K = \rho c_p \kappa$, an equivalent question is: Which of κ and c_p are needed to compute the cooking time? It could be one or both. Maybe we had better sort out:

What is cooking?

Does it depend on getting a certain amount of energy (heat flow) into the egg? Or does it depend on raising it to a certain temperature? The centre warms last, so cooking requires raising the centre to a given temperature without burning the outside. That's why sending a huge, fast blast (e.g. a blowtorch) is not a good way to cook. The centre will cook more quickly than it would if you used boiling water, but the rest will become charcoal.

Cooking involves denaturing (unfolding) proteins. Proteins fold into a designed shape to catalyse a particular reaction (e.g. amylase) or to support a particular structure (collagen). The folded shape is a result of competition between electrostatic energy (the amino acids have partial charges all over) on the one hand and entropy, or disorder, on the other. Electrostatics tries to curl the protein into a ball. In such a state, however, it has little scope for disorder – in other words, its *entropy* is low; entropy tries to unfold the protein. Systems like to have low energy (E) and high entropy (S). In particular, they like to minimise the combination $E - TS$, known as the *free energy*.

Don't worry about the particular combination for now. The important point is that the goal is low energy and high entropy, and that the entropy goal becomes more important at higher temperatures. A protein's shape depends on temperature because temperature determines how important the two opposing forces are. As a protein is heated, entropy becomes more important and the protein unfolds. For most proteins, this change happens around 50 or 60 °C. A class of bacteria live near deep-ocean hot springs, and get their energy from sulphur compounds rather than sunlight (no sunlight at the bottom of the ocean!). Proteins in these bacteria have evolved to withstand high temperatures, so they unfold at much higher temperatures.

The unfolding reaction is reasonably fast, perhaps on the order of milliseconds. The reverse problem, of folding, is also reasonably fast, which is surprising. Imagine a protein composed of 100 amino acids, and each amino acid could be in one of 4 orientations. Then the entire protein has $4^{100} \approx 10^{30}$ possible shapes. A typical thermal vibration frequency is 10^{13} Hz, so let's guess that a protein can investigate one such shape every 10^{-13} s. Finding the folded shape would then take 10^{17} s, or roughly 10 billion years. Hmm. What's wrong with this argument?

Cooking an egg

Back to cooking the egg. Imagine a new type of egg, perhaps a GM egg. It has the same κ but twice the c_p as a normal egg. Because its c_p is doubled, bringing the GM egg to the denaturing temperature will require twice as much heat as for a normal egg. So the cooking time looks like it'll be larger. But the heat gets in twice as fast, because K is twice as large ($K \propto c_p$). Therefore the cooking time is *unchanged*.

So the cooking time depends on the diffusivity κ . How? Imagine a regular egg and an egg twice as large (in radius). Heat travels by a random walk, so it will take four times as long to walk into the centre of the large egg as for the small egg. The walk time is, as in all random walks, proportional to distance squared:

$$\tau \propto \ell^2,$$

where ℓ is a length related to the size of the object. What is the constant of proportionality? The walk time depends also on κ (the point of all the long discussion), and the larger κ the faster heat walks. Perhaps

$$\tau \propto \ell^2 / \kappa?$$

The dimensions work because diffusivities (also known as diffusion constants) have dimensions of length squared per time. If ℓ is chosen to be roughly $r/2$, then the missing dimensionless constant is roughly 1:

$$\tau \sim \frac{\ell^2}{\kappa}.$$

Let's put in numbers. An egg has diameter roughly 5 cm, so $\ell \sim 1$ cm. But:

What is κ for egg?

Who knows, but eggs are mostly water, so I'll use κ for water. If an egg were really water, then it would convect and would cook much faster than a real egg, but the proteins in a real egg block convection, so it's okay to use κ for water and assume that heat travels by diffusion. A great example of two errors cancelling.

Putting in numbers

Putting in the numbers and using the value of κ_{water} worked out in lecture 6:

$$\tau \sim \frac{10^{-4} \text{ m}^2}{1.5 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}} \sim 10 \text{ min.}$$

This value seems reasonable or is perhaps a bit long.

Adiabatic and isothermal

This course has lots of everyday application, and here's another: cycle theft. Where I was an undergraduate, cycle theft was rampant in spite of tough U-locks. One method involved spraying liquid carbon dioxide (or back then, freon) under high pressure onto the lock. As it leaves the cannister, it expands and cools, and then freezes the lock.

Which equation(s) apply during the expansion?

- $p = nkT$ (ideal gas law in my favourite form)
- $pV^\gamma = \text{const}$
- Both
- Neither

Several arguments came up. It's a quick expansion, so heat has no time to flow, so it is adiabatic. Therefore pV^γ applies. Another argument is that carbon dioxide is roughly an ideal gas, at least once it evaporates, so $p = nkT$ should apply. Another argument is that both relations apply.

But, you ask, aren't they inconsistent? To see how they could be inconsistent, rewrite $p = nkT$ using volume V :

$$pV = NkT,$$

where N is the number of molecules (n is number density). How can pV be proportional to T , yet maintain pV^γ at a constant value? Ah, because the temperature changes in an adiabatic expansion. So both relations can apply.

Moral

Both relations do apply, by the arguments you gave. The ideal gas law $p = nkT$ applies because carbon dioxide is an ideal gas. And the adiabatic law pV^γ applies because the expansion is too fast for much heat to flow. Meanwhile as it expands, it cools. If it cools enough, it can freeze a cycle lock into brittleness. (How does freezing the lock make it more brittle?)

What happens if the expansion is very slow?

The cannister starts out at room temperature. I find this fact a bit surprising. Knowing that carbon dioxide is liquid inside the cannister makes me think it must be damn cold inside. But that reasoning is bogus: The cannister has plenty of time to get to room temperature.

Now imagine letting the cannister grow one percent in volume every week. A week is plenty of time for it to exchange heat with the rest of the world, and stay at room temperature. So eventually I'll have a huge cannister of carbon dioxide, at room temperature. Not much use for nicking cycles.

Microscopic reason for $pV^\gamma = \text{const}$

Where does that γ come from?! To get an intuitive idea, imagine a moving wall (piston) and molecules bouncing around. What happens to a molecule's speed as the wall closes in and it collides with the wall (Figure 1)?

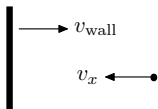


Figure 1. Molecule heading for wall. What happens after the collision?

What is the molecule's change in speed after it collides with the wall?

- a. v_{wall}
- b. $v_x v_{\text{wall}}$
- c. $v_x/2$
- d. 0

Think about this question for the next lecture.

References and further reading

Gas laws, adiabatic changes.

Adkins, pp. 40–42; Baierlein, pp. 13–16.

Entropy demonstration!

Alan Chapman has built a demonstration for us. In the first act: Using a nice block as the cargo, the cart slides down the plane, bounces off the wall, then travels roughly 80 cm up the plane (Figure 1). In the second act: Using a mess of springs and other junk as the payload, the cart slides down the plane and bangs into the wall, and then travels roughly 65 cm up the plane. Why less than in the first act? Because the impact rattles the junk around, and 15 cm worth of potential energy is lost to the shaking. In the third act, I set the junk cart sit at the bottom next to the wall, and I give it a smack. The junk starts shaking, like in the second act. Sadly, the shaking does not combine into useful energy that moves the cart 15 cm up the hill. You are seeing *entropy*, or disorder. The energy that goes into shaking the junk is disordered. It will not combine into ordered energy that can do mechanical work. In other words, entropy never decreases. You will see this interpretation of entropy in much greater depth in the statistical physics course, and you can read lots about it in P.W. Atkins, *The Second Law*.

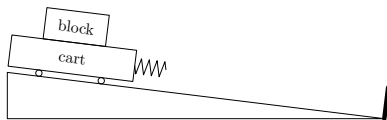


Figure 1. Cart sliding down plane. The cart's wheels are nearly frictionless, so it loses hardly any energy to friction. The spring in front is a low-loss bumper for the collision. In this case, the cargo is a single block.

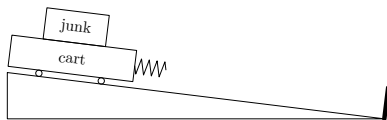


Figure 2. Cart sliding down plane with its cargo a hodgepodge of springs and junk.

Adiabatic expansions and compressions

Here was the question from the end of the last lecture. What happens to a molecule's speed as the wall closes in and it collides with the wall? The wall moves to the right with speed v_{wall} and the molecule moves to the left with speed v_x .

What is the molecule's change in speed after it collides with the wall?

- a. v_{wall}
- b. $v_x v_{\text{wall}}$
- c. $v_x/2$
- d. 0

How do you support or argue against these choices?

For a start, imagine an *extreme case*: The peaceful little molecule is sitting quietly ($v_x = 0$) and the big nasty wall smashes into it. Extreme cases are easy to analyse,

so start with them. The speed afterwards cannot be zero, because then the molecule would have to pass through the wall. So a zero change in speed cannot be right. Thus choices (b), (c), and (d) are out. Choice (b) is doubly out because its dimensions of velocity squared are bogus.

GRE

Many of you may apply to a PhD program in America. You might even go to one if you don't mind being fingerprinted by the Ministry of Fatherland Security. Almost every PhD program requires the GRE and the TOEFL (Test of English as a Foreign Language). Once in a while they even require British people to take the TOEFL, as a friend who went to Harvard found out. He refused, and they told him to go home to England, so he said he'd see what the newspapers thought of kicking out an English person for not taking the TOEFL. They let him stay.

So normally you'll just face the GRE. It has a general part and a subject part. The physics subject test is maybe 80 or 100 multiple-choice questions. In many questions, I could eliminate a lot of choices by using dimensions. For example, one question asked for the ground-state energy of a quantum particle in an unpleasant potential (it might have been $V = x^4$). Who has time to solve the Schrödinger equation in a minute or two? However, one answer had dimensions of energy squared, another had dimensions of area; they were easy to eliminate. Others had the right dimensions but looked like

$$\frac{\text{some big mess}}{\hbar}.$$

In the classical limit (extreme cases again!), where $\hbar \rightarrow 0$, the energy would be infinite! So toss out that choice as well. Just using dimensions and a bit of physical reasoning, you can often quickly eliminate most of the choices, sometimes even all but one choice. Then you save time for the questions where you don't spot a trick right away.

What about choice (a)?

Back to the wall collision. Only choice (a) survived the extreme-cases arguments. How reasonable is it? In the same extreme case of $v_x = 0$, this choice says that the final speed is v_{wall} : The molecule sticks to the wall. I'll experiment. I put a light plastic water bottle on the desk and move a coffee mug along. After the collision, the water bottle seems to leap off the mug rather than stick to it. So the final speed should be greater than v_{wall} . But let's calculate by changing frames.

Changing frames

In the rest frame of the wall, the molecule approaches with speed v , bounces, and leaves with speed v (Figure 3). Why the same speed? One reason might be conservation of momentum. Momentum is mv and the speed is preserved by the collision. The confusion is that I've used v for the speed (the magnitude of velocity). However, momentum is a vector so the $P = mv$ has a sign. Therefore mv changes in a collision. Another reason could be conservation of energy, because kinetic energy involves v^2 , which means the sign of the velocity does not matter. If the energy of the ball is preserved by the collision, then the energy of the wall must also be preserved. So the collision doesn't change the speed of the wall. Since the wall is infinitely massive, this



Figure 3. Collision with stationary wall. The molecule's speed is the same before and after the collision. Why?

result is reasonable. So conservation energy produces a decent explanation for why the molecule leaves with the same speed at which it approaches the wall.

In the wall's frame, the gas molecule approaches, and therefore leaves with speed $v_{\text{wall}} + v_x$. In the lab frame, the molecule leaves with speed $v_{\text{wall}} + 2v_x$, so its change in speed is $2v_{\text{wall}}$. The extra boost is consistent with the table-top experiment where the light water bottle leapt away from the mug. But it's not one of the choices that I offered you!

Am I careless or nasty?

Most of you thought I was nasty rather than careless. Thanks, I think. And you are right. I left out the right answer to show you a general point. We hear endlessly how UK universities are 'in trouble'. They do not have enough money when compared with their wealthier American cousins. Suppose you are working in government and are asked to decide whether to (a) increase student fees or (b) cut lecturer salaries. If you stick to the assigned choices, you will miss a third choice: cut management salaries and hire no more managers. So, come up with your answers – and even better, your own questions – before looking at what others offer you!

Examples of this speed change

In football the goal keeper often has to kick the ball across the pitch. Her infinitely massive foot hits the ball with speed v_{wall} . The ball is initially at rest, so its final velocity is $2v_{\text{wall}}$. How fast can you move your foot? Maybe you can move swing your leg one-quarter of an arc in 0.1 s (if you are a professional footballer!). The speed is roughly 10 m s^{-1} , so the ball leaves with speed 20 m s^{-1} . The distance travelled is roughly v^2/g (check it by using dimensions) or 40 m. This distance seems reasonable: It is about one-half of a football pitch.

Another example of this kind of collision is used by NASA. Often a spacecraft, say Voyager, needs a boost along the way, but carrying fuel from earth is too difficult. For one, carrying fuel means a heavier payload for the rocket sending the spacecraft into orbit, which greatly increases the cost. Fortunately the solar system has many infinitely massive, moving walls. For example, Jupiter. The spacecraft approaches Jupiter moving opposite to its orbital motion (Figure 4). In the rest frame of Jupiter, the probe approaches, swings around, and then leaves in (almost) the opposite direction. In the frame of the solar system, the probe gets a kick from Jupiter. This is a *gravity slingshot*. *Puzzle:* Where does the extra energy for the spacecraft come from?

A third example of the bounce is the problem we began with: molecules colliding with a wall. The principle applies to microscopic systems (molecules colliding with a wall), mesoscopic systems (kicking a football), and macroscopic systems (gravity slingshots in the solar system): a range of perhaps 20 orders of magnitude in length.



Figure 4. Bouncing off Jupiter. In the lab frame, a spacecraft approaches Jupiter with speed v , as shown in (a). Meanwhile Jupiter is doing its usual orbital motion, giving it speed v_J in the opposite direction. In Jupiter's frame, shown in (b), the spacecraft approaches with speed $v + v_J$, so it bounces off with the same speed. Transforming back to the lab frame shows that the spacecraft leaves Jupiter with speed $v + 2v_J$.

Fractional change in energy

The speed of the gas molecule went from v_x to $v_x + 2v_{\text{wall}}$, which is a fractional change of

$$\frac{\Delta v_x}{v_x} = \frac{2v_{\text{wall}}}{v_x}.$$

What is the fractional change in energy in terms of the fractional change in velocity? Since kinetic energy is proportional to v^2 , a reasonable conclusion is that the fractional changes behave similarly:

$$\frac{\Delta E}{E} = \left(\frac{\Delta v_x}{v_x} \right)^2.$$

Let's check it in a simple example. Imagine a square with side $x = 1$ and area $A = 1$. Now increase x by 10%: a fractional increase of 0.1 (Figure 5). Does the area increase by 0.1²? The area becomes $1.1^2 \approx 1.2$, which is an increase of 20%. Here is another example. Increase x to 1.05. The area becomes $1.05^2 \approx 1.1$, so a 5% increase in x turns into a 10% increase in A . The general rule would then be

$$\frac{\Delta E}{E} = 2 \left(\frac{\Delta v_x}{v_x} \right).$$

It still has a 2 but the 2 has come in front as a factor rather than living as an exponent. Here's a rough derivation of that result using *logarithmic differentiation*. If $A = x^2$ then $\log A = 2 \log x$. Now differentiate:

$$\frac{dA}{A} = 2 \frac{dx}{x}.$$

And you can easily generalise this result to higher powers.

But, you ask, the energy formula is slightly different from $A = x^2$ because it has a constant in front. So let's try $A = bx^2$ where b is a constant. Then $\log A = \log b + 2 \log x$. Since b is a constant, the differentiation step is the same:

$$\frac{dA}{A} = 2 \frac{dx}{x}.$$

Next time we'll use the result for fractional change in energy to work out the pressure and volume change when you compress a gas.

0.1	0.01
1	0.1

Figure 5. Increasing the area of a square. Originally there was a unit square (heavy outline). The side length increases by 10% (not drawn to scale), so the area increases, approximately, by the two rectangles. Their area is 0.2.

Problem solving

Here is a description of Los Alamos when the news came back that Hiroshima had been bombed:

He entered the room like a prize fighter. As he walked through the hall there were cheers and shouts and applause all round and he acknowledged them in the fighter's salute – clasping his hands together above his head as he came to the podium.

The prize fighter was Robert Oppenheimer. Here is Hans Bethe describing a later era at Los Alamos:

Grim as the subject was, it was a most exciting enterprise. The ideas we had about triggering an H-bomb turned out to be all wrong but the intellectual experience was unforgettable.

Solving problems is often lots of fun. But which problems are you solving?

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

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

where the \dots 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 $R = N_A k$ shows up). So for an ideal gas

$$c_v = d \times \frac{k}{2},$$

and

$$c_p = c_v + k = (d + 2) \times \frac{k}{2}.$$

Then $1 + 2/d = (d + 2)/d$ has a simple expression as c_p/c_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.

Light bulb filaments

Alan Chapman set up a demonstration about light bulb filaments. Under the microscope, you can see that it has coils within the coils. The wire itself looks about $50\text{ }\mu\text{m}$ in diameter, which is reasonably close to the value predicted in problem C1 of sheet 2.

Adiabatic changes

Last time we got to

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

If you integrate both sides, you get

$$\ln p = \text{const} - \gamma \ln V.$$

This form is just the logarithm of the more familiar form:

$$pV^\gamma = \text{const}.$$

I prefer the fractional-change form: It shows more clearly that pressure drops more in an adiabatic expansion than in an isothermal expansion. This fact has an important consequence for the temperature. The ideal gas law says that $pV \propto T$. The fractional change in pV is the sum of the fractional changes in p and V (an idea used in lecture 9):

$$\frac{d(pV)}{pV} = \frac{\Delta p}{p} + \frac{\Delta V}{V} = (1 - \gamma) \frac{\Delta V}{V}.$$

In air ($\gamma = 1.4$), a 5% increase in volume produces a 7% decrease in pressure and a 2% decrease in temperature. The sign is correct: Adiabatic expansions reduce temperature as the gas does work on the surroundings, or equivalently, as the gas molecules collide with a receding wall.

Rain shadows

Now imagine a mountain range and winds bringing moist air towards it (the moist air come from the ocean). As the air parcel rises up the mountain, the surrounding air pressure falls. Why? Because of gravity. One picture of air pressure (there are a few gotchas in this picture, but it's mostly right) is as the weight per area of a column of air above you. At higher altitudes less air sits on top of your head. So the pressure drops and the parcel expands until its pressure matches the external pressure. The expansion is adiabatic, so the parcel cools as it rises. Cooler air holds less water vapour. We'll sort out why in a minute, but let's take it as a given for now. What happens to the excess water vapour? It condenses into water and turns into rain! So the windward side of the mountain gets lots of rain.

As the dry parcel descends the other side of the mountain, the surrounding pressure increases so the parcel contracts. In this adiabatic expansion the temperature rises, as does the capacity to hold water vapour. Oh, not so good for the plants: The water-hungry air sucks up water from the ground, so it dries out (it gets 'anti-rain'). The net effect of the parcel of air is to transfer rain from the far side of the mountain to the windward side.

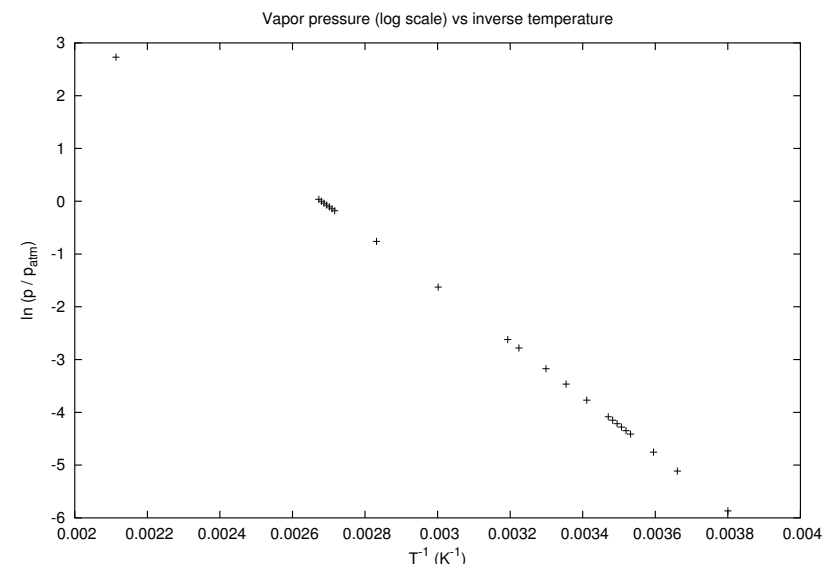
Adiabatic atmosphere

Knowing the pressure at the top of the mountain, we can calculate the temperature of the air parcel (using the adiabatic law). This temperature is also the temperature of the surrounding air in an adiabatic atmosphere (see problem B1 on sheet 3). How does an atmosphere become adiabatic?

Imagine an atmosphere where the temperature is constant with height. The pressure drops with height – because of gravity. You studied this *isothermal atmosphere* in IA physics as an example of the Boltzmann factor. It is stable as long as nothing disturbs it. Now add a tiny bit of convection: A bit of air near the ground heats up slightly (perhaps it's near a hot tarmac), so it becomes less dense than the surrounding air and therefore rises (buoyancy). As it rises, it follows the same life history as the air parcel going up the mountain: It expands (because of lower surrounding pressure) and therefore cools adiabatically. Heat flows in from the surrounding air, raising the temperature of the parcel and lowering the temperature of the surrounding air. This process of parcel circulation continues to reduce the temperature until the temperature at that height is what it would be in an adiabatic change. The isothermal atmosphere is *convectively unstable* and turns into an adiabatic atmosphere.

Vapour pressure

How does vapour pressure vary with temperature? Here is vapour pressure data for water:



Note the special axes. The pressure is on a log scale and the temperature is plotted as $1/T$. Those choices make the data fall on a straight line. So

$$\ln p = \ln p_0 - \frac{T_0}{T},$$

where p_0 and T_0 are constants determined by fitting a straight line to the data. Thus

$$p \propto e^{-T_0/T}.$$

Why does the pressure have this form?

Boltzmann!

The answer is the Boltzmann factor: the same factor that you used last year to work out the pressure versus height in an isothermal atmosphere. It says that

$$\text{probability of being in a state} \propto e^{-E/RT},$$

where E is the energy of a state and R is the usual gas constant. Here the two states are gaseous water (steam) and liquid water. Imagine a box containing liquid water and vapour. The ratio of probabilities to be in vapour relative to liquid is

$$\frac{P(\text{steam})}{P(\text{liquid})} \propto e^{-\Delta E/RT},$$

where ΔE is the energy difference between vapour and liquid. It takes energy to remove a molecule from the liquid (you have to break hydrogen bonds) so the vapour has higher energy than the liquid ($\Delta E > 0$). As temperature changes, more liquid turns into vapour, but the amount of liquid hardly changes (gases are so much less dense than liquids). So $P(\text{liquid})$ is roughly constant, and then

$$P(\text{steam}) \propto e^{-\Delta E/RT}.$$

Furthermore, probability is proportional to density and pressure is proportional to density by the ideal gas law. So

$$p_{\text{vapour}} \propto e^{-\Delta E/RT}.$$

Looking at the graph, you can find that $T_0 \sim 5000 \text{ K}$ (see also problem B1 on sheet 4). In the exponential form above, $RT_0 = \Delta E$. So

$$\Delta E \sim 8 \text{ J mol}^{-1} \text{ K}^{-1} \times 5000 \text{ K} = 4 \times 10^4 \text{ J mol}^{-1}.$$

One mole of water has a mass of 18 g, so

$$\Delta E \sim 4 \times 10^4 \text{ J mol}^{-1} \times \frac{1 \text{ mol}}{1.8 \times 10^{-2} \text{ kg}} \sim 2 \text{ MJ kg}^{-1}.$$

Hmm, that looks familiar: It's the heat of vaporisation of water (lecture 3). This result makes sense, since it is the energy to remove a water molecule from the liquid to the vapour. Thus

$$p \propto e^{-L_{\text{vap}}/RT}.$$

The constant of proportionality is determined by setting $p = 1 \text{ atm}$ at $T = 100^\circ \text{C}$ (don't forget to convert to Kelvin!).

Results

Everywhere you find the results of Boltzmann and adiabatic expansions. In North America, winds bring moist air from the Pacific Ocean towards the east. They eventually hit the Rocky Mountains ($h \sim 3000 \text{ m}$), dumping water on the western slopes and making them bountiful and green. From the solution to problem B1 on sheet 3, the temperature in an adiabatic atmosphere is

$$T = T_0 \left(1 - \beta \frac{z}{H}\right),$$

where $\beta = 1 - 1/\gamma \approx 0.3$, $T_0 \sim 300 \text{ K}$, and $H \sim 10 \text{ km}$. So at the top of the Rocky Mountains, the temperature has dropped by

$$\Delta T \sim 300 \text{ K} \times 0.3 \times \frac{3 \text{ km}}{10 \text{ km}} \sim 30 \text{ K}.$$

Which seems reasonable. Even in summer, where perhaps $T = 30^\circ \text{C}$ at the bottom of the mountains, the tops have a bit of snow (at least in the shady regions). What fraction of the water is dumped because of this temperature change? The fraction retained is given by

$$e^{-T_0/T_{\text{final}}} / e^{-T_0/T_{\text{initial}}}.$$

The initial temperature is say 300 K and the final temperature is 270 K . So the exponent in the Boltzmann factor goes from $5000/300$ to $5000/270$ (leaving out the minus sign). The first quotient is roughly 17, and the second is roughly 10% higher (because 270 is 10% lower than 300). The exponent then changes by 1.7, and the fraction retained is roughly $e^{-1.7}$ or 0.2. So four-fifths of the water is dumped on the western slopes, and perhaps that much water is absorbed from the eastern slopes. No wonder it is so dry.

East of the Rocky Mountains is the Great Plains where farming is difficult because it is so dry. In the 1930s a further drop in rainfall turned parts of the Great Plains into a dust bowl: the dirt was so dry that winds could blow it around. Farmers went bankrupt and many families fled to California in mass migrations. Their sad tale is the subject of John Steinbeck's classic novel *The Grapes of Wrath*.

Here is a European example of rain shadows, from Mark Mazower, *The Balkans: A Short History* (Modern Library, 2000):

Over millions of years, the play of the earth's tectonic plates pushed up a series of mountain ranges in the Mediterranean along the geological frontier between Europe and Africa. Stretching from the Iberian peninsula in the west to the ranges of southeastern Europe in the east, they eventually link up with the mountain chains of Asia Minor and central Asia. To their north, the great Eurasian lowlands extend with scarcely a break from Calais to the Urals. There rainfall is abundant, arable land is plentiful and numerous navigable rivers connect the interior with the sea. To the south, it is a different story: good farming land becomes scarcer, the ground is more broken and rainfall less frequent.

The effect of mountains is felt everywhere from the skies to the sea. Rain shadows deprive much of the peninsula of the moisture found in Europe's continental climatic zone. Kolain in Montenegro has an average annual rainfall of 104 inches, while a little way east, Skopje in Macedonia has only 18 inches per year. A tiny

coastal strip running down the Dalmatian coast to western Greece enjoys sufficient rain to soften the impact of the harsh Mediterranean summers.

On Corfu the vegetation is luxuriant; the Cyclades, by contrast, are parched and dry. The former is able to support itself, the latter—as wartime starvation revealed—relies on food imports to keep going.

What is the Carnot cycle?

These so-often studied engines (ways of turning heat flow into mechanical work) are important not because a real engine looks that much like a Carnot cycle. Rather, they show the maximum efficiency an engine can have and then lead to the idea of entropy.

The ingredients are reservoirs at T_{hot} and at T_{cold} and an ideal gas whose volume can be varied with a piston. The piston is surrounding by vacuum, so if we don't want the piston to expand we have to lock it down. The gas has four states, and begins in state 1 with the piston locked:

State	Temp	Volume
1	T_{hot}	V_1
2	T_{hot}	V_2
3	T_{cold}	V_3
4	T_{cold}	V_4

It goes through four changes, steps A–D:

Step	States	Type of change	Heat flow?
A	1 → 2	Isothermal at T_{hot}	Heat flows in (Q_{hot})
B	2 → 3	Adiabatic	No heat flow
C	3 → 4	Isothermal at T_{cold}	Heat flows out (Q_{cold})
D	4 → 1	Adiabatic	No heat flow

Step A: Isothermal expansion at T_{hot}

Connect the gas to the hot reservoir (which could be for example a giant metal block at T_{hot}). Reservoir just means: 'huge object whose temperature does not change even as heat enters or leaves' (infinite heat capacity). Just as a voltage source means: 'ideal source that supplies the same voltage no matter how much current is needed.' Neither a true reservoir nor a true voltage exists, but they are useful approximations.

Nothing happens when you first connect the reservoir, since the gas was already at T_{hot} . The gas tries to shove the piston outward, but no luck because the piston is locked. Unlock the piston and let it *slowly* creep outward. To prevent it from accelerating, you must balance the pressure from the gas. As the piston moves outward, the gas does mechanical work against your force on the piston. Without the reservoir, the gas would cool as it expands (it would be an adiabatic expansion). The reservoir supplies the heat needed to keep the temperature constant. Call this heat Q_{hot} . We'll compute it later. In this step, the volume has grown and the pressure has fallen, but the temperature remained T_{hot} . The gas is now ready for the next step.

Step B: Adiabatic expansion from $T_{\text{hot}} \rightarrow T_{\text{cold}}$

Disconnect the reservoir and let the gas expand further. Without the reservoir to supply heat, the temperature drops in this adiabatic expansion. Keep expanding – and doing work on the environment – until the gas cools to T_{cold} . No heat flows in this step.

Step C: Isothermal compression at T_{cold}

Now attach the cold reservoir and squeeze the gas until it reaches a special volume (which we won't need to calculate). Without the reservoir the gas temperature would rise, but the reservoir maintains the temperature by sucking heat from the gas. Call this heat Q_{cold} . The compression requires mechanical work from the environment to do work against the gas pressure.

After this step, the gas has neither the starting temperature (T_{hot}) nor the starting volume (V_1). Alas! The fourth step fixes these problems and makes the four steps a cycle.

Step D: Adiabatic compression from $T_{\text{cold}} \rightarrow T_{\text{hot}}$

Now remove the reservoir and compress the gas until it reaches T_{hot} . If in step C you chose the right stopping volume (V_3), then when the gas reaches T_{hot} in this step it will also have the initial volume V_1 . The cycle will then be complete and can start over. Never mind what the magic volume V_3 is. As you will see, adiabatic magic means that we don't need to compute it. All that matters is that such a volume exists.

Diagram of the Carnot cycle

Most texts plot the states of a Carnot cycle on a pV diagram. I prefer to use a log–log diagram. So I plot $\ln p$ versus $\ln V$. But I do not want to commit dimension crimes by taking the logarithm of a pressure. For an example of the trouble that would get me into:

$$\ln(10 \text{ Pa}) = \ln 10 + \ln \text{ Pa}.$$

But what on earth is the logarithm of a Pascal? So I better make sure I use a dimensionless pressure. The most natural way is to plot $\ln(p/p_1)$, where p_1 is the pressure in state 1. Similarly, I plot $\ln(V/V_1)$ on the x axis. Thus for state 1, both logarithms are zero, so state 1 lies on the origin. I'll plot the other three states by going one step at a time. Figure 1 has the result.

Step A: Isothermal expansion at T_{hot}

In an isothermal expansion, $p \propto V^{-1}$, so

$$\ln p = \text{const} - \ln V,$$

where all the dimension crimes hide in the constant. So on the log–log diagram, an *isotherm* is a line of slope -1 . Hence I plot state 2 some distance along such a line.

Step B: Adiabatic expansion from $T_{\text{hot}} \rightarrow T_{\text{cold}}$

In an adiabatic expansion, $p \propto V^{-\gamma}$, so on the diagram the system moves along a line of slope $-\gamma$. Because $\gamma > 1$ an *adiab*t is steeper than an isotherm. So I move along an adiabat and plot state 3.

Step C: Isothermal compression at T_{cold}

Now the system moves up an isotherm (slope -1) until it reaches state 4. As discussed above, we don't know where state 4 is, but we will choose it so that step D completes the cycle. How? By considering what happens in step D.

Step D: Adiabatic compression from $T_{\text{cold}} \rightarrow T_{\text{hot}}$

Now the system moves up an adiabat (they all have the same slope) to return to state 1. So state 4 is the intersection of the adiabat from state 1 and of the isotherm from state 3.

Plotting it all

Figure 1 puts together all the plotting.

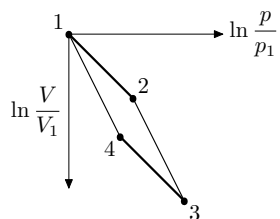


Figure 1. Carnot cycle on a log-log pV diagram. The two isothermal steps, with slope -1 , are shown as thicker lines. The adiabatic steps have slope -7 .

Analysis of the Carnot cycle

There are many subtle points about the cycle, best brought out after analysing the heat flows and mechanical work. Only in steps A and C does heat flow: Q_{hot} is slurped from the hot reservoir, and Q_{cold} is dumped into the cold reservoir.

Computing Q_{hot} and Q_{cold}

These heat flows arose during the isothermal changes. The energy in an ideal gas depends only on temperature (and on the number of molecules, but the number never changes in any step). So the energy remains fixed during an isothermal change. But heat flowed, and heat is a form of energy. Where did that energy go? Oh, right, it all got turned into mechanical work. In step A, the incoming heat flow Q_{hot} is the mechanical work done by the gas in the expansion. In step B, the outgoing heat flow Q_{cold} is the mechanical work done on the gas during the isothermal contraction.

By computing the mechanical work, we can compute the heat flows. We know how to compute the mechanical work:

$$W = \int p dV,$$

which is a fancy way of saying work is force (from the pressure) times distance (from the volume change). For an ideal gas $pV = N_{\text{moles}}RT$ so

$$W = N_{\text{moles}}RT \int \frac{dV}{V} = N_{\text{moles}}RT \ln \left(\frac{V_f}{V_i} \right),$$

where V_f and V_i are the final and initial volumes, respectively. This value is easy to read on the log-log plot because it is just proportional to the x -axis distance between the final and initial volumes.

In step A, the initial and final volumes are V_1 and V_2 , respectively, and the temperature is T_{hot} . The work done *by the gas*, and therefore the incoming heat flow (where the gas gets the energy to do the work), is:

$$Q_{\text{hot}} = N_{\text{moles}}RT_{\text{hot}} \ln \left(\frac{V_2}{V_1} \right).$$

Careful about the sign! Q_{hot} should be positive. Luckily it is since $V_2 > V_1$. Similarly for Q_{cold} :

$$Q_{\text{cold}} = N_{\text{moles}}RT_{\text{cold}} \ln \left(\frac{V_3}{V_4} \right).$$

Again a sign check. Q_{cold} should be positive since it represents the heat flowing out during the isothermal compression, and $V_3 > V_4$, so all is well.

Did you forget the heat flows in steps B and D?

No, they are adiabatic and no heat flows.

Computing work done

After the four steps of the cycle, the gas is in its original state with its original (thermal) energy. The net heat flow, $Q_{\text{hot}} - Q_{\text{cold}}$, changed neither the state of the gas nor its energy. But heat flow is energy flow so the net heat flow must have turned into another kind of energy: mechanical work. This statement, which nobody today doubts, is another way of stating the *first law of thermodynamics* or conservation of energy. At the time of its discovery in the 19th century, debates raged on what heat was; was it a substance (the so-called caloric)? Nobody was sure. But especially now that we have microscopic models of matter, we can see that heat has a mechanical interpretation in the potential and kinetic energies of molecules.

Using the almost-obvious first law, the net work is

$$W_{\text{net}} = Q_{\text{hot}} - Q_{\text{cold}} = N_{\text{moles}}R \left(T_{\text{hot}} \ln \left(\frac{V_2}{V_1} \right) - T_{\text{cold}} \ln \left(\frac{V_3}{V_4} \right) \right).$$

Despair! We don't know either V_3 or V_4 . But that's where the connecting adiabatic expansions save us.

Adiabatic magic

States 2 and 3, like states 4 and 1, are connected by an adiabatic change. Figure 1 shows the happy consequences. Because the figure is a parallelogram, the vector \mathbf{r}_{12} is identical to \mathbf{r}_{43} . In particular, the x distance between states 1 and 2 is the same as the x distance between states 4 and 3. Since the x axis is logarithmic:

$$\ln \frac{V_4}{V_3} = \ln \frac{V_2}{V_1},$$

which is just what we needed to know. The simplicity of this method is why I like to plot pV on a log-log graph rather than on the usual linear axes.

A more complicated way to get the same result is to wade through the algebra of the gas laws. Since $pV^\gamma = \text{const}$ for such changes and $pV \propto T$ always for an ideal gas, then by dividing these two relations you get

$$V^{\gamma-1} \propto T^{-1}$$

in an adiabatic change. So $V \propto T^{1/(1-\gamma)}$. The exponent itself will turn out not to matter, so for good hygiene I'll define

$$\alpha \equiv \frac{1}{\gamma - 1}$$

With that definition, the volume-temperature relation is

$$V \propto T^{-\alpha}.$$

For an expansion going from $T_i \rightarrow T_f$, the volume ratio is

$$\frac{V_f}{V_i} = \left(\frac{T_f}{T_i} \right)^{-\alpha},$$

where T_i and T_f are the starting and final temperatures, respectively. Let's check sanity. If the gas expands adiabatically, so $V_f > V_i$, then the final temperature is less than the initial temperature; this fact we know from the freezing of the bicycle U-lock. Since the exponent $-\alpha$ is negative, all is well.

Using this result for step B:

$$\frac{V_3}{V_2} = \left(\frac{T_{\text{cold}}}{T_{\text{hot}}} \right)^{-\alpha},$$

because the gas starts at T_{hot} and finishes at T_{cold} . And for step D:

$$\frac{V_1}{V_4} = \left(\frac{T_{\text{hot}}}{T_{\text{cold}}} \right)^{-\alpha},$$

since the gas starts at T_{cold} and finishes at T_{hot} . There's the magic we needed, because the two results combine to show $V_3/V_2 = V_4/V_1$ and therefore $V_3/V_4 = V_2/V_1$. This result is what we found so easily using the log-log diagram.

Using this result we can finally get the net work:

$$\begin{aligned} W_{\text{net}} &= N_{\text{moles}} R \left(T_{\text{hot}} \ln \left(\frac{V_2}{V_1} \right) - T_{\text{cold}} \ln \left(\frac{V_3}{V_4} \right) \right) \\ &= N_{\text{moles}} R \left(T_{\text{hot}} \ln \left(\frac{V_2}{V_1} \right) - T_{\text{cold}} \ln \left(\frac{V_2}{V_1} \right) \right) \\ &= N_{\text{moles}} R (T_{\text{hot}} - T_{\text{cold}}) \ln \left(\frac{V_2}{V_1} \right). \end{aligned}$$

How simple! And it makes sense from what you know about real engines. Powerful car engines have a large *displacement* because it allows large volume changes. The T_{hot} in W_{net} means that engines run hot, and indeed much effort goes into making materials that withstand such heat for many, many cycles.

Efficiency

The efficiency of an engine is the ratio of work done to heat taken in (at the hot temperature):

$$\begin{aligned} \eta &\equiv \frac{\text{work done}}{\text{heat taken in}} \\ &= \frac{N_{\text{moles}} R (T_{\text{hot}} - T_{\text{cold}}) \ln \left(\frac{V_2}{V_1} \right)}{N_{\text{moles}} R T_{\text{hot}} \ln \left(\frac{V_2}{V_1} \right)} \\ &= 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}. \end{aligned}$$

More interesting than the efficiency

More interesting than the efficiency is a quantity suggested by this derivation. It's not the heat. Heat is not so interesting because, even though the system returns to the same state after one cycle, the incoming heat is not the same as the outgoing heat. It's therefore impossible to inspect a system and say: 'It has this much heat in it.' To see why, imagine that you could identify a property called 'heat'. After you one full Carnot cycle on your system, it will return to the original state, but the 'total heat' will be larger because more heat flowed in than flowed out! So 'total heat' cannot be a property of a system, and it is meaningless to ask what the total heat of a system is. (When you ask this question, you probably mean to ask for the energy of the system.)

But a close relative of heat can have a meaning. Here are the heats themselves:

$$Q_{\text{hot}} = N_{\text{moles}} R T_{\text{hot}} \ln \left(\frac{V_2}{V_1} \right),$$

and

$$Q_{\text{cold}} = N_{\text{moles}} R T_{\text{cold}} \ln \left(\frac{V_2}{V_1} \right).$$

Look at the close cousin Q/T for each heat flow:

$$\frac{Q_{\text{hot}}}{T_{\text{hot}}} = N_{\text{moles}} R \ln \left(\frac{V_2}{V_1} \right),$$

and

$$\frac{Q_{\text{cold}}}{T_{\text{cold}}} = N_{\text{moles}} R \ln \left(\frac{V_2}{V_1} \right).$$

These ratios are equal! In one cycle the system gains and loses equal amounts of this quantity. When Q is the heat flowing into a system, we call Q/T the *entropy change* of the system. So a cycle preserves the entropy of the gas: The incoming entropy all departs. Thus entropy can be a property of a system.

The second law of thermodynamics

You already know that heat flows from hot to cold. This empirical statement is the Clausius statement of the second law of thermodynamics. Let's apply our concept of entropy to it. Imagine tanks of hot and cold water separated by an insulating membrane. After you replace the membrane with a conducting membrane (one that allows heat to flow), the tanks will come to the same temperature: heat flows from the hot to the cold one. Consider one tiny time interval of this flow, before equilibrium is reached. A bit of heat, ΔQ flows from hot to cold. The entropy of the hot water falls by $\Delta Q/T_{\text{hot}}$ and the entropy of the cold water rises by $\Delta Q/T_{\text{cold}}$. But $T_{\text{hot}} > T_{\text{cold}}$ (heat flows from hot to cold!), so

$$\frac{\Delta Q}{T_{\text{cold}}} > \frac{\Delta Q}{T_{\text{hot}}},$$

and the combined entropy increases. In other words, whenever heat flows from hot to cold, entropy increases. And heat never flows from cold to hot, so

Entropy never decreases!

Statistics!

We defined entropy in terms of macroscopic quantities (heat and temperature). In Bill Allison's course (for those in Advanced Physics) or in the beautifully illustrated book by Atkins, *The Second Law*, you will learn that entropy has a microscopic, statistical interpretation. This interpretation was such a surprise to Boltzmann that he put it on his tombstone.

A clever little device

Here is a situation that connects the micro- and macroscopic interpretations of entropy. Imagine gas in a box. The box has two halves separated by a partition. The partition has a slider door (like on bottles of salt), and you in very tiny form open and close the door. As one of you pointed out when I was approximating everything away to compute $pV^\gamma = \text{const}$, gas molecules have a distribution of speeds. Some are fast, some are slow, and some are just average. When you see a fast molecule coming from the left side, you quickly open the door, let the molecule into the right side, and shut the door. When you see a slow molecule coming from the right side, you quickly open the door, let the molecule into the left side, and shut the door. The left side will steadily cool (lower average energy of the molecules) and the right side will steadily warm (higher average energy of the molecules), even though the total energy of the two sides will not change.

After the temperature gets sufficiently far apart, you connect them to a Carnot engine. The right side is the hot reservoir and the left side is the cold reservoir. You extract mechanical work from the system as heat flows from the hot reservoir to the cold. When the two reservoirs are at the same temperature (which is the initial temperature of the gas before you did your sliding door tricks), you take away the Carnot engine, do the sliding door tricks again, and then reconnect the engine to extract still more mechanical work...

What's wrong with this picture?

By the door tricks, you made heat flow from cold to hot; this change violates the second law (entropy never decreases). Using the Carnot engine, you also extract energy forever. This extraction violates the first law of thermodynamics (energy conservation). This sliding-door system indicates that the first law is somehow contained in the second law because it shows you how to take any system that can violate the second law and use it to violate the first law.

Macroscopically you can forbid these door tricks using the first and second laws. You can say, 'No, such a system cannot exist.' But that kind of legal barrier does not leave one entirely at ease. If it's wrong macroscopically, it should be wrong microscopically since macroscopic quantities arise from microscopic pictures. The microscopic picture should not give a different answer! Thermodynamics, after all, is supposed to be independent of the microscopic model. This generality is its great strength and also why it is so abstract and confusing if taught entirely independent of microscopic models. So, *how can you bring together the micro- and macroscopic pictures that this example tears asunder?*

References and further reading

Phase changes and vapour pressure.

Adkins, pp. 64–66, 81–83, and 110–111; or Baierlein, pp. 270–76 and (although a bit overloaded with equations) pp. 280–282.

Heat engines and entropy.

Adkins, pp. 104–110 and 114–116; or Baierlein, pp. 34–35 and 51–70.

The end

In this course I hope you've seen how physics surrounds us. On the one hand, physics has invented terrible weapons and served the powerful. On the other hand, physical principles explain so much of the world around us. The mass migrations of people looking for good farming land are an aspect of human culture resulting from $pV^\gamma = \text{const}$. Wearing clothes is a consequence of

$$F = K \frac{\Delta T}{\Delta x}.$$

Our earth is the right temperature for life because of $F = \sigma T^4$. Who can say whether war or explanation and wonder will be the main result of physics. As physicists, you have a place in deciding.

Concern for man himself and his fate must always form the chief interest of all technical endeavours. ... Never forget this in the midst of your diagrams and equations.

–Albert Einstein