6 THERMAL PROPERTIES

How fast does a turkey cook? How quickly does the moon cool? Why are wooden spoons useful for cooking? Why does water boil at 373 K? Such questions depend on the thermal properties of materials. To warm up, try thermal expansion.

6.1 Thermal expansion

Most materials expand when they get hotter and contract when they get cooler. If bridge designers forget this fact, and design a bridge so that its joints exactly mate in the summer, then it will fall down in the winter. We would like to understand why materials expand, and by how much.

So imagine a piece of material, heated from 0 K to a temperature T. How much does it lengthen? Before trying dimensional analysis, you can sharpen the question. Materials lengthen because their atoms move apart. So a long rod probably expands more than a short rod does. A physically reasonable quantity to analyze is

$$\frac{\text{change in length}}{\text{length}}, \tag{6.1}$$

which is the fractional length change. This quantity is intensive, usually a good quality, and dimensionless, always a good quality. So the revised question is: In heating the material from 0 K to temperature T, by what fraction does it lengthen? Time for the list of variables. With a as the usual bond length, let Δr be the change in length. Then $\Delta r/a$ is the fractional change. As the goal, it goes on the list. The temperature is on the list. As a rule of thumb, include temperature as the energy kT, where k is Boltzmann's constant. If you include it as T, you add a fourth dimension, temperature. To deal with a fourth dimension, you then need to include a constant to convert temperature to energy; that constant is k. Including T and k separately adds two variables and one dimension, which increases the number of dimensionless groups by one. Equivalently – and more simply – include kT, which adds one variable and no new dimensions. This simpler alternative also adds also one new dimensionless group. So kT goes on the list. Strong bonds imply a stiff, hard-to-stretch material, so the bond strength – or cohesive energy ϵ_c – might affect thermal expansion as well. Perhaps the bond length a matters as well. The list is shown in Table 6.1.

Var.	*Dim.*	*Description*
$\Delta r/a$	$--$	fractional expansion
a	L	bond length at $T=0$
ϵ_c	$\mathrm{ML}^2\mathrm{T}^{-2}$	bond energy
kT	$\mathrm{ML}^2\mathrm{T}^{-2}$	thermal energy

Table 6.1. *Variables that determine thermal expansion. The goal, $\Delta r/a$, is in red.*

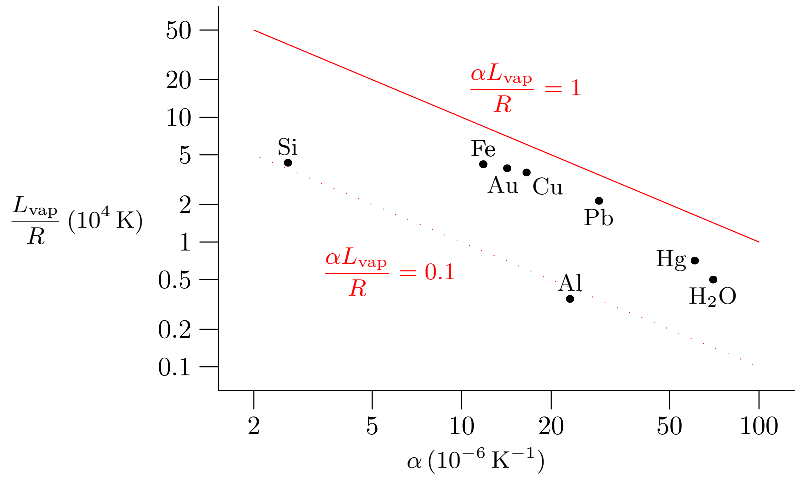

Figure 6.1. *Cohesive energy vs thermal expansion coefficient. The cohesive energy is represented by L_{vap}/R, where L_{vap} is the molar heat of vaporization. The solid red line is the curve $\alpha(L_{\text{vap}}/R) = 1$ and the dotted red line is $\alpha(L_{\text{vap}}/R) = 0.1$. Most substances lie between these lines.*

Although this list contains three dimensions (L, M, and T), it contains only *two* independent dimensions. You can form the dimensions of every variable using only L and $\mathrm{ML^2T^{-2}}$. Four variables and two independent dimensions produce two dimensionless groups. The first one is free because $\Delta r/a$ is already dimensionless. So

$$\Pi_1 = \frac{\Delta r}{a}. \tag{6.2}$$

The other group is almost as easy. Both ϵ_c and kT are energies, so

$$\Pi_2 = \frac{kT}{\epsilon_c} \tag{6.3}$$

is dimensionless. Two groups complete the set. Only one variable, a, has dimensions of length, so a does not make it into a dimensionless group. To solve for $\Delta r/a$, use the form $\Pi_1 = f(\Pi_2)$:

$$\frac{\Delta r}{a} = f\left(\frac{kT}{\epsilon_c}\right). \tag{6.4}$$

A reasonable guess is that expansion is proportional to temperature, so $f(x)$ would be linear. Then

$$\frac{\Delta r}{a} \sim \frac{kT}{\epsilon_c} = \frac{k}{\epsilon_c} T. \tag{6.5}$$

where the factor in red is the **thermal expansion coefficient** α. Then

$$\alpha \sim \frac{k}{\epsilon_c}. \tag{6.6}$$

The coefficient varies with temperature. Rather than changing the temperature from 0 to T, over which range the coefficient might vary, imagine a small temperature change ΔT around the current temperature. The more exact definition of α uses ΔT instead of T:

$$\alpha \equiv \frac{\text{fractional length change}}{\Delta T}. \tag{6.7}$$

In an approximate analysis, you can often ignore the distinction between T and ΔT.

Table 6.2 lists thermal-expansion coefficients for various materials, and Figure 6.1 shows how the data compare to the dimensional-analysis prediction (6.6). If the missing constant in (6.6) is β, then all substances would lie on the line $\alpha(L_{\mathrm{vap}}/R) = \beta$. Most substances shown on the scatterplot have values between 0.1 (dotted red line) and 1 (solid red line). So dimensional analysis produces a reasonable result. Even using a fixed value of ϵ_c, say $\epsilon_c = 10\,\mathrm{eV}$, in (6.6) produces a reasonable, easy-to-remember value:

$$\alpha \sim \frac{\overbrace{10^{-4}\,\mathrm{eV\,K^{-1}}}^{k}}{10\,\mathrm{eV}} \sim 10^{-5}\,\mathrm{K}^{-1}. \tag{6.9}$$

Beyond dimensional analysis, you might wonder about the mechanism of thermal expansion. The mechanism also shows where the missing constant in (6.6) comes from. Look at the potential energy between two atoms or molecules (as in water). When $T = 0$ the atoms have zero kinetic energy, the bond does not vibrate, and the atoms are separated by a distance a (the minimum-energy distance). Quantum mechanics prevents the kinetic energy from being zero, even at $T = 0$, but that complication does not change the reasoning, so ignore the so-called zero-point energy. Once you are happy with the rest of the argument, you can improve the argument by adding it back.

As T increases so does the kinetic energy of the atoms. The bond vibrates, and the potential-energy curve says how much. Think of the bond as a vibrating spring. It expands until all kinetic energy converts to potential energy. Without kinetic energy, it stops expanding; that point is the maximum extension. The restoring force then pulls the bond back toward its equilibrium length a, but it overshoots (like any spring) and keeps shrinking until, again, all kinetic energy converts to potential energy. That point is the minimum extension. A reasonable guess is that the bond's average extension is midway between the minimum and maximum extensions. Figure 6.2 shows these midway points for a true spring potential. The points do not vary with temperature, so there is no thermal expansion! *Thermal expansion requires an asymmetric potential,* such as the Lennard–Jones potential (Figure 6.3) or the potential (5.14) for hydrogen including the confinement energy.

Figure 6.3 shows the midpoints shifting with increasing temperature. To find an expression for their position, solve for the minimum and maximum distances as a function of kinetic energy. The kinetic energy is roughly kT, so $kT = U(r_\pm) - U(a)$, where r_+ is the maximum extension and r_- is the minimum extension. This equation is easier to analyze in dimensionless form. It has lengths and energies, and they have a natural scale: ϵ_c for energy and a for length. So use

Substance	α $(10^{-6}\,\mathrm{K}^{-1})$	L_{vap}/R $(10^{4}\,\mathrm{K})$
Au	14.2	3.90
Al	23.1	0.350
Cu	16.5	3.61
Si	2.6	4.32
Fe	11.8	4.20
Pb	28.9	2.14
Hg	60.7	0.71
Steel (carbon)	10.7	
C		
diamond	1.0	
graphite	7.1	
Wood		
along gr.	3–6	
against gr	35–60	
Water	70	0.500
Granite	4–7	
Brick	3–10	
Cement	7–14	
Glasses		
Pyrex	3.2	
crown	7–8	
flint	8–9	
Vycor	0.75	

Table 6.2. *Thermal-expansion coefficients at room temperature. The third column gives, where available, ϵ_c in temperature units:*

$$\frac{\epsilon_c}{k} \times \frac{N_{\mathrm{A}}}{N_{\mathrm{A}}} = \frac{L_{\mathrm{vap}}}{R}. \tag{6.8}$$

For the liquids (water and mercury), the tables quote the volume-expansion coefficient; the linear-expansion coefficient above was obtained by dividing by 3. Source: Kaye and Laby [30, §2.3.5, 3.10.1, 3.11.2], Elements *[13].*

a and ϵ_c to define dimensionless variables:

$$\begin{aligned}\bar{T} &\equiv \frac{kT}{\epsilon_c},\\ \bar{U} &\equiv \frac{U}{\epsilon_c}+1,\\ \bar{r} &\equiv \frac{r}{a}-1.\end{aligned} \tag{6.10}$$

The definition of $\bar{U}$ includes a +1 so that the minimum $\bar{U}$ is 0 rather than -1. Similarly, the definition of $\bar{r}$ includes a -1 so that $\bar{U}$ has a minimum at $\bar{r}=0$ instead of at $\bar{r}=1$. This choice – placing a special point (the minimum) at a special location (the origin) – makes subsequent calculations slightly simpler and shorter. With this notation, the problem becomes one of solving

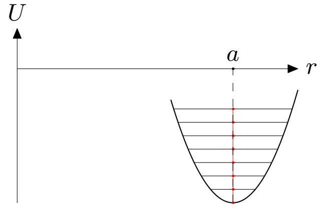

Figure 6.2. *Symmetric potential. As the temperature increases (horizontal lines), the bond oscillates between two extreme lengths. In this symmetric spring potential, the point (in red) midway between these extremes does not vary with temperature.*

$$\bar{T}=\bar{U}(\bar{r}). \tag{6.11}$$

Around its minimum, any function looks like a parabola. So

$$\bar{U}(\bar{r})=\beta\bar{r}^2+\cdots, \tag{6.12}$$

where β is a constant. Without the $\bar{r}^3$ term in the dots, the $\bar{U}$ is symmetric and the substance does not expand thermally (Figure 6.2). A Taylor series produces the $\bar{r}^3$ term:

$$\bar{U}(\bar{r})=\frac{1}{2}\bar{U}''(0)\bar{r}^2+\frac{1}{6}\bar{U}'''(0)\bar{r}^3+\ldots. \tag{6.13}$$

The constant term vanishes because $\bar{U}$ is defined so that $\bar{U}(0)=0$. The linear term $\bar{U}'(0)\bar{r}$ vanishes because the expansion is about the minimum, where the first derivative is zero.

In this dimensionless world, $\bar{U}''(0)$ and $\bar{U}'''(0)$ are dimensionless constants. Follow the usual practice and pretend that they are 1. Better: Pretend that $\bar{U}''(0)=2$ and $\bar{U}'''(0)=-6$, to make the formula as simple as possible. Choose $\bar{U}'''(0)$ to be negative so that $\bar{U}$ behaves correctly: Compared to a pure spring ($\bar{U}=\bar{r}^2$), the true $\bar{U}$ has stronger repulsion at short distances and weaker attraction at long distances. With these choices,

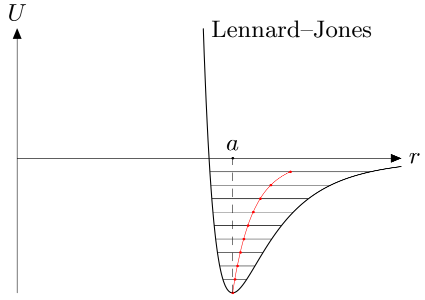

Figure 6.3. *An asymmetric potential (the Lennard–Jones potential). Here the midpoint (in red) varies with temperature.*

$$\bar{U}(\bar{r})\sim\bar{r}^2-\bar{r}^3. \tag{6.14}$$

This function is sketched and analyzed in Figure 6.4. The result is that the equilibrium point of the bond shifts to $\bar{r}=\bar{T}/2$. The definition of $\bar{r}$ is $\bar{r}=r/a-1$, so $\bar{r}=\bar{T}/2$ becomes $\Delta r/a=\bar{T}/2$. Since $\bar{T}=kT/\epsilon_c$, the result in regular dimensions is:

$$\frac{\Delta r}{a}\sim\frac{1}{2}\frac{k}{\epsilon_c}T. \tag{6.15}$$

The thermal expansion coefficient is everything on the right except for the T (in red), so

$$\alpha \sim \frac{1}{2}\frac{k}{\epsilon_c}. \tag{6.16}$$

To play fair we should drop the 1/2, as with the other dimensionless constants. But including the 1/2 makes the thermal-expansion prediction too accurate for us to resist temptation. In Figure 6.1, the line $\alpha(L_{\text{vap}}/R) = 1/2$ would pass very near most of the points.

The analysis in Figure 6.4 assumes that $\bar{r}$ is small. Is this assumption justified? Although the analysis using a spring potential does not explain thermal expansion, it does give us the estimate that $\bar{r} \sim \sqrt{\bar{T}}$ (in dimensionless units). A typical kT is 0.025 eV; a typical covalent bond energy is $\epsilon_c \sim 2.5\,\text{eV}$. In dimensionless units, $\bar{T} \sim 0.01$ and $\bar{r} \sim 0.1$. For most order-of-magnitude calculations, 0.1 is a small dimensionless number. Here its smallness justifies the approximations made in analyzing Figure 6.4.

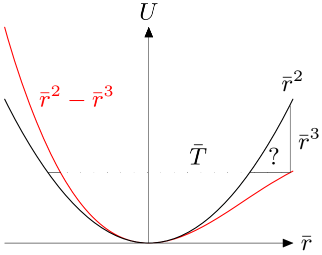

Figure 6.4. *Rescaled (dimensionless) potential energy. The red curve includes the $-\bar{r}^3$ term. The black curve is the symmetric potential energy. The thermal expansion due to a scaled temperature $\bar{T}$ is caused by the difference between these curves, and it is the average of the two little horizontal lines. For the right-hand line, the height of the triangle is $\bar{r}^3$ because it is the difference between the symmetric $\bar{r}^2$ curve and the asymmetric $\bar{r}^2 - \bar{r}^3$ curve. The slope of the symmetric curve is $2\bar{r}$, so the horizontal piece has length $\bar{r}^3/2\bar{r} = \bar{r}^2/2$. Since $\bar{T} \approx \bar{r}^2$ (except for the $\bar{r}^3$ term, which is small), the length is $\bar{T}/2$. By symmetry, the left-hand shift is also $\bar{T}/2$, so the midpoint shifts by $\bar{T}/2$ going from the black curve to the red curve.*

6.2 Boiling

To vaporize or boil a liquid requires energy to move molecules from the liquid into the gas phase. How much energy is required? Per molecule, the energy required is roughly the cohesive energy ϵ_c. The molar heat of vaporization (or enthalpy of vaporization) is the energy required to boil one mole of a substance, and we can estimate it from the cohesive energy:

$$L_{\text{vap}} \sim N_{\text{A}}\epsilon_c \sim 100\,\text{kJ}\,\text{mol}^{-1} \times \left(\frac{\epsilon_c}{1\,\text{eV}}\right). \tag{6.17}$$

For water, $\epsilon_c \sim 0.5\,\text{eV}$ so $L_{\text{vap}} \sim 50\,\text{kJ}\,\text{mol}^{-1}$. This estimate of the enthalpy leaves out a small contribution: the energy to make room in the vapor for the evaporating molecules. This energy is PV in the expression $H = E + PV$ for the enthalpy. The heat of vaporization is the change in H:

$$L_{\text{vap}} \equiv \Delta H = \Delta E + \Delta(PV). \tag{6.18}$$

Once you look at data for boiling temperature, you find that $\Delta(PV)$ is small compared to ΔE. But dot the i's at the end!

Predicting L_{vap} from ϵ_c is straightforward. Instead use L_{vap}, for which accurate experimental data are available, to determine ϵ_c (the second column of Table 6.3). Now knowing ϵ_c you can predict the boiling temperature. As a substance heats up, more molecules leave the liquid and become vapor; the pressure of the vapor increases. The boiling temperature is the temperature at which the vapor pressure reaches atmospheric pressure (at sea level, roughly 10^5 Pa or 1 atm). Atmospheric pressure is arbitrary; it is lower on Mount Everest, for example, and far lower on Mars. It is unrelated to the properties of the substance being boiled – although it helps to determine the boiling

	ϵ_c	T_{vap} (*K*)	
Substance	(eV)	*actual*	*pred.*
Water	0.50	373	580
NH_3	0.31	240	348
HCl	0.21	188	244
O_2	0.071	90	82
Au	3.35	3130	3884
Xe	0.13	165	150
He	0.00086	4.2	1
Hg	0.61	630	707
N_2	0.058	77	67

Table 6.3. *Cohesive energy, ϵ_c, per atom or molecule; actual and predicted boiling temperatures (at 1 atm). The cohesive energy is $L_{\text{vap}}/N_{\text{A}}$, where L_{vap} (the latent heat of vaporization) is from experimental data. The predicted boiling point comes is $\epsilon_c/10k$, the prediction of (6.20). Source:* CRC *[41,* ***6-106ff****]*

temperature. A more general question is how boiling temperature depends on atmospheric pressure. You can generalize the upcoming methods to answer this question.

For a first guess for the boiling temperature, convert the cohesive energy into a temperature using Boltzmann's constant:

$$T_{\text{vap}} = \Pi \frac{\epsilon_c}{k}, \tag{6.19}$$

where Π is a dimensionless constant. The conversion factor k is $1\,\text{eV} \simeq 10^4\,\text{K}$ (accurate to 20 percent). Table 6.3 shows how inaccurate this guess is. For water, the predicted boiling temperature would be 5000 K rather than 373 K: Tea kettles would be difficult to boil. For gold, the predicted temperature would be 30,000 K instead of $\sim 3000\,\text{K}$. So by fiat insert a factor of 10 to improve the prediction to:

$$T_{\text{vap}} \sim \frac{\epsilon_c}{10k}, \tag{6.20}$$

If T_{vap}, ϵ_c, and k are the only relevant variables for the boiling temperature, then there is a constant Π such that $T_{\text{vap}} = \Pi\epsilon_c/k$. A few minutes with the data in Table 6.3 will convince you that, although the factor is nearly 0.1 as in (6.20), it is not a constant. However, even the approximate result helps check that PV can be neglected in the heat of vaporization (6.18). For one molecule in a gas at the boiling temperature, $PV = kT_{\text{vap}}$. From (6.20), $kT_{\text{vap}} \sim \epsilon_c/10$ so PV is also $\epsilon_c/10$. Thus PV is much smaller than ϵ_c, which is the consistency check that we promised.

6.3 Heat flow

The previous sections discussed what happens when you heat or cool a substance. Heating or cooling requires sending heat from one substance to another. But how does heat travel? And how fast? These questions lead to the subject of heat flow, upon which many interesting phenomena depend: Why can people (who are not too confident of success) walk on hot coals without getting burned? How long does the 3-inch layer of frost in the freezer take to melt? Heat flow is the topic of the rest of the chapter.

Charge flow (current) and heat flow share a key property: They flow in response to a drive. Charge flows from high potential to low potential. Heat flows from high temperature to low temperature. Charge flow is measured by current density, also known as charge flux:

$$\text{charge flux} = \frac{\text{charge transported}}{\text{area} \times \text{time}}. \tag{6.21}$$

That is the definition of charge flux. It is produced by an electric field:

$$\underbrace{\text{charge flux}}_{J} = \underbrace{\text{conductivity}}_{\sigma} \times \underbrace{\text{drive}}_{E}. \tag{6.22}$$

The electric field E is produced by the potential difference and is driving the charges. Imagine a slab of material, perhaps a wire or a block of seawater (Section 4.6), of length Δx. Then the electric field is

$$E = \frac{V_1 - V_2}{\Delta x}, \tag{6.23}$$

where V_1 and V_2 are the potentials at the ends. Imagine heat flowing in the same slab. Heat flow is measured by heat flux,

$$\text{heat flux} = \frac{\text{energy transported}}{\text{area} \times \text{time}}. \tag{6.24}$$

The analogy to heat flow suggests a form for heat flux similar to the charge flux (6.22):

$$\underbrace{\text{heat flux}}_{F} = \underbrace{\text{thermal conductivity}}_{K} \times \underbrace{\text{drive}}_{?}. \tag{6.25}$$

The following symbols are conventional: F for flux and K for thermal conductivity. Again by analogy to charge flow, the drive for heat flow should be similar to the drive (6.23) for charge flow, so try

$$\text{drive} = \frac{T_1 - T_2}{\Delta x}. \tag{6.26}$$

Then the heat flux (6.25) becomes

$$F = K\,\frac{T_1 - T_2}{\Delta x}. \tag{6.27}$$

This argument by analogy does not explain the mechanism, but it structures the analysis of the thermal conductivity.

The mechanism is easiest to understand in gases, so study them first. Studying gases is also enjoyable: We are surrounded by them (air), so their properties explain many everyday thermal phenomena (feeling cold standing outside in a thin shirt, for example).

Fluxes, by construction, divide out the cross-sectional area. However, you can understand phenomena more easily with a mental picture, and it is difficult to imagine a substance without cross-sectional area. So imagine a slab of gas with cross-sectional area A, knowing (hoping, expecting) that A cancels when computing any intensive quantity such as thermal conductivity. The length Δx is already required, in order to compute the drive $(T_1 - T_2)/\Delta x$, where the slab has temperature T_1 in the left half and T_2 in the right half (Figure 6.5). To find K, use this model to estimate the flux F, then match the result against the general form (6.27). To compute the flux using (6.24) requires knowing the: (1) energy transported, (2) time taken, and (3) cross-sectional area. The area A is specified in the thought experiment. The other two require further analysis.

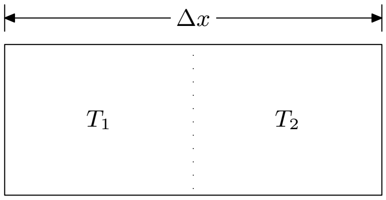

Figure 6.5. *Slab of gas. The slab has cross-sectional area A (not shown). As molecules from the left side diffuse into the right side, and vice versa, the temperatures equalize. The heat flow is from hot to cold, and can be estimated from knowing the heat content in each half and the time it takes to diffuse.*

Energy is transported because, after waiting a while, the temperatures equalize. So energy has flowed from left to right. This energy is, except for dimensionless constants (ignore them!),

$$\Delta E \sim \text{energy in left side} - \text{energy in right side}. \tag{6.28}$$

Each portion can be estimated by estimating the energy per molecule. This so-called internal energy is a function of T, call it $u(T)$, where u is the traditional label for internal energy, and it is in lower case to indicate that it is the energy per molecule. Each side contains $N \sim nA\Delta x$ molecules, where n is their number density. So

$$\Delta E \sim (u(T_1) - u(T_2))nA\Delta x. \tag{6.29}$$

As long as u has constant slope, or T_1 and T_2 are close, this becomes

$$\Delta E \sim \frac{\partial u}{\partial T}(T_1 - T_2)nA\Delta x. \tag{6.30}$$

The factor $T_1 - T_2$ has appeared! The factor $\partial u/\partial T$ appears so often that it has a name, the specific heat:

$$c_{\mathrm{p}} \equiv \frac{\partial u}{\partial T}. \tag{6.31}$$

The 'p' in the subscript is for pressure, meaning that this quantity is measured by heating a gas while keeping the pressure fixed (the alternative is to keep the volume fixed, which gives c_{v}). Then

$$\Delta E \sim c_{\mathrm{p}} nA\Delta x(T_1 - T_2). \tag{6.32}$$

Now for the time required to transport this much energy. The energy is transported by the molecules moving from one side to the other. How long before the two sides mix? Except for a dimensionless constant, this time is the same as the time for a molecule to wander from one side to the other. We say 'wander', because the molecules do a random walk. In a random walk of N steps, the molecules travel a typical distance $\propto \sqrt{N}$. This result is fundamentally different from a regular walk. In a regular walk, $x \propto t$, where t is the time taken to make N steps. The interesting quantity is not x or t itself, since they can grow without limit, but their ratio x/t, also known as the speed. In a random walk, where $\langle x^2\rangle \propto t$, the interesting quantity is $\langle x^2\rangle/t$, which is the analogue of speed for a random walk. It is the diffusion constant and has dimensions of $\mathrm{L}^2\mathrm{T}^{-1}$. For more on random walks, see the classic book *Random Walks in Biology* [3], full of fascinating examples.

Since the gas molecule walks randomly, the time it requires to cross from one side to the other, a distance Δx, is

$$t \propto (\Delta x)^2. \tag{6.33}$$

The constant that makes the dimensions correct is κ, the diffusion constant:

$$t \sim \frac{(\Delta x)^2}{\kappa}. \tag{6.34}$$

With this time and the energy transported (6.32), the heat flux (6.24) becomes

$$F = \frac{\Delta E}{At} \sim \frac{\overbrace{c_\mathrm{p} n A \Delta x (T_1 - T_2)}^{\Delta E}}{A \underbrace{(\Delta x)^2/\kappa}_{t}}. \tag{6.35}$$

As expected, the area cancels and

$$F = \underbrace{n c_\mathrm{p} \kappa}_{K} \times \underbrace{\frac{T_1 - T_2}{\Delta x}}_{drive}. \tag{6.36}$$

Matching this form to the form for the flux (6.27) gives

$$K = n c_\mathrm{p} \kappa. \tag{6.37}$$

Let's check upstairs and downstairs. As the gas becomes concentrated, it contains more energy so it can transport energy more rapidly: n should be on top. If each molecule's capacity to hold energy increases, then the same diffusive wandering transports more energy: c_p should be on top. As the gas molecules diffuse more easily, they transport energy more rapidly: κ should be on top. The thermal conductivity (6.37) passes these tests. The problem of heat flow has simplified to problem of finding K. The problem of finding K is the problem of finding the specific heat c_p and the diffusivity κ. This thought experiment used a gas, and the same ideas will apply for liquids and solids. We continue with the thermal conductivity of gases by estimating c_p and κ for gases. After that we turn to liquids and solids.

6.4 Diffusivity of gases

The diffusion constant, or diffusivity, measures how rapidly the gas molecules wander. Molecules travel until they hit another one, then they bounce in a random direction: These ingredients make a random walk. All we have to know is how far they wander before colliding, and how often they collide. These natural units of space and unit time characterize the random walk; the nature of the particle doing the walking doesn't matter beyond those two facts. Try dimensional analysis. The relevant variables are κ, the goal; the collision time τ; and the mean free path λ. Three variables containing two independent dimensions (L and T) make one dimensionless group: $\kappa\tau/\lambda^2$. So

$$\kappa \sim \frac{\lambda^2}{\tau}. \tag{6.38}$$

In terms of the molecular velocity $v = \lambda/\tau$,

$$\kappa \sim v\lambda. \tag{6.39}$$

The missing constant depends a more exact calculation of the behavior of a random walk, and also on the definition of κ. Several definitions are possible, each with its own dimensionless constant buried in the definition. So these variations, not only the approximations in the analysis, affect the constant. The convention for κ is to make the diffusion equation,

$$\nabla^2 T = -\kappa\frac{\partial T}{\partial t}, \tag{6.40}$$

look elegant by not having a dimensionless constant (or rather by making the constant unity). Using this definition of κ, a proper calculation gives:

$$\kappa = \frac{1}{3}v\lambda, \tag{6.41}$$

where the magic constant is in red. Here v is the thermal velocity obtained from

$$\text{thermal energy} = \frac{1}{2}mv_{\text{t}}^2, \tag{6.42}$$

where m is the molecular mass. The thermal energy is $(3/2)kT$, so

$$v_{\text{t}} = \sqrt{\frac{3kT}{m}}. \tag{6.43}$$

For air, which is mostly diatomic nitrogen, $m = 28m_{\text{p}}$. The speed of sound (within 15 percent) is

$$c_{\text{s}} \approx \sqrt{\frac{kT}{m}}, \tag{6.44}$$

so

$$v_{\text{t}} \approx \sqrt{3}\,c_{\text{s}}. \tag{6.45}$$

Since $c_{\text{s}} \sim 300\,\text{m}\,\text{s}^{-1}$, $v_{\text{t}} \sim 500\,\text{m}\,\text{s}^{-1}$. As a check, let's do the calculation directly. To convert between different energy units, multiply (6.43) by unity:

$$v_{\text{t}} = \sqrt{\frac{3kT}{m}} \times \frac{c}{c} = \sqrt{\frac{3kT}{28m_{\text{p}}c^2}}\,c. \tag{6.46}$$

Now the energies in the square root have convenient values:

$$\begin{aligned} m_{\text{p}}c^2 &\approx 10^9\,\text{eV}, \\ kT_{\text{room}} &\approx \frac{1}{40}\,\text{eV}. \end{aligned} \tag{6.47}$$

The electron–Volts cancel and

$$v_{\text{t}} \sim \left(\frac{3}{40 \times 28 \times 10^9}\right)^{1/2} c \sim \frac{1}{6}\cdot 10^{-5}c = 500\,\text{m}\,\text{s}^{-1}. \tag{6.48}$$

To compute λ see Figure 6.6. It is determined by the molecular diameter d and by the number density n:

$$n\sigma\lambda \sim 1, \tag{6.49}$$

here σ is the scattering cross section. You can also recreate this relation by ensuring that the dimensions match: n has dimensions of 1/volume, σ is an area, and λ is a length, so the left side has no dimensions, and neither does the right side. To compute n you need σ, which is πd^2. Why is it πd^2 rather than the more intuitive area of a circle πr^2? Because two molecules collide if their centres come within a distance $d = 2r$. So you can consider the moving molecule as having a radius $R = 2r$ and all the other molecules being points. Then the relevant cross-sectional area is πR^2 or πd^2.

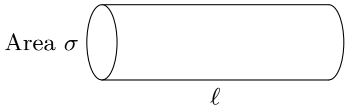

Figure 6.6. *Mean free path. A molecule has scattering area σ, which is πd^2. Once it sweeps out a volume containing one molecule, then it is likely to collide. The distance λ that makes the cylinder contain one molecule is then the mean free path. Its volume is $\sigma\lambda$, so the number of molecules it contains is $n\sigma\lambda$. Hence $n\sigma\lambda \sim 1$.*

To compute λ for air, we need its molecular diameter. Air is N_2. Guessing that $\lambda \sim 3\,\mathring{A}$ or $d \sim 3\,\mathring{A}$ is always reasonable. Then

$$\begin{aligned}\lambda &\sim \frac{1}{n\sigma} \sim \underbrace{\frac{2.4\cdot 10^{-2}\,\mathrm{m}^3}{6\cdot 10^{23}}}_{n} \times \frac{1}{\underbrace{3}_{\pi} \times \underbrace{9\cdot 10^{-20}\,\mathrm{m}^2}_{d^2}} \\ &\sim 10^{-7}\,\mathrm{m}\end{aligned} \tag{6.50}$$

and

$$\kappa \sim \frac{1}{3} \times \underbrace{500\,\mathrm{m\,s}^{-1}}_{v_\mathrm{t}} \times \underbrace{10^{-7}\,\mathrm{m}}_{\lambda} \sim 1.5\cdot 10^{-5}\,\mathrm{m}^2\,\mathrm{s}^{-1}. \tag{6.51}$$

In decently sized units (cgs units),

$$\kappa \sim 0.15\,\mathrm{cm}^2\,\mathrm{s}^{-1}. \tag{6.52}$$

That value is suspiciously similar to the viscosity of air (4.45). The connection is not accidental. Thermal diffusivity is the diffusion constant for heat. Kinematic viscosity is the diffusion constant for momentum. In a gas, molecular motion carries heat and momentum, so their respective diffusion constants are closely related. Their ratio is dimensionless. It is such an important number that it is given a name, the **Prandtl number**:

$$\mathrm{Pr} \equiv \frac{\nu}{\kappa}, \tag{6.53}$$

It is close to unity in gases and even in many solids and liquids (for water, it is 6).

Example 6.2 *Sniffing perfume*

You open a bottle of perfume at one end of a room. How long before people at the other end can smell it? If you make enough approximations, you can apply the preceding results. Pretend that perfume molecules are merely labelled air molecules (imagine that they are green, although that makes no physical sense). How long before a green air molecule wanders across the room? The time is $t \sim l^2/\kappa$, where l is the length of the room, say 5 m. Then

$$t \sim \frac{(5\,\mathrm{m})^2}{1.5 \cdot 10^{-5}\,\mathrm{m}^2\,\mathrm{s}} \sim 10^6\,\mathrm{s}. \tag{6.54}$$

A day is 10^5 s, so the green wandered takes 10 days to reach the other noses. This estimate is far too high! The method ignores a few minor effects. For example, noses are extremely sensitive, and can detect even a handful of molecules (for certain molecules), but that effect turns out to reduce t by only a small factor, perhaps 5. The method also ignores the size and mass of perfume molecules. They are much heavier and larger than air molecules, which slows their diffusion. Perhaps that effect cancels the factor from nose sensitivity. Even if it does not fully cancel the factor, the resulting t is still far too long. But do not spend too much time correcting the small mistakes. Otherwise you fall into a trap [1]:

> In other words – and this is the rock solid principle on which the whole of the Corporation's Galaxy-wide success is founded – their fundamental design flaws are completely hidden by their superficial design flaws.

By agonizing over the superficial flaws, you will the fundamental flaw, which is that the perfume odors are transported mostly by convection. The room is full of tiny air currents, due to temperature differences between the floor and ceiling, due to people walking, due to doors opening, etc. These currents, whjich are minature winds, move perfume molecules much more efficiently than diffusion does. The calculation of the diffusion time is correct, and is not a total waste because it shows you that odors must travel using another mechanism.

6.5 Specific heat of gases

The thermal conductivity K requires the thermal diffusivity, the subject of the previous section, and the specific heat, the subject of this section. How much energy does it take to heat water to bath temperature? How many days of solar heating can the oceans store? The answers to these questions depend on the energy that the substance stores per unit temperature change: the **specific heat**.

Before thinking about the physics of specific heats, make the usual dimensional estimate. The dimensions of specific heat are

$$[\text{specific heat}] = \frac{\text{energy}}{\text{temperature} \times \text{amount of substance}}. \tag{6.55}$$

The amount can be whatever size is convenient: one mole, one gram, or one molecule. The molecule is a natural size: It involves the fewest arbitrary parameters. A mole, or a gram, for example, depends on human-chosen sizes. You know one quantity with units of energy per temperature: the Boltzmann constant. So a first estimate is

$$\begin{aligned}\frac{\text{specific heat}}{\text{molecule}} &\sim k,\\ \frac{\text{specific heat}}{\text{mole}} &\sim kN_\mathrm{A} = R.\end{aligned} \tag{6.56}$$

Substance	c_p/k
I_2	4.4
Cl_2	4.1
O_2	3.5
N_2	3.5
Ni	3.1
Au	3.1
Zn	3.1
Fe	3.0
Xe	2.5
He	2.5
Diamond	
0 °C	0.6
223 °C	1.6
823 °C	2.6

Table 6.4. *Specific heats at constant pressure. All data are for room temperature (unless otherwise noted) and atmospheric pressure. The specific heats are in dimensionless form – in units of k per atom or molecule – because we already know that the specific heat must contain a factor of k. Source:* Smithsonian Physical Tables *[17, p. 155].*

Table 6.4 lists the specific heat of various substances.

For nitrogen (or air),

$$c_{\mathrm{p}} = \frac{7}{2}k, \tag{6.57}$$

A useful way to remember k as $0.8 \times 10^4\,\mathrm{eV\,K^{-1}}$ and convert it to SI units when you need to:

$$k \approx \frac{0.8\,\mathrm{eV}}{10^4\,\mathrm{K}} \times \frac{1.6 \cdot 10^{-19}\,\mathrm{J}}{\mathrm{eV}} = 1.3 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}. \tag{6.58}$$

So

$$c_{\mathrm{p}} = 4.5 \cdot 10^{-23}\,\mathrm{J\,K^{-1}}. \tag{6.59}$$

Now you have the ingredients to compute K for air (which is mostly nitrogen). The number density is

$$n = \frac{6 \cdot 10^{23}}{1\,\mathrm{mol}} \times \frac{1\,\mathrm{mol}}{24\,\ell} \times \frac{1\,\ell}{10^{-3}\,\mathrm{m}^3} = 2.5 \cdot 10^{25}\,\mathrm{m}^{-3}. \tag{6.60}$$

With κ from (6.51) and c_{p} from (6.59), the thermal conductivity is

$$\begin{aligned} K = nc_{\mathrm{p}}\kappa &\sim 2.5 \cdot 10^{25}\,\mathrm{m}^{-3} \times 4.5 \cdot 10^{-23}\,\mathrm{J\,K^{-1}} \times 1.5 \cdot 10^{-5}\,\mathrm{m^2\,s^{-1}} \\ &\sim 1.7 \cdot 10^{-2}\,\mathrm{W\,m^{-1}\,K^{-1}}. \end{aligned} \tag{6.61}$$

Now imagine air at the same temperature but different density (and pressure). For concreteness, imagine decreasing the density by a factor of 4 and consider the effect on each factor in the product $K = nc_{\mathrm{p}}\kappa$. The number density decreases by a factor of 4. The c_{p} is the specific heat per molecule, so it does not change. What about κ? As a result of n decreasing, the mean free path, which is $l \sim 1/n\sigma$, increases by a factor of 4. Since the diffusivity is $\kappa \sim v_{\mathrm{t}}l$, and v_{t} remains the same (T is constant), the diffusivity increases by a factor of 4. The product $nc_{\mathrm{p}}\kappa$ therefore does not change, so *thermal conductivity is independent of density* over a wide range of densities – and this result holds not just for air, but for any ideal gas. Once the mean free path gets comparable to the size of the container, however, this analysis breaks down. One system with a huge container is the atmosphere. Figure 6.7 shows how little K varies despite ρ varying over many orders of magnitude. A similar result holds for the dynamic viscosity $\eta = \rho\nu$. For ideal gases, $\nu \sim \kappa$. So ν inherits the ρ^{-1} dependence from

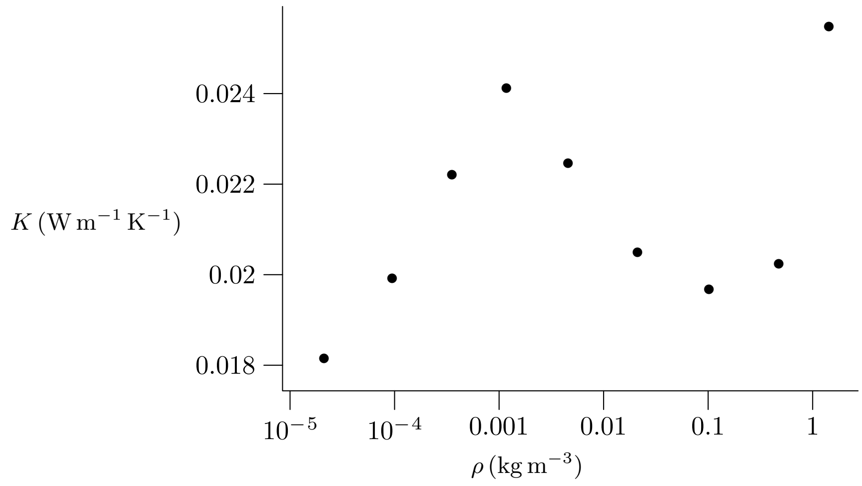

Figure 6.7. *Thermal conductivity vs density. The data are from the 'U.S. Standard Atmosphere (1976)' at various heights up to* 80 km*. The density varies over five orders of magnitude, whereas the thermal conductivity varies by 30 percent. Source:* CRC *[41, pp.* ***14****-20ff].*

κ (which got it from the mean free path), and $\eta = \nu\rho$ is a constant.

6.6 Diffusivity of liquids and solids

Many of these ideas for gases apply to liquids and solids. Most important, the formulas for flux and thermal conductivity are the same. So to find the thermal conductivity K, it is a matter of finding c_{p} and κ. In a liquid or a solid, heat is not transported by molecular motion. Heat *is* molecular motion but, unlike in a gas, it is not transported by molecular motion. In a solid, for example, the molecules hardly leave their sites. They vibrate but do not wander much. In a liquid, molecules wander but only slowly: The tight packing means that the free path is very short. Yet everyday experience suggests that liquids and solids can be excellent conductors of heat. The reason is that heat is transported by sound waves or **phonons** rather than by molecular motion. One molecule vibrates, shaking the next molecule, which shakes the next molecule, and so on.

Using this idea we can compute a thermal diffusivity. Heat is the vibration of atoms. In a solid, the atoms are confined in a lattice, and the vibrations can be represented as combinations of many sound waves. More precisely, the waves are phonons, which are sound waves that can have polarization (just as light waves have polarization). Heat diffusion is the diffusion of phonons.

Phonons act like particles: They travel through lattice, bounce off impurities, and bounce off other phonons. The same random-walk analysis for gases works for solids and liquids, perhaps with a different velocity or mean free path. The phonon mean free path λ measures how far a phonon travels before bouncing (or scattering), and then heading off in a random direction. In a solid without too many defects, at room temperature, a phonon travels a few lattice spacings before scattering. Let's say

$$\lambda = fa, \tag{6.62}$$

where a is the lattice spacing and f is a dimensionless number that says how many lattice spacings the phonons survives. Now for the speed. In a gas the relevant speed for computing κ was the speed at which the molecules move; this speed is roughly the sound speed. In a liquid or solid, the phonon speed is the relevant speed, and it is also the sound speed, but it has no relation to the thermal speed. To see why, recall the sound speed (5.61):

$$c_{\mathrm{s}} \sim \sqrt{\frac{\epsilon_c}{m}}, \tag{6.63}$$

where ϵ_c is the cohesive energy and m is the atomic or molecular mass. A typical thermal speed is $v_{\mathrm{t}} \sim \sqrt{kT/m}$, so the dimensionless ratio $c_{\mathrm{s}}/v_{\mathrm{t}}$ is

$$\frac{c_{\mathrm{s}}}{v_{\mathrm{t}}} \sim \sqrt{\frac{\epsilon_c}{m}} \Big/ \sqrt{\frac{kT}{m}} = \sqrt{\frac{\epsilon_c}{kT}}. \tag{6.64}$$

At room temperature, $kT \sim 1/40\,\mathrm{eV}$. For a typical solid, $\epsilon_c \sim 10\,\mathrm{eV}$. So the ratio is $\sqrt{400}$ or 20. Compare that value to its counterpart in an ideal gas:

$$\frac{c_{\mathrm{s}}}{v_{\mathrm{t}}} \sim \frac{1}{\sqrt{3}} \qquad \text{(ideal gas)}. \tag{6.65}$$

With the mean free path (6.62), the thermal diffusivity is

$$\kappa = \frac{1}{3} c_{\mathrm{s}} f a. \tag{6.66}$$

For most solids or liquids, $c_{\mathrm{s}} \sim 3\,\mathrm{km\,s^{-1}}$ (see Table 5.5 on p. 80) and $a \sim 3\,\text{Å}$. Then

$$\kappa \sim \frac{1}{3} \times \underbrace{3 \cdot 10^{3}\,\mathrm{m\,s^{-1}}}_{c_{\mathrm{s}}} \times \underbrace{f \times 3 \cdot 10^{-10}\,\mathrm{m}}_{\lambda} \sim \frac{f}{3} \times 10^{-6}\,\mathrm{m^2\,s^{-1}}. \tag{6.67}$$

For a typical solid, take $f = 3$. Then

$$K \sim 10^{-6}\,\mathrm{m^2\,s^{-1}} = 10^{-2}\,\mathrm{cm^2\,s^{-1}}. \tag{6.68}$$

For our favorite substance, water, $c_{\mathrm{s}} \sim 1.7\,\mathrm{km\,s^{-1}}$ and $a \sim 3\,\text{Å}$, so

$$\kappa \sim f \times 1.7 \cdot 10^{-7}\,\mathrm{m^2\,s^{-1}} \qquad \text{(water)}. \tag{6.69}$$

In cgs units,

$$\kappa \sim f \times 1.7 \cdot 10^{-3}\,\mathrm{cm^2\,s^{-1}}. \tag{6.70}$$

For water, the value is exact if you take $f = 1$, an easy result to remember. So phonons travel only one lattice spacing before being scattered. This short distance is because water has no lattice, so the molecules are highly disordered. The many irregularities scatter the phonons. Let's look at two examples of thermal diffusion.

Example 6.3 *Cooking a turkey*

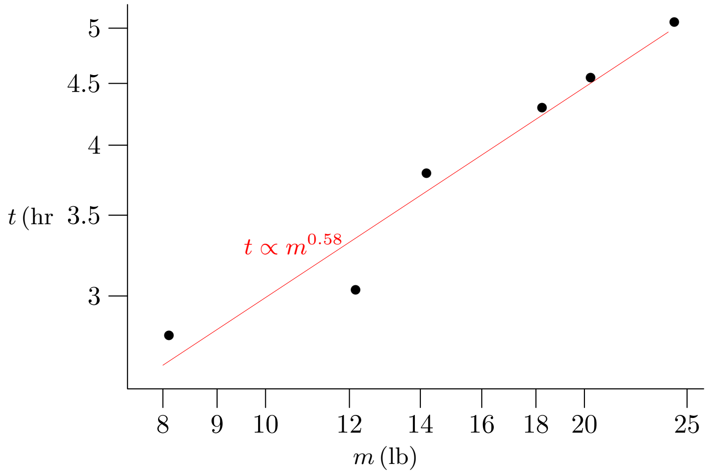

Figure 6.8. Turkey cooking times (log–log plot). The times are typical recommended times. The nontraditional units for mass are appropriate, since the major application is for an American holiday. These data are taken from [49] (for an unstuffed turkey). The red line is the best power-law fit to the data. Its exponent of 0.58 is not far from the prediction of $2/3$.

During Thanksgiving, an American holiday in which large turkeys are cooked, many people give thanks once all the turkey leftovers are finished. How long does it take to cook a typical turkey? Consider a spherical turkey with, say, $r \sim 10\,\mathrm{cm}$. A turkey is roughly water, so that radius would have $m \sim 4\,\mathrm{kg}$, reasonable for feeding a family of 10. The time for heat to diffuse from the edge, where the air and pan are hot, to the center, is roughly $t \sim r^2/\kappa$. Using the cgs value (6.70) for κ:

$$t \sim \frac{(10\,\mathrm{cm})^2}{1.7\cdot 10^{-3}\,\mathrm{cm}^2\,\mathrm{s}^{-1}} \sim 6\cdot 10^4\,\mathrm{s}, \qquad (6.71)$$

or roughly 15 hours! This estimate is too large, perhaps by a factor of 4. Still, start cooking in the morning if you want dinner before midnight. Even though the missing dimensionless constant is significant, the derivation suggests an extension. Imagine turkeys of varying size or mass: How does the cooking time vary? This extension calls for a scaling analysis. The size is $r \propto m^{1/3}$ so the cooking time is $t \propto r^2 \propto m^{2/3}$. Figure 6.8 shows that this analysis is reasonably accurate.

The estimate of the cooking time ignored an important parameter: the oven temperature. So the result implicitly assumes that the turkey will cook in the time t no matter what the oven temperature is. Diffusion equalizes the temperature at the center of the turkey to the oven temperature. Equalization is necessary but not sufficient. The inside must cook (the proteins must denature) after reaching the oven temperature. So that is why the oven must be hot: A cold oven would not cook the meat, even after the meat reached oven temperature. What oven temperature is hot enough? Protein physics is complicated so this temperature is difficult to estimate by theoretical calculations while sitting an armchair, so use experimental data. From experience pan frying a thin filet of fish, you can guess that a thin piece of meat next to a hot skillet (perhaps at $200\,^\circ\mathrm{C}$) cooks in a few minutes. If the skillet is only at $50\,^\circ\mathrm{C}$, the meat will never cook ($50\,^\circ\mathrm{C}$ is not much hotter than body temperature). So with the oven at $200\,^\circ\mathrm{C}$, the center of the turkey turkey will cook in a few minutes after it reaches oven temperature. So as long as the oven is hot enough, most of the cooking time is spent attaining this temperature, which is the assumption behind the estimate of r^2/κ for the cooking time.

Example 6.4 *Cooling the moon*

How long does the moon take to cool? Its size is $r \sim 2 \cdot 10^6\,\mathrm{m}$, as you estimated in (2.5). For the thermal diffusivity of rock, use the typical value (6.67). What f is reasonable? Rock is highly disordered, so f (the number of lattice spacings that the phonons travel) is not large – at most perhaps 3. Then $\kappa \sim 10^{-6}\,\mathrm{m^2\,s^{-1}}$. So

$$t \sim \frac{(2 \cdot 10^6\,\mathrm{m})^2}{10^{-6}\,\mathrm{m^2\,s^{-1}}} \sim 4 \cdot 10^{18}\,\mathrm{s} \sim 10^{11}\,\mathrm{yr}. \tag{6.72}$$

[Another useful number: $1\,\mathrm{yr} \sim 3 \cdot 10^7\,\mathrm{sec}$.] The universe has been around for only 10^{10} yr; so why is the moon already cold? This problem is similar to the paradox in the perfume example (Example 6.2): How does a person at the other end of the room smell the perfume if molecules takes 10 days to diffuse there? In both cases the answer is little winds (convection). Rock seems like a solid, but it flows on a billion-year timescale, and this flow transports heat to the surface much faster than molecular motions could.

This example shows a merit of order-of-magnitude physics: efficiency. You could – with lots of computer time – solve the diffusion equation for a mostly-spherical body like the moon. You might show that the accurate cooling time is, say, $2.74 \cdot 10^{11}$ yr. What would that result gain you? The more accurate time is still far longer than the age of the universe, so the same paradox remains. It has the same conclusion: convection. Order-of-magnitude analysis allows you to determine quickly which approaches are worth pursuing, so you can then spend more time refining productive approaches and less time chasing unproductive ones.

6.7 Specific heat of liquids and solids

The remaining piece in the thermal conductivity is the specific heat, either c_p or c_v. Liquids and solids hardly change volume, even if the volume is not held constant, so the two specific heats are almost equal. If each molecule sits in a three-dimensional harmonic potential produced by the rest of the lattice, each molecule has three potential-energy degrees of freedom. Combining them with the three translational degrees of freedom produces six degrees of freedom. Each degree of freedom contributes $kT/2$ to the internal energy so the energy per molecule is $3kT$. Since $c_\mathrm{p} \sim u/T$:

$$c_\mathrm{p} \sim 3k. \tag{6.73}$$

The specific heat per mole is

$$C_\mathrm{p} \sim 3R \sim 25\,\frac{\mathrm{J}}{\mathrm{mol\,K}}. \tag{6.74}$$

which is a useful number to remember. This value is the lattice heat due to phonons transporting energy. The prediction is accurate for most of the solids and liquids (Ni, Au, Zn, and Fe) in Table 6.4.

6.8 Thermal conductivity of solids and liquids

Now the pieces are assembled to estimate a typical K:

$$K \sim \underbrace{\left(\frac{1}{3\,\text{Å}}\right)^3}_{n} \times \underbrace{3 \times 1.3\cdot 10^{-23}\,\mathrm{J\,K^{-1}}}_{c_\mathrm{p}} \times \underbrace{10^{-6}\,\mathrm{m^2\,s^{-1}}}_{\kappa} \tag{6.75}$$
$$\sim 1\,\mathrm{W\,m^{-1}\,K^{-1}}.$$

Table 6.5 lists useful thermal conductivities.

Substance	K $\mathrm{W\,m^{-1}\,K^{-1}}$	T °C
Diamond	1000	0
H_2O		
water	0.6071	25
snow	0.16	0
ice	2.3	−5
Glass		
borosilicate crown	1.1	25
pyrex	1.1	25
Wood		
oak	0.16	20
plywood	0.11	20
pine, ⊥	0.11	60
pine, ∥	0.26	60
Wool	0.04	30
Rock		
granite	2.2	20
limestone	1	20
basalt	2	20
Cork	0.06	0
Asphalt	0.06	20
Sand, dry	0.33	20
Concrete	0.8	0
Ethanol	0.169	25
Quartz		
∥ to c-axis	11	25
⊥ to c-axis	6.5	25
Paper	0.06	25
Asbestos	0.09	0

Table 6.5. *Thermal conductivities for common liquids and solids. The table uses the SI unit for K, not only because it is a standard unit but also because it is a typical size for K as predicted in (6.75). Tabulate values relative to a reasonable estimate, so that typical values come out near unity. Source: Kaye and Laby [30, §2.3.7] and the* CRC *[41,* ***6-190, 12-224****ff].*

6.9 Thermal conductivity: Metals

A curious fact in Table 6.4 is that nickel, gold, and zinc have c_p slightly greater than $3k$! From where did the extra specific heat come? These substances are all metals, so the estimate in (6.74) probably neglects an important feature of metals. Metals are different from other solids because their electrons are free to roam and to absorb thermal energy. Therefore the total specific heat should include the specific heat of the electrons. Their contribution is small, enough to raise c_p by $0.1k$ above the prediction of $3k$.

But this small contribution does not explain why metals feel colder to the touch than, say, concrete does. If phonons are the only mechanism for conducting heat, then metals and concrete would not have such a great disparity in conductivity. That they do is a consequence of the large contribution to the thermal conductivity from free electrons in a metal. The typical phonon contribution (6.75) is $K \sim 1\,\mathrm{W\,m^{-1}\,K^{-1}}$. Rather than computing the electron contribution from scratch, scale it relative to the phonon contribution. Because

$$\text{conductivity} = \text{diffusivity} \times \text{specific heat}, \tag{6.76}$$

the problem of finding the ratio of conductivities becomes the problem of finding the ratio of diffusivities and of specific heats. First, the ratio of electronic to phonon diffusivities. Diffusivity is

$$\text{velocity} \times \text{mean free path}, \tag{6.77}$$

so split the estimate of the diffusivity ratio into estimates of the velocity ratio and of the mean-free-path ratio.

Phonons move at speeds similar to the speed of sound – a few kilometers per second. Electrons move at the **Fermi velocity** v_F. Electrons are confined by electrostatics (a metal is like a giant hydrogen atom). In both systems, confinement gives electrons a velocity and a kinetic energy. Let n_e be the number density of free electrons in the metal. Then $\Delta p \sim \hbar/\Delta x \sim \hbar n_\mathrm{e}^{1/3}$, where Δp is the momentum uncertainty produced by confinement, and Δx is the position uncertainty. The velocity $\Delta p/m_\mathrm{e}$ is the Fermi velocity:

$$v_\mathrm{F} \sim \frac{\hbar n_\mathrm{e}^{1/3}}{m_\mathrm{e}}. \tag{6.78}$$

A typical metal has one or two free electrons per atom. Pretend it is one electron per atom. Then $n_e^{1/3} = 1/a$, where $a = 3\,\text{Å}$ is the interatomic spacing. To evaluate v_F, multiply by unity:

$$\begin{aligned} v_F &\sim c\frac{\hbar c n_e^{1/3}}{m_e c^2} \\ &\sim 3\cdot 10^5\,\mathrm{km\,s^{-1}} \times \frac{\overbrace{2000\,\mathrm{eV}\,\text{Å}}^{\hbar c} \times \overbrace{0.3\,\text{Å}^{-1}}^{n_e^{1/3}}}{\underbrace{5\cdot 10^5\,\mathrm{eV}}_{m_e c^2}} \\ &\sim 500\,\mathrm{km\,s^{-1}}. \end{aligned} \tag{6.79}$$

This velocity is much faster than a typical sound wave, which may have $c_s \sim 2$ or $3\,\mathrm{km\,s^{-1}}$. So the velocity ratio is ~ 200 (electrons win). Not only are electrons faster than phonons, but for reasons related to the Fermi surface, they travel farther before scattering than phonons do. In copper, $\lambda_e \sim 100a$, where $a \sim 3\,\text{Å}$ is a typical lattice spacing. The phonon mean free path is $\lambda_p \sim 10\,\text{Å}$. So the mean-free-path ratio is ~ 30. The diffusivity ratio is therefore $200 \times 30 \sim 10^4$ in favor of the electrons.

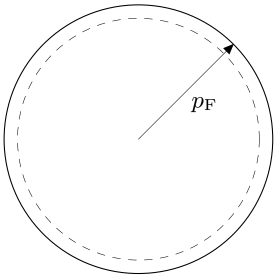

Figure 6.9. *Fermi sphere. It is a sphere in momentum space with radius p_F, which is the Fermi momentum $m_e v_F$. If an electron absorbs a packet of energy, it gets a new momentum and moves to a new point in the sphere. However, most points are not accessible. The lower-energy states in the sphere are filled and the Pauli principle will not allow an electrons to join the others in that state. So it has to go to an empty state. But if $kT \ll \mathcal{E}_F$, only electrons in the tiny ring beyond the dashed ring have enough energy to move to an empty state. So most electrons are immune from thermal fluctuations.*

Now for the specific-heat ratio. The phonons win this race because only a small fraction of the electrons carry thermal energy. To understand why, revisit the Fermi-velocity argument. A more accurate picture is that the metal is a three-dimensional potential well (the electrons are confined to the metal). There are many energy levels in the well, labeled by the momentum of the electrons that occupy it. The free electrons fill the lowest levels first. The Pauli principle allows only two electrons to share an energy level. The electrons in the highest levels have velocity v_F or momentum $m_e v_F$. As vectors, the momenta of the highest-energy electrons are uniformly distributed over the surface of a sphere in momentum space; the sphere has radius $m_e v_F$ and is called the Fermi sphere (Figure 6.9). To carry thermal energy, an electron has to be able to absorb and deposit energy; the typical package size is kT. Consider an electron that wants to absorb a thermal-energy package. When it does so, it will change its energy – it will move outward in the Fermi sphere. But can it? If it is in most of the sphere, it cannot, because the sphere is packed solid – all interior levels are filled. Only if the electron is near the surface of the sphere can it absorb the package. How near the surface must it be? It must have energy within kT of the Fermi energy $\mathcal{E}_F$ (the Fermi energy is $\sim m_e v_F^2$). The fraction of electrons within this energy range is $f \sim kT/\mathcal{E}_F$. Typically, $kT \sim 0.025\,\mathrm{eV}$ and $\mathcal{E}_F \sim$ few eV, so $f \sim 10^{-2}$. This fraction is also the specific-heat ratio. To see why, consider the case $f = 1$ (when every electron can carry thermal energy). Each atom contributes $3k$ to the specific heat, and each electron contributes one-half of that amount $(3k/2)$ because there is no spring potential for the electrons (they contribute only their three translational degrees of freedom). The number of free electrons is typically twice the number of atoms, so the total electron and phonon contributions to specific heat are roughly equal. When $f \sim 10^{-2}$, the contributions have ratio 10^{-2}.

Now assemble all the pieces. The conductivity ratio is

$$\frac{K_{\text{metal}}}{K_{\text{dielectric}}} \sim \underbrace{10^4}_{\kappa} \times \underbrace{10^{-2}}_{nc_{\text{p}}} = 10^2. \tag{6.80}$$

No wonder metals feel much colder than glass or wood! The typical dielectric thermal conductivity (6.75) is $1\,\mathrm{W\,m^{-1}\,K^{-1}}$. So

$$K_{\text{metal}} \sim 10^2\,\mathrm{W\,m^{-1}\,K^{-1}}. \tag{6.81}$$

Table 6.6 contains data on the thermal conductivities of common metals. The estimate (6.81) is more accurate than it has a right to be, given the number of approximations that made in deriving it.

Substance	$K\ \left(10^2\,\mathrm{W\,m^{-1}\,K^{-1}}\right)$
Ag	4.27
Al	2.37
Cr	0.937
Cu	4.01
Fe	0.802
Ni	0.907
W	1.74
Hg	0.0834

Table 6.6. *Thermal conductivities for common metals at room temperature. Metals should have thermal conductivities of roughly* $10^2\,\mathrm{W\,m^{-1}\,K^{-1}}$*, so we measure the actual values in that unit. We are being gentle with our neural hardware, giving it the kind of numbers that it handles with the least difficulty: numbers close to 1. The good electrical conductors (copper, silver, and gold) have high thermal conductivities. In both cases, electrons do the transporting, either of charge (for electrical conductivity) or of heat (for thermal conductivity), and the electron mean free path is long. Mercury, the only liquid in the table (in red), has a low thermal conductivity, because the lack of a lattice shortens the electron mean free path to only one or two lattice spacings.*

6.10 What you have learned

- *Approximate first, check later:* Many analyses are simpler if a dimensionless parameter is small. So assume that it is small, as we did when computing the thermal expansion in Figure 6.4, arrive quickly at a result, and then use it to check whether the assumption was justified.
- *The microscopic basis of thermal diffusivity and viscosity:* Particles (or phonons) move in steps whose size is equal to the mean free path, λ. The particles' velocity v determines the time to take one step and the diffusion constant, which is $\kappa \sim v\lambda$.
- *Viscosity:* For gases, kinematic viscosity ν and thermal diffusivity κ are approximately the same. In other words, the ratio ν/κ, known as the Prandtl number, is roughly 1.
- *Formula hygeine:* Convert formulas to dimensionless form, as for the calculation of thermal expansion, so that equations are simpler and reasoning is easier.
- *Metals:* In metals, electrons *transport* most of the heat; phonons *store* most of the heat.
- *Typical values:* Typical thermal conductivities are

$$K \sim \begin{cases} 0.02 & \text{for air,} \\ 1 & \text{for non-metals,} \\ 100 & \text{for metals.} \end{cases} \times\ \mathrm{W\,m^{-1}\,K^{-1}} \tag{6.82}$$

6.11 Exercises

▶ **6.28** *Losing heat*

At what rate do you lose heat when standing outside in a T-shirt on a winter day?

► **6.29** *Wooden spoons*
Why are wooden spoons useful for cooking?

► **6.30** *Eggs*
How long should it take to hardboil an egg?

► **6.31** *Sweating*
How much water do you sweat away while bicycling at your full speed for 10 km?

► **6.32** *Earth cooling*
How long should the earth take to cool? Interpret your estimate.