Physics of Matter

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14 January, 2020

These are my notes for the *matter* part of the *physics of fields and matter* course from the University of Edinburgh as part of the second year of the theoretical physics degree. When I took this course in the 2019/20 academic year it was taught by Dr Stewart McWilliams[1] and Dr Simon Titmuss[2]. These notes are based on the lectures delivered as part of this course, and the notes provided as part of this course. The content within is correct to the best of my knowledge but if you find a mistake or just disagree with something or think it could be improved please let me know.

These notes were produced using LaTeX[3]. Graphs where plotted using Python[4], Matplotlib[5], NumPy[6], and SciPy[7]. Diagrams were drawn with tikz[8]. Some images were taken from the lecture notes provided.

This is version 1.0 of these notes, which is up to date as of 04/01/2021.

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[3] https://www.latex-project.org/
[4] https://www.python.org/
[5] https://matplotlib.org/
[6] https://numpy.org/
[7] https://scipy.org/scipylib/
[8] https://www.ctan.org/pkg/pgf

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Part I

Fluids

1 The Basics

1.1 Scale

This course is mostly interested in large collections of particles where large is approximately $1\,\mathrm{mol}$. The mole is defined as the one Avogadro's number N_A of particles, that is the number of particles in $12\,\mathrm{g}$ of carbon-12.

$$N_A = 6.022 \times 10^{23}$$

This is such a large number that considering individual particles to see macroscopic effects is a hopeless task. The size of molecules is measured in angstroms Å where $1\,\text{Å} = 10^{-10}\,\mathrm{m}$.

1.2 Brownian Motion

Brownian motion is the random movement of particles suspended in a fluid. It arises as the net effect of many molecular impacts. This was key evidence for the molecular nature of matter.

1.3 Random Walks

A random walk is a path characterised by a number of equal sized steps that are equally likely to be in any direction. Random walks have structure at every level. What this means is that if you where to take steps more frequently you would still have a random walk.

We use the notation $\langle x \rangle$ to represent the average value of x, theoretically over an infinite number of measurements. If a random walk of N steps ends at $\boldsymbol{r}_N$ then

$$\langle \boldsymbol{r}_N \rangle = \boldsymbol{0}$$

This is because steps in all directions are equally likely so over many walks cancel out. The average distance from the origin squared is given by

$$\langle r_N^2 \rangle = N\lambda^2$$

where λ is the step length and $r_N^2 = \boldsymbol{r}_N \cdot \boldsymbol{r}_N$. This is easily shown in 1 dimension.

$$\boldsymbol{r}_N = \boldsymbol{r}_{N-1} \pm \boldsymbol{\lambda}$$

$$\langle r_N^2 \rangle = \langle r_{N-1}^2 \rangle + 2\langle \boldsymbol{r}_{N-1} \cdot \boldsymbol{\lambda} \rangle + \lambda^2$$

Forward and backward steps are equally likely so $\langle \boldsymbol{r}_{N-1} \cdot \boldsymbol{\lambda} \rangle = 0$. Our basis case is one step, $N = 1$. After one step the distance from the origin in λ regardless of direction so $r_N^2 = \lambda^2$. Now assume that $\langle r_k \rangle = k\lambda^2$. Hence the distance squared after $k + 1$ steps is

$$\langle r_{k+1} \rangle = \langle r_k^2 \rangle + \lambda^2 = k\lambda^2 + \lambda^2 = (k+1)\lambda^2$$

so by induction

$$\langle r_N^2 \rangle = N\lambda^2$$

If one step is taken every Δt seconds then in time t $N = t/\Delta t$ steps are taken. Hence $\langle r_N^2 \rangle \propto N \propto t$. This comes in useful when considering diffusion which is characterised by

$$\langle r_N^2 \rangle \propto Dt$$

where D is the diffusion coefficient.

If molecules are so small and the particles the hit are (relatively) big and molecules are going at (relatively) low speeds ($100\,\mathrm{m/s}$ to $1000\,\mathrm{m/s}$) then how do they impart enough of a change of momentum to be noticeable? Einstein realised that we don't see the effects of the rapid motion of individual impacts but that we only see the rare large displacements.

2 Maxwell–Boltzmann Distribution

2.1 Equipartition

Einstein realised that colloidal particles behave just like solute particles but bigger. The equipartition theory is that energy is shared equally between all modes of a system. The mean energy of each quadratic mode (any mode with dependence on something squared) is $\frac{1}{2}k_B T$ where k_B is the Boltzmann constant $k_B = 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$ and T is the temperature in kelvin. For example if each particle has kinetic energy E_K then

$$\langle E_K \rangle = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle\right) = \frac{3}{2}k_B T$$

We can be precise about average molecular energies but not individual particles.

2.2 Probability Recap

If we measure some property x N times and we find x_i N_i times then the mean is

$$\langle x \rangle = \sum_i \frac{N_i}{N}x_i = \sum_i P_i x_i$$

where $P_i = N_i/N$ is the probability of x_i. This is for a discrete distribution. We can extend it to a continuous distribution by using an integral over all possible values of x and a probability distribution function P in place of P_i:

$$\langle x \rangle = \int_{-\infty}^{\infty} xP(x)\,dx$$

When we are talking about molecule's speeds the probability distribution we use is the Maxwell–Boltzmann distribution f.

2.3 Maxwell–Boltzmann Distribution

Let $g(v_x)dv_x$ be the fraction of particles with velocities $v_x \to v_x + dv_x$. The velocity distribution function g is proportional to the Boltzmann constant. The Boltzmann constant in general is proportional to the probability P that a system is in a state with energy E.

$$P \propto e^{-E/k_B T}$$

where E is the energy in question. In the case of particle speeds E is the kinetic energy so

$$g(v_x) \propto \exp\left(-\frac{mv_x^2}{2k_B T}\right)$$

We need to normalise the distribution:

$$\int_{-\infty}^{\infty} g(v_x)dv_x = 1$$

$$\int_{-\infty}^{\infty} \exp\left(-\frac{mv_x^2}{2k_B T}\right) = \sqrt{\frac{2\pi k_B T}{m}}$$

$$g(v_x) = \sqrt{\frac{m}{2\pi k_B T}} \exp\left(-\frac{mv_x^2}{2k_B T}\right)$$

The fraction with velocities $v_x \to v_x + dv_x$, $v_y \to v_y + dv_y$, $v_z \to v_z + dv_z$ is given by

$$g(v_x)dv_x g(v_y)dv_y g(v_z)dv_z = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) dv_x dv_y dv_z$$

Since all directions are equally likely the situation in velocity space is spherically symmetric. The volume of velocity space corresponding to speeds $v \to v + dv$ is a spherical shell with inner radius v and outer radius

$v + dv$. The volume of this shell is $4\pi v^2 dv$. As v increases there are more ways to combine v_x, v_y and v_z to get v hence as v increases so does the volume. The fraction of particles with speeds $v \to v + dv$ is

$$f(v)dv = 4\pi v^2 g(v_x)g(v_y)g(v_z)dv$$

$$f(v)dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T} \right)$$

The most probable speed v^* is found by requiring $f(v^*)$ to be a maximum:
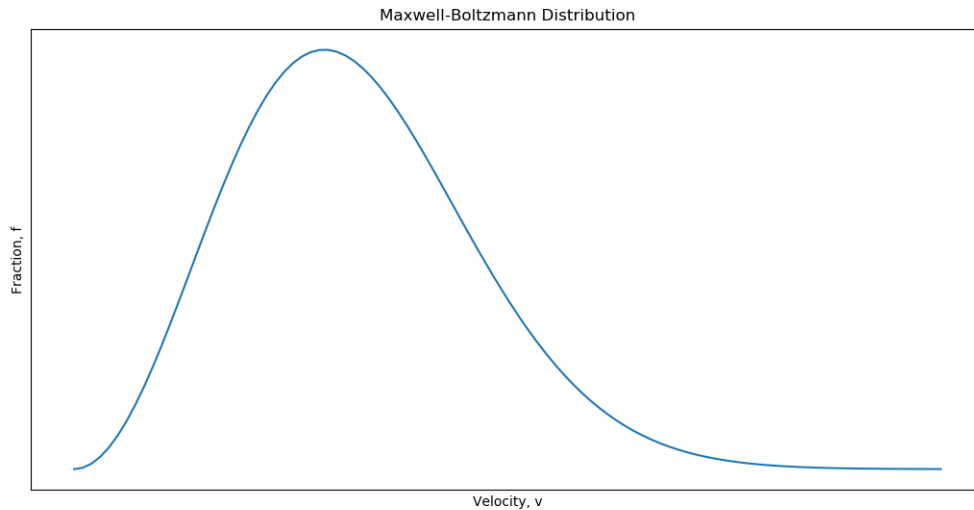
Figure 2.1: The Maxwell–Boltzmann distribution

$$\left. \frac{\partial f}{\partial v} \right|_{v^*} = 0$$

$$\frac{\partial f}{\partial v} = \frac{4}{\sqrt{\pi}} \left(-\frac{m}{2k_B T} \right)^{3/2} \left[2v \exp\left(-\frac{mv^2}{2k_B T} \right) - \frac{mv^3}{2k_B T} \exp\left(-\frac{mv^2}{2k_B T} \right) \right] = 0$$

The value in the square brackets must be 0. This gives

$$v^* = \sqrt{\frac{2k_B T}{m}}$$

We can also find the expected value of the velocity:

$$\langle v \rangle = \int_0^\infty v f(v) \, dv$$

$$= \frac{4}{\sqrt{\pi}} \left(-\frac{m}{2k_B T} \right)^{3/2} \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2k_B T} \right) \, dv$$

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

From this and the mean kinetic energy we can also work out the root mean square:

$$\langle E_K \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \implies \sqrt{\langle v^2 \rangle} = v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$$

By looking purely at the numerical factors it is clear that the most probable speed is the lowest, then the mean speed and the root mean square speed is highest (note that $2 < 8/\pi < 3$).

Example 2.1
What is the mean speed of N_2 at $300\,K$?

The molar mass of N_2 is $28\,g\,mol^{-1}$. This means that the mass of one molecule is $28 \times 10^{-3}/N_A\,kg$. This gives $\langle v \rangle = 476\,m\,s^{-1}$. This is comparable to the speed of sound in air.

We can now show that Equipartition works for kinetic energy:

$$\begin{aligned}
\langle E_K \rangle &= \frac{1}{2}m \left\langle v^2 \right\rangle \\
&= \frac{1}{2}m \int_0^\infty v^2 f(v)\,dv \\
&= \frac{1}{2}m \frac{4}{\sqrt{\pi}} \left(\frac{m}{(2k)BT}\right)^{3/2} \int_0^\infty v^4 \exp\left(-\frac{mv^2}{2k_BT}\right)\,dv \\
&= \frac{3}{2}k_BT
\end{aligned}$$

The temperature provides a measure of mean kinetic energy which is independent of mass. Equipartition generally only applies at high temps where the energy levels are close enough together to approximate as continuous, how high depends on the specific energy levels.

Equipartition applies to any quadratic mode, for example a mass spring system has $\langle E_P \rangle = kx^2/2$.

$$\langle E_P \rangle = \frac{k}{2} \frac{\int_{-\infty}^\infty x^2 \exp\left(-\frac{kx^2}{2k_BT}\right)\,dx}{\int_{-\infty}^\infty \exp\left(-\frac{kx^2}{2k_BT}\right)\,dx} = \frac{1}{2}k_BT$$

If we inject fast moving particles they collide lots and quickly slow down so we return rapidly to a Maxwell–Boltzmann distribution at a slightly higher temperature.

2.4   Effusion

The process of molecules escaping from a small hole is known as effusion. The distribution of velocities is not the same as the Maxwell–Boltzmann distribution, instead it is proportional to

$$v^4 \exp\left(-\frac{mv^2}{2k_BT}\right) = v^2 f(v)$$

The additional factor of v^2 comes from two effects:

- Escape favours faster particles
- The finite size of the hole means that a range of velocities is transmitted and that range is proportional to the velocity

3   Ideal Gasses

In the following section n is the number of molecules per unit volume which is known as the number density. The molar volume V_m is the volume one mole of a substance. For an ideal gas at pressure p, volume V and temperature T if there are N molecules then the ideal gas equation is

$$pV = Nk_BT$$

For one mole of the gas $V = V_m$ and $N = N_A$ so the equation is

$$pV_m = N_Ak_BT$$

we define the molar gas constant $R = N_A k_B = 8.314 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1}$ so the ideal gas equation for n_m of gas can also be written as

$$pV = n_m R T$$

This comes from combining three laws:

- Boyle's law: $p \propto 1/V$ at constant temperature

- Charles' law: $V \propto T$ at constant pressure

- Gay-Lussac's law $p \propto T$ at constant volume

There are two key assumptions for an ideal gas:

- There is a large number of molecules so we can average out fluctuations

- The volume of a molecule is much less than the volume per molecule. Or equivalently the molecules behave as if they where point particles. This means that collisions between molecules are rare (compared to collisions with the container) and intermolecular forces are negligible.

The first assumption depends on the system of interest. In macroscopic amounts of gas where we use this equation it is clearly true. Assuming that the second assumption holds we can predict the average distance $\langle s \rangle$ between molecules under standard conditions. Standard conditions are $T = 273.15 \, \text{K}$ and $10^5 \, \text{Pa}$. So for one mole of gas the volume V_m is given by

$$V_m = \frac{RT}{p} = 0.022\,71 \, \text{m}^3 \, \text{mol}^{-1} = 22.71 \, \text{dm}^3 \, \text{mol}^{-1}$$

So at standard temperature and pressures the volume per molecule is

$$\frac{V_m}{N_A} = \frac{4}{3} \pi \left(\frac{\langle s \rangle}{2} \right)^2 \implies \langle s \rangle \approx 4 \, \text{nm}$$

Comparing this to the diameter of a molecule which is about $0.4 \, \text{nm}$ we see that the separation is about ten times the diameter. This means that the volume per molecule is about one thousand times the volume of the molecule.

The thermodynamic limit is when numbers are big enough that we can ignore fluctuations as they cancel when we average.

3.1   Pressure

The pressure in a container of gas is due to molecular impacts with the walls causing a change in momentum and hence force. We will consider only elastic (momentum and energy conserved) and specular (angle of incidence equals angle of reflection) collisions.

We will consider a cube of side length L. We define our coordinate axis as the normals to the faces of this cube. A molecule mass m that has velocity v_x in the x direction will collide with the wall and have velocity $-v_x$. This results in a change of momentum $2mv_x$. The frequency of collisions with one face depends on the speed and twice the distance between faces (since it has to hit the face and then bounce back off the other face before it collides again) this gives a frequency of $v_x/2L$. So for N molecules this gives

$$2m v_x \frac{v_x}{2L} N = m \left\langle v_x^2 \right\rangle \frac{N}{L}$$

The pressure is the force per area and the area is L^2 so the pressure is

$$m \left\langle v_x^2 \right\rangle \frac{N}{L^3} = m \left\langle v_x^2 \right\rangle \frac{N}{V}$$

Note that $N/V = n$ the number density. The velocity of the particle in general is equally likely to be in any direction and can be split into components. When averaged all of these components should be the same:

$$\left\langle v^2 \right\rangle = \left\langle v_x^2 \right\rangle + \left\langle v_y^2 \right\rangle + \left\langle v_z^2 \right\rangle \implies \left\langle v_x^2 \right\rangle = \frac{1}{3} \left\langle v^2 \right\rangle$$

Hence the pressure is given by

$$p = \frac{1}{3}nm \left\langle v^2 \right\rangle$$

where we can find $\left\langle v^2 \right\rangle$ from the Maxwell–Boltzmann distribution.

3.2   Solid Angles

We will need to know the fraction of molecules that are travelling in a certain direction. To do this we can use solid angles. A solid angle Ω is defined by

$$\Omega = \frac{A}{r^2}$$

the units are known as steradians. A is the area covered on the surface of a sphere radius r by a solid angle Ω from the centre. There are 4π steradians in a sphere.

If molecules are travelling in all directions with equal probability then the fraction of molecules with trajectories in a solid angle $d\Omega$ is

$$\frac{d\Omega}{4\pi}$$

The fraction of molecules travelling at angles $\vartheta \to \vartheta + d\vartheta$ to a particular direction (often the normal to a wall) is given by the area of the surface of a sphere that can be reached by molecules at that angle starting at the centre divided by the total surface area of the sphere. The area in question is the circumference of the ring $2\pi \sin \vartheta$ times the width of the ring $d\vartheta$ so $d\Omega = 2\pi \sin \vartheta d\vartheta$ which means that the fraction of the molecules travelling in the desired direction is

$$\frac{d\Omega}{4\pi} = \frac{2\pi \sin \vartheta d\vartheta}{4\pi} = \frac{1}{2} \sin \vartheta d\vartheta$$

3.3   Derivation of Pressure

We will now try and derive the result from above using statistical mechanics. Molecules that have a speed v and are travelling at an angle ϑ to the surface normal will strike the surface in time dt if they are in the shaded box shown in figure 3.1. The volume of the box is $Avdt \cos \vartheta$. The number of molecules per unit
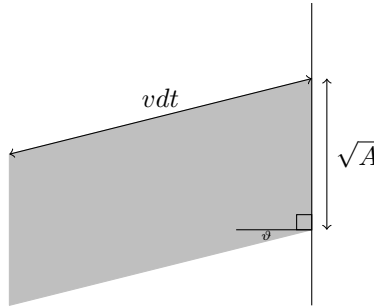
Figure 3.1: Molecules travelling at speed v at an angle ϑ to the surface normal will hit the wall in time dt if they are in the shaded box.

volume which have speeds $v \to v + dv$ and angles to the surface normal $\vartheta \to \vartheta + d\vartheta$ is

$$n \left(\frac{1}{2} \sin \vartheta d\vartheta \right) f(v) dv$$

The first term n accounts for the number of molecules per unit volume, the second term $\sin \vartheta d\vartheta / 2$ accounts for the fraction of molecules with the desired angle and the final term $f(v) dv$ accounts for the fraction of molecules that have the desired speed. The number of impacts in an area A in time interval dt is given by

$$Avdt \cos \vartheta n \left(\frac{1}{2} \sin \vartheta d\vartheta \right) f(v) dv$$

The flux Φ is the number of impacts per unit area per unit time. The flux due to molecules travelling at speed v at angle ϑ is $d\Phi_{v\vartheta}$ and is given by

$$d\Phi_{v\vartheta} = n(v\cos\vartheta)\frac{1}{2}\sin\vartheta d\vartheta f(v)dv$$

The pressure is the force per area which by Newton's second law is the change of momentum per area which is

$$dp = 2mv\cos\vartheta d\Phi_{v,\vartheta}$$

Where the term $2mv\cos\vartheta$ accounts for the change in momentum per collision and the flux accounts for the number of collisions per unit area.

$$dp = nm\sin\vartheta\cos^2\vartheta d\vartheta v^2 f(v)dv$$

$$p = nm\int_0^{\pi/2}\sin\vartheta\cos^2\vartheta\,d\vartheta\int_0^\infty v^2 f(v)\,dv$$

$$I = \int_0^{\pi/2}\sin\vartheta\cos^2\vartheta\,d\vartheta$$

$$\frac{\mathrm{d}(\cos\vartheta)}{\mathrm{d}\vartheta} = -\sin\vartheta \implies d\vartheta = \frac{d(\cos\vartheta)}{-\sin\vartheta}$$

$$\implies I = \int_{\vartheta=0}^{\vartheta=\pi/2}\sin\vartheta\cos^2\vartheta\frac{d(\cos\vartheta)}{-\sin\vartheta} = \int_{\vartheta=0}^{\vartheta=\pi/2} -\cos^2\vartheta\,d(\cos\vartheta)$$

$$\implies I = \left[-\frac{1}{3}\cos^3\vartheta\right]_{\vartheta=0}^{\vartheta=\pi/2} = \frac{1}{3}\left(-\cos^3\frac{\pi}{2}+\cos^3 0\right) = \frac{1}{3}$$

$$\int_0^\infty v^2 f(v)\,dv = \langle v^2\rangle$$

$$p = \frac{1}{3}nm\langle v^2\rangle$$

We can use the facts that $n = N/V$ and $\langle v^2\rangle = 3k_B T/m$ to write the pressure as

$$p = nk_B T$$

$$pV = Nk_B T$$

$$p = \frac{2\langle E_K\rangle}{3V}$$

the last one means that we can think of the pressure of an ideal gas as the kinetic energy density (times a constant $2/3$).

3.4   Effusion

We can now come back to the process of effusion. The rate of effusion through a small hole area A is given by

$$\Phi A$$

where Φ is the total flux.

$$\Phi = \frac{n}{2}\int_0^{\pi/2}\sin\vartheta\cos\vartheta\,d\vartheta\int_0^\infty vf(v)\,dv$$

$$= \frac{n\langle v\rangle}{2}\frac{1}{2}\int_0^{\pi/2}\sin 2\vartheta\,d\vartheta$$

$$= \frac{n\langle v\rangle}{4}\left[-\frac{\cos 2\vartheta}{2}\right]_0^{\pi/2} = \frac{n\langle v\rangle}{4}$$

$$\Phi = \frac{p}{\sqrt{2\pi m k_B T}}$$

The fact that $p \propto 1/\sqrt{m}$ is known as Graham's law. It was used in the Manhattan project to separate $^{238}\text{UF}_6$ and $^{235}\text{UF}_6$.

The molecules that start at a distance $v\cos\vartheta dt$ from the hole will escape in a time dt if $\vartheta \in [0, \pi/2]$. The number escaping per unit time per area of hole is

$$d\Phi_{v\vartheta} = nv\cos\vartheta\frac{1}{2}\sin\vartheta d\vartheta f(v)dv$$

The extra factor of v at the start is important. When considering the kinetic energies of the particles we must consider this factor of v for example the average kinetic energy of escaping molecules is

$$\langle E_K \rangle = \frac{\int_0^\infty v^3 f(v)\, dv}{\int_0^\infty v f(v)\, dv} = 2k_B T$$

Notice that it is $v^3 f(v)$ and $vf(v)$ in the integrands that would normally just be $v^2 f(v)$ and $f(v)$. The angle integrals are the same in the numerator and denominator so cancel. The faster moving molecules (higher temperature) are more likely to escape.

3.5   Exponential Atmosphere

From section 2.3 we saw that
$$P \propto e^{-E/k_B T}$$

We will use this to approximate the air pressure at the peak of Mount Everest. We are interested in a change in height so the relevant energy is gravitational potential energy.

$$mgh \sim 4 \times 10^{-21}\,\text{J}$$

where $h = 8.8\,\text{km}$ is the height of Mount Everest. By coincidence at standard temperatures $k_B T \sim 4 \times 10^{-21}$ J so the number of molecules per unit volume at the peak is

$$n = n_0 \exp\left(-\frac{mgh}{k_B T}\right) = n_0 e^{-1}$$

where n_0 is the number of particles per molecule at sea level Since the number of molecules is proportional to the pressure
$$p = p_0 e^{-1} \approx 3.7 \times 10^4\,\text{Pa}$$

We can make the same prediction with (mostly) macroscopic physics. We assume a constant temperature (isothermal atmosphere). The hydrostatic pressure change dp due to a fluid of density ρ over a height dh is

$$dp = -\rho g dh$$

We consider a gas in a cylinder supporting a piston with its underside at height h and its top surface at height $h + dh$. We must allow some method for the gas below the piston and above to reach a thermal equilibrium. The pressure difference times the area of the piston must be equal to the force due to the displacement of gas upwards by the piston:

$$(p - (p + dp))A = n(Adh)mg$$

The first two terms on the left hand side give the pressure below and above the piston.

$$-\frac{\mathrm{d}p}{\mathrm{d}h} = nmg$$

$$p = nk_B T$$

$$dp = -\frac{mg}{k_B T} dh$$

$$p = p_0 \exp\left(-\frac{mgh}{k_B T}\right)$$

So we get the same result if we make the same assumptions required for the Maxwell–Boltzmann distribution, ie isothermal atmosphere and equilibrium.

4   Transport

Some properties of fluids can be thought of as transport of something:

- Diffusion is transport of molecules
- Viscosity is transport of momentum
- Thermal conductivity is transport of heat

These processes are all driven by a gradient, for these cases the gradient is concentration, velocity and temperature respectively.

4.1   Mean Free Path

The key length scale in all of these cases is the mean free path length λ. It is the average distance between molecular collisions. To find λ consider a frame where all but one particle is stationary. The moving molecule sweeps out an imaginary collision tube. If the centre of another molecule is in this tube then it will collide with the moving molecule. The cross sectional area σ of this tube is

$$\sigma = \pi(a_1 + a_2)^2$$

where a_1 is the radius of the moving molecule and a_2 is the radius of all of the other molecules. This follows from the fact that two spheres will overlap if and only if the distance between them is less than or equal to the sum of their radii. In time t the molecule collides with $\sigma v t n$ molecules where we use $v = \langle v_r \rangle$ as the average velocity of the moving molecule relative to the other molecules. The molecule also travels a distance of $\langle v \rangle t$. This gives us the mean free path length as the length of the path divided by the number of collisions:

$$\lambda = \frac{\langle v \rangle t}{\sigma \langle v_r \rangle tn}$$

For the Maxwell–Boltzmann distribution we can make an approximation of $\langle v_r \rangle$. For this distribution we have

$$\frac{\langle v \rangle}{\sqrt{\langle v^2 \rangle}} = \sqrt{\frac{8}{3\pi}} = 0.92 \approx 1$$

so we can approximate $\langle v \rangle \approx \sqrt{\langle v^2 \rangle}$ that is we can approximate the mean as the root mean square. We can thus approximate $\langle v_r \rangle \approx \sqrt{\langle v_r^2 \rangle}$. We now consider two molecules with velocities $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$. This gives us a relative velocity

$$\boldsymbol{v}_r = \boldsymbol{v}_1 - \boldsymbol{v}_2$$

$$v_r^2 = \boldsymbol{v}_r \cdot \boldsymbol{v}_r = (\boldsymbol{v}_1 - \boldsymbol{v}_2) \cdot (\boldsymbol{v}_1 - \boldsymbol{v}_2) = v_1^2 + v_2^2 - 2\boldsymbol{v}_1 \cdot \boldsymbol{v}_2$$

$$\langle v_r^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle - 2 \langle \boldsymbol{v}_1 \cdot \boldsymbol{v}_2 \rangle$$

Since all directions are equally likely $\langle \boldsymbol{v}_1 \cdot \boldsymbol{v}_2 \rangle = 0$, as well as this $\langle v_1^2 \rangle = \langle v_2^2 \rangle = \langle v^2 \rangle$

$$\langle v_r^2 \rangle = 2 \langle v^2 \rangle$$

$$\langle v_r \rangle \approx \sqrt{\langle v_r^2 \rangle} = \sqrt{2 \langle v^2 \rangle} \approx \langle v \rangle \sqrt{2}$$

so we can approximate $\langle v_r \rangle \approx \langle v \rangle \sqrt{2}$. Going back to the mean free path length we can now write this as

$$\lambda = \frac{\langle v \rangle t}{\sigma \langle v \rangle \sqrt{2}tn} = \frac{1}{\sigma n \sqrt{2}}$$

We can use $p = nk_BT$ to write this as

$$\lambda = \frac{k_BT}{p\sigma\sqrt{2}}$$

From this it is clear that increasing pressures decreases λ. This is because the molecules become closer together on average so more collisions occur in the same time.

For this derivation we have assumed that there are no intermolecular forces. If there where then they would simply have the effect of increasing the effective collision cross section as the molecules would no longer need to actually touch to collide but just come close to each other.

Example 4.1
What is the mean free path length of N_2 at $300\,\mathrm{K}$ and $10^5\,\mathrm{Pa}$? The molecular diameter d is $d = 0.37\,\mathrm{nm}$. This gives a cross section $\sigma = \pi d^2 = 4.3 \times 10^{-19}\,\mathrm{m}^2$. The mean free path is then $\lambda = 6.8 \times 10^{-8}\,\mathrm{m}$.

In general the mean free path $\lambda \approx 100\,\mathrm{nm}$. For comparison the average intermolecular separation is $\langle s \rangle \approx 4\,\mathrm{nm}$ and the molecular diameter is usually about $d = 0.4\,\mathrm{nm}$. The time τ between collisions is

$$\tau = \frac{\lambda}{\langle v \rangle} \approx 0.14\,\mathrm{ns}$$

4.2   Diffusion

Diffusion is transport of molecules driven by a concentration gradient. Molecules spread away from an area of high concentration. We will start by considering one dimensional random walks. If all of the volume of fluid is split by planes area A into bins then we define $N(z)$ to be the number of molecules in the bin containing the point z. If all of the planes are a distance L apart then the number of molecules in the plane to the left of the plane containing z is $N(z - L)$. The volume of a bin is LA if the number density of the
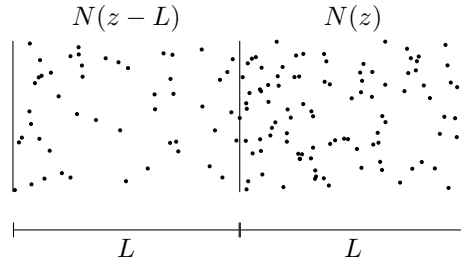
Figure 4.1: Gas divided into bins width L containing N molecules

fluid defusing is n^* then $N = ALn^*$. If in time τ half the molecules step from left to right an half step from right to left then the net nuber crossing from left to right is given by

$$\frac{1}{2}(N(z - L) - N(z)) = \frac{L}{2}\frac{\mathrm{d}N}{\mathrm{d}z}$$

The flux Φ is given by

$$\Phi = -\frac{L}{2A\tau}\frac{\mathrm{d}N}{\mathrm{d}z} = -\frac{L^2}{2\tau}\frac{\mathrm{d}n^*}{\mathrm{d}z} = -D\frac{\mathrm{d}n^*}{\mathrm{d}z} \tag{4.1}$$

We can identify that $L \leftrightarrow \lambda$ since this is the length of one step. D is the diffusion coefficient.
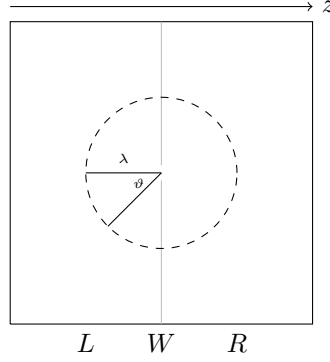
Figure 4.2: Concentration gradient decreases from left to right.

4.3   Diffusion Coefficient and Fick's Law

Figure 4.2 shows a box with a concentration gradient. We place an imaginary window in the plane dividing the box in half at W. Recall that $\Phi \propto n^*$. One question that we can ask is how much higher is the concentration at L than at R? This depends on the positions of L and R and also on the value of $\partial_z n^*$. The last change in direction of a particle before it went through the window must have occurred somewhere on the circle if we assume all steps are of size λ. This means that it occurred at a distance $\lambda \cos \vartheta$ along the z axis. The excess concentration at L is

$$-\lambda \cos \vartheta \partial_z n^*$$

The flux approaching W from the left exceeds that leaving by the right by

$$d\Phi_{\vartheta v} = -\frac{\partial n^*}{\partial z} \lambda \cos \vartheta \frac{1}{2} sin\vartheta \cos \vartheta d\vartheta v f(v) dv$$

The total excess flux is

$$\Phi_z = -\frac{1}{2} \frac{\partial n^*}{\partial z} \lambda \int_0^\pi \cos^2 \vartheta \sin \vartheta \, d\vartheta \int_0^\infty v f(v) \, dv$$

$$\Phi_z = -\frac{\lambda}{3} \langle v \rangle \frac{\partial n^*}{\partial z}$$

This last line is Fick's law. From this we can equate with equation 4.1 and we get

$$D = \frac{\lambda}{3} \langle v \rangle$$

$$[D] = \mathrm{m^2 \, s^{-1}}, \qquad D \propto p^{-1} \propto T^{3/2}, \qquad \langle v \rangle \propto T^{1/2}$$

Diffusion is faster at higher temperatures as the particles are faster and at lower pressures as the mean free path is longer.

We can treat diffusion as a large number of random walks. The expected square of the length of an N step walk of step length l is $\langle x_N^2 \rangle = N l^2$. The step size $l = \lambda$ and in time t the number of steps is given by the number of collisions so $N = t \langle v \rangle / \lambda$.

$$\langle x_N^2 \rangle = \langle v \rangle \lambda t$$

$$D = \frac{\lambda}{3} \langle v \rangle$$

$$\sqrt{x_N^2} \propto \sqrt{Dt}$$

we can take $\sqrt{x_N^2}$ as a measure of the width of the distribution so we can also do the same with $\sqrt{Dt}$. So if D is very high or after a long time we would expect the distribution to look wide and flat as the gas is

evenly spread. If D is very low or for small t we would expect a sharp distribution with all the gas in one place.

We used the molecular diameter to construct this entire argument but we can work back and measure D to get d. When we do this we find that the value of d is in agreement with other methods such as those that depend on different transport properties. This was important evidence for the molecular nature of matter early on in statistical mechanics.

4.4   Viscosity

Consider two plates area A sandwiching a fluid. The top plate moves with velocity u relative to the bottom plate. This establishes a velocity gradient as the fluid near a wall has a velocity that matches that of the wall. We imagine the fluid as a series of layers. Molecules in the layer next to the top plate will collide with the layer below and in doing so lose some momentum and cause the layer below to gain some. Like wise molecules in the lowest layer will collide with molecules in the layer above and gain some of their momentum. In this way momentum is transferred from the top plate to the bottom plate.
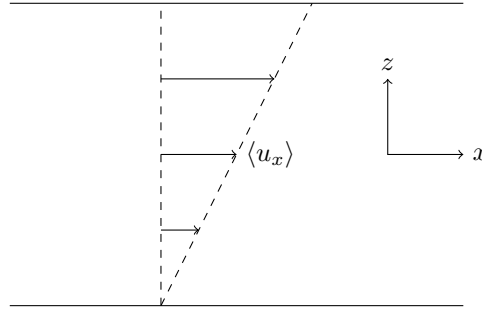
Figure 4.3: Velocity Gradient

We define the shear stress τ_{xz} to be the force per unit area which is equivalently the flux of momentum which is in turn the rate of transfer of momentum per unit area. The flux is given by

$$d\Phi_{v\vartheta} = \frac{1}{2}\sin\vartheta\cos\vartheta d\vartheta nv f(v)dv$$

A molecule a distance $\lambda\cos\vartheta$ up the velocity gradient carries additional momentum given by

$$-m\frac{\partial\langle u_x\rangle}{\partial z}\lambda\cos\vartheta$$

where $\langle u_x\rangle$ is the average velocity in the x at a heigh z and m is the mass of the . The flux of the momentum is then given by

$$\Phi = -\frac{1}{2}nm\lambda\frac{\partial\langle u_x\rangle}{\partial z}\int_0^\pi \cos^2\vartheta\sin\vartheta\,d\vartheta\int_0^\infty vf(v)\,dv$$

$$\Phi = -\frac{1}{3}nm\lambda\langle v\rangle\frac{\partial\langle u_x\rangle}{\partial z}$$

We define the viscosity η to be

$$\eta = \frac{1}{3}nm\lambda\langle v\rangle$$

which allows us to write

$$\tau_{xz} = \eta\frac{d\langle u_x\rangle}{dz}$$

We can substitute in

$$\lambda = \frac{1}{\sigma n\sqrt{2}}$$

to get

$$\eta = \frac{1}{3}\frac{nm}{\sigma n \sqrt{2}} = \frac{\sqrt{2}}{6}\frac{m}{\sigma}\langle v \rangle$$

we see that η is independent of n and hence independent of pressure. This is because when the pressure increases the number of collisions increases but the efficacy of the collisions transferring momentum decreases and these effects cancel out. For a gas $\eta \propto \sqrt{T}$ so increasing temperature increases the viscosity. For most liquids increasing temperature decreases velocity.

5 Thermodynamics

5.1 Heat Flux

The flux of heat is given by

$$\frac{1}{A}\frac{\mathrm{d}Q}{\mathrm{d}T} = -\kappa \frac{\mathrm{d}T}{\mathrm{d}y}$$

where

$$\kappa = \frac{1}{3}n\langle v \rangle \lambda C_{\mathrm{molecule}}$$

Where Q is the heat, A is the area and C_{molecule} is the heat capacity of one molecule. Since the temperature is related to the average kinetic energy then a transfer of kinetic energy by collision is related to a transfer of heat and hence the mechanism for temperature transfer is collisions.

5.2 What is Thermodynamics

Thermodynamics connects energy, heat work and temperature. Classical thermodynamics as a framework was established before the molecular nature of matter was widely accepted. Statistical thermodynamics was established after. We will be using which ever is more convenient in this course. Thermodynamics is interested in how macroscopic variables are related.

5.3 Zeroth Law of Thermodynamics

The zeroth law was added after the other three laws when it became clear that a definition of thermal equilibrium was needed. Two bodies are defined to be in thermal equilibrium if they are the same temperature. The zeroth law states

> Two bodies A and B that are separately in thermal equilibrium with a third body C they are also in thermal equilibrium with each other.

Thermal equilibrium is an equivalence relation since all objects are in thermal equilibrium with themselves, thermal equilibrium is symmetric and the zeroth law states the transitivity of thermal equilibrium.

This law is the basis for how thermometers work since they are calibrated from one object and then allowed to reach a thermal equilibrium with another. Then they give the temperature under the assumption that the calibration object and object being measured are in thermal equilibrium if the associated pressure change in the thermometer is the same.

If two systems are in thermal contact then there will be an energy transfer, on average, from the hotter object of temperature T_2 to the cooler object of temperature T_1 and eventually thermal equilibrium will be achieved. The temperature T at thermal equilibrium will be $T_1 < T < T_2$.

5.4 First Law of Thermodynamics

Joule did experiments where he did work on a system in various ways, for example dropping a weight or with an electric current. He observed that the heat transfer is the same for the same amount of work. This established that heat and work are equivalent ways of increasing the internal energy of a system.

Heat Q is thermal energy in transit. Work W is also energy in transit but it is motion against a force. Work is done if the process could be used to change the height of a weight. If the weight is raised work is done by the system. If the weight is lowered work is done on the system. An important distinction is that heat is transfer of energy by disorderly thermal motion whereas work is transfer of energy by organised motion.

Energy is the capacity to do work. Internal energy U is the total energy of all internal degrees of freedom that the system possesses. The internal energy is the sum of the kinetic and potential energies.

A state function depends only on the condition of the system. A path function depends on how the system got into that state.

Internal energy change $\Delta U = U_f - U_i$ is a state function. The first law of thermodynamics is

> If a system absorbs heat Q and work W is done on the system then the change in internal energy is

$$\Delta U = Q + W$$

This is often written in terms of infinitesimal changes:

$$dU = dQ + dW$$

5.4.1   Work done in Gas Expansion

A piston area A is compressed by a force F due to an external pressure p_{ext}. The piston moves a distance dx. What is the work done?

We consider the external pressure to be a constant. The force is given by

$$F = p_{\text{ext}} A$$

The work done is then

$$dW = F dx$$

$$dW = p_{\text{ext}} A dx$$

The change in volume of the gas in the piston is

$$dV = -A dx$$

where the negative denotes a decrease in volume. Hence the work done is

$$dW = -p_{\text{ext}} dV$$

$$W = -p_{\text{ext}} \int_{V_i}^{V_f} dV = -p_{\text{ext}}[V_f - V_i]$$

If the gas is compressed then the work is positive and we say work has been done on the gas in the piston. The internal energy of the gas in the piston increases and its temperature increases.

If we consider work done in a reversible isothermal (constant temperature) expansion. A reversible change is one that can be reversed by an infinitesimal change in a variable. If the internal pressure is only infinitesimally greater than the external pressure then the piston moves out infinitely slowly and the motion can be reversed by an infinitesimal increase in the external pressure. The pressures are balanced so the system is always at equilibrium. In this case we can ensure reversibility by setting $p_{\text{int}} = p_{\text{ext}}$.

The pressure of the gas in the piston is

$$p_{\text{int}} = \frac{n_m RT}{V}$$

for an ideal gas. The work done is

$$dW = -p_{\text{ext}} dV$$

$$W = -\int_{V_i}^{V_f} p_{\text{int}}\, dV = -n_m RT \int_{V_i}^{V_f} \frac{1}{V}\, dV = -n_m RT \ln\left(\frac{V_f}{V_i}\right)$$

Work done reversibly is a maximum. At higher temperatures if everything else is unchanged more work will be done. For an ideal gas undergoing an isothermal change since all energy is kinetic $\Delta U = 0$. The heat transfer in this case is

$$Q = -W = n_m RT \ln\left(\frac{V_f}{V_i}\right)$$

In an adiabatic process no heat is transferred so $Q = 0$. The temperature can still change if the volume or pressure changes. We can approximate the work done as somewhere between the work done in an isothermal change at the start temperature and the work done in an isothermal change at the final temperature.

5.5   Heat Capacity

We define the heat capacity, C, of an object as

$$C = \frac{dQ}{dT}$$

We generally consider two different cases where we want to know the heat capacity. At constant pressure or at constant volume. These are denoted with a subscript p or V respectively and are defined as

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p, \qquad C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

To keep the pressure constant the gas must expand so it has to do work against the atmosphere. For this reason we expect that $C_p > C_V$.

We consider a system where the internal energy is defined by two, independent, thermodynamic variables T and V such that $U = U(T, V)$. A small change (dT, dV) in (T, V) will result in a small change dU in the internal energy:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

From before we have the first law $dU = dQ + dW = dQ - p\,dV$ which allows us to write dQ as $dQ = dU + p\,dV$

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV$$

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\frac{dV}{dT} \tag{5.1}$$

At a constant volume the second term is 0 so the first term is equal to dQ/dT and can be identified as the heat capacity at a constant volume.

$$\frac{dQ}{dT} = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\frac{dV}{dT}$$

For an ideal gas all internal energy is kinetic so $\partial_V U = 0$:

$$\frac{dQ}{dT} = C_V + p\frac{dV}{dT}$$

For one mole of an ideal gas the volume is

$$V = \frac{RT}{p}$$

$$\frac{\mathrm{d}V}{\mathrm{d}T} = \frac{R}{p}$$

$$\frac{\mathrm{d}Q}{\mathrm{d}T} = C_V + p\frac{R}{p}$$

$$\frac{\mathrm{d}Q}{\mathrm{d}T} = C_V + R$$

for one mole of an ideal gas. If instead we take equation 5.1 at a constant pressure then we get C_p instead

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

6 Degrees of Freedom and Entropy

6.1 Quadratic Modes

Equipartition applies to any quadratic mode for example the potential energy of a mass on a spring: $E_p = kx^2/2$. For equipartition to apply however the energy of the system must be such that all energy levels are reachable. Up to now we have considered ideal, monatomic gases. If instead we consider an ideal, diatomic gas then there are more degrees of freedom:

- Translational - There are 3 translational degrees of freedom due to the three different directions a molecule's centre of mass can be translated. The quadratic mode here is the kinetic energy associated with this motion. The energy levels for translational degrees of freedom are available at any non-zero temperature

- Rotational - There are 2 rotational degrees of freedom. There are three axis along which rotation is possible but the one that is collinear with the bond results in a very low moment of inertia since only electrons are being rotated so this degree of freedom is actually associated with electron energy levels so isn't considered a rotational degree of freedom. The quadratic mode here is the kinetic energy associated with this motion. The energy levels for these degrees of freedom are available a temperature of

$$T = \frac{\hbar^2}{2Ik_B}$$

  where I is the moment of inertia. For a heavy molecule like Br_2 the temperature is $\sim 20\,\mathrm{K}$. For a lighter molecule like H_2 the temperature is $\sim 100\,\mathrm{K}$.

- Vibrational - There are 2 vibrational degrees of freedom. The quadratic modes here are the kinetic energy due to the shortening and lengthening of the bond and the potential energy due to this vibration. Note that one vibrational mode gives rise to two degrees of freedom. The energy levels for these degrees of freedom are available at a temperature of

$$T = \frac{\hbar\omega}{k_B}$$

  where ω is the angular frequency of the vibration.

The total number of quadratic modes is $f = 7$. At sufficiently high temperatures using equipartition we get

$$\langle U \rangle = \frac{7}{2}k_B T$$

At these same high temperatures for a mole of ideal, diatomic gas

$$C_V = \frac{7}{2}R = 29.1\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

In general for an ideal gas:

$$C_V = \frac{3}{2}R + \frac{f_{\mathrm{rot}}}{2}R + f_{\mathrm{vib}}R$$

where f_{rot} and f_{vib} are the number of rotational and vibrational degrees of freedom respectively.

An N atom molecule has $3N$ degrees of freedom. Of these 3 are translational degrees of freedom. If it is linear then there are 2 rotational degrees of freedom and if it is non-linear then there are 3 rotational degrees of freedom. The rest are vibrational. This gives the number of vibrational degrees of freedom as

$$f_{\mathrm{vib}} = 3N - 3 - 2 = 3N - 5$$

$$f_{\mathrm{vib}} = 3N - 3 - 3 = 3N - 6$$

for a linear and non-linear molecule respectively.

Example 6.1
CO_2 has three atoms so it has 9 degrees of freedom. It is a linear molecule so it has 3 translational and 2 rotational degrees of freedom. It has $9 - 3 - 2 = 4$ vibrational degrees of freedom. One of these is the carbon atom staying stationary while the bonds change length together, one is one bond shortening and the other lengthening and the other two are degenerate and correspond to scissoring of the molecule in two different planes.

Example 6.2
A ratio of $\gamma = C_p/C_V$ is measured as $7/5$. What can be deduced about the gas?

$$\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V} = \frac{7}{5}$$

$$\implies \frac{C_V}{R} = \frac{5}{2}$$

hence $C_V = 5R/2$. This means that there are 5 degrees of freedom. 3 degrees of freedom must be translational so there are two rotational degrees of freedom meaning the molecule is linear. The fact that there aren't more means that the temperature isn't high enough for the quadratic modes of vibration to be available.

6.2   Entropy

Entropy S is a measure of the distribution of energy. Spontaneous processes increase the number of ways in which energy can be distributed and so increase entropy. It is easy to convert work to heat but not the other way around. This idea is formalised in the second law of thermodynamics.

6.3   Second Law of Thermodynamics

There have been multiple statements of this law each one improving on the last. Clausius stated this law as

> No process is possible whose sole result is the transfer of heat from a colder to a hotter body

Lord Kelvin improved on this stating

> No process is possible whose sole result is the complete conversion of heat into work

Now this law is best understood as all processes increase or leave unchanged the entropy of the universe:

$$\Delta S_{\mathrm{univ}} \geq 0$$

We can further split this into two cases. If $\Delta S_{\mathrm{univ}} > 0$ then the process is spontaneous. If $\Delta S_{\mathrm{univ}} = 0$ then the process is reversible since the reversal necessarily has equal and opposite entropy change so this must be zero to avoid violating the second law of thermodynamics.

6.4   Statistical Definition of Entropy

Lord Kelvin defined entropy as

$$S = k_B \ln \Omega$$

where Ω is the number of ways of distributing a fixed number of particles with a fixed amount of energy.

6.4.1   Joule Expansion of a Gas

An ideal gas, at constant temperature, is kept in a container split in to two parts of volume V. At first the gas is in one part at pressure p_i and the other part is a vacuum. The boundary is removed. What is the change in entropy. Say the gas is now at pressure p_f.

Removing the block doubles the number of ways that each molecule could be positioned giving

$$\frac{\Omega_{\text{after}}}{\Omega_{\text{before}}} = 2^{N_A}$$

$$\Delta S = k_B \ln \Omega_{\text{after}} - k_B \ln \Omega_{\text{before}} = k_B \ln \left(\frac{\Omega_{\text{after}}}{\Omega_{\text{before}}} \right) = k_B \ln 2^{N_A} = N_A k_B \ln 2 = R \ln 2$$

6.5   Thermodynamic Definition of Entropy

In thermodynamics entropy is defined in terms of heat transferred in the process if it where reversible even if it isn't. For an infinitesimal, reversible, heat transfer dQ_{rev} at temperature T the entropy change is

$$dS = \frac{dQ_{\text{rev}}}{T}$$

From this definition we can see that entropy is a state function

6.5.1   Joule Expansion of a Gas

We consider the same set up as before but now we use this other definition of entropy to see if we get the same result. The expansion is isothermal so $dU = 0$. The first law of thermodynamics $dU = dQ + dW$ gives us

$$0 = dQ + dW \implies dQ = -dW = -(-pdV) = \frac{RT}{V}dV$$

for one mole of an ideal gas. Hence the entropy change is

$$dS = \frac{dQ_{\text{rev}}}{T} = \frac{R}{V}dV$$

$$\Delta S = \int_{V_i}^{V_f} \frac{1}{T}\,dQ_{\text{rev}}$$
$$= R \int_{V_i}^{V_f} \frac{1}{V}\,dV$$
$$= R \ln \left(\frac{V_f}{V_i} \right)$$
$$= R \ln 2$$

Which is the same result as the statistical method gave us.

6.6   Surroundings

So far we have only considered the entropy change ΔS_{sys} of the system in question. We also need to consider the entropy change ΔS_{surr} of the surroundings. These quantities combined give us the entropy change of the universe

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

The heat flow from the surroundings Q_{surr} must be equal and opposite to the heat flow Q_{sys} from the system:

$$Q_{\text{surr}} = -Q_{\text{sys}}$$

The surroundings are the rest of the universe so very big. For this reason we can consider heat transfer to the surroundings to be reversible.

Consider a gas expanding reversibly. The entropy change of the system is ΔS_{sys}. The heat flows from the surroundings to the system. The entropy of the surroundings therefore decreases by

$$\Delta S_{\text{surr}} = - \int \frac{1}{T} \, dQ_{\text{rev}} = -\Delta S_{\text{sys}}$$

The total entropy change is then

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

. This is a general result for a reversible process.

If instead we consider the Joule expansion as before then since it is isothermal $\Delta U = 0$. No heat is transferred to or from the surroundings so $Q_{\text{rev}}^{\text{surr}} = 0$. The entropy change of the surroundings is then 0. The entropy change of the system is still $R \ln 2$.

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + 0 = R \ln 2 > 0$$

This makes sense as expansion into a vacuum is spontaneous.

7   Enthalpy and Gibbs Free Energy

Recall the definition of heat capacity:
$$C = \frac{\mathrm{d}Q}{\mathrm{d}T}$$

At constant pressure this becomes

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p \implies (\mathrm{d}Q)_p = C_p \mathrm{d}T$$

This gives us an alternative way to write entropy at constant pressure:

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} = \frac{C_p \mathrm{d}T}{T}$$

$$S(T_2) - S(T_2) = \int_{T_1}^{T_2} \mathrm{d}S = \int_{T_1}^{T_2} \frac{C_p(T)}{T} \, \mathrm{d}T$$

At very low temperatures $C_p \propto T^3$. This is Debye's law, we will come back to it later.

7.1   Third Law of Thermodynamics

The third law of thermodynamics is:

> At absolute zero the entropy of a substance is fixed at a constant value.

For most substances this value is zero since there is only one minimum energy state and this is the state at absolute zero so $S = k_B \ln 1 = 0$. There are substances with non-unique minimum energy states where the entropy is not zero at absolute zero, rather $S = k_B \ln \Omega$ where in this case Ω is the number of distinct, minimum energy states. In this course we can assume that the entropy is zero at absolute zero.
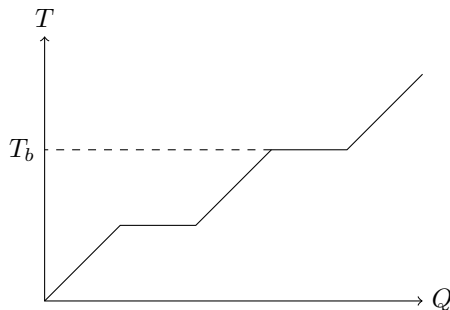
Figure 7.1: Temperature as a substance is heated

7.2   Latent Heat

Figure 7.1 shows how the temperature changes as a substance that starts solid is heated. The temperature starts a solid and the temperature climbs until the melting point is reached. The temperature then plateaus while the substance melts and the temperature starts to rise again. The same happens when the boiling point is reached. The reason for this happening is that changing phase from solid to liquid or liquid to gas results in a large increase in entropy. At the boiling point the state change from liquid to vapour is reversible and the temperature is constant. The entropy change of the system is

$$\Delta S_{\text{sys}} = S_{\text{vap}} - S_{\text{liq}} = \int_{\text{liq}}^{\text{vap}} \frac{\mathrm{d}Q_{\text{rev}}}{T} = \frac{Q_{\text{rev}}}{T_b}$$

where T_b is the boiling point of the substance. We identify this heat absorbed as the latent heat $L = Q_{\text{rev}}$.

$$\Delta S_{\text{sys}} = \frac{L}{T_b}$$

Since the change is reversible we know that $\Delta S_{\text{univ}} = 0$. This means that the entropy change of the surroundings $\Delta S_{\text{surr}} > 0$ so the latent heat comes from the surroundings.

We can estimate the latent heat of vaporisation.

$$\Delta S_{\text{vap}} = \frac{L_{\text{vap}}}{T_b}$$

$$\frac{\Omega_{\text{vap}}}{\Omega_{\text{liq}}} = \left(\frac{V_{\text{vap}}}{V_{\text{liq}}}\right)^{N_A}$$

The volume per gas molecule is about 10^3 times the volume of a single molecule so $V_{\text{vap}}/V_{\text{liq}} \approx 10^3$. This gives

$$\Delta S_{\text{vap}} = k_B \ln\left(\frac{\Omega_{\text{vap}}}{\Omega_{\text{liq}}}\right) \approx k_B \ln\left(\left(10^3\right)^{N_A}\right) = R \ln\left(10^3\right) \approx 7R$$

Comparing this with measured values in 7.1 we can see that this is approximately right for simple molecules like Ne with only one atom. Once there is more than one molecule it is less accurate. Especially for molecules like water with strong intermolecular forces.

7.3   Internal Energy and Entropy

The first law gives us

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$$

and we have previously shown that

$$\mathrm{d}W = -p\mathrm{d}V$$

Material	L/RT_b
Ne	7.85
Ar	8.98
Kr	9.06
Xe	9.21
He	2.39
H_2O	13.1
CH_4	8.80
c_6H_6	10.5

Table 7.1: Latent heat divided by R times the boiling point

In this section we have seen that the entropy is

$$\mathrm{d}S = \frac{\mathrm{d}Q}{T} \implies \mathrm{d}Q = T\mathrm{d}S$$

Combining these we get

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

We have assumed a reversible pressure for the entropy term but since all functions are state functions this holds for irreversible processes. This means that internal energy changes can be considered to be changes of entropy or volume only.

7.4   Enthalpy

We define the enthalpy H of a substance as the heat absorbed at a constant pressure. The enthalpy is

$$H = U + pV$$

To show that this function is what we have said it is we differentiate:

$$\begin{aligned}
\mathrm{d}H &= \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p \\
&= \mathrm{d}Q - p\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p \\
&= \mathrm{d}Q - V\mathrm{d}p
\end{aligned}$$

At constant pressure $\mathrm{d}p = 0$ so

$$\mathrm{d}H = \mathrm{d}Q$$

Integrating gives

$$H = Q$$

assuming the constant of integration to be zero. This shows that this function does indeed calculate what we have stated it does. This is a useful value as constant pressure is a common lab condition.

7.5   Gibbs Free Energy

The second law gives us

$$\Delta S_{\mathrm{sys}} + \Delta S_{\mathrm{surr}} \geq 0$$

At constant temperature and pressure

$$\Delta S_{\mathrm{surr}} = \frac{\Delta Q_{\mathrm{surr}}}{T} = \frac{\Delta H_{\mathrm{surr}}}{T} = -\frac{\Delta H_{\mathrm{sys}}}{T}$$

where the first equality comes from the fact that at constant temperature

$$\int \frac{\mathrm{d}Q}{T} = \frac{\Delta Q}{T}$$

and the second equality comes from the fact that we are at constant pressure so by the definition of enthalpy $\Delta Q = \Delta H$. The final equality is that, due to the conservation of energy, the enthalpy change of both the system and surroundings must be opposite and equal so that there is no overall change. This allows us to restate the second law as

$$\Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} \geq 0$$

$$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \leq 0$$

We define the Gibbs free energy as

$$G = H - TS$$

If the change in Gibbs free energy $\Delta G = \Delta H - T\Delta S \leq 0$ is zero then the process is reversible. If instead it is negative then the process is spontaneous.

7.6 Master equation for $\mathrm{d}G$

$$G = H - TS$$

$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T \qquad\qquad \text{Differentiate}$$

$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T \qquad \text{Substitute for differential form of enthalpy}$$

$$\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T$$

This is known as the master equation for $\mathrm{d}G$. One difference between entropy and Gibbs free energy is that the entropy increases to a maximum at equilibrium whereas the Gibbs free energy decreases to a minimum. We can think of the Gibbs free energy as the maximum amount of work that can be done without changing pressure or volume.

7.7 Phase Change

At a liquid–vapour phase boundary the phases are in equilibrium. The molecules transfer from liquid to vapour and vice versa until $\Delta G = G_{\text{vap}} - G_{\text{liq}} = 0$. This means that $G_{\text{vap}} = G_{\text{liq}}$ so

$$\mathrm{d}G_{\text{vap}} = \mathrm{d}G_{\text{liq}}$$

A change in pressure of $\mathrm{d}p$ will result in a change of boiling point by $\mathrm{d}T$. From here we will consider molar amounts of a substance. We can write the infinitesimal changes of Gibbs free energy as

$$\mathrm{d}G_m^{\text{state}} = V_m^{\text{state}}\mathrm{d}p - S_m^{\text{state}}\mathrm{d}T$$

where the subscript m means that this is for one mole of a substance and the superscript state is either vap or liq. Equating this for vapour and liquid gives

$$V_m^{\text{vap}}\mathrm{d}p - S_m^{\text{vap}}\mathrm{d}T = V_m^{\text{liq}}\mathrm{d}p - S_m^{\text{liq}}\mathrm{d}T$$

$$[V_m^{\text{vap}} - V_m^{\text{liq}}]\mathrm{d}p = [S_m^{\text{vap}} - S_m^{\text{liq}}]\mathrm{d}T$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{S_m^{\text{vap}} - S_m^{\text{liq}}}{V_m^{\text{vap}} - V_m^{\text{liq}}}$$

This is the Clapeyron equation. We can identify that the numerator as $\Delta S_{\text{sys}} = L/T_b$ and the denominator as ΔV_{sys} and we can write this as

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T_b \Delta V_{\text{sys}}}$$

While this derivation was for a liquid to solid phase transition this equation works just as well for a solid to liquid phase change. The quantity $\mathrm{d}p/\mathrm{d}T$ is the gradient of the line on phase diagram of pressure against temperature where the two phases in question coexist.

We can make further assumptions to simplify this. The first such assumption is that since the volume of a gas is far greater than the volume of a liquid

$$V_m^{\mathrm{vap}} - V_m^{\mathrm{liq}} \approx V_m^{\mathrm{vap}}$$

We can also assume that the system acts like an ideal gas so

$$V_m^{\mathrm{vap}} = \frac{RT}{p}$$

Substituting this into the Clapeyron equation we get

$$\frac{\mathrm{d}p}{\mathrm{d}T} \approx \frac{\Delta S^{\mathrm{vap}} p}{RT}$$

As before we identify $\Delta S^{\mathrm{vap}} = \Delta H^{\mathrm{vap}}/T = L^{\mathrm{vap}}/T$ to get

$$\frac{\mathrm{d}p}{\mathrm{d}T} \approx \frac{\Delta H^{\mathrm{vap}} p}{RT^2}$$

We can solve this differential equation:

$$\frac{1}{p}\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta H^{\mathrm{vap}}}{RT^2}$$

$$\int_{p_1}^{p_2} \frac{1}{p}\,\mathrm{d}p = \ln\left(\frac{p_2}{p_1}\right) = \int_{T_1}^{T_2} \frac{\Delta H^{\mathrm{vap}}}{RT^2}\,\mathrm{d}T$$

If we assume ΔH^{vap} is constant over the temperature range we get

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H^{\mathrm{vap}}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

8   Van der Waal's Equation

8.1   Phase Boundaries

The critical point (T_c, p_c) is defined as the temperature and pressure at which a supercritical fluid is formed (ie its hot enough that gas and liquid become indistinct). The triple point (T_{tr}, p_{tr}) is defined as the temperature and pressure at which a substance can exist as a solid, liquid and gas at the same time. Supercritical fluids are good solvents.

At temperatures $T \in [T_{tr}, T_c]$ there is an interface between liquid and vapour phases. Vapour can be condensed into a liquid by increasing the pressure or decreasing the temperature (while keeping it greater than T_{tr}). Above the critical pressure and temperature this interface disappears.

An ideal gas has only kinetic energy. We have previously seen that $p \sim n \langle E_K \rangle$, ie the pressure is a measure of kinetic energy density. From the first law of thermodynamics we know

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V \implies p = -\left(\frac{\partial U}{\partial V}\right)_S$$

ie the pressure is the negative of the rate of change of the internal energy as the volume changes at constant entropy. An ideal gas only has kinetic energy so it can't form the intermolecular bonds necessary to condense into a liquid. Real gasses can as they have a potential energy contribution to their internal energy. This accounts for the discrepancy in the values of L_{vap} from the approximation in table 7.1. The potential when measured looks something like the potential in figure 8.1. The minimum potential energy is ϵ.

The Lennard-Jones Potential
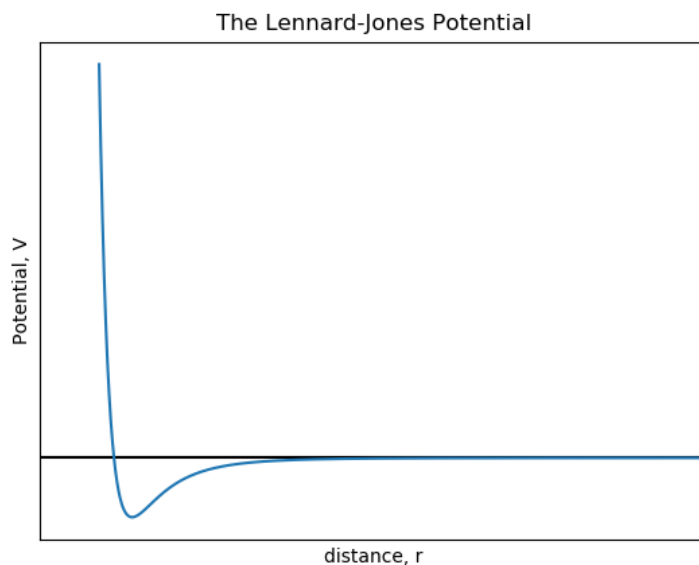
Figure 8.1: The potential energy of a molecule as a function of molecule separation r

8.2 Van der Waal's Equation

We can modify the ideal gas law for one mole:

$$pV = RT$$

to get the van der Waal's equation

$$(p + \frac{a}{V_m^2})(V_m - b) = RT$$

The first term $p + a/V_m^2$ is a modification of the pressure that takes into account the attractive inter molecular forces. The second term $V_m - b$ modifies the volume term to subtract the excluded volume, b, due to the non zero size of the molecules. b is the molar excluded volume. That is the volume in a mole of gas where there can be no other molecules. Figure 8.2 shows the excluded volume of molecule A as the dashed line.
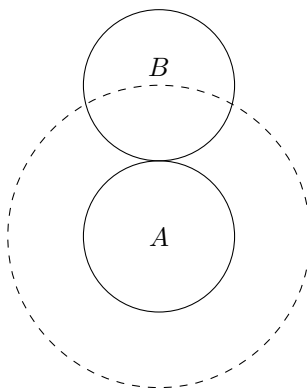
Figure 8.2: The excluded volume of one molecule

The excluded region is everywhere that molecule A makes it impossible for the centre of a molecule to be. Molecule B is as close to molecule A as possible. The exclusion region of a molecule of diameter d is a sphere

of diameter $2d$. The molecular volume is

$$v = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3$$

The volume of the exclusion region is

$$\frac{4}{3}\pi d^3 = 8v$$

This is shared between two molecules as the exclusion regions can overlap. This gives an excluded volume per molecule of $4v$. This gives a molar excluded volume of

$$b = 4N_A v$$

The a/V_m^2 term originates from the potential energy. Each pairwise interaction lowers the internal energy by ϵ. The number of pairwise interactions for each molecule is proportional to the number of moles divided by the volume, n_m/V. The potential energy changes the internal energy of n_m moles by

$$U_{PE} = a n_m \frac{n_m}{V}$$

The internal energy change due to changing the volume of the container is

$$\mathrm{d}U_{PE} = -\frac{a n_m^2}{V^2}\mathrm{d}V$$

We associate this with the effective pressure, p_{eff}. The actual pressure is

$$p = p_{\text{eff}} + p_{\text{ideal}} = p_{\text{eff}} + \frac{RT}{V_m}$$

The last one is for one mole of gas. Rearranging we get

$$\frac{RT}{V_m} = p - p_{\text{eff}} = p + \frac{a}{V_m^2}$$

since $n_m = 1\,\text{mol}$. We then adjust the volume $V_m \to V_m - b$ to take account of the excluded volume and we get

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

We only account for the excluded volume in the first order term as the difference is negligible for the second order term.

8.3   Van der Waal's instability

Figure 8.3 shows the isotherms (lines of constant temperature) of van der Waal's equation. Shown in red is the critical isotherm where the temperature is the critical temperature. Van der Waal's equation is only valid for temperatures above the critical temperature. The reason for this can be seen in the lower temperature isotherms which behave weirdly at lower volumes and also start to increase slightly at higher volumes when they should asymptote zero.

The isothermal compressibility is less than zero for the isotherms a temperature less than the critical temperature. This is because the isothermal compressibility is defined as.

$$B = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

This should always be positive.
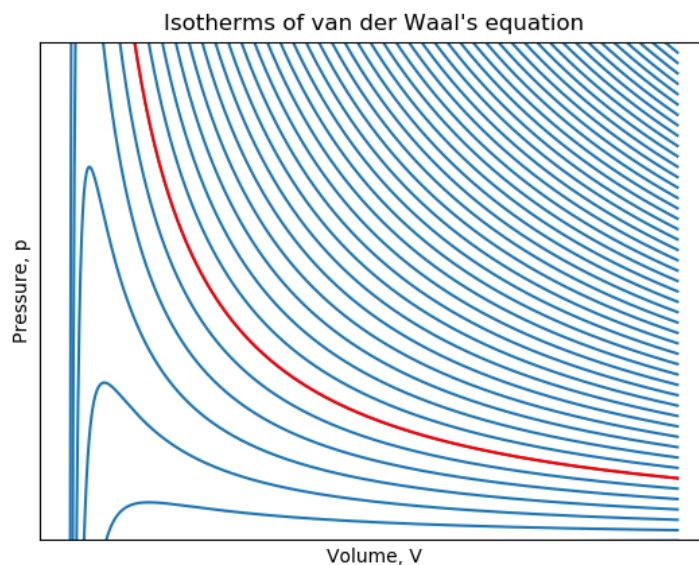
Figure 8.3: Isotherms (lines of constant temperature) of van der Waal's equation. The isotherm in red is the critical isotherm at the critical temperature.

8.4   Maxwell's Construction

What we actually see experimentally is a horizontal line where condensation happens allowing compression without a pressure increase. Over the region where this happens liquid and vapour phases are in equilibrium. This means that the Gibbs free energy $\Delta G = 0$. Recall that

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$$

We define two points B_1 and B_2 which are the edge points of the region where van der Waal's equation predicts that the compressibility is negative. We integrate along the isotherm between these two points. We get

$$G(p_{B_1}, T) = G(p_{B_2}, T) + \int_{B_1}^{B_2} V \, \mathrm{d}p$$

since temperature is constant so $\mathrm{d}T = 0$. For ΔG to be zero we require

$$\int_{B_1}^{B_2} V \, \mathrm{d}p = 0$$

This means that the area above the isotherm and below the line connecting B_1 and B_2 must be the same as the area below the isotherm and above that line. This can in turn be used to find B_1 and B_2.

For temperatures $T < T_c$ the calculated isotherms from van der Waal's equation oscillate and each passes through a minimum and then a maximum. These extrema converge as $T \to T_c$ and coincide at $T = T_c$ (ie a point of inflection). We can find this from van der Waal's equation:

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3} = 0$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4} = 0$$

$$RT = \frac{2a(V-b)^2}{V^3} = \frac{3a(V-b)^3}{V^4}$$

$$\frac{3(V-b)}{V} = 2$$

This is true only at the critical volume V_c. We can substitute this into the second derivative to get

$$T_c = \frac{8a}{27Rb}$$

Substituting T_c and V_c into van der Waal's equation we get the critical pressure

$$p_c = \frac{a}{27b^2}$$

At temperatures $T < T_c$ how much liquid is present depends on how far along the coexistence region V is. The fraction of the sample that is vapour is given by

$$f_{\text{vap}} = \frac{V - V_{\text{liq}}}{V_{\text{vap}} - V_{\text{liq}}}$$

This is known as Lever's rule. As the temperature increases f_{vap} increases and V is a constant. If the number of moles of vapour increases the density of the vapour increases. At the critical temperature the point of inflection in p means that

$$B = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \to \infty$$

The compressibility diverges. This means that there are large fluctuations in the density. This gives rise to critical opalescence where these fluctuations in density cause light to be bounced around a lot and the fluid becomes opaque.

9   Liquids

We can estimate the critical temperature, T_c, using equipartition. We know that

$$\langle E_K \rangle = \frac{3}{2}k_B T$$

At the critical point the kinetic and potential energies sum to zero. The potential energy is $-\epsilon$. Hence

$$\frac{3}{2}k_B T_c \approx \epsilon$$

Often prefactors are dropped in approximations like this giving

$$T_c \approx \frac{\epsilon}{k_B}$$

9.1   Lennard–Jones Potential

The Lennard–Jones potential is a mathematical model for the potential shown in figure 8.1. It gives the potential between two particular molecules It is a function of distance, r, between the molecules. If there are more than two molecules then the total potential due to intermolecular forces is just the sum of the individual potentials between each pair. The Lennard–Jones potential is

$$U_{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

where σ is a constant. The r^{-12} term represents the close range repulsive nature of the potential. The r^{-6} term represents attraction at larger distances. Both terms go to zero at infinity as one would expect.

Compare this to the hard ball model potential where at the molecular diameter the repulsion is infinite and elsewhere it is zero. This is basically the same as the Lennard–Jones model but with only two values allowed. The Lennard–Jones potential is a bit like having slightly squashable balls instead of hard ones.

The r^{-6} long range attractive term comes from the attractive van der Waal's interaction:

$$U(r) = -\frac{C}{r^6} = -\frac{C_{\text{dipole}} + C_{\text{inuction}} + C_{\text{Dispersion}}}{r^6}$$

The first term comes from the average potential of the dipoles as shown in figure 9.1. This term is

$$\langle U \rangle = -\frac{2}{3k_B T} \frac{\mu_1^2 \mu_2^2}{(4\pi\varepsilon_0)^2 r^6} = -\frac{C_{\text{dipole}}}{r^6}$$

where μ_1 and μ_2 are the dipole moments of the two dipoles. There are two dipoles so the normal factor of r^{-3} is squared. This term is temperature dependent as the temperature effects how easy it is to move to a more favourable condition. The second term appears because of induced dipoles from pre-existing dipoles
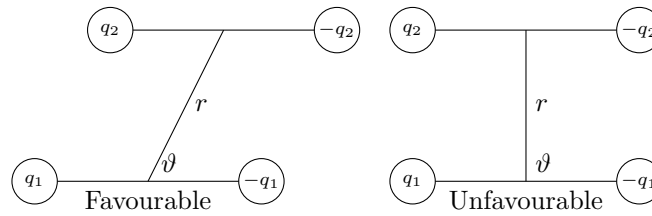
Figure 9.1: Two dipoles in a favourable and unfavourable configuration

like in figure 9.2. This term is

$$U_{\text{ind}}(r) = -\frac{\mu_1^2 \alpha_2}{(4\pi\varepsilon_0)^2 r^6} = -\frac{C_{\text{induction}}}{r^6}$$

where μ_1 is the dipole moment of the dipole and α_2 is a measure of the strength of the induced dipole. The strength of the dipole and the induced dipole both depend on r^{-3} which explains the factor of r^{-6}. The
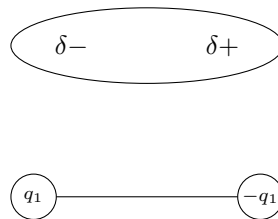
Figure 9.2: Induced dipole

third term comes from the different ways that electron spins and can line up and is given by

$$U_{\text{disp}}(r) = -\frac{3}{4} \frac{\alpha_0^2 I}{(4\pi\varepsilon_r\varepsilon_0)^2 r^6} = -\frac{C_{\text{dispersion}}}{r^6}$$

9.2   Basic Liquid Properties

Liquids exist between the triple and critical points. There is a steep gradient on a pressure–volume diagram for a liquid. This gives rise to a low compressibility:

$$B = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

There is typically a 10 % to 15 % increase in volume on melting. This is not the case for water or silicon because of their tight packing crystal structures as solids. Liquids can't withstand a shear stress. The balance between kinetic and potential energy makes theoretical treatment of liquids challenging. We will treat liquids as a dense gas (ie the molecular separation is approximately the molecular diameter). Liquids have a lower entropy per molecule than a gas. This is because there is *some* molecular level order to a liquid.

9.3   Radial Distribution Function

A radial distribution function is a measure of how many molecules there are at a certain distance from a particular molecule. To construct it we start by picking an arbitrary test molecule. Around this test molecule
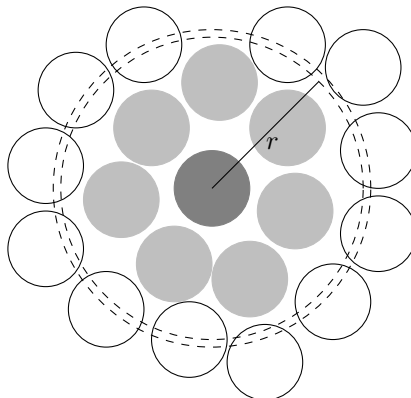
Figure 9.3: Test molecule and spherical shell

we construct a spherical shell of radius r and thickness $\mathrm{d}r$. The volume of this shell is

$$\frac{4}{3}\pi((r+\mathrm{d}r)^3 - r^3) = \frac{4}{3}\pi(r^3 + 3r^2\mathrm{d}r + 3r\mathrm{d}r^2 + \mathrm{d}r^3 - r^3) = 4\pi r^2\mathrm{d}r$$

Where we have disregarded any second order or higher $\mathrm{d}r$ terms. We define the radially averaged number density function, ρ, as a function of r such that for a spherical shell of radius r the number, N, of molecules that intersect the shell is

$$N(r) = \rho(r)4\pi r^2\mathrm{d}r$$

That is $\rho(r)$ gives the number of molecules per unit volume at a distance r from the test molecule. We then define $\langle\rho\rangle$[9] as the average number density over the whole sample. The radial distribution function, g, is then

$$g(r) = \frac{\rho(r)}{\langle\rho\rangle}$$

This means that the number of molecules intersecting the spherical shell of radius r is

$$N(r) = g(r)\langle\rho\rangle\,4\pi r^2\mathrm{d}r$$

N can be measured with x-ray or neutron scattering. Due to the finite size of the molecules $\rho(r) = 0$ for $r < d$ the molecular diameter since we don't count the test molecule and no molecules can be inside the test molecule. There is then a spike at about d where there is a ring of molecules. There is then another dip and a smaller spike at $2d$. This is because of the local structure where molecules tend to form spherical shells known as coordination shells. At larger distances the number of molecules in the shell tends to a constant amount as there is only local structure in a liquid so $g(r) \to 1$. For an ideal gas we would expect that g is zero for $r < d$ and constant for $r > d$. For a real gas we actually see a peak as there is still some local structure but it very quickly tends to a constant.

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[9]In the notes this is denoted ρ but this is confusing as ρ is already a function so I've decided on a different notation.
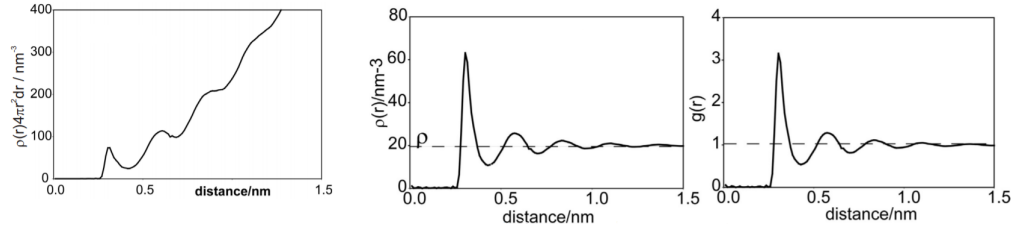
Figure 9.4: N, ρ and g for argon
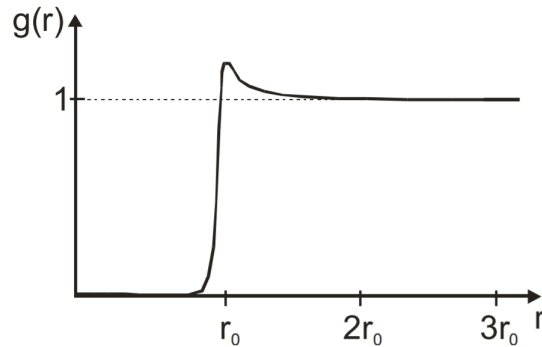
Figure 9.5: g for a real gas

We define the number of nearest neighbours (also known as the coordination number) as

$$\int_0^B N(r)\, \mathrm{d}r = \int_0^B \langle \rho \rangle \, g(r) 4\pi r^2 \, \mathrm{d}r$$

where B is the distance at which the first trough appears. The coordination number is the area under the first peak and is a measure of how many molecules are in the first coordination shell. The interaction energy of the test particle with all other molecules is

$$U' = \int_0^\infty u(r) N(r)\, \mathrm{d}r = \int_0^\infty u(r) \, \langle \rho \rangle \, g(r) 4\pi r^2 \, \mathrm{d}r$$

where $u(r)$ is the pair potential for example Lennard–Jones or the hard sphere potential.

9.4 Interfacial Properties

The surface area to volume ratio for a sphere of radius r is

$$\frac{4\pi r^2}{4\pi r^3 / 3} = \frac{3}{r}$$

This shows that interfaces are important when objects are small (as in measured in µm or nm). The surface free energy, γ, is also the surface tension and is the energy cost to create $1\,\mathrm{m}^2$ of surface. The units are $\mathrm{J\,m}^{-2} = \mathrm{N\,m}^{-1}$. The reason that it takes energy to create surfaces is that in the bulk of the material the potential is lowered by intermolecular interactions. To move a molecule to the surface or remove a layer of molecules to expose a molecule reduces the number of nearest neighbours which increases the potential so work must be done to do this.

In the bulk each molecule has N_{nn} nearest neighbours and each nearest neighbour reduces the energy by ϵ. At the surface the number of nearest neighbours is reduced by ΔN_{nn}. Therefore there is a higher energy than a molecule in the bulk by $\epsilon \Delta N_{nn}$. The number of molecules in an area A is given by A/r_0^2 where r_0 is the side length of the largest cube that can be constructed around a molecule without including other molecules. That is the square with sides r_0 is the area per molecule.

Imagine a column of liquid cut in half to create two surfaces of area A. The total new surface area is $2A$. The total free energy cost to do this is the number of molecules now at the surface times the energy increase due to loss of nearest neighbours. That is

$$\epsilon \frac{A}{r_0^2} \Delta N_{nn}$$

The total free surface energy is the amount γ such that the area created times γ is the energy used to create the surface:

$$2\gamma A = \epsilon \frac{A}{r_0^2} \Delta N_{nn}$$

$$\gamma = \frac{1}{2} \frac{\epsilon}{r_0^2} \Delta N_{nn}$$

We can use this to approximate the latent heat of vaporisation. Supplying energy ϵ separates two molecules. To become a vapour a molecule needs to be separated from all of its nearest neighbours so $\Delta N_{nn} = N_{nn}$. The energy needed to transfer one molecule to the vapour phase is ϵN_{nn}. The energy needed to transfer one mole of molecules to the vapour phase is

$$L_{\text{vap}} = \frac{1}{2} \epsilon N_{nn} N_A$$

The factor of $1/2$ accounts for the fact that each pair potential needs breaking only once not once per molecule involved.

We can approximate r_0^3 as the volume per molecule giving

$$r_0 = \left(\frac{V}{N} \right)^{\frac{1}{3}}$$

where V is the volume and N is the number of molecules. For a liquid with van der Waal's forces $N_{nn} = 12$ this is the most spheres that can touch one sphere all at the same time, known as the kissing number.

Up to now we have considered the surface free energy. We will now show that this is the same as the surface tension. consider a rectangle of width L and initial length L. Applying a force, F, along the length increases it by dx. Increasing the length by dx increases the area by $dA = Ldx$. The work done is $\gamma dA = \gamma Ldx = Fdx$ so $\gamma = F/L$. This is a tension and is in fact the surface tension.

For simple liquids $\gamma \sim 30\,\text{mJ}\,\text{m}^{-2} - 100\,\text{mJ}\,\text{m}^{-2}$.

10   Wetting Surfaces and Bernoulli

A liquid resting on a solid can do one on the following:

- Wet the surface. Wetting occurs when the liquid forms a film over the surface. The contact angle $\vartheta = 0$.

- Partially wet the surface. Partial wetting occurs when the liquid forms a hemisphere or similar on the surface. The contact angle $\vartheta \in (0, \pi/2)$.

- Non-wetting occurs when the liquid forms a bead on the surface. The contact angle $\vartheta > \pi/2$.

Liquids with low surface free energy wet most solids as the liquid easily spreads out to create a large interfacial area. Liquids with high surface free energies in comparison have a non zero contact angle. The liquid–liquid interactions are preferable over the liquid–solid interactions and the surface tension acts to keep the liquid together rather than spreading out.

10.1   Young's Equation

The three phase contact line is the line where the solid, liquid and gas are in contact. It occurs around the base of a droplet on a solid surface. The surface free energy depends on the two materials at the phase boundary. To increase the area of solid wetted by $\mathrm{d}A$ the surface energy of the solid–liquid interface increases by $\gamma_{SL}\mathrm{d}A$. Like wise the surface energy of the solid–vapour interface decreases by $\gamma_{SV}\mathrm{d}A$. Both of these are due simply to the increase in area of the surface–liquid boundary and the necessary decrease in area of the solid–vapour boundary that is replaced by solid–liquid boundary. Less obviously the area of liquid–vapour boundary increases by $\mathrm{d}A\cos\vartheta$ so the surface energy increases by $\gamma_{LV}\mathrm{d}A\cos\vartheta$. Conserving energy we get

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\vartheta$$

This is Young's equation. We could find the same result by balancing the forces that act due to the surface tension given that the droplet must be at rest.

10.2   Laplace Pressure

Suppose a syringe has a drop of liquid of radius r hanging off the end. The pressure of the liquid in the syringe is p_1. The pressure outside the syringe is p_2. If the piston moves down a distance $\mathrm{d}x$ it does work $\mathrm{d}W = F\mathrm{d}x = (p_1 - p_2)\mathrm{d}V$ where $\mathrm{d}V$ is the change in volume of the droplet. If the radius of the drop increases by $\mathrm{d}r$ then

$$\mathrm{d}V = \frac{4}{3}\pi((r + \mathrm{d}r)^3 - r^3) = \frac{4}{3}\pi(r^3 + 3r^2\mathrm{d}r + 3r\mathrm{d}r^2 + \mathrm{d}r^3 - r^3) \approx 4\pi r^2\mathrm{d}r$$

Neglecting $\mathrm{d}r$ terms raised to powers greater than 1. The surface area increases by

$$\mathrm{d}A = 4\pi((r + \mathrm{d}r)^2 - r^2) = 4\pi(r^2 + 2r\mathrm{d}r + \mathrm{d}r^2 - r^2) \approx 8\pi r\mathrm{d}r$$

The increase in surface energy must be equal to the work done:

$$\mathrm{d}W = (p_1 - p_2)\mathrm{d}V = 4\pi r^2\mathrm{d}r(p_1 - p_2) = \gamma\mathrm{d}A = 8\pi r\mathrm{d}r\gamma$$

$$r(p_1 - p_2) = 2\gamma$$

$$p_1 - p_2 = \frac{2\gamma}{r}$$

This is called the Laplace pressure.

We can do something similar for a bubble. p_0 is the pressure outside the bubble and p_{bubble} is the pressure in the bubble. Since there are two interfaces we get an extra factor of two:

$$p_{\text{bubble}} - p_0 = \frac{4\gamma}{r}$$

If a surface isn't spherical then we can identify two principle radii of curvature, R_1 and R_2. The Laplace pressure is then

$$p_1 - p_2 = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

In the case of a sphere $R_1 = R_2 = r$ and this reduces to $2\gamma/r$ as expected. Two parallel plates are a distance $2R_1$ apart. The gap is partially filled with liquid. The liquid naturally sits in a u shape extending along the length of the plates. The first radius of curvature is perpendicular to the plates and has radius R_1. The second radius of curvature is parallel to the plates and has an infinite radius of curvature (ie there is no curvature). This gives $p_1 - p_2 = \gamma/R_1$. As the plates become further apart $R_1 \to \infty$ and the surface becomes flatter and flatter. Eventually there is no curvature and hence no pressure difference.

10.3   Capillary Rise

Dip a narrow tube of radius R into a liquid which wets the tube. This means that the contact angle $\vartheta = 0$. This must be true all around the tube so a cross section along the tube will have a U shaped liquid–vapour interface. This is known as a meniscus. The radius of curvature of the meniscus will be R. The Laplace pressure will be

$$p_A - p_B = \frac{2\gamma}{R}$$

where p_A is the pressure in the tube above the liquid and p_B is the pressure in the tube in the liquid. The pressure $p_{A'}$ outside of the tube and liquid at the same height as p_A was measured must be equal to p_A and approximately equal to the pressure just above the surface of the liquid and all of these must be approximately atmospheric pressure.

$$p_C - p_B = h\rho g$$

where h is the height the liquid is drawn up the tube (to the bottom of the meniscus) and ρ is the density of the liquid. Since $p_C = p_A$ we can say

$$p_C - p_B = p_A - p_B \implies \frac{2\gamma}{R} = h\rho g$$

If instead $\vartheta \neq 0$ then the radius of curvature is $R/\cos\vartheta$. Balancing the pressure differences again we get

$$h\rho g = \frac{2\gamma\cos\vartheta}{R}$$

This even holds for $\vartheta > 90°$. For example mercury $\vartheta = 140°$ so $\cos\vartheta < 0$. This agrees with what we see which is that the mercury is actually pushed down by the tube rather than being drawn up.

10.4   Surfactants

Water has a high surface tension of $\gamma = 72\,\mathrm{N\,m^{-1}}$. Surfactants are molecules that absorb at interfaces lowering the surface tension. For example in our lungs there are surfactants in the alveoli. Normally $\gamma = 50\,\mathrm{N\,m^{-1}}$ and $R \sim 10^{-4}\,\mathrm{m}$. The required pressure difference to inflate the lungs against surface tension is then $p_1 - p_2 = 2\gamma/R = 500\,\mathrm{Pa}$. This is very big. With surfactants $\gamma = 3\,\mathrm{N\,m^{-1}}$. This reduces the required pressure difference to $30\,\mathrm{Pa}$. This is much more manageable.

Alcohol is a surfactant for water. This gives rise to the Marangoni effect where wine near the edge of the glass is drawn upwards in the meniscus and due to the increased surface area more alcohol evaporates from this part of the wine so the surface tension increases pulling the wine upwards leading to "tears" on the wine glass.

10.5   Fluid Dynamics

Motion of real fluids is very complicated. We simplify it by considering two schema:

- Only steady flow with no viscous forces (high Reynold's numbers)
- Only steady flow with no inertial forces (low Reynold's numbers)

We will simplify further by only considering ideal fluids. An ideal fluid will in static conditions only undergo steady flow, that is the velocity at a point is constant, ie there is no acceleration at a point (there is still acceleration between points). It is also incompressible, that is the density, ρ is constant. The fluid is also non–viscous so there are no viscous losses of energy. The flow is irrotational. These properties are necessary for us to be able to use conservation of mass and energy.

A streamline is the trajectory followed by a tracer particle. It is the path taken by a fluid element. Streamlines can't intersect as the velocity is tangent to the streamline so if two intersected it would imply that a fluid element had two different velocities. In steady flow streamlines don't move. A stream tube is an imaginary tube with stream lines at the boundary. Since streamlines can't intersect all fluid in a stream tube remains in the stream tube.

10.6   Continuity Equation

If we apply conservation of mass we get the continuity equation. The cross sectional area of a stream tube has the values A_1 and A_2 at two points. The velocity at these two points is v_1 and v_2 respectively. The volume of fluid through one of these surfaces in time Δt is given by $v_1 A_1 \Delta t$ and $v_2 A_2 \Delta t$ respectively. The mass of fluid through one of these surfaces is then $\rho_1 v_1 A_1 \Delta t$ and $\rho_2 v_2 A_2 \Delta t$. These values must be the same by conservation of mass. Also for an ideal fluid $\rho_1 = \rho_2$ is constant so

$$v_1 A_1 = v_2 A_2$$

This is the continuity equation. For this to hold everywhere along the stream tube we require that in general $v \propto 1/A$.

10.7   Bernoulli's Equation

Bernoulli's equation is a statement of conservation of energy per unit mass of fluid. It only applies if there are no sources or sinks of fluid or energy. We start with the same stream tube as from the last section. The work done on the system as fluid enters through A_1 is

$$W_1 = p_1 A_1 \Delta v_1 \Delta t = p_1 \frac{\Delta M}{\rho}$$

since $p_1 A_1$ is the force it imparts and $\Delta v_1 \Delta t$ is the distance it moves the system. Likewise the work done on the system as fluid exits through A_2 is

$$W_2 = p_2 A_2 \Delta v_2 \Delta t = p_2 \frac{\Delta M}{\rho}$$

The net work done is $W_1 - W_2$ and is the change in energy between 1 and 2.

$$W_1 - W_2 = p_1 \frac{\Delta M}{\rho} - p_2 \frac{\Delta M}{\rho} = \frac{1}{2} \Delta M v_2^2 - \frac{1}{2} \Delta M v_1^2 + \Delta M \varphi_2 - \Delta M \varphi_1$$

The first two terms account for change in kinetic energy and the second two for change in potential energy. Barring a few weird cases where there is some other potential the potential in question is gravitational and $\varphi_1 = gh_1$ and $\varphi_2 = gh_2$ where h_1 and h_2 are the heights of the points 1 and 2 respectively. This can be rearranged to give

$$\frac{p_1}{\rho} + \frac{v_1^2}{2} + \varphi_1 = \frac{p_2}{\rho} + \frac{v_2^2}{2} + \varphi_2 = \text{const}$$

This is Bernoulli's equation.

Example 10.1
A tank with $z = 0$ defined as the start height of the water has a hole at $z = -h$. What is the velocity v_{out} at which the water flows out of the tank?

The pressure everywhere is the same and equal to atmospheric pressure. The velocity at the top of the tank is zero for a sufficiently large tank. The output velocity is v_{out}. $\varphi_1 = 0$ and $\varphi_2 = -gh$. This gives

$$\frac{p_{\text{atm}}}{\rho} = \frac{p_{\text{atm}}}{\rho} + \frac{v_{\text{out}}^2}{2} - gh$$

$$v_{\text{out}} = \sqrt{2gh}$$

This is the same as the velocity of an object that has fallen through a distance h. The liquid loses potential energy but gains kinetic energy.

10.8   Viscosity

Viscosity characterises resistance to flow. In a viscous fluid kinetic energy is turned into heat. Viscosity characterises to what level the shear forces in the fluid are important. Consider two planes parallel to each other with a fluid between. The top plane moves at a speed, v, relative to the bottom plane. This results in a velocity gradient in the fluid. The planes exert a shear force on the fluid. This shear force is proportional to the shear rate which is the velocity gradient.

$$\frac{F}{A} = \eta \frac{\mathrm{d}v}{\mathrm{d}y}$$

where v is the velocity of the fluid, F is the force moving the top plate and A is the area of the plates.
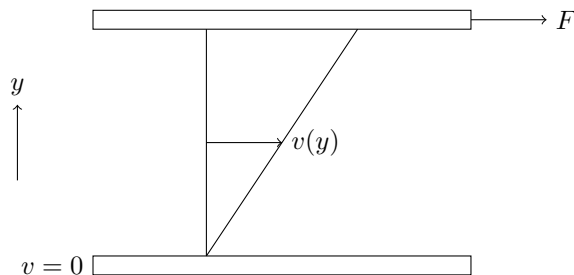
Part II

Solids

11   Pair Potentials

Any two atoms experience a pair potential. Wherever this pair potential is at a minimum the atoms are in a stable configuration. One such stable configuration occurs at distances on the order of 10^{-10} m as in chemical bonds. This is the main region of interest for solids. One of the most common pair potential models is the Lennard–Jones potential

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

The equilibrium point, r_0, occurs when the forces balance. The force is given by

$$F = -\frac{\mathrm{d}U}{\mathrm{d}r} = 4\epsilon \left[-12 \frac{\sigma^{12}}{r^{13}} + 6 \frac{\sigma^6}{r^7} \right]$$

$$F(r_0) = 0 \implies r_0 = 2^{1/6}\sigma$$

$$U(r_0) = -\epsilon$$

so the depth of the potential well is ϵ. For argon atoms $\epsilon = 0.01$ eV and $\sigma = 3.4$ Å. So even a low temperature $T \approx 100$ K, or $k_B T \approx \epsilon$ is enough to disrupt bonding. This is seen in the low boiling point of argon at 87 K.

11.1   Ionic Bonding

Ionic bonding is the attraction via electron exchange to produce filled orbitals that then results in oppositely charged particles that attract each other through Coulomb forces. Assuming only one electron is exchanged the attractive Coulomb force has a potential energy of

$$U_C = \pm \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r}$$

where the $\pm$ accounts for the possible pairings of positive and negative charge. There is also a repulsive term determined experimentally as

$$U_R = \frac{A}{r^9}$$

for some constant A. The total potential is then

$$U = U_C + U_R = \pm\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} + \frac{A}{r^9}$$

This system can only be at equilibrium for a negative Coulomb potential, when this is the case the equilibrium position is

$$F = -\frac{\mathrm{d}U}{\mathrm{d}r} = 0$$

$$\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_0^2} - \frac{9A}{r_0^{10}} = 0$$

hence

$$A = \frac{1}{9}\frac{e^2}{4\pi\varepsilon_0}r_0^8$$

$$U = \frac{e^2}{4\pi\varepsilon_0}\left[\pm\frac{1}{r} + \frac{r_0^8}{9r^9}\right]$$

The depth of the potential well for a pair of dissimilar charges is

$$U(r_0) = -\frac{e^2}{4\pi\varepsilon_0}\frac{8}{9}\frac{1}{r_0}$$

This can be written in a form analogous to the Lennard–Jones potential:

$$U = \epsilon^*\left[\pm\left(\frac{\sigma}{r}\right)^1 + \left(\frac{\sigma}{r}\right)^9\right]$$

We find that the minimum occurs at $r_0 = 9^{1/8}\sigma$ and at this distance we get

$$U(r_0) = \epsilon^*\left[9^{-9/8} - 9^{-1/8}\right]$$

giving

$$U = 1.481\epsilon\left[\pm\left(\frac{\sigma}{r}\right)^1 + \left(\frac{\sigma}{r}\right)^9\right] \tag{11.1}$$

where ϵ is the binding energy.

This is an ionic pair potential. For NaCl molecules $\epsilon = 5.32\,\mathrm{eV}$ and $\sigma = 1.83\,\mathrm{Å}$. This is about 500 times stronger bonding energy than between argon molecules.

11.2   Other Bonds

A pair potential like this can only be defined for van der Waal's forces and ionic bonds other types of bond don't have such a nice potential.

Covalent bonds occur when electrons are shared between two or more atoms. Because it relies so heavily on the aim of gaining a full subshell it requires quantum mechanics to explain the potential so is beyond the scope of the course.

Metallic bonding occurs when electrons are denoted to a sea of delocalised electrons which then acts like glue between molecules. Again to find the potential we require quantum mechanics.

Hydrogen bonding occurs when a hydrogen atom forms a covalent bond with a highly electronegative element (O, N, F) and since Hydrogen has only one electron this exposes the nucleus (which is just a proton) which leaves part of the molecule slightly positively charged allowing for a Coulomb potential with another negative molecule. Hydrogen bonds are the reason for water's high surface tension.

11.3   Solid Characteristics

- Exist in a vacuum - solids require no external forces to pack the particles together as the bonds are strong enough to do this themselves. Liquids on the other hand need a pressure greater than that at the triple point to exist.

- Ubiquitous - solids occur in almost all materials at low enough temperatures.

- Strength - solids can withstand a shear stress, unlike fluids.

- Melting and sublimation - the melting and sublimation points of solids depend on the strength of the bonds, stronger bonds will hold together at higher temperatures

- Order - solids, especially crystals, have long range structure.

11.4   Crystals

Apart from a few exceptions the lowest energy state of matter, which is what will form at the lowest temperatures, is a crystalline solid. Diffraction studies show that crystals have long range order; they form a regular array over macroscopic distances. Recall the radial distribution function that was derived for fluids, it also describes solids well but $g(r)$ and $\rho(r)$ will be different to a liquid.

$$\mathrm{d}N(r) = \rho(r)4\pi r^2 \mathrm{d}r = \langle \rho \rangle\, g(r)4\pi r^2 \mathrm{d}r$$

For a solid because of the long range structure $g(r)$ is zero at most values of r and then forms sharp peaks at specific values of r. Where these peaks occur depends on the crystal structure. Since the order is long range $g(r)$ doesn't tend to a particular value as it did for disordered matter.

Crystals are described by a lattice and a basis. A crystal lattice is an infinite grid of identical points representing the repetition of the structure. We will start with the way we describe the lattice. It can be described by three vectors $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ and the angles between them. These three vectors make up a (normally not orthonormal) basis set that spans the lattice. The lattice is then given as the set of all vectors $\boldsymbol{R} = n_1\boldsymbol{a} + n_2\boldsymbol{b} + n_3\boldsymbol{c}$ where $n_i \in \mathbb{Z}$. A unit cell is a what you get if you take the basis vectors as the edges of a volume. Each unit cell contains at least one lattice point. Note that a lattice point can be shared between multiple unit cells. In this case it contributes only part of a lattice point to each. For example the corner of a unit cell is also the corner of seven other unit cells so only contributes 1/8th of a lattice point to each unit cell. A lattice point on the face of a unit cell is in two unit cells so contributes half a lattice point to each.

There can be multiple, equally valid, unit cells (and hence basis vectors) for each crystal structure. It is always possible to find a unit cell that contains exactly one lattice point. This is known as the primitive unit cell. It isn't necessarily useful as it may be less regular than a larger unit cell and so harder to work with. The cells can be described by where in them there are lattice points (other than the corners) and their shapes. For example a lattice point in the centre of a unit cell makes it a body–centred unit cell, one lattice point on the face of the unit cell makes it one–face–centred (note that there will be half a lattice point on one face and half on the opposite face) and one lattice point in the middle of each face makes it face–centred.

The lengths of the basis vectors/edges of the unit cell are a, b and c. Denoting the angle between two vectors $\boldsymbol{x}$ and $\boldsymbol{y}$ as $\boldsymbol{x}\angle\boldsymbol{y}$ we get $\boldsymbol{a}\angle\boldsymbol{b} = \gamma$, $\boldsymbol{a}\angle\boldsymbol{c} = \beta$ and $\boldsymbol{b}\angle\boldsymbol{c} = \alpha$. Combined a, b, c, α, β and γ are known as the lattice parameters or cell dimensions.

The basis of a crystal is a list of all atoms in the unit cell and their positions in terms of the basis vectors. The point $\boldsymbol{P} = x\boldsymbol{a} + y\boldsymbol{b} + z\boldsymbol{c}$ is usually given as (x, y, z). For a simple cubic structure there is one basis point on every single corner. This gives a basis of $(0, 0, 0)$ for the unit cell since each corner of the unit cell is at the origin of one unit cell so we only need to specify that there is an atom at the origin. A body centred basis is the same as simple cubic but with a basis point in the centre so its basis is $(0, 0, 0)$ and $(1/2, 1/2, 1/2)$. One–face–centred has a basis $(0, 0, 0)$ and $(1/2, 1/2, 0)$. Face–centred has a basis $(0, 0, 0)$, $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$ and $(0, 1/2, 1/2)$.

Note that the lattice points all have to have the same type of atom at the corner if there is more than one type of atom.

12   Crystal Structure

12.1   The Seven Unit Cells

There are seven fundamentally different unit cells. They can be distinguished by so the side lengths and angles relate to each other.

- Cubic - $a = b = c$ and $\alpha = \beta = \gamma = 90°$ - It is a cube

- Tetragonal - $a = b \neq c$ and $\alpha = \beta = \gamma = 90°$ - Cube stretched in one direction

- Orthorhombic - $a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$ - Cuboid

- Monoclinic - $a \neq b \neq c$ and $\alpha = \gamma = 90°$ and $\beta \neq 90°$ - Cuboid pushed over

- Hexagonal - $a = b \neq c$ and $\alpha = \beta = 90°$ and $\gamma = 120°$ - Three of these share an edge and the resulting shape has a hexagonal cross section

- Trigonal - $a = b = c$ and $\alpha = \beta = \gamma \neq 120°$ - Cube pushed over

- Triclinic - $a \neq b \neq c$ and all angles different and not $90°$ - as irregular as possible

In this course we are mostly interested in the two simplest, cubic and tetragonal, and the face/body–centred versions of these.
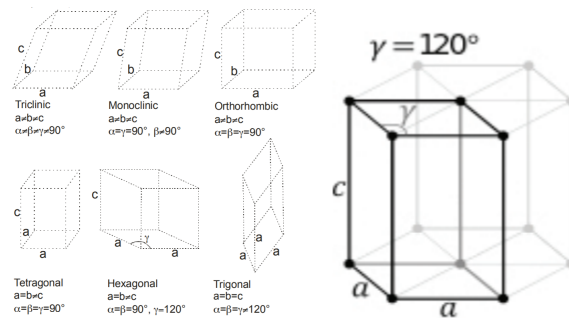
Figure 12.1: The different crystal structures and the reason hexagonal is called hexagonal

12.2   Planes

Planes in a crystal are defined by their Miller indices, (hkl). These planes are actually sets of equally spaced, parallel, planes. To find the Miller indices we take the plane closest to the origin that doesn't contain the origin and we look at where it intercepts the unit cell axes. The plane with Miller indices (hkl) intercepts the x axis at a/h, the y axis at b/k and the z axis at c/l. This value of (hkl) then describes any set of parallel planes to this which are then called the (hkl) planes. If a plane is parallel to an axis then it intercepts that axis at infinity so the corresponding index is 0. If the plane cuts the axis on the negative side of the origin then the relevant Miller index is negative which is usually denoted with a bar such as $(1\bar{1}0)$ is the set of planes parallel to the plane which crosses the x axis at a, the y axis at $-b$ and is parallel to the z axis.

We consider a plane through the origin and the nearest parallel plane. The distance between the planes is $d(hkl)$ often abbreviated d if there is only one set of planes in consideration. Define the angle from the x, y and z axis to the perpendicular to the plane as ψ_1, ψ_2 and ψ_3 respectively. Since the planes are parallel the normal to the planes is the shortest distance between them. We find that

$$d = \frac{a}{h} \cos \psi_1 = \frac{b}{k} \cos \psi_2 = \frac{c}{l} \cos \psi_3$$

In the case where $\alpha = \beta = \gamma = 90°$ we get that

$$\cos^2 \psi_1 + \cos^2 \psi_2 + \cos^2 \psi_3 = 1$$

so

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

for a cubic cell this simplifies to

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \tag{12.1}$$

A set of lattice planes is referred to with brackets as (hkl). When this set is identical to another by virtue of symmetry the two sets are equivalent and belong to a family, referred to using curly brackets as $\{hkl\}$.

The planes parallel to (hkl) on the opposite side of the origin, that is $(\bar{h}\bar{k}\bar{l})$ are always equivalent to (hkl). After this the planes that are equivalent depend on the symmetry of the crystal. For the least symmetric crystal unit cell (triclinic) the only equivalent planes are (hkl) and $(\bar{h}\bar{k}\bar{l})$. For the most symmetric crystal unit cell (cubic) all possible arrangements of h, k and l and their negatives are equivalent so for distinct h, k and l there are 24 equivalent ways to describe (hkl).

Directions in the unit cell are denoted with square brackets as $[hkl]$ for a specific direction or with angle brackets $\langle hkl \rangle$ for a family. For a cubic lattice these are perpendicular to the corresponding planes (hkl) or $\{hkl\}$.

12.3 Counting Particles and Density

The number of particles in a unit cell is given by the sum of the particles partly in the unit cell weighted by how much of the particle is in the unit cell. This means that if a particle is only half in the unit cell it only counts as half a particle. It is often convenient to think of the particles as spheres with the largest radius possible so that they don't overlap. If the number of particles in the unit cell is N_p and the particles have mass M_p and the unit cell has volume V_{UC} then the density of the solid is

$$\rho = \frac{N_p M_p}{V_{UC}}$$

If there is more than one type of particle then this extends to

$$\rho = \frac{1}{V_{UC}} \sum_i N_{pi} M_{pi}$$

where N_{pi} is the number of particles of the ith type of particle and M_{pi} is the mass of the ith type of particle.

12.4 Coordination and Packing

The coordination of a particle is the number of nearest neighbours that it has in a given crystal structure. The nearest neighbours are the particles that are the minimum distance from the particle. In a crystal the coordination of a particle is an integer and the nearest neighbours are at a set distance.

Different crystal structures have different efficiencies when it comes to fitting in particles into a set volume. One measure of efficiency is the packing fraction which is the fraction of space that is occupied by hard spheres of maximum radius in place of the particles. If the volume of the unit cell is V_{UC}, the number of particles in the unit cell is N_p and the volume of one of the hard spheres is V_p then the packing fraction PF is given by

$$PF = \frac{N_p V_p}{V_{UC}}$$

The fraction of open space is then $1 - PF$.

The packing fraction and coordination number are both higher for denser lattices. When maximised the structure is said to be close packed. For a one component crystal face centred cubic lattices are close packed and so are hexagonal close packed lattices. These have a maximum packing fraction of $PF \approx 0.74$ and coordination number of $CN = 12$.

12.5   Typical Crystal Structures

12.5.1   Simple or Primitive Cubic (sc)

One atom at each corner of a cubic lattice. Each atom has coordination number $CN = 6$ and packing fraction $PF = 0.524$.

12.5.2   Body Centred Cubic (bcc)

One atom at each corner of a cubic lattice and one in the centre of the lattice. Each atom has coordination number $CN = 8$ and packing fraction $PF = 0.68$.

12.5.3   Face Centred Cubic (fcc)

One atom at each corner of a cubic lattice and one atom in the centre of each face of the lattice. Each atom has coordination number $CN = 12$ and packing fraction $PF = 0.74$.

The reason that both fcc (also known as cubic close packed) and hexagonal close packed are both close packed is that by moving layers of atoms it is possible to move from one to the other without changing the density.

13   Lattice Energy and Diffraction

We used pair potentials earlier to describe boding effects in a pair of free particles such as a diatomic molecule. For N interacting particles the total potential, U_T, is the sum of the pair potentials $U(r_{ij})$ where r_{ij} is the distance between the ith and j^{th} atoms. Note the factor of $1/2$ that stops double counting:

$$U_T = \frac{1}{2} \sum_{i \neq j} U(r_{ij}) = \sum_{i > j} U(r_{ij})$$

If this is a gas then as it becomes denser or becomes a liquid then the total potential becomes very complicated and would be best defined by a computer simulation. For a crystal however the structure allows for a well defined set of distances for each set of nearest neighbours. Even for an ideal crystal where there is an infinite number of particles since pair potentials generally scale as $1/r^x$ we can often ignore the terms from particles more than a certain distance away.

We expect that U_T will have a solution in the case of an infinite crystal and wit a goal to find it we rewrite U_T as a sum over increasing radial distance about the jth particle with the distance from this particle being denoted r_i and the number of nearest neighbours at this distance being N_i. Then

$$U_T^j = \sum_{i=1}^{\infty} N_i U(r_i)$$

Converting this to a quantity per mole we get the total potential is

$$U_T = \frac{1}{2} \sum_{j=1}^{N_A} U_T^j$$

we get the potential is

$$U_T = \frac{1}{2} N_A \sum_{i=1}^{\infty} N_i U(r_i)$$

where again the factor of $1/2$ stops double counting. This is the lattice energy or lattice potential and the sum is a lattice sum.

13.1 Van der Waals Solid

A van der Waals solid has a pair potential given by the Lennard–Jones potential:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

where the lone pair separation is $r_0 = 1.12\sigma$ and the potential well depth is ϵ. When calculating U_T we can

i	$r_i(a)$	$r_i(r_1)$	N_i
1	$a/\sqrt{2}$	r_1	12
2	a	$r_1\sqrt{2}$	6
3	$a\sqrt{3/2}$	$r_1\sqrt{3}$	24
4	$a\sqrt{2}$	$r_1\sqrt{4}$	12
5	$a\sqrt{5/2}$	$r_1\sqrt{5}$	24
6	$a\sqrt{3}$	$r_1\sqrt{6}$	8
$\vdots$	$\vdots$	$\vdots$	$\vdots$

Table 13.1: The first six nearest neighbours for a face centred cubic crystal. The distance to the nearest neighbour is given in terms of the lattice parameter, a, and the distance to the first nearest neighbour, r_1.

safely assume that the very short range repulsive force is only important for the first nearest neighbour. For the values given in table 13.1 the lattice potential for a fcc crystal is

$$U_T = \frac{N_A}{2} 4\epsilon \left[12 \left(\frac{\sigma}{r_1} \right)^{12} - 12 \left(\frac{\sigma}{r_1} \right)^{6} - 6 \left(\frac{\sigma}{r_1\sqrt{2}} \right)^{6} - 24 \left(\frac{\sigma}{r_1\sqrt{3}} \right)^{6} \right.$$

$$\left. -12 \left(\frac{\sigma}{r_1\sqrt{4}} \right)^{6} - 24 \left(\frac{\sigma}{r_1\sqrt{5}} \right)^{6} - 8 \left(\frac{\sigma}{r_1\sqrt{6}} \right)^{6} - \cdots \right]$$

$$= 2\epsilon N_A \left[12 \left(\frac{\sigma}{r_1} \right)^{12} - \left(\frac{\sigma}{r_1} \right)^{6} (12.0 + 0.750 + 0.888 + 0.188 + 0.192 + 0.037 + \cdots) \right]$$

Noting that the series is rapidly decreasing we ignore further terms to get

$$U_T \lesssim 2\epsilon N_A \left[12 \left(\frac{\sigma}{r_1} \right)^{12} - 14.05 \left(\frac{\sigma}{r_1} \right)^{6} \right]$$

where $\lesssim$ indicates that further terms would reduce U_T but not by much. Evaluating for

$$F = -\frac{\mathrm{d}U}{\mathrm{d}r} = 0$$

we find that the equilibrium first nearest neighbour distance is $r_1 \lesssim 1.09\sigma$ which is about 3% less than the free pair solution of $r_0 = 1.12\sigma$. So we find that condensation to a solid causes bond lengths to contract. Each atom is now feeling the attractive force of more atoms. The depth of the potential well for each ion is $U_T/N_A = 8.2\epsilon$. This is much lower than for the free particle case. This deepening, by a factor of about 12.6, can be attributed almost entirely to the 12 nearest neighbours.

13.2 Ionic Solid

For an ionic solid the potential is different. This is the potential derived in equation 11.1:

$$U(r) = 1.481\epsilon \left[\left(\frac{\sigma}{r} \right)^{9} \pm \left(\frac{\sigma}{r} \right)^{1} \right]$$

i	$r_i(a)$	$r_i(r_1)$	N_i	(C_i)
1	$a/2$	r_1	6	-1
2	$a/\sqrt{2}$	$r_1\sqrt{2}$	12	$+1$
3	$a\sqrt{3/4}$	$r_1\sqrt{3}$	8	-1
4	a	$r_1\sqrt{4}$	6	$+1$
5	$a\sqrt{5/4}$	$r_1\sqrt{5}$	24	-1
6	$a\sqrt{3/2}$	$r_1\sqrt{6}$	24	$+1$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$

Table 13.2: The first six nearest neighbours for a face centred cubic crystal of NaCl. The distance to the nearest neighbour is given in terms of the lattice parameter, a, and the distance to the first nearest neighbour, r_1. (C_i) is the sign of the Coulomb term.

We will consider the case of NaCl which is fcc with a basis of Na^+ at $(0,0,0)$ and Cl^- at $(0.5,0,0)$ and the nearest neighbours given in table 13.2. The lone pair separation is $r_0 = 1.32\sigma$ and the potential well depth is ϵ. Using the same method as before where the $(\sigma/r)^9$ term is only considered for the nearest neighbours we get

$$U_T = \frac{N_A}{2}1.481\epsilon\left[6\left(\frac{\sigma}{r_1}\right)^9 - 6\left(\frac{\sigma}{r_1}\right) + 12\left(\frac{\sigma}{r_1}\right) - 8\left(\frac{\sigma}{r_1}\right) + 6\left(\frac{\sigma}{r_1}\right) - 24\left(\frac{\sigma}{r_1}\right) + 24\left(\frac{\sigma}{r_1}\right) - \cdots\right]$$

$$= 0.741\epsilon N_A\left[6\left(\frac{\sigma}{r_1}\right)^9 + \left(\frac{\sigma}{r_1}\right)(-6 + 8.49 - 4.62 + 3 - 10.73 + 9.79)\right]$$

This series does not seem to converge. Not only does the magnitude of terms not decrease with distance but the alternating positive and negative terms are of equal magnitude so even the sign of the potential can't be determined. This is not surprising as $U \propto 1/r$ and $N \propto r^2$ so the potential contributions to U_T do not dissipate with distance. Lattice sums of ionic substances do in fact converge to known values called the Madelung constants. In the case of NaCl the coefficient of the σ/r term sums to -1.75.

$$U_T = 0.741\epsilon N_A\left[6\left(\frac{\sigma}{r_1}\right)^9 - 1.75\frac{\sigma}{r_1}\right]$$

Again setting $F = 0$ we find that $r_1 = 1.54\sigma$ and $U(r_1) = -1.50\epsilon$ per pair of ions. Hence the potential well has deepened by a factor of 1.5 which is about 50 %. This effect is much smaller than with the van der Waals molecule due to the alternating signs of the Coulomb term. More notably the atomic bond distance increases by a factor of 17 % as the molecules condense to a solid. This is because there is no Coulomb repulsion in the molecule to drive the molecules apart but in the solid there is. This means that for the electrostatic, ionic, case the lattice sum is a non-local quantity and depends on ions a long way away.

13.3   Heat of Vaporisation and Lattice Potentials

When a solid transforms to a gas the potential changes as bonds break and distances increase. This is measured by the latent heat of vaporisation, L_V. It is equivalent to the heat of formation, that is the energy released by condensing a solid from a gas.

A reasonable approximation is that L_V is equivalent to the lattice energy, that is the energy needed to separate all atoms to an infinite distance. This gives

$$L_V \approx U_T$$

This works well for a simple van der Waals solid but for an ionic material we find that $L_V < U_T$. This can be explained if instead of forming a gas of separate ions a gas of NaCl ions is formed giving a potential difference between states of

$$L_V \approx U_T - U(r_0)$$

This is a better result. This means that a NaCl gas is actually a bonded vapour of molecules or clusters.

13.4   X–ray Diffraction

The wavelength of x–rays is $\sim 1\,\text{Å}$. This is of the same order of magnitude as the interplanar distance in crystals. This means that crystals act as a 3D diffraction grating for x–rays. In an optical diffraction experiment the distance between maxima allows for the deduction of the spacing of the slits and the intensity of different orders allows for more information about the structure to be gleaned. Similarly for x–ray diffraction the separation gives the size of the unit cell and the intensity of the different maxima gives the arrangement of atoms within the cell.

In x–ray diffraction incident light will reflect off of parallel planes of atoms and will interfere with other light, mostly destructively, leaving reflection only at particular angles where the light happens to travel an integer number of wavelengths more than the other light. It can be seen from figure 13.1 that the light is in phase
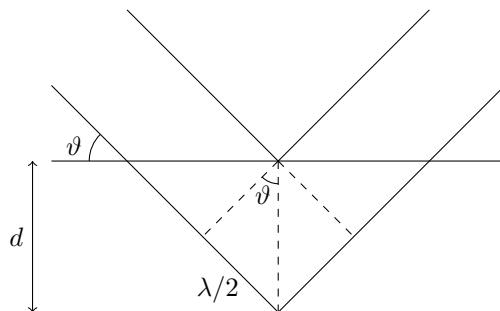
Figure 13.1: X–ray diffraction with constructive interference

when

$$\sin\vartheta = \frac{n(\lambda/2)}{d}$$

where n is a positive integer. Rearranging this gives Bragg's law:

$$n\lambda = 2d\sin\vartheta \tag{13.1}$$

This is the condition for in phase scattering from planes a distance d apart. This depends only on d and λ not on which atoms or where in the plane they are.

We can use the Miller indices, (hkl), of the planes to label the diffraction maxima. In general monochromatic light will not be reflected and either λ or ϑ must be changed until Bragg's law is satisfied. Usually it is easier to change ϑ. A given lattice will have a set diffraction pattern. If we know λ and the diffraction angles then the unit cell dimensions can be deduced. Combining Bragg's law (equation 13.1) and the equation for $d(hkl)$ (equation 12.1) for a cubic lattice we get

$$\sin^2\vartheta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2)$$

assuming first order diffraction so $n = 1$. Plotting $\sin^2\vartheta$ against $h^2 + k^2 + l^2$ will give a straight line of gradient $\lambda^2/4a^2$ for any cubic system. We will see later how the crystal structure also defines the intensities of the different orders.

14   Diffraction Orders

14.1   Higher Order Diffraction

In Bragg's law (equation 13.1) the factor of n determines the order of diffraction. Consider a cubic crystal with lattice parameter a. It is clear from Bragg's law that the lowest diffraction angle corresponds to the largest plane spacing and smallest value of n. This implies that only one of h, k and l is non–zero and equal

to 1 and the other two are zero. This gives $d = a$. This occurs for the $\{100\}$ family of planes. The second order diffraction from (100) occurs at

$$\vartheta = \arcsin\left(2\frac{\lambda}{2a}\right) = \arcsin\left(\frac{\lambda}{a}\right)$$

Now if we consider the (200) planes we get $d(200) = a/2 = d(100)/2$. The angle for first order diffraction from the (200) planes is

$$\vartheta = \arcsin\left(1\frac{\lambda}{2(a/2)}\right) = \arcsin\left(\frac{\lambda}{a}\right)$$

These angles are identical and hence the different maxima from the different planes coincide. For most purposes though we only need to consider the first order diffraction as at higher orders they are much weaker.

14.2   Reflection Intensity

As previously mentioned the reflection intensity can be used to determine the position of atoms in the unit cell. Consider the body centred cubic crystal CsCl. $a = 4.11\,\text{Å}$ and $\lambda = 1.54\,\text{Å}$. Assume

- Negligible amount of incident beam is scattered

- All atoms have the same amplitude of incident light

- Atomic reflecting power is proportional to the number of ions so $Z - n$ for Z^{n+} ions and $Z + n$ for Z^{n-} ions

Cs^+ has $Z = 55$ so has 54 electrons. Cl^- has $Z = 17$ so has 18 electrons.

First we will consider the reflection from the (100) planes. The density of ions in each plane is identical (1 ion per $a^2/2$ area). All of the Cs^+ ions scatter in phase at $\vartheta(100)$ so there is a reflection at this angle. However, all of the Cl^- atoms in the planes between the 100 planes also scatter in phase with each other at $\vartheta(100)$ but since they are directly between the Cs^+ planes this reflection is exactly out of phase so the amplitude, A, of the total reflected beam from the (100) planes is

$$A(100) = (54 - 18) \cdot \text{const}$$

where const is some constant of proportionality. The intensity $I = A^2$ so

$$I(100) = 1296 \cdot \text{const}^2$$

Next we consider the scattering from the (200) planes. Now there is no plane between planes so all scattering at angle $\vartheta(200)$ is in phase so

$$A(200) = (54 + 18) \cdot \text{const}$$

$$I(200) = 5184 \cdot \text{const}^2$$

The same occurs for the (110) planes so they also have

$$I(110) = 5184 \cdot \text{const}^2$$

The (111) planes again have a plane of Cl^- ions between them so scatter out of phase with

$$I(111) = 1296 \cdot \text{const}^2$$

This analysis works well and reproduces the positions exactly and roughly the correct amplitude, it can be improved by noting that const is not the same for all reflections.

14.3   Systematic Absences

Considering a bcc crystal with identical atoms at the centre instead we get that when there is destructive interference since both atoms have the same number of electrons the intensities are now reduced to zero. These are called systematic absences. There are some simple conditions that determine whether a crystal of a certain structure will have a systematic absence for a particular plane. For first order reflection the restrictions on the possible values of h, k and l for there to be no systematic intensity are

- Simple cubic: No restriction on h, k or l

- Body centred cubic: $h + k + l =$ even for non–zero intensity

- Face centred cubic: h, k and l all even or all odd for non–zero intensity

14.4   Experimental Methods of X–ray Diffraction

Note that if an angle is measured relative to the path the x–ray would have taken if not for the crystal (as it almost always is) then the angle measured is 2ϑ. A detector of some sort is placed behind the crystal. Commonly a CCD is used now but in the past film or even and image plate would have been used.

14.4.1   Rotation Method

A single crystal is exposed to collimated, monochromatic x–rays. Initially no diffraction is expected as it is unlikely that Bragg's law will be satisfied. The crystal is rotated about a fixed axis perpendicular to the beam of x–rays until diffraction occurs. This is done to find as many diffraction angles as needed.

14.4.2   Powder Method

A powder of the crystal is placed in a collimated, monochromatic beam of x–rays. Since the powder contains crystals of all orientations diffraction will occur and causes a set of rings to appear. Integrating the intensity around the rings gives the total intensity. This method guarantees that all possible diffraction angles are found (although the intensity may be too low to actually use).

14.4.3   Laue Method

White (continuous spectrum) x–rays are used with a single stationary crystal. Each set of planes will satisfy Bragg's law for some wavelength and the resulting diffracted beams generate a pattern. The symmetry of the diffraction pattern reflects the symmetry of the crystal when viewed along the x–ray beam.

14.5   Types of Diffraction

14.5.1   X–ray Diffraction

So far we have only considered x–ray diffraction X–rays scatter from electrons in the atom and the reflecting power of the atom depends on the number of electrons. Traditional x–ray tubes use a Cu or Mo target to produce x–rays and can produce x–rays of wavelength $1.54\,\text{Å}$ or $0.71\,\text{Å}$ respectively. X–rays can also be obtained from magnetically accelerated electron beams but this requires a lot of equipment (as in a literal particle accelerator).

14.5.2   Neutron Diffraction

We can obtain neutrons with a wavelength $\sim 1\,\text{Å}$. For this we need a neutron with a velocity $\sim 4\,\text{km}\,\text{s}^{-1}$. This is easily produced by a fission reaction. The neutrons scatter off of the nucleus of the atoms. The reflection power does not vary simply with atomic number. It depends heavily on the properties of the nucleus.

15   Vibrating Solids

15.1   Harmonic Oscillators

Vibrations of bonded atoms are important whenever there is a bond in a single molecule or a large crystal. Two particles are joined by a bond with a potential given by the Lennard–Jones potential:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

The equilibrium separation is $r_0 = 2^{1/6}\sigma \approx 1.12\sigma$ which corresponds to the deepest part of the potential well where $U(r_0) = -\varepsilon$.

In reality particles don't just sit at the equilibrium separation. They oscillate around it. Classically any system with non–zero thermal energy must have some vibrational energy. In the quantum view vibrations have some non–zero zero point energy. The potential is almost symmetric near the base of the potential well and as such oscillations of a small amplitude are approximately harmonic. To see this we Taylor expand the Lennard–Jones potential:

$$U(r) = U(r_0) + U'(r_0)(r - r_0) + \frac{U''(r_0)}{2!}(r - r_0)^2 + \frac{U'''(r_0)}{3!}(r - r_0)^3 + \mathcal{O}\left((r - r_0)^4\right)$$

$$U(r_0) = -\epsilon, \qquad U'(r_0) = 0, \qquad U''(r_0) = \frac{4\epsilon}{\sigma}\frac{18}{2^{1/3}}, \qquad U'''(r_0) = -\frac{4\epsilon}{\sigma}\frac{378}{2^{1/2}}$$

$$U(r) = -\epsilon \left[1 - \frac{2^{2/3} \cdot 18}{\sigma^2}(r - r_0)^2 + \frac{2^{1/2} \cdot 126}{\sigma^3}(r - r_0)^3 + \mathcal{O}\left((r - r_0)^4\right) \right]$$

Considering only small displacements and so disregarding higher order terms we get

$$U(r) \approx -\epsilon + \epsilon \frac{2^{2/3} \cdot 18}{\sigma^2}(r - r_0)^2$$

This second order expansion has the same form as a simple harmonic oscillator of potential $u(x)$:

$$u(x) = u_0 + \frac{1}{2}k_{\text{spring}}x^2$$

Where k_{spring} is the "spring constant" and is

$$k_{\text{spring}} = (2^{2/3} \cdot 36)\frac{\epsilon}{\sigma^2}$$

This turns out to be a fairly good approximation. The particle will oscillate at angular frequency

$$\omega = \sqrt{\frac{k_{\text{spring}}}{m}}$$

where m is the mass of the particle. For the Lennard–Jones potential we get

$$\omega = \frac{2^{1/3} \cdot 6}{\sigma}\sqrt{\frac{\epsilon}{m}}$$

For argon with $m = 40\,\text{amu}$ this gives $\omega = 3.45 \times 10^{12}\,\text{rad s}^{-1}$ so the atom oscillates at $f = \omega/2\pi = 5.5 \times 10^{11}\,\text{s}^{-1} = 0.55\,\text{THz}$ and has period $T = 1/f = 1.8 \times 10^{-12}\,\text{s} = 1.8\,\text{ps}$. This is actually relatively slow compared to other materials with stronger bonding, note that f scales as $\sqrt{\epsilon}$.

15.2   Heat Capacity of Solids

Bonds in the solid state can execute nearly harmonic motion in the form of vibrations. These vibrations carry thermal energy and as such will contribute to its heat capacity. Recall that for an ideal gas at constant volume:

- Monatomic gases have 3 degrees of freedom from translations in three directions so have a heat capacity of
$$C_V = 3 \cdot \frac{1}{2}R = \frac{3}{2}R$$

- Diatomic gases have, in addition to the translational degrees of freedom:

  - 2 rotational degrees of freedom for orthogonal rotations to the bond axis. Each contributes
    $$2 \cdot \frac{1}{2}R = R$$
    for a total heat capacity of
    $$C_V = \frac{3}{2}R + R = \frac{5}{2}R$$

  - 1 vibrational degree of freedom with a potential and kinetic quadratic mode contributing
    $$2 \cdot \frac{1}{2}R = R$$
    for a total heat capacity of
    $$C_V = \frac{3}{2} + R + R = \frac{7}{2}R$$

- The temperature must be sufficiently high for these degrees of freedom to be accessible.

This is all for a gas, but what about a solid? In a solid the particles aren't free to move about, instead they are confined by their position in the lattice, this is like being enclosed in a small box. Hence translational degrees of freedom are not available. Bonds between particles in the crystal can't rotate so rotational degrees of freedom aren't free. Particles can vibrate and as such only vibrational modes are available. Vibration can occur in any three orthogonal directions and each direction has a kinetic and potential quadratic mode.

15.3   Classical Picture of Solid Heat Capacity

Consider a simple cubic crystal. Each atom is bonded to its 6 nearest neighbours. Each bond can be approximated as a harmonic potential. We can model this as each particle being suspended by 6 springs running along the positive and negative coordinate axes. For now we will ignore the fact that the vibrational modes are quantised and assume we are at a high enough temperature that they are all available. For each particle in the lattice there are three independent harmonic oscillators in the x, y and z directions having energy similar to
$$u_x = \frac{1}{2}k(x - x_0)^2 + \frac{1}{2}mv_x^2$$

And an average energy given by
$$\langle u_x \rangle = \frac{1}{2}k \left\langle (x - x_0)^2 \right\rangle + \frac{1}{2}m \left\langle v_x^2 \right\rangle$$

Each degree of freedom then contributes $0.5R$ to the heat capacity so the heat capacity is
$$C_V = 6 \cdot \frac{1}{2}R = 3R = 24.94 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1}$$

This was first observed experimentally by Dulong and Petit and is referred to as the law of Dulong and Petit. However it isn't the complete picture. It works well when bonds aren't too strong which can be seen in table and only near room temperature. 15.1 This rule is also known as the Dulong Petit limit as $C_V = 3R$ is the limiting value reached at high temperatures. This is due to the quantum nature of the vibrational degrees of freedom and the fact that stronger bonds have higher values of k and therefore are further apart so not available until a higher temperature is reached.

Material	C_V/R
Copper	2.92
Aluminium	2.82
Gold	3.03
Lead	3.21
Iron	2.98
Sodium	3.32
NaCl	2.96
Silicon	2.62
Diamond	0.60

Table 15.1: The value of C_V/R for some common materials at $300\,\mathrm{K}$

15.4   Quantum Picture of Solid Heat Capacity

Like molecular vibrations lattice vibrational energies are quantised. The difference between energy levels is comparable to thermal energies. We start with a quantum harmonic oscillator with energy

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

where $n = 0, 1, 2, \ldots$ The energy needed to excite the system from its ground state ($n = 0$, $\epsilon_0 = 0.5\hbar\omega$) is $\hbar\omega$. Hence thermal energies must be of a similar order so $k_B T \sim \hbar\omega$ to allow for excitation into higher vibrational states. Recall in section 15.1 the angular frequency for argon was found to be $\omega = 3.45 \times 10^{12}\,\mathrm{rad\,s^{-1}}$ so the temperature at which a significant population of excited vibrational modes is possible is

$$T \sim \frac{\hbar\omega}{k_B} = 165\,\mathrm{K}$$

Below this temperature excited vibrational modes are mostly unavailable. The boiling point of argon at atmospheric pressure is $83\,\mathrm{K}$ so argon doesn't normally reach this Dulong Petit limit unless the pressure is much greater than atmospheric pressure.

At sufficiently low temperatures we expect that no vibrational degrees of freedom are available and as such the heat capacity drops to zero. This same behaviour does not occur for an ideal gas which always has translational degrees of freedom since these are classical and always available.

15.5   Einstein Model

A simple and empirically successful model to track the occupation of excited vibrational modes is the Einstein Model. Consider the energy of a simple harmonic oscillator in one dimension:

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

We redefine energy levels as the energy above the zero point energy of $0.5\hbar\omega$ so

$$\epsilon_n = n\hbar\omega$$

we will add the zero point energy back in later. We can use the Boltzmann factor to describe the spread over the different states at a specific temperature:

$$N_n = A\exp\left(-\frac{\epsilon_n}{k_B T}\right) = A\exp\left(-\frac{n\hbar\omega}{T}\right) = A\exp(-n\chi)$$

where $\chi = \hbar\omega/k_B T$. To determine the value of the constant A we require that the total number of states across all atoms is equal to the number of oscillators, N:

$$N = \sum_{n=0}^{\infty} N_n = \sum_{n=0}^{\infty} Ae^{-n\chi}$$

Some useful exponential series rules here are

$$\sum_{n=1}^{\infty} e^{-kz} = \frac{1}{e^z - 1}, \qquad \sum_{n=0}^{0} e^{-kz} = e^0 = 1$$

$$N = \sum_{n=0}^{\infty} Ae^{-n\chi} = \sum_{n=1}^{\infty} Ae^{-n\chi} + \sum_{n=0}^{0} Ae^{-n\chi}$$

$$= \frac{1}{e^\chi - 1} + 1 = \frac{1}{e^\chi - 1} + \frac{e^\chi - 1}{e^\chi - 1} = \frac{1 + e^\chi - 1}{e^\chi - 1} = \frac{e^\chi}{e^\chi - 1} = \frac{1}{1 - e^{-\chi}}$$

Rearranging we get

$$A = N(1 - e^{-\chi})$$

So the number of atoms in the nth state is

$$N_n = N(1 - e^{-\chi})e^{-n\chi}$$

The total energy for vibrations summed over all particles is

$$U = \sum_{n=0}^{\infty} N_n \epsilon_n = \sum_{n=1}^{\infty} \left[N(1 - e^{-\chi})e^{-n\chi} n\hbar\omega \right]$$

Note that the sum starts as $n = 0$ but after substitution is from $n = 1$. This is allowed as $\epsilon_0 = 0$ since we took this as the base energy for all others. Considering a molar amount and that there are three independent dimensions we get $N = 3N_A$ and

$$U = 3N_A \sum_{n=1}^{\infty} \left[n\hbar\omega(1 - e^{-\chi})e^{-n\chi} \right]$$

This sum can be simplified:

$$U = 3N_A \sum_{n=1}^{\infty} \left[n\hbar\omega(1 - e^{-\chi})e^{-n\chi} \right]$$

$$= 3N_A\hbar\omega \sum_{n=1}^{\infty} \left[ne^{-n\chi} - ne^{-\chi}e^{-n\chi} \right]$$

$$= 3N_A\hbar\omega \sum_{n=1}^{\infty} \left[ne^{-n\chi} - ne^{-(n+1)\chi} \right]$$

$$= 3N_A\hbar\omega \sum_{n=1}^{\infty} \left[ne^{-n\chi} - ne^{-(n+1)\chi} - e^{-(n+1)\chi} + e^{-(n+1)\chi} \right]$$

$$= 3N_A\hbar\omega \sum_{n=1}^{\infty} \left[ne^{-n\chi} - (n+1)e^{-(n+1)\chi} + e^{-(n+1)\chi} \right]$$

$$= 3N_A\hbar\omega \left[\sum_{n=1}^{\infty} ne^{-n\chi} - \sum_{n=2}^{\infty} ne^{-n\chi} + \sum_{n=2}^{\infty} e^{-n\chi} \right]$$

$$= 3N_A\hbar\omega \left[e^{-\chi} + \sum_{n=2}^{\infty} ne^{-n\chi} - \sum_{n=2}^{\infty} ne^{-n\chi} + \sum_{n=2}^{\infty} e^{-n\chi} \right]$$

$$= 3N_A\hbar\omega \left[e^{-\chi} + \sum_{n=2}^{\infty} e^{-n\chi} \right]$$

$$= 3N_A\hbar\omega \sum_{n=1}^{\infty} e^{-n\chi}$$

Which using the rules for sums of exponentials from before is

$$U = \frac{3N_A \hbar \omega}{e^\chi - 1} = \frac{3N_A \hbar \omega}{\exp(\hbar\omega/k_B T) - 1}$$

Finally we add the zero point energy back as a constant shift for all of the $3N_A$ nodes:

$$U = 3N_A \hbar \omega \left[\frac{1}{2} + \frac{1}{\exp(\hbar\omega/k_B T) - 1} \right]$$

The heat capacity at constant volume is

$$\begin{aligned}
C_V &= \left(\frac{\partial U}{\partial T} \right)_V \\
&= \frac{\hbar\omega \exp(\hbar\omega/k_B T)}{k_B T^2} \frac{3N_A \hbar \omega}{[\exp(\hbar\omega/k_B T) - 1]^2} \\
&= 3N_A k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp(\hbar\omega/k_B T)}{[\exp(\hbar\omega/k_B T) - 1]^2} \\
&= 3R \left(\frac{\vartheta_E}{T} \right)^2 \frac{\exp(\vartheta_E/T)}{[\exp(\vartheta_E/T) - 1]^2}
\end{aligned}$$

Where we have used the fact that $N_A k_B = R$ and defined the Einstein temperature $\vartheta_E = \hbar\omega/k_B$. This is the Einstein Model for specific heat. This form of the Einstein temperature is the same as the order of magnitude estimate for the temperature at which excited states are populated in a quantum harmonic oscillator.

At high temperatures

$$\exp\left(\frac{\hbar\omega}{k_B T} \right) \approx 1 + \frac{\hbar\omega}{k_B T} = 1 + \frac{\vartheta_E}{T}$$

so the Einstein model reduces to

$$C_V \approx 3R \left(\frac{\vartheta_E}{T} \right)^2 \frac{1 + \vartheta_E/T}{(\vartheta_E/T)^2} = 3R \left(1 + \frac{\vartheta_E}{T} \right)$$

$$C_V \approx 3R$$

assuming that the ϑ_E/T term is negligible. This agrees with the earlier analysis that lead to the Dulong Petit law. The Einstein model works well at high temperatures but at low temperatures requires a fix given in the Debye model for heat capacity.

16   Debye Model for Heat Capacity

So far we have assumed that the lattice is fixed apart from one molecule which is oscillating. In reality all molecules are oscillating and we need to consider these coupled oscillations to get a full picture. We consider phonons which are the wave-like collective vibrations of the whole lattice. In the Debye model the phonons are treated as standing waves or normal modes of the lattice but it is possible to treat them as a particle as well. The Debye phonons have a range of frequencies. The lower the frequency the longer the length scale over which the phonon needs to be considered. The Einstein Model can be thought of as only dealing with high frequency phonons and hence only close by oscillation. As temperature is lowered the high frequency modes become unavailable so the low frequency modes are more populated which is why the Einstein model fails at low temperatures.

By considering lower frequency modes the Debye model makes a higher prediction for lower temperatures than the Einstein model does. The Debye model is

$$C_V = 9R \left(\frac{T}{\vartheta_D} \right)^3 \int_0^{\vartheta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} \, dx$$

where ϑ_D is the Debye frequency. The integral does not have a closed form solution. ϑ_D is analogous to ϑ_E and indeed, they usually have similar values. We can also define the Debye frequency $\omega_D = k_B \vartheta_D / \hbar$. This represents the maximum phonon frequency of the lattice.

The Debye model is so accurate that ϑ_D is considered a fundamental material constant. Because it characterises the vibrational properties of the material it is useful for more than just specifying heat capacities. For example it can be seen that the higher the value of ϑ_D (or ϑ_E) the stronger the bonds are. For example for lead $\vartheta_D = 88\,\mathrm{K}$ and for diamond $\vartheta_D = 1860\,\mathrm{K}$. This corresponds to the fact that lead is much softer than diamond.

Even the Debye model still makes assumptions about the behaviour of phonons. In the Einstein model it is assumed that all phonons are oscillating at frequency ω. The Debye model assumes that all phonons are oscillating at less than ω_D and are distributed with more at higher temperature increasing smoothly. The more advanced density functional theory uses the density of states to give a more accurate prediction based on which states are filled. For most cases the Debye model is more than good enough.

16.1   Solid Heat Capacity at constant Pressure

So far we have only dealt with heat capacity at a constant volume for solids and like gases the heat capacity at a constant pressure is different. In practice the heat capacity at constant pressure is best determined empirically. It is often assumed for solids that C_p and C_V are approximately the same. The heat capacity at constant volume *and* pressure is

$$C_{V,p} = \left(\frac{\partial Q}{\partial T}\right)_{V,p}$$

$$\mathrm{d}U = \mathrm{d}Q + \mathrm{d}W$$

$$\mathrm{d}Q = \mathrm{d}U + p\,\mathrm{d}V$$

Internal energy, U, is usually specified by the thermodynamic variables T and V.

$$U = U(T, V)$$

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

$$\mathrm{d}Q = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \mathrm{d}V$$

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \left(\frac{\partial V}{\partial T}\right)_p$$

For an ideal gas the internal energy only depends on temperature so we only keep the p as the internal energy is constant with volume so the first term is zero.

$$U = f(t)$$

$$C_p - C_V = p \left(\frac{\partial V}{\partial T}\right)_p$$

$$V = \frac{RT}{p}$$

$$C_p - C_V = R$$

For an ideal, monatomic, gas $C_V = 3R/2$ so

$$\frac{C_p - C_V}{C_V} = \frac{R}{3R/2} = \frac{2}{3} = 67\,\%$$

so the difference between C_p and C_V is significant. For a solid the internal energy depends on temperature and volume so we have to keep both terms.

$$U = f(T, V)$$

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

At finite temperatures $(\partial V/\partial T)_p$ (the thermal expansion) is very small. This means that $C_p - C_V$ is very small so $C_p \approx C_V$.

The reason that C_P is higher than C_V for a gas is that the gas must do work on its surroundings to expand so it can stay at a constant pressure. A solid doesn't need to expand that much when heated to keep a constant pressure and so it doesn't need to do much work on its surroundings.

Alternatively for a solid as $T \to 0$ $C_V \to 0$.

$$dU = T dS - p dV = -p dV$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -p$$

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p = [-p + p]\left(\frac{\partial V}{\partial T}\right)_p = 0$$

The fact that $C_V \to 0$ as $T \to 0$ is a separate, quantum phenomenon.

16.2   Thermal Expansion of Solids

Solids expand as they are heated however in our harmonic approximation while at high temperatures the maximum deviation from the equilibrium position may increase the average position is still the same. How does a solid expand with T if the average bond length doesn't change? The answer is that the interatomic potential is not actually symmetrical as assumed for the harmonic approximation. This means that oscillations aren't entirely harmonic. The Taylor series of the Lennard–Jones potential is

$$U(r) = -\epsilon\left[1 - \frac{2^{2/3} \cdot 18}{\sigma^2}(r - r_0)^2 + \frac{2^{1/2} \cdot 126}{\sigma^3}(r - r_0)^3 + \mathcal{O}\left((r - r_0)^4\right)\right]$$

Before we truncated at the $(r - r_0)^2$ term. If we keep the next term we better reproduce the asymmetry of the potential. This additional term beyond the harmonic term is called the anharmonic term and is proportional to $(r - r_0)^3$. As the vibrational energy increases the mean position of the vibrating bond length will shift to positive r with temperature, away from the "cold" equilibrium position, r_0. So the anharmonic nature of the true potential is the reason for thermal expansion. However since the anharmonic terms are so small the bond length doesn't change by that much so the thermal expansion is small. The thermal expansivity, β, is

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

For an ideal gas

$$V = \frac{RT}{p} \implies \frac{1}{V} = \frac{p}{RT}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} \implies \beta_{\text{gas}} = \frac{p}{RT}\frac{R}{p} = \frac{1}{T}$$

$$\beta_{\text{gas}} = \frac{1}{T} \approx 10^{-2}\,\text{K}^{-1} - 10^{-3}\,\text{K}^{-1}$$

near ambient conditions. For solids

$$\beta_{\text{solid}} \approx 10^{-4}\,\text{K}^{-1} - 10^{-5}\,\text{K}^{-1}$$

so the thermal expansivity of solids is 10 to 1000 times smaller than for a gas.

16.3   Thermal Conductivity of Solids

Energy is transported across crystals by some carrier of energy such as a phonon, electron, photon, etc. For insulators the energy is transported by atomic motion such as vibrations, phonons and sound waves. In the case of metals the free electrons carry the bulk of the thermal energy. For now we consider the case of insulators. If there is a temperature difference between two regions in thermal contact then we know that they will tend toward thermal equilibrium with each other. In fluids mixing and flow make heat transfer a fast but complicated process following fluid dynamic as well as thermodynamic laws. In a solid there can't be mixing or flowing and all heat is spread only by conduction. This is significantly slower but much simpler.

We have a steady state, one dimensional, heat transfer. We can write the heat flux, q, which is the heat flow per unit area as

$$q = \frac{1}{A}\frac{dQ}{dt}$$

where A is the area and dQ/dt is the rate of heat flow. Fourier's law relates this to the gradient:

$$q = -\kappa\frac{dT}{dx}$$

where κ is the thermal conductivity. In the case of non–steady state heat transfer in one dimension the relationship is

$$\frac{\partial T}{\partial t} = D\frac{\partial^2 T}{\partial x^2}$$

This comes from the continuity equation, which in one dimension is

$$\frac{\partial \varphi}{\partial t} = -\frac{\partial q}{\partial x}$$

in this context $d\varphi$ is the energy change per volume:

$$d\varphi = \rho C_p dT$$

Substituting in the expression for q from Fourier's law we get

$$\frac{\partial T}{\partial t} = \frac{\kappa}{\rho C_p}\frac{\partial^2 T}{\partial x^2} = D\frac{\partial^2 T}{\partial x^2}$$

where $D = \kappa/\rho C_p$ is the thermal diffusivity. Looking at the units of D we see

$$[D] = \frac{\text{length}^2}{\text{time}}$$

for an object of size ℓ we may suppose that the cooling time is

$$\tau \sim \frac{\ell^2}{D}$$

Example 16.1
Consider a chicken, which is mostly water ($D = 10^{-7}\,\text{m}^2\,\text{s}^{-1}$), which is $0.2\,\text{m}$ in diameter. The chicken is placed in a hot oven. The time taken for the chicken to reach thermal equilibrium is to an order of magnitude

$$\tau = \frac{(0.1\,\text{m})^2}{10^{-7}\,\text{m}^2\,\text{s}^{-1}} = 100\,000\,\text{s} = 28\,\text{hrs}$$

In reality to cook something we don't need it to reach thermal equilibrium with the oven, rather we have a desired temperature of say 70 °C and an oven of 200 °C. This only takes a few hours to happen. A more accurate estimate can be made by assuming a spherical chicken and solving the time dependent heat equation. This gives a similar amount of time, within a factor of 2 of our answer of 28 hrs, for the time to reach thermal equilibrium.

16.4   Lattice Thermal Conductivity

The thermal conductivity κ is generally a result of three primary microscopic transport processes:

- Conduction by lattice vibrations, known as lattice conduction, has associated thermal conductivity κ_l, this is what we covered above

- Conduction by free electrons, known as electronic conduction, has associated thermal conductivity κ_e, see the section on this later

- Conduction by photons, known as radiative conduction, has associated thermal conductivity κ_r, relevant mainly at high temperatures

The total thermal conductivity is

$$\kappa = \kappa_l + \kappa_e + \kappa_r$$

For an insulator near room temperature this is approximately $\kappa - \kappa_l$. As an analogy to the kinetic theory of gases we can write the thermal conductivity as

$$\kappa = \frac{1}{3} n \langle v \rangle \lambda C_V$$

where n is the number density, v is the velocity of the vibration and λ is the mean free path of the vibration.

Einstein proposed that heat could be transported by a random walk of localised (Einstein) oscillations. We consider the oscillations to transfer there energy every half a period as this is how long it takes to bounce between neighbours. This time is τ_E. From our previous treatment of the Einstein temperature we get

$$\tau_E = \frac{1}{2} \frac{2\pi}{\omega} = \frac{\hbar \pi}{k_B \vartheta_E}$$

We take C_V per atom from the Einstein model:

$$C_V = 3 k_B \frac{x^2 e^x}{(e^x - 1)^2}$$

where $x = \vartheta_E / T$. The scattering length is approximately the distance between atoms which is

$$\lambda = V^{-1/3} = n^{-1/3}$$

Similarly the effective velocity of the atom is

$$v = \frac{\lambda}{\tau_E} = \frac{-1/3}{\tau_E}$$

Combining this we get

$$\kappa = \frac{k_B^2 \vartheta_E}{\hbar \pi} \frac{x^2 e^x}{(e^x - 1)^2} n^{1/3}$$

This works well for amorphous solids where each atom can be thought of as an independent oscillator but for crystals we have already seen that we need to consider phonons across all length scales. For this reason crystals actually transmit heat faster than amorphous solids.

This model can be better fitted to the empirical results for a crystal if we treat v as an elastic wave velocity in the lattice (ie the speed of sound) or as the speed of an acoustic (travelling) phonon. This gives a mean free path larger than the interatomic spacing which shows the need for consideration of large scale vibrations in a crystal.

17   Mechanical Properties of Solids

A stress is a force per unit area (like a pressure but directional). An elastic response to a stress is one with a reversible deformation. An inelastic response is not reversible. Fluids, by definition, have a purely inelastic response to a stress (excluding weird, non–Newtonian fluids). We are only going to consider mechanically isotropic solids here. These are solids where the mechanical properties are independent of the sample orientation. Crystals have intrinsic anisotropic mechanical properties but in the case of multiple small crystals such as in a crystalline solid these tend to cancel.

17.1   Elasticity

For an elastic deformation there is generally an applied stress, σ, causing a resulting strain, ε.[10] These are proportional with the constant of proportionality, C, being called the elastic modulus.

$$\sigma = C\varepsilon$$

σ is a force per unit area and has units of $\mathrm{N\,m^{-2}}$ and ε is a fractional strain and is dimensionless. This means that C has units of $\mathrm{N\,m^{-2}}$. We will consider several common deformations.

17.2   Compressibility: The Bulk Modulus

The simplest deformation occurs when the stress, σ, is the same everywhere. This is known as an isotropic stress (isotropic meaning same everywhere), hydrostatic stress (hydrostatic meaning as if the stress where from submersion in a fluid) or simply a pressure, denoted p. For a small change, ΔV, in the volume, V the stress strain relationship is

$$\Delta p = -K\frac{\Delta}{V}$$

where K is a constant known as the bulk modulus. In differential form this is

$$K = -V\frac{\partial p}{\partial V}$$

Taking the partial derivative under specific conditions such as constant temperature or entropy gives slightly different constants denoted K_T and K_S respectively.

K is an elastic constant but it is also a thermodynamic constant and relates volume and pressure changes. The higher K is the less compressible a material is. The compressibility of a material is B and is given by

$$B = \frac{1}{K}$$

We can estimate K from the lattice potential and the thermodynamic relationship:

$$dU = T dS - p dV$$

Assuming an isothermal process at $T = 0\,\mathrm{K}$ this is

$$dU = -p dV$$

$$-p = \left(\frac{\partial U}{\partial V}\right)_T$$

Hence the bulk modulus at constant temperature is

$$K_T = -V\left(\frac{\partial p}{\partial V}\right)_T = V\left(\frac{\partial^2 U}{\partial V^2}\right)_T$$

---

[10]Both ε, the strain, and ϵ, the binding energy, are being used in this section

This is then evaluated by assuming that $r = V^{1/3}$ so $U(r) = U(V^{1/3})$.

Example 17.1

For NaCl we have the potential per atom of

$$U(r) = 0.741\epsilon \left[6 \left(\frac{\sigma}{r} \right)^9 - 1.75 \left(\frac{\sigma}{r} \right) \right]$$

Hence the potential in terms of volume is

$$U = 0.741\epsilon \left[6\sigma^9 V^{-3} - 1.75\sigma V^{-1/3} \right]$$

$$\left(\frac{\partial U}{\partial V} \right)_T = 0.741\epsilon \left[6(-3)\sigma^9 V^{-4} - 1.75 \left(-\frac{1}{3} \right) \sigma V^{-4/3} \right]$$

$$\left(\frac{\partial^2 U}{\partial V^2} \right)_T = 0.741\epsilon \left[6(-3)(-4)\sigma^9 V^{-5} - 1.75 \left(-\frac{1}{3} \right) \left(-\frac{4}{3} \right) \sigma V^{-7/3} \right]$$

$$= 0.741\epsilon \left[72\sigma^9 V^{-5} - 0.778\sigma V^{-7/3} \right]$$

$$K_T = V \left(\frac{\partial^2 U}{\partial V^2} \right)_T = 0.741\epsilon \left[72\sigma^9 V^{-4} - 0.778\sigma V^{-4/3} \right]$$

This gives K_T as a function of the ionic volume. To find K_T at the equilibrium volume insert the equilibrium value $V = r_1^3$ where $r_1 = 1.54\sigma$ and $\sigma = 1.83\,\text{Å}$.

$$K_T = 0.741\epsilon \left[72 \left(\frac{r_1}{1.54} \right)^9 (r_1)^{-4} - 0.778 \left(\frac{r_1}{1.54} \right) (r_1^3)^{-4/3} \right]$$

$$= 0.741\epsilon [1.47 - 0.505] r_1^{-3}$$

$$= 0.2 \frac{\epsilon}{\sigma^3}$$

$$= 21 \times 10^9 \, \text{Pa} = 21 \, \text{GPa}$$

This is close to the experimental value of $23.8\,\text{GPa}$. Elastic moduli are typically measured in GPa.

According to our model changing the volume of the crystal by applying a stress or changing the temperature will effect the elastic constants of the material.

The bulk modulus increases with compression. In terms of the interatomic potential this is because the repulsive force increases as atoms are forced closer together so it becomes harder to compress the material so the bulk modulus must increase. Integrating the stress strain relationship we ge that to make a certain compression we need a pressure given by

$$p = \int \mathrm{d}p = -\int \frac{K}{V} \, \mathrm{d}V$$

If the volume change is small then we use the linear elastic approximation where K_T is a constant so

$$\Delta p = -K_T \frac{\Delta V}{V}$$

The bulk modulus decreases with expansion as the distance between atoms decreases so the effects of the repulsive term decrease. This effect is called softening. Since increasing temperature causes an expansion the effect of increasing temperature is to soften a material. The limit of this is when the material becomes a liquid or even a gas when it becomes very compressible compared to a solid.

17.3   Young's Modulus

If a force F is applied in one direction to a material with cross sectional area A perpendicular to the force then we call this a uniaxial stress. The force causes the material to extend from a length x by a small amount Δx. Equally it could cause a compression by the same amount and the same maths would hold. The stress strain behaviour is given by Young's modulus, E. For a small deformation

$$\frac{F}{A} = E\frac{\Delta x}{x}$$

Consider an atomic bond parallel to the force. If the bond length before the force is applied is r_0 and it is stretched by x by the force then we can use the harmonic approximation of the potential to describe the deformation:

$$U(x) = U_0 + \frac{1}{2}k(x)^2$$

where for the Lennard–Jones potential the spring constant is

$$k = \frac{\epsilon(2^{2/3} \cdot 36)}{\sigma^2} = \frac{72\epsilon}{r_0^2}$$

The force applied to a spring is equal and opposite to the restoring force so

$$F = -\left(-\frac{\mathrm{d}U}{\mathrm{d}x}\right) = kx$$

The force is applied over an area $A = r_0^2$ assuming a cubic lattice. Hence

$$\sigma = \frac{F}{A} = \frac{kx}{r_0^2}$$

The strain is

$$\varepsilon = \frac{x}{r_0}$$

so the Young's modulus is

$$E = \frac{\sigma}{\varepsilon} = \frac{72\epsilon}{r_0^2}\frac{x}{r_0^2}\frac{r_0}{x} = \frac{72\epsilon}{r_0^3}$$

For argon this gives a value of $E \approx 2\,\mathrm{GPa}$ which compares favourably with experimental values of $E = 2\,\mathrm{GPa} - 3\,\mathrm{GPa}$. If instead we assume a fcc structure then we find that

$$E = \frac{77\epsilon}{r_0^3}$$

which is slightly better.

17.4   Shear Modulus

A stress applied parallel to a surface is called a shear stress. A shear deformation is characterised by the shear modulus, μ. Consider the deformation shown in figure 17.1. If the area of the face parallel to the force
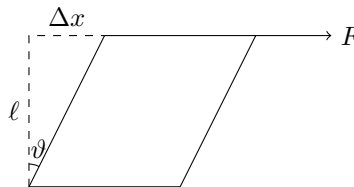

Figure 17.1: Shear stress

is A then

$$\frac{F}{A} = \mu\frac{\Delta x}{\ell} \approx \mu\vartheta$$

using the small angle approximation.

17.5   Poisson's Ratio

Going back to uniaxial stress (as with Young's modulus). If the bar is stretched then there must be contraction in the perpendicular directions. This is characterised by Poisson's ration, ν. Poisson's ratio is the strain perpendicular to the stress divided by the strain parallel to the stress. In the 2D case a stress in the y direction causes a longitudinal strain $\varepsilon_L = y/\Delta y$ where Δy is the expansion in the y direction from initial length y. A the same time the stress also causes a translational stress $\varepsilon_T = \Delta x/x$ where Δx is the contraction along the x direction from the original length x. This gives a Poisson's modulus of

$$\nu = \frac{\varepsilon_T}{\varepsilon_L} = \frac{\Delta x/x}{\Delta y/y} = \frac{y\Delta x}{x\Delta y}$$

In reality things aren't 2D. A cube, side length L, with a stress applied perpendicular to one face extends by a length ΔL along the direction of the stress. The other faces are contracted in by the stress by a distance of $\Delta L'$. Poisson's ratio is

$$\nu = \frac{\Delta L'/L}{\Delta L/L} = \frac{\Delta L'}{\Delta L}$$

For a small deformation the volume gained by the extension is

$$V_{\text{gained}} \approx L^2 \Delta L$$

and the volume lost by the contraction is

$$V_{\text{lost}} \approx 2L^2 \Delta L'$$

note the factor of 2 since there are two perpendicular directions both contracted by $\Delta L'$. The change in volume is then

$$\Delta V = L^2(\Delta L - 2\Delta L')$$

$$\frac{\Delta V}{V} = \frac{\Delta V}{L^3} = \frac{\Delta L - 2\Delta L'}{L} = \frac{\Delta L}{L} - 2\frac{\Delta L'}{L}$$

Note that $\Delta L'/L = \nu \Delta L/L$ giving

$$\frac{\Delta V}{V} = \frac{\Delta L}{L}(1 - 2\nu)$$

There are two extreme cases to consider. First if $\nu = 0.5$ which occurs for a fluid. The fluids volume is conserved as it flows as soon as a stress is applied. Rubber also has $\nu \sim 0.5$ The second is $\nu = 0$ which is generally not found in nature. Cork has $\nu \sim 0$. Most dense solids have $\nu \in [0.2, 0.4]$. Poisson's ratio (unlike the other elastic constants) is dimensionless.

17.6   Independent Elastic Constants

So far we have defined four elastic constants: K, E, μ and ν. These are not all independent. For any elastically isotropic material there are only two independent elastic constants. Any two of the four can be used and the relationships between them are

$$K = \frac{2\mu(1+\nu)}{3(1-2\nu)} = \frac{\mu E}{3(3\mu - E)} \quad = \frac{E}{3(1-2\nu)}$$

$$E = 2\mu(1+\nu) \quad = \frac{9K\mu}{3K+\mu} \quad = 3K(1-2\nu)$$

$$\mu = \frac{E}{2(1+\nu)} \quad = \frac{3K(1-2\nu)}{2(1+\nu)} = \frac{3KE}{9K-E}$$

$$\nu = \frac{E}{2\mu} - 1 \quad = \frac{3K-2\mu}{2(3K+\mu)} \quad = \frac{3K-E}{6K}$$

An anisotropic material may require up to 21 independent elastic constants to characterise its elastic response.

17.7   General Elasticity and Hooke's Law

The above deformations are specific examples of Hooke's law. Hooke's law for a spring is that a deformation x is linearly proportional to the applied force F:

$$F = kx$$

where k is known as the spring constant. This can be generalised for a linear elastic response of solid matter as

$$\sigma = C\varepsilon$$

where σ is a stress, ε is a strain and C is a constant. This can be further generalised by taking ω and ε to be 2-tensors and C to be a 4-tensor. Imposing a basis the stress and strain tensors can be represented as 3×3 matrices. These must be symmetric to ensure that there is no rotation of the element. The diagonal terms of σ represent normal stresses and the off diagonal terms are shear stresses. Likewise the diagonal terms of ε represent contraction and extension whereas the off diagonal terms are shear deformations. Hooke's law is then

$$\sigma_{ij} = -\sum_{k=1}^{3}\sum_{l=1}^{3} C_{ijkl}\varepsilon_{kl}$$

C is a 4-tensor so it is a $3 \times 3 \times 3 \times 3$ array of 81 constants. Symmetry reduces this to 2 constants for an isotropic material, 3 constants for a cubic crystal and 21 for an arbitrary anisotropic material.

We can show that this reduces to the familiar form of Hooke's law in sufficiently nice scenarios. Consider a compression of an isotropic material. This is controlled by the bulk modulus, K. The shear stress and strain are zero so we have

$$\sigma = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix}, \qquad \varepsilon = \begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{22} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix}$$

Since the off diagonal components represent shear stress and strain which are zero. If we further consider this to be an isotropic stress then the stress and strain are the same in all directions and we get[11]

$$\sigma = \begin{pmatrix} p & 0 & 0 \\ 0 & p & 0 \\ 0 & 0 & p \end{pmatrix}, \qquad \varepsilon = \begin{pmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & \varepsilon \end{pmatrix}$$

Hooke's law then gives

$$p = -(C_{1111} + C_{1122} + C_{1133})\varepsilon$$

We can define

$$\varepsilon = \frac{\Delta L}{L} = \frac{1}{3}\frac{\Delta V}{V}$$

$$p = -\frac{1}{3}(C_{1111} + C_{1122} + C_{1133})\varepsilon$$

Comparing this to the definition of K:

$$p = -K\frac{\Delta V}{V} \implies K = \frac{1}{3}(C_{1111} + C_{1122} + C_{1133})$$

It turns out that $C_{1122} = C_{1133}$ for an isotropic material so

$$K = \frac{1}{3}(C_{1111} + 2C_{1122})$$

Often C_{1111} and C_{1122} are shortened to C_{11} and C_{12}. This shows that Hooke's law fully describes elastic deformation. The other elastic constants only apply for specific deformations.

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[11]The fact that ε appears as a component in the tensor ε is an abuse of notation, the components are not the tensor.

17.8 Speed of Sound

Sound waves propagating is an example of elastic behaviour in a solid. Consider the classical wave equation in one dimension:

$$\frac{\partial^2 u}{\partial t^2} = v^2 \frac{\partial^2 u}{\partial x^2}$$

where u is displacement, x is position, t is time and v is the wave speed. For a sound wave we can show that

$$v = \left(\frac{\mathrm{d}p}{\mathrm{d}\rho}\right)^{1/2}$$

where p is the pressure applied in the direction of wave propagation and ρ is the density of the medium. We note a similarity in the definition of v in the wave equation and of K:

$$K = -V\frac{\partial p}{\partial V}$$

Noting that $p = p(V(\rho))$ and $V = V(\rho) = m/\rho$ we take the derivative of p with respect to ρ and we get

$$\frac{\partial p}{\partial \rho} = \frac{\partial p}{\partial V}\frac{\mathrm{d}V}{\mathrm{d}\rho} = -\frac{m}{\rho^2}\frac{\partial p}{\partial V}$$

$$\implies \frac{\partial p}{\partial V} = -\frac{\rho^2}{m}\frac{\partial p}{\partial \rho}$$

$$\implies V\frac{\partial p}{\partial V} = -\frac{m}{\rho}\frac{\rho^2}{m}\frac{\partial p}{\partial \rho} = -\rho\frac{\partial p}{\partial \rho}$$

$$\implies K = \rho\frac{\partial p}{\partial \rho}$$

$$\implies \frac{\partial p}{\partial \rho} = \frac{K}{\rho}$$

assuming the relationship between p and ρ is that of bulk compression we get

$$v_B = \sqrt{\frac{K}{\rho}}$$

where v_B is the bulk sound velocity. This is the sound velocity for a gas and a liquid. It is applicable to fluids as the pressure is the same in all directions.

In a solid the situation is more complex. Solids can support shear stresses as well so the stress in the direction of propagation can be different to the stress in the other directions. One simple case is sound propagating along a thin solid bar with stress applied along the bar only. Here the relationship between p and ρ is described by uniaxial stress and Young's Modulus. It can be shown that the speed of sound in a bar is

$$v_{\mathrm{bar}} = \sqrt{\frac{E}{\rho}}$$

The bar can expand and contract perpendicular to its length. This isn't the case for a bulk solid. For a planar compressional sound wave in a solid the longitudinal speed is

$$v_L = \sqrt{\frac{K + 4\mu/3}{\rho}}$$

Because of the ability for solids to withstand shear stresses (known as having strength) the moduli of elasticity relevant to sound wave propagation must include information about the shear stresses and strains such as

μ or ν. The cases above are only for compression (longitudinal) wave propagation. A solid can also support shear (transverse) wave propagation (a fluid can't). The speed of a pure shear wave in a solid is

$$v_S = \sqrt{\frac{\mu}{\rho}}$$

Liquids, gases and other materials with $\mu = 0$ or $\nu = 0.5$ can't propagate shear waves. In all cases the general form for the speed of sound is

$$v = \sqrt{\frac{\text{elastic modulus}}{\text{density}}}$$

Sound propagation is fast enough that heat conduction has no time to occur so the compression is adiabatic (no heat transfer). In principle we should use adiabatic elastic constants but these are similar to isothermal heat constants for a solid so the error is small.

We can estimate the speed of sound by treating sound propagation as a sequence of atomic vibrations across the solid with each vibrating atom hitting its neighbour to pass on vibration. We can estimate this this speed as the interatomic distance r_0 divided by one quarter of the time period T (one quarter as if both atoms are moving towards each other, as they will be once the vibrations are set up, this is the time it takes for them to reach the mid point between them where they collide).

$$v \approx \frac{4r_0}{T}$$

For example with argon this gives a value of $v = 822\,\text{m}\,\text{s}^{-1}$. The measured speed of sound in liquid argon is $v_B = 813\,\text{m}\,\text{s}^{-1}$. The difference with solids is that shear stresses and the surrounding atoms mean that the atom oscillating back and forth is too simple a model to work.

18 Inelasticity and Electronic Properties

All materials can only withstand so much elastic deformation. At some point the stress on the material becomes so large that it causes an inelastic deformation. This can occur in two ways:

- Fracturing - Bonds are broken and cracks appear
- Plasticity - Atoms slip past each other leading to a permanent deformation

Consider a tensile stress on a bar as with the Young's Modulus. As the bonds are stretched the harmonic approximation breaks down and there is a maximum restoring force where

$$\frac{\mathrm{d}^2 U}{\mathrm{d}r^2} = 0$$

Beyond this point the force decreases again so if the force is equal or more than this maximum restoring force the bar will break and atoms will be moved apart. The critical stress at which this occurs is called the elastic limit or yield strength. For the Lennard–Jones potential the position r_{max} at which the maximum force occurs is $r_{\text{max}} \approx 1.1r_0$ so the breaking strain is $\sim 10\,\%$. In practice imperfections will cause the solid to break when the strain is maybe only $\sim 1\,\%$.

18.1 Beyond the Elastic Limit

Brittle materials such as glass display elastic behaviour up to the elastic limit and then break catastrophically. This is known as fracturing. Ductile materials such as metals display elastic behaviour up to the elastic limit and then at first deform plastically. This means that the material starts to flow. At the level of the lattice what is happening is atoms are moving past each other. The crystal structure is generally maintained and dislocations in the lattice propagate across it and this allows for macroscopic flow. This requires bonds to be broken and made again so can only occur for sufficiently weak bonds. Eventually the stress will be too high and then the material will also break.

18.2   Hardness

Hardness is not well defined alone. A material that can withstand elastic deformation can be thought of as hard but would be better thought of as stiff (having high elastic moduli). A material that has a high elastic limit can also be thought of as hard but is better thought of as strong.

18.3   Electrons in Gases

So far we have considered gases to consist of inert particles. Electrons are important for bonding and particle interactions but are bound to there nucleus. This works well since to remove atoms we need to be at temperatures where $k_B T \sim E_i$ where E_i is the ionisation energy for the ith electron. This is on the order of $1\,\text{eV}$ or $11\,604\,\text{K}$. As a gases temperature is raised to values approaching the ionisation energy free electrons appear in the gas. At high enough temperatures they can be separated entirely from their nucleus. It is also possible to cause ionisation by other stimuli such as electrical discharge as you see with an arc of electricity. The collection of ions and free electrons is called a plasma.

Plasma is another state of matter. Excluding dark matter and the likes plasma is actually the most common form of matter as stars are made of plasma.

An ideal plasma at a thermodynamic equilibrium is similar to an ideal gas.

$$p_{\text{ideal gas}} = \frac{n_i}{V} k_B T$$

where n_i is the number of ions. For a plasma this becomes

$$p_{\text{plasma}} = \left(\frac{n_i}{V} + \frac{n_e}{V} \right) k_B T$$

where n_e is the number of free electrons.

18.4   Free Electron Gas

Consider a gas of only free electrons. At high temperatures this scenario is basically the same as a plasma. At low temperatures the electrons cool and adopt a minimum energy configuration. If electrons were bosons then they would all have the same zero point energy. This isn't the case though. Electrons are fermions and as such obey the Pauli exclusion principal. Each quantum state can only be occupied by one electron. This means that the electrons are forced to adopt a range of energies in their ground state from near zero to a maximum energy known as the Fermi energy. This is analogous to electrons in a ground state atom filling up from the $1s^1$ shell up to some other shell.

Consider electrons of mass m in a potential well of size L. The solutions to the Schrödinger equation imply energy levels of

$$\epsilon_n = \frac{\hbar^2}{2m} \left(\frac{n\pi}{L} \right)^2$$

where $n = 1, 2, 3, \ldots$ In the 1D case for N particles with 2 fermions per energy level (one spin up the other spin down) the Fermi energy is

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{N\pi}{2L} \right)^2$$

The three dimensional case yields a slightly different Fermi energy

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3N\pi^2}{V} \right)^{2/3}$$

where N/V is the concentration of electrons.

18.5   Metals as Electron Gases

This scenario of a cold electron gas can be used to model the electrons in a metal if we ignore the ionic configuration and threat the electrons as being completely free. For a given density, N/V, of electrons there is a corresponding range of energies from 0 to E_F at which the electrons exist in the ground state. Typically $E_F = 1\,\text{eV} - 10\,\text{eV}$ for a metal.

Electrons in lone atoms have discrete energies. As atoms are brought together the electron shells, particularly the outer shell, distort. As orbitals start to overlap the Pauli exclusion principle starts to apply to the whole system of overlapping orbitals as well as individual atoms. As more orbitals overlap more energy levels exist and the energy levels become close enough that they are approximately continuous from $E = 0$ to $E = E_F$. This broadened energy domain is the conduction band.

18.6   Electronic Heat Capacity

In metals free electrons can move and therefore contribute to the heat capacity, similarly to how an ideal gas has translational degrees of freedom that contribute to its heat capacity. Electrons in their ground state do not contribute to the materials heat capacity. Electrons need to be excited to retain thermal energy. This means the temperature must be comparable to the Fermi energy in the same way that vibrational energy levels are unavailable until the temperature is comparable to $\hbar\omega$. This point corresponds to the Fermi temperature:

$$T_F = \frac{E_F}{k_B}$$

at which point a significant number of electrons are excited out of the ground state. The Fermi temperature for most metals is very large, easily exceeding $20\,000\,\text{K}$ so electronic contributions aren't important a lot of the time. For comparison the Einstein or Debye temperature, at which lattice vibrations contribute to the heat capacity, is around $100\,\text{K}$ for most metals. Most metals melt below their Fermi temperature at atmospheric pressure.

When a metal is heated from absolute zero to a temperature T the electrons gain an average energy of $k_B T$. Only electrons within $k_B T$ of the Fermi energy can be excited as the rest are trapped by degeneracy (analogous to how the first electrons in an atom that are excited are the electrons in the outer shell). When these electrons are excited they gain energy of the order $k_B T$ again. For N total electrons a fraction of order T/T_F can be excited thermally since that is the fraction that lie within an energy range $k_B T$ of E_F Each of these NT/T_F electrons has thermal energy on the order of $k_B T$ so the total electronic thermal energy is

$$\Delta E \approx \frac{NT}{T_F} k_B T$$

The electronic heat capacity is

$$C_{el} = \frac{\partial(\Delta E)}{\partial T} \approx N k_B \frac{T}{T_F}$$

At room temperature C_{el} is a few orders of magnitude smaller than the ideal gas value of $C_V = 3Nk_B/2$. A more detailed calculation gives

$$C_{el} = \frac{1}{2}\pi^2 N k_B \frac{T}{T_F}$$

Which is only about 5 times bigger than our order of magnitude approximation.