

Stat Mech for Hobos

Before moving into heat transfer, mechanics of materials, and sound, it is useful to touch on a few topics in statistical mechanics, at the approximate level suited to this course.

Heat Capacity

We already have made a fair bit of use of heat capacity (especially of water) in the course. Most stuff (air, wood, plastic) tends to have a heat capacity around 1000 J/kg/K. Water is exceptional at 4184 J/kg/K (definition of kcal), other liquids tend to be around 2000, and metals dip to the 500 range or a bit less. Compared to properties like thermal or electrical conductivity, density, etc. heat capacity tends to occupy a relatively small range. Why is that?

At the atomic level, we know that the thermal energy of a particle is $\frac{1}{2}kT$ per degree of freedom. Atoms in a solid may experience 3 degrees of translation. Single, loose atoms also have three available degrees of freedom, so $\frac{3}{2}kT$ comes up a lot. A diatomic molecule (as in air) will have 6 degrees of freedom: three translations, two rotations, and one vibration. But this is still three per atom. Larger molecules have a rich spectrum of vibrational modes, but again working out to a total of three degrees of freedom per atom.

If we add thermal energy to a substance in the amount ΔE , it distributes among the N atoms such that each atom gets an amount $\Delta E/N \sim \frac{3}{2}k\Delta T$. We can count the number of atoms as the mass of the bulk object, m , divided by the mass of an individual atom, $m_{\text{atom}} = \mu/N_A$, where μ is the molar mass (kg/mol, for instance) and N_A is Avogadro's number. Thus we compute that the total energy added is

$$\Delta E = \frac{3}{2}Nk\Delta T = \frac{3}{2} \frac{m}{m_{\text{atom}}} k\Delta T = \frac{3}{2} \frac{N_A k}{\mu} m\Delta T \equiv c_p m\Delta T,$$

where we have rearranged terms and posited that the energy change is the heat capacity, c_p times the mass and temperature change involved. Thus we identify the heat capacity as approximately

$$c_p \approx \frac{3N_A k}{2\mu}.$$

The two constants in the numerator have giant and minuscule exponents (-23 and 23 , respectively), multiplying to a tidy 8.3 J/K/mol (known as the gas constant, R , often used in chemistry). We therefore end up with $c_p \sim 12/\mu$. Most stuff is made of atoms averaging something like 15 g/mol, or $\mu = 0.015$ kg/mol (consider the prevalence of hydrogen in the average), in which case we compute a heat capacity around 800 J/kg/K—approximately on target. Now we have a better sense as to why heat capacities are not wildly different among different substances. Metals have heavier atoms, thus lower heat capacity (though free electrons share the thermal energy).

Collisions

Let's think of a gas in which particles act essentially as billiard balls bouncing into each other. We consider collisions as purely geometrical encounters of otherwise non-interacting spheres bumping into each other.

Thermal Velocity

Each particle (could be atom or molecule) has $\frac{3}{2}kT$ of energy dedicated to translation (additional energy may be absorbed in vibrations), or in other words to $\frac{1}{2}mv^2$. Equating these says that thermal velocity is

$$v_{\text{th}} = \sqrt{\frac{3kT}{m}}. \quad (1)$$

The Boltzmann constant is $k = 1.38 \times 10^{-23}$ J/K, so that at room temperature we get 4×10^{-21} J, equivalent to $\frac{1}{40}$ eV (worth committing to memory). The mass of an air molecule, at about 30 nucleons per molecule, is about $(0.03 \text{ kg/mol}) / (6 \times 10^{23} \text{ mol}^{-1}) \approx 5 \times 10^{-26}$ kg. Sticking these into Eq. 1 yields

$$v_{\text{th}} \approx \sqrt{\frac{12 \times 10^{-21}}{0.5 \times 10^{-25}}} = \sqrt{24 \times 10^4} \approx 500 \text{ m/s}.$$

Sound speed is approximately this divided by $\sqrt{3}$, based on the fact that the velocity of the particle is split over three dimensions (one third of its energy is in the direction of interest). It is actually a little more than that by a factor of $\sqrt{\gamma}$, where $\gamma = \frac{7}{5}$ for a diatomic gas.

Space Density

We use the symbol, n , to describe the number density of particles, in units $\#/\text{m}^3$, or simply m^{-3} . You may remember from chemistry classes that gases occupy 22.4 L/mol at STP (standard temperature and pressure; where $T = 0^\circ\text{C}$). This translates to about 45 moles in a cubic meter. Multiply this by Avogadro's number and we find that the number density for any gas at STP is

$$n = 2.7 \times 10^{25} \text{ m}^{-3}. \quad (2)$$

While we're here we may as well enjoy the relation to mass density, whereby we can take the 45 mol/ m^3 multiplied by molar mass (kg/mol) to get mass density. For air, composed of about three-quarters N_2 (28 g/mol) and one-quarter O_2 (32 g/mol), the weighted mean is very close to 29 g/mol to yield 1.3 kg/ m^3 at 0°C . Warmer air is slightly less dense, making 1.25 kg/ m^3 a convenient rational number.

Incidentally, we can take the species-independent number from Eq. 2 and note it to be $27 \times 10^{24} \text{ m}^{-3}$, which is a perfect cube of $3 \times 10^8 \text{ m}^{-1}$, indicating that the typical inter-particle separation is 3 nm (roughly 10 diameters, so 0.001 volume density, which relates to why gases are less dense than their equivalent fluids by approximately this factor).

Colliding Spheres

We want to establish the cross section, σ , for collisions. This is just a geometrical area, in square meters. A sphere of radius R has a cross section of πR^2 to a point particle trying to hit it. But when another sphere of radius R comes at it, they will hit if the impact parameter is less than $2R$, so that $\sigma = \pi(2R)^2 = 4\pi R^2$. A characteristic scale for R for atoms is 1 Å, or 10^{-10} m.

At what point would we expect a sphere of interest to run into another? Let's imagine a slab of gas, with area A and thickness λ . Within this volume we have $nA\lambda$ particles. Each particle has an associated "collision area" σ , so that the whole mess adds to a blockage area $nA\lambda\sigma$. We "fill" the area, A , when the total area occupied by collision cross sections equals A . This happens at a thickness

$$\lambda = \frac{1}{n\sigma}. \quad (3)$$

We call this the *mean free path*, representing the distance one particle might expect to travel uninterrupted before hitting another particle when the cross section for doing so is σ .

For the diatomic molecules of air, we are not dealing with spheres but with oblong things roughly 2×4 Å in scale. If we take a characteristic diameter of 3 Å, we have $\sigma \approx \pi(3 \times 10^{-10})^2$, or $3 \times 10^{-19} \text{ m}^2$. Using our value for n , we find that $\lambda = 1/n\sigma \approx 10^{-7}$ m, or 100 nm. The "official" answer is 70 nm (sail past about 20 before hitting one), which we would get if we had adopted a characteristic diameter of 4 Å.

Diffusion

First we'll look at this in a more formal way, then devise a reasonable hobo-style shortcut. The diffusion equation reads thusly:

$$\frac{\partial \phi}{\partial t} = D \nabla^2 \phi, \quad (4)$$

where ϕ might represent temperature (then this is called the Heat Equation), mass density, number density, etc. For our purposes, we will concentrate on number density, n . As a hobo preview, we might say that at some location of interest n changes by some amount Δn in a time Δt , and spatially changes by a similar amount over spatial scale Δx . We then write the diffusion equation as

$$\frac{\Delta n}{\Delta t} = D \frac{\Delta n}{\Delta x^2},$$

by which we relate the diffusion constant $D \sim \Delta x^2 / \Delta t$, having units m^2/s , or area per time.

Let's try Eq. 4 on a trial function:

$$n(r, t) = n_0 e^{-r/R}, \text{ where } R \rightarrow R(t).$$

This is a centrally concentrated (peaked) function at the origin with characteristic radial scale R . Nothing interesting happens in the angular dimensions, and I need the spherical Laplacian to handle the r -derivatives. Shortcutting a few manipulation steps,

$$\nabla^2 n = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial n}{\partial r} \right) = \frac{n_0}{R^2} \left(1 - 2 \frac{R}{r} \right) e^{-r/R},$$

while the time derivative yields

$$\frac{\partial n}{\partial t} = -n_0 \left(\frac{r}{R^2} \dot{R} \right) e^{-r/R}.$$

Equating these two with the diffusion constant and eliminating the exponential from both sides, we find that

$$r \dot{R} = D \left(2 \frac{R}{r} - 1 \right) \rightarrow D = \frac{r \dot{R}}{2 \frac{R}{r} - 1}.$$

Evaluated at $r = R$, we find that $D = R \dot{R} = \frac{\partial}{\partial t} (\frac{1}{2} R^2)$. Because D is a constant, we have the result that R^2 **grows linearly in time**. This is the key to diffusion: the boundary's area grows linearly in time, or the radius of influence grows as the square-root of time. Think of the diffusion constant as the rate at which area grows (or at least radius-squared, or area/ 4π).

Hobo Diffusion

Now we will approach diffusion from a simple perspective: partial differential equations be damned. The fundamental process is a random walk, the steps governed by collisions. We have already established the mean free path, $\lambda = 1/n\sigma$ in Eq. 3. We also know that the mean thermal velocity of the particles as given in Eq. 1. We can combine these two to establish a mean time between subsequent collisions:

$$\tau = \frac{\lambda}{v}.$$

In time Δt , we therefore expect to see $N = \Delta t / \tau$ collisions, which we can also write as $N = v \Delta t / \lambda$, carrying the simple and satisfying interpretation that in time Δt , the total distance traveled by the particle (if the jagged path is stretched out) is $v \Delta t$, composed of many steps averaging λ in length.

In three dimensions, we essentially have three independent random walks going on at once. Heuristically, we might imagine that every third collision results in motion along the x -axis, so that progress along the x -dimension random walk scales as $\sqrt{N/3}$. Of course the particle does not partition its time this way, but

one can equivalently say that the average step projects only partially onto a particular axis, represented by this factor of three.

Thus in a particular dimension, our particle effectively takes $N/3$ steps of length λ , accruing an expected net progress of $\lambda\sqrt{N/3}$ in time Δt , which we might take to be a radius (excursion distance from starting point). Then we can make the association

$$R^2 = \frac{N}{3}\lambda^2 = \frac{v\Delta t}{3\lambda}\lambda^2 = \frac{1}{3}v\lambda\Delta t.$$

Finally, associating the diffusion constant, D , with the rate of change of R^2 , we have that

$$D \sim \frac{R^2}{\Delta t} \sim \frac{1}{3}v\lambda.$$

Worth remembering. By the techniques described earlier, we can get the thermal velocity and mean free path of particles in a gas. Now we know the associated scale of diffusion.

For air, with $v \approx 500$ m/s and $\lambda \approx 70$ nm, we find that $D \approx 1.2 \times 10^{-5}$ m²/s. How do we interpret this? We have two choices. How far does something diffuse in a given time, or how much time does it take to go a certain distance? For the former, $R \sim \sqrt{D\Delta t}$, and for the latter, $\Delta t \sim R^2/D$. We try some things for air particles in the following table (the arrow indicating the direction of calculation).

Δt	direc.	R
1 s	→	3.5 mm
1 hr	→	200 mm
$\sim 10^5$ s (~ 1 day)	←	1 m
$\sim 10^7$ s (~ 4 months)	←	10 m

The square root of time is a killer. Molecules cover short distances rather efficiently, but take ages to move far.

How is it we can smell perfume soon after someone walks into the room, even if meters away? Surely the perfume molecules are bumping around in a random walk in the air. Clearly diffusion is not the only way to get around.