Physics 114 Statistical Mechanics Spring 2021

Week 7 Conceptual Overview

Concept checklist from Readings:

- The *pressure* of a gas on a wall is the force normal to the wall, divided by the wall area: $P = F/A$. (It's important to specify "normal to" because when we talk about viscosity, we'll be talking about shearing forces which are parallel to the wall.)
- Say the wall is oriented in the $x - y$ plane; so its surface normal points in the z direction. One molecule hitting the wall supplies an quick, impulsive, normal force of $F = dp_z/dt$. Our job is to calculate how much force comes from molecules at a density of $n = N/V$, traveling in random directions. B&B Eq's 6.10-12 construct this argument, arriving at an expression for molecules that hit in a certain angular range within $d\theta$ of θ.

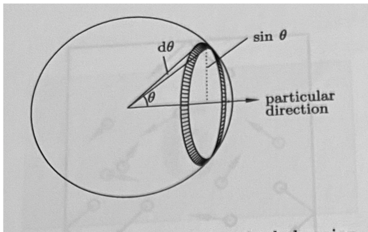

Fig. 6.4 The area of the shaded region on this sphere of unit radius is equal to the circumference of a circle of radius $\sin\theta$ multiplied by the width $d\theta$ and is hence given by $2\pi \sin\theta \, d\theta$.

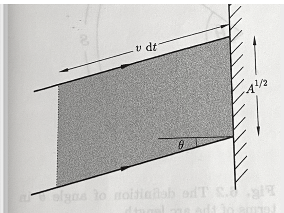

Fig. 6.5 Molecules hit a region of wall (of cross-sectional area $A^{1/2} \times A^{1/2} = A$) at an angle θ. The number hitting in time dt is the volume of the shaded region ($A v dt \cos\theta$) multiplied by $n f(v) dv \frac{1}{2} \sin\theta$.

- The number of molecules per unit volume, per unit time, with speed near v, hitting the wall near angle θ is:

$$v \; cos\theta \; n \; f(v) dv \; \frac{1}{2} sin\theta \; d\theta \qquad (6.12)$$

  Above, $f(v)$ is the Maxwellian speed distribution familiar to us from last week :-). We can then integrate over angle and speed in order to find:

$$p = \frac{1}{3} nm < v^2 > \qquad (6.15)$$

- The Maxwellian distribution is then used to find $< v^2 > = \frac{3k_BT}{m}$. This leads to what else ... the ideal gas law. Nice!

$$p = nk_BT \qquad (6.18)$$

- One can find the proportionality between pressure p and u, the energy per unit volume. This is most interesting, perhaps, when one contrasts different systems. For example, we will later do this for a "gas" of photons at thermal equilibrium. For now, for the ideal gas the constant is 2/3: $p = \frac{2}{3}u$.

- *Dalton's law* is just common sense. The sum of the "partial pressures" due to different kinds of gasses is the total pressure in a gaseous mixture:

$$\Sigma_i \; p_i = p$$

- *Effusion* is when gas escapes from a tiny hole. *Grahm's law* applies when the hole is tiny. How tiny? It must be the case that the hole's diameter is much less than λ, the mean free path that a molecule travels in-between collisions. To understand this phenomenon, we define the *flux*, Φ, the number of particles per unit time hitting an imagined unit area. B&B Eq. 7.5 (again, using the Maxwellian distribution $f(v)$ of speeds) yields

$$\Phi = \frac{1}{4} n < v >= \frac{p}{\sqrt{2\pi m k_B T}} \qquad (7.6), (7.9)$$

  Then, the effusion rate is ΦA, for a hole of area A. The rate of change of mass in the system is $dM/dt = -m\Phi A$ where m is the molecular mass.

- The rate of effusion thus gives us a way of determining gas pressure. It also gives us a way of separating molecules by mass, since the effusion rate $\propto 1/\sqrt{m}$. It also predicts that if hole's diameter is much less than λ, setting $\Phi_1 = \Phi_2$ means $p_1/\sqrt{T_1} = p_2/\sqrt{T_2}$. [1]

- Finally we get to the idea that gas particles can collide! We start with the idea that a particle with an effective cross section σ will sweep out a volume $\sigma \; v \; dt$ in time dt, and if another, stationary molecule's center lies in that volume (see the picture below), there will be a collision. The effective cross section, σ, for a collision is the area of the "tube" of volume below - the *collision cross-section.* This model is predicated on the particles interacting like hard-spheres ... they miss each other unless their actual surfaces impinge on one another. The simplest model is that all particles have the same radii, making $\sigma = \pi d^2$ where d is a particle diameter.

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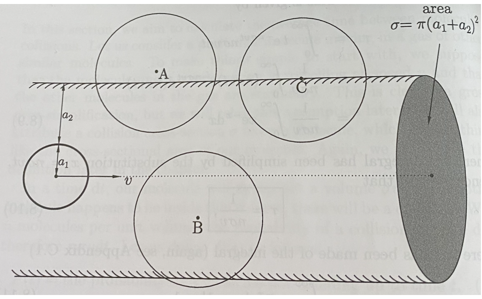
[1] This supports something that we discussed weeks ago, the Joule-Kelvin"throttling process" where two gasses had different pressures on either side of a a tiny connector between the two containers. I am not claiming that this is the exact relationship between pressures and temperatures for the Joule-Kelvin effect! I'm just saying that here is another situation in which a pressure difference can exist between two containers of gas, when molecules must make their way through a tiny hole into the adjacent container.



- B&B derive that the probability that a molecule has *not* suffered a collision over a time interval t is

$$p_{no\ collision\ before\ t} = e^{-n\sigma v t} \qquad (8.5)$$

- It follows that the likelihood of having no collision up to a time t, then colliding in the next dt is $p_{collision\ near\ t} = e^{-n\sigma v t}\ n\sigma v\ dt$. This permits us to calculate the *mean scattering time* τ, which is the expected time between collisions:

$$\tau = \frac{1}{n\sigma v} \qquad (8.10)$$

- The *mean free path* λ is the typical distance a particle goes between collisions. B&B Section 8.3 makes one common-sense modification to the ultra-simple model that would suggest $\lambda =< v > \tau$. One realizes that particles collide more often, hence have a shorter mean free path, b/c they are all moving relative to one another. With this modification:

$$\lambda = \frac{1}{\sqrt{2}n\sigma} = \frac{k_B T}{\sqrt{2}p\sigma} \qquad (8.20), (8.21)$$

  It is also the case that the mean free time is modified, to:

$$\tau = \frac{1}{\sqrt{2}n\sigma < v >}$$

- *Transport* of momentum, energy, and matter are found in B&B Ch. 9. All three of these quantities are described in terms of their *flux*. Fluxes are introduced by referring to an imaginary area in the xy plane ... and the transport occurs in the z direction. These concepts are generalized later. Fluxes of energy and particles are both vectors. Problems involving these fluxes can be done in cylindrical or spherical geometries, as boxed examples on pages 80, 83 and 84 show.
  - The *transverse momentum flux*, Π_z, is how much x momentum is transported per unit area per unit time. (One could have also talked about y momentum; the idea is that this is a component of momentum transverse to the direction in which it is transported.)

  - The *heat flux*, J_z is how much thermal energy is transported per unit area per unit time.
  - The *flux of labelled particles*, Φ_z, is how many labelled particles are transported per unit area per unit time.

- A key geometry we use for all three transport properties is this one:

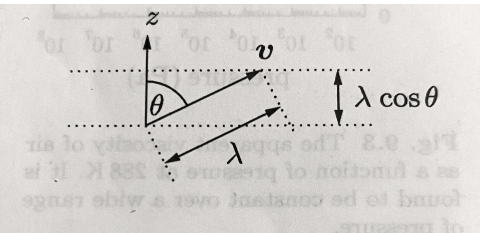


Fig. 9.2 Molecular velocity $\boldsymbol{v}$ for molecules travelling at an angle θ to the z-axis. These will have travelled on average a distance λ since their last collision, and so they will have travelled a distance $\lambda\cos\theta$ parallel to the z-axis since their last collision.

  We want to know the excess transverse momentum (Eq. 9.3) or net thermal energy (Eq. 9.16), or net flow (implicit in Eq 9.37) for a single particle which has travelled its mean free path, moving at angle θ and speed v, moving from lower to higher z. The z direction is relevant due to B&B's choice of how to shear the system, or set up a temperature or concentration gradient (for viscosity, thermal conductivity and diffusion, respectively).

- A key approximation in what follows is that the system size L is much greater than the mean free path, λ, which is in turn much greater than the diameter d of the molecules.

- *Momentum transport* is determined by *viscosity*. Its SI units are Ns/m^2.
  - The *momentum* we discuss is parallel to some shearing force. The simplest geometry is having the fluid confined between two plates, which are in steady, relative motion, say in the x direction. Even without modeling the particles as having any "sticky" interactions with other particles or the walls, you will get a gradient of the average x velocity, $< u_x(z) >$ from the top plate to that of the bottom plate. A more practical geometry with rotating cylindrical walls is discussed in the box on B&B p. 80. In that case, the "transverse" momentum is in the $\hat{\theta}$ direction, and it varies with the radial position in the cell.

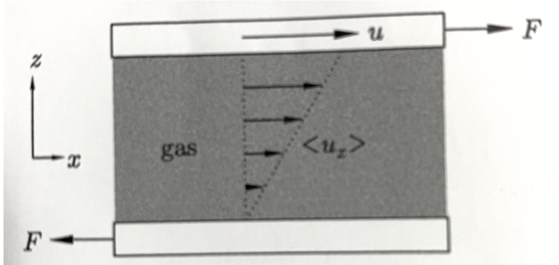


Fig. 9.1 A fluid is sandwiched between two plates of area A which each lie in an xy plane (see text).

- The *shear stress* $\tau_{xz} = F/A$. It is proportional to the transverse momentum gradient, with the coefficient of proportionality being the *viscosity* η:

$$F/A = \eta \frac{d < u_x >}{dz} \qquad (9.1)$$

- This shearing produces a *transverse momentum flux* $\Pi_z = -\tau_{xz} = -\eta \frac{d<u_x>}{dz}$. $\Pi_z(\theta, v)$ is a product of two terms: the number of particles impinging at angle θ and speed v on an imaginary area in the xy plane, and the x component of momentum they carry. One then integrates over angle using Eq. (6.12), and speed using the Maxwellian distribution $f(v)$, to obtain:

$$\eta = \frac{1}{3} nm\lambda < v > \qquad (9.5)$$

- Interesting facts are that η is independent of p. However, all other things being fixed: $\eta \propto \sqrt{T}$ (which is *not* what you'd expect from a liquid), $\eta \propto \sqrt{m}$, and $\eta \propto 1/d^2$.

- Thermal energy transport is characterized by the *thermal conductivity*, κ. Its SI units are $Wm^{-1}K^{-1}$.
  - We imagine a cell with a temperature gradient so heat flows from low to high z (hot to cold).

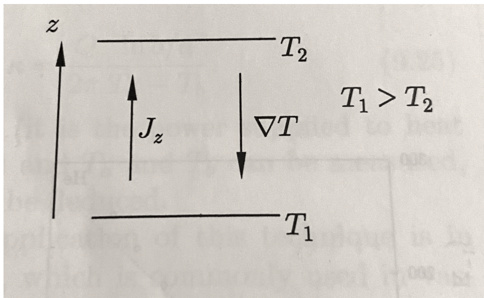


Fig. 9.7 Heat flows in the opposite direction to the temperature gradient.

- The temperature differential produces a *heat flux* $J_z = -\kappa \frac{dT}{dz}$. $J_z(\theta, v)$ is a product of two terms: the number of particles impinging at angle θ and speed v on an imaginary area in the xy plane, and the amount of heat they carry. For a single molecule, B&B calls the latter $C_{molecule}\Delta T$. For a molecule traveling a single mean free path's distance, $\Delta T = dT/dz \ \lambda cos\theta$. As with viscosity, one integrates over angle and speed to obtain:

  $$\kappa = \frac{1}{3} n C_{molecule} \lambda < v > \equiv \frac{1}{3} C_V \lambda < v > \tag{9.18}$$

  where C_V is the heat capacity per unit volume.
- Interesting facts are that κ is independent of p. Also, all other things being fixed: $\kappa \propto \sqrt{T}$, $\kappa \propto 1/\sqrt{m}$, and $\kappa \propto 1/d^2$.

- Mass transport which B&B characterize as the motion of some subset of labelled particles is characterized by the *self diffusion constant*, D. Its SI units are m^2/s.
  - We imagine a cell with a concentration $n^*(z)$ of labelled particles, where a concentration gradient $\partial n^*/\partial z$ has been set up. The *particle flux*, Φ_z is the number crossing an imaginary area in the xy plane, per unit area per unit time. Flux is proportional to the concentration gradient, with *self diffusion constant* D the constant of proportionality: $\Phi_z = -D\frac{\partial n^*}{\partial z}$.

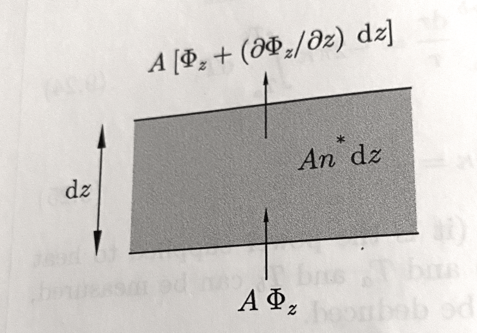


Fig. 9.11 The fluxes into and out of a thin slab of gas of thickness dz and area A.

  - B&B go further to derive the 1d *Diffusion Equation*, predicated on the idea that particles are conserved; i.e. $\frac{\partial n^*}{\partial t} = -\frac{\partial \Phi_z}{\partial z}$. This leads to
$$\frac{\partial n^*}{\partial t} = D\frac{\partial^2 n^*}{\partial z^2} \qquad (9.31)$$
    This is generalized to 3 dimensions. (See Ch. 10 if you wish ... perhaps this is math you did in Phys 17?). Further, diffusion can be connected to random walk theory. There are many places one can go with diffusion, but we haven't the bandwidth to go there now :-} .
  - In the same way as was done for the other two transport quantities, one integrates $\Phi_z(\theta, v)$ for a single particle over all angles and speeds, weighted by the Maxwellian speed distribution, to obtain
$$D = \frac{1}{3}\lambda < v > \qquad (9.38)$$
  - Interesting facts are that D is *not* independent of p ... but goes like p^{-1} at fixed temperature, because $\lambda \propto n^{-1}$. Also, all other things being fixed: $D \propto T^{3/2}$, $D \propto 1/\sqrt{m}$, and $D \propto 1/d^2$. Finally, there is a weirdly direct relationship between diffusion constant and viscosity: $D\ n\ m = \eta$.

- B&B gives us "less memorable" formulae for η, κ, and D in Eqs. (9.6), (9.19), (9.40). These have all the constants and thermodynamic parameters shown. While they do fairly well reproducing experimental data, a more careful theory (not assigned, mentioned in B&B Section 9.4) has slightly better predictions for the constants that agree even better with experiment.