14. Kinetic Theory

Read: Chapter 14
Do: Problems 1, 2, 3, 4

Kinetic theory aims to understand macroscopic phenomena from microscopic point of view. We'll first consider ideal gas (in *classical* physics) as a collection of noninteracting particles. Then we'll consider (again classically) *nonideal* behavior, effects of interactions. (Gas behavior on distance scales >> mean-free-path) theory of diffusion, with many ramifications:

- Dynamical mixing of gases
- Heat conduction
- electrical conduction
- viscosity

} all *transport* processes (diffusive)

As a prelude to kinetic theory of ideal gas --

Equipartition of Energy in Classical Statistical Mechanics

(see Chapter 3)

In general, internal energy is

$$U = \langle E \rangle = \frac{\sum_{\text{states}} E e^{-E/\tau}}{\sum_{\text{states}} e^{-E/\tau}}$$

or --

$$U = \tau \frac{\left(\sum E/\tau \, e^{-E/\tau}\right)}{\left(\sum e^{-E/\tau}\right)}$$

In certain cases we can evaluate this dimensionless number in the $\tau \to \infty$ (classical) limit

dimensionless number

Example: Classical Ideal Gas

If we ignore (Bose or Fermi) statistics, and consider large volume (so allowed $\vec{K}$ can be regarded as continuum)

specify microscopic state by momenta of N particles $\vec{p_1}, \vec{p_2}, \vec{p_3} --, \vec{p_N}$ (3N components

and positions $\vec{q_1}, \vec{q_2}, -- \vec{q_N}$

- 6N dimensional phase space

Remember -- in quantum mechanics, for a single free particle

$$\sum_{\text{states}} \to \frac{V}{(2\pi\hbar)^3} \int d^3p \quad \text{or} \quad \int \frac{d^3q \, d^3p}{(2\pi\hbar)^3}$$

- a state "occupies" volume $h^3 = (2\pi\hbar)^3$ in q-p space

The pioneers of 19th century (classical) Stat Mech (Boltzmann, Maxwell, --) did not know about $\hbar$ — so they didn't know how to normalize density of space. But for many purposes (calculating expectation values) this normalization does not matter. In classical physics, sum over states becomes

$$C\int d^3q\, d^3p$$

("Fundamental assumption of classical stat. mech.")

irrelevant constant

For N-particle ideal gas

$$E = \frac{1}{2M}\left(\vec{p}_1^{\,2} + \vec{p}_2^{\,2} + \cdots + \vec{p}_N^{\,2}\right)$$

$$U = \frac{\int d^3q_1 d^3p_1 \cdots d^3q_N d^3p_N \; E e^{-E/\tau}}{\int d^3q_1 \cdots d^3p_N \; e^{-E/\tau}}$$

3N Terms in $E = \frac{1}{2M}\left(\vec{p}_1^{\,2} + \cdots + \vec{p}_N^{\,2}\right)$; each Factorizes into 3N Gaussian integrals:

$$3N \; \frac{\int dp \, \frac{1}{2M} p^2 e^{-p^2/2M\tau}}{\int dp \; e^{-p^2/2M\tau}} = 3N\tau \underbrace{\frac{\int_{-\infty}^{\infty} dx\, x^2 e^{-x^2}}{\int_{-\infty}^{\infty} dx\, e^{-x^2}}}_{=\frac{1}{2}}$$

$$U = 3N\left(\tfrac{1}{2}\tau\right)$$ ~ contribution does not depend on M

Kinetic Energy (on average) is $\frac{3}{2}\tau$ per particle.

<u>Generalization</u> - "<u>Equipartition of Energy</u>"

<u>Any</u> phase space variable that appears quadratically in Hamiltonian carries energy $\frac{1}{2}\tau$ on average (in <u>classical</u> statistical mechanics).

- E.g. same for different gas molecules
- System of oscillators

$$H = \sum_i \left(\frac{1}{2m_i} p_i^2 + \frac{1}{2} m_i \omega_i^2 q_i^2 \right)$$

Different masses and frequencies

But energy $= \frac{1}{2}\tau + \frac{1}{2}\tau = \tau$ in classical stat mech.

For elastic solid with 3N atoms

$$U = 3N\tau, \quad C_V = 3N$$

(Dulong + Petit)
- see p 4.17

For classical stat mech to apply, need

$\tau \gg \hbar\omega$ — so can replace sum over states by integral — ignore splittings

For oscillator of frequency ω
(cf Planck, page 4.2)

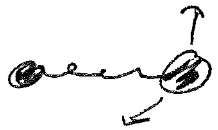
$$\langle E \rangle = \frac{\hbar\omega}{e^{\hbar\omega/\tau}-1} \Rightarrow \begin{cases} \overset{\text{equipartition}}{\tau}, & \tau \to \infty \\ \underset{\text{Boltzman suppression}}{\hbar\omega e^{-\hbar\omega/\tau}}, & \tau \to 0 \end{cases}$$

Oscillators freeze out at low τ (Einstein 1906)

Equipartition: $\frac{1}{2}\tau$ per (accessible) degree of freedom

○ Vibration and Rotation of Molecules

N_2



1 vibrational mode
2 rotational mode

$$H_{\text{rotation}} = \frac{1}{2I}\left(L_1^2 + L_2^2\right) \to \frac{\hbar^2}{2I}\left(l_1^2 + l_2^2\right),$$

$$H_{\text{vibration}} = \frac{1}{2m}p^2 + \frac{1}{2}m\omega^2 q^2$$
$$\to \hbar\omega(n)$$

Another quadratic Hamiltonian
$H = \frac{1}{2} I \dot{\theta}^2$

Rotation accessible for
$\tau \gg \hbar^2/2I$

Vibration accessible for
$\tau \gg \hbar\omega$

Typical molecules at room temperature:
Rotation accessible, Vibration frozen out

For H_2

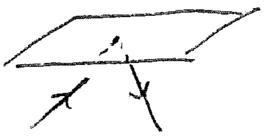
Very low τ $C_v \to 0$ (quantum gas)

low τ $C_v \to \frac{3}{2}N$

intermediate τ $C_v \to (\frac{3}{2}+1)N = \frac{5}{2}N$ (rotation)

high τ $C_v \to (\frac{3}{2}+1+1) = \frac{7}{2}N$ (rot and vib)

Pressure in Kinetic Theory



Ideal gas molecules collide with wall

$p = \langle$(impulse per collision)(No of collisions per area and time)$\rangle$

particle flux $\vec{J} = n\vec{v}$

Half of particles are moving each way, so $J_{up} = \frac{1}{2} n v_z$

Impulse $\Delta p = 2Mv_z$

$$p = \langle \tfrac{1}{2} n v_z \, 2M v_z \rangle = nM\langle v_z^2 \rangle$$

Now: use equipartition: $\langle \frac{1}{2} M v_z^2 \rangle = \frac{1}{2}\tau$

So we find $p = n\tau = \frac{N}{V}\tau$

— once again, the ideal gas law

Maxwell Distribution

Probability distribution for velocity in a classical ideal gas

Recall counting of states

$$\sum \to V\int \frac{d^3p}{(2\pi\hbar)^3} = V\int \frac{4\pi p^2\,dp}{(2\pi\hbar)^2}$$

and $p = Mv \Rightarrow \quad = V\,C\int v^2\,dv$

combine with Boltzman $e^{-\frac{1}{2}Mv^2/\tau}$

$$\Rightarrow \underset{\text{(prob dist for speed)}}{P(v)\,dv} = \frac{v^2\,dv\,e^{-\frac{1}{2}Mv^2/\tau}}{\int_0^\infty dv\,v^2 e^{-\frac{1}{2}Mv^2/\tau}}$$

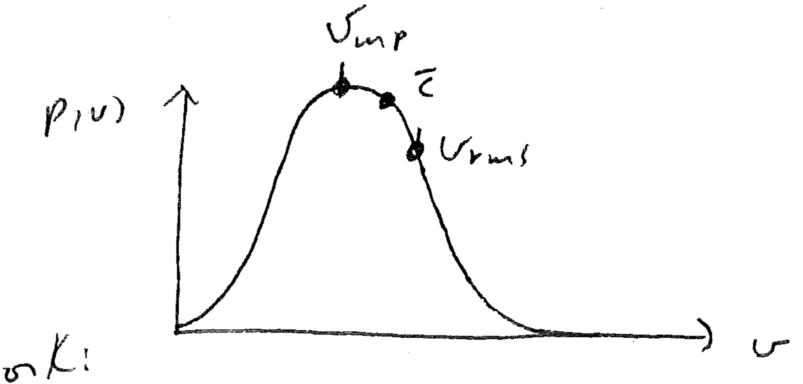
— Again, the normalization drops out; this is a classical distribution in which $\hbar$ does not appear

$$\text{Denominator} = \left(\frac{2\tau}{M}\right)^{3/2}\int_0^\infty dx\,x^2 e^{-x^2} = \frac{\sqrt{\pi}}{4}\left(\frac{2\tau}{M}\right)^{3/2}$$

$$= \frac{\sqrt{2\pi}}{2}\left(\tau/M\right)^{3/2}$$

$$\boxed{P(v)\,dv = \frac{2}{\sqrt{2\pi}}\left(\frac{M}{\tau}\right)^{3/2} v^2 e^{-\frac{1}{2}Mv^2/\tau}\,dv}$$

— the maxwell distribution of velocities



Homework:

Peak (most probable) $\quad v_{mp} = \left(\frac{2\tau}{M}\right)^{1/2}$

i.e. $\tau = \frac{1}{2} M v_{mp}^2$

(temperature is **most probable** K.E.)

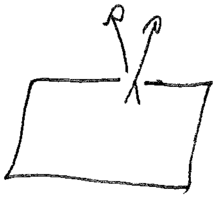
Root-Mean-Square $\quad v_{rms} = \left(\frac{3\tau}{M}\right)^{\frac{1}{2}}$

or $\frac{1}{2} M v_{rms}^2 = \frac{3}{2}\tau$

– as equipartition demands, and we knew from $U = \frac{3}{2}N\tau$

Mean
$\bar{c} = \left(8\tau/\pi M\right)^{1/2} \qquad$ so $v_{rms} > \bar{c} > v_{mp}$

Gas coming out of a hole in a hot oven:
(Note: hole small so viscosity negligible)



$v_z = v\cos\theta \qquad P_{beam} = \underbrace{\langle\cos\theta\rangle}_{\text{average over hemisphere}} v\, P_{maxwell}$

$$\int_0^1 d\cos\theta \cos\theta = \frac{1}{2}$$

$$P_{beam} = \frac{1}{2} v\, P_{maxwell} \sim v^3 e^{-\frac{1}{2}Mv^2/\tau}$$

(Faster molecules more likely to come out.)

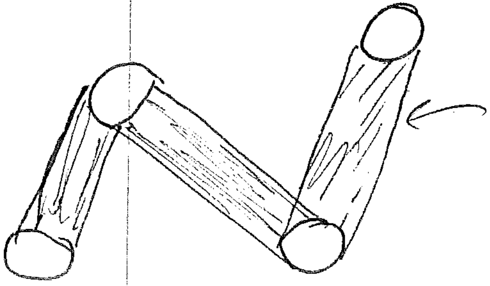
Mean Free Path

consider collisions — nonideal behavior

suppose molecules are billiard balls with radius d

collision "cross section"

Area $= \pi d^2$



volume $L\pi d^2$

(Molecule moves distance $L \Rightarrow$ sweeps out volume $L\pi d^2$)

on average, 1 molecule per volume $\frac{V}{N} = n^{-1}$

So $\# \text{ of collisions} = n\pi d^2 L$

or $L = \frac{1}{n\pi d^2}$ = average distance between collisions

(cf: dimensional analysis) — the mean free path

Typical atomic size: few × 10^{-8} cm

Ideal gas at STP (0°C and 1 atm) $\Rightarrow 2.7 \times 10^{19}$ molecules/cm^3

$L \sim 10^{-5}$ cm — few hundred times atomic size

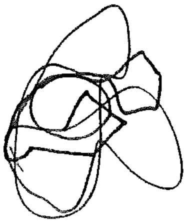
(Also large compared to typical separations $n^{-1/3} \simeq 3 \times 10^{-7}$ cm)

(which is why gas is reasonably close to ideal)

$$L \cong n^{-\frac{1}{3}} \left(\frac{n^{-\frac{1}{3}}}{d}\right)^2 \frac{1}{\pi}$$

Transport

concerns behavior at distance >> mean free path



Each atom makes a random walk

$\Rightarrow$ Diffusion

Diffusion has many ramifications:

- Mixing (determines timescale)
- Diffusion of energy — thermal conductivity
- Diffusion of electric charge — electrical conductivity
- Diffusion of momentum — viscosity

Particle Diffusion

put an ink drop in water - How does it spread out?

Empirical Law (Fick's Law)

$$\vec{J} = -D\vec{\nabla} n$$

ink flux

Flow from high to low density

"diffusivity"
"diffusion constant"

ink density

We wish to understand the law in microscopic terms, and relate D to mean free path and molecular velocity of ink molecules

Can rewrite Fick's law as a PDE for n by using continuity eqn.

Flux out of cell $= \int d\vec{a}\cdot\vec{J} = \int d^3x\, \vec{\nabla}\cdot\vec{J}$

$= -\frac{d}{dt}\int d^3x\, n = -\int d^3x\, \frac{\partial}{\partial t} n(\vec{x},t)$

So $\frac{\partial}{\partial t} n = -\vec{\nabla}\cdot\vec{J}$

$\Rightarrow n(\vec{x},t)$ satisfies $\boxed{\frac{\partial n}{\partial t} = D\nabla^2 n}$

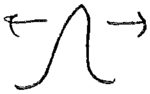
<u>Diffusion Equation</u>

<u>Microscopic Derivation of Diffusion Equation</u>

(Einstein 1905)

- the key thing is to regard $n(\vec{x},t)$ as a <u>probability</u> distribution for ink molecules
- Each molecule is executing random walk ⇒ we know how the distribution evolves
- Derive diffusion eqn — as a statistical statement

E.g. (to start): Diffusion in one dimension



Prob distribution <u>spreads</u>

Each molecule is as likely to move left as right

But more move from high to low density than from low to high.

To start: $\cdot\ \cdot\ \overset{\leftarrow\ \rightarrow}{\cdot}\ \cdot\ \cdot\ \cdot$

one-dimensional diffusion

"Lattice" Model: in each time interval ϵ, particle takes a step to left or right by distance Δ

$$P(x,t) \longrightarrow P(s,n) \qquad \begin{aligned} x &= \Delta s \\ t &= \epsilon n \end{aligned}$$

E.g. suppose the particle starts out at $s=0$ at $n=0$ (with prob 1)

At later time
$$\begin{aligned} s &= n_{right} - n_{left} \\ n &= n_{right} + n_{left} \end{aligned}$$

If L and R each have $p = \frac{1}{2}$, this is exactly the same problem as flipping a fair coin n times.

So probability distribution is binomial $\Rightarrow$ Gaussian for large n (cf Chapter I)

$$P(s,n) = \frac{1}{\sqrt{2\pi n}} e^{-s^2/2n}$$

or
$$\underset{\substack{\Uparrow \\ \text{Probability \underline{density}}}}{P(x,t)} = \frac{1}{\Delta}\frac{1}{\sqrt{2\pi n}} e^{-s^2/2n} = \frac{1}{\sqrt{2\pi \frac{\Delta^2}{\epsilon} t}} e^{-\left(\frac{\epsilon}{2\Delta^2} x^2/t\right)}$$

We will arrive at this Gaussian by a different argument

14.13

Write down a difference equation for $\rho(s,n)$

$$\rho(s,n) = \tfrac{1}{2}\rho(s-1,n-1) + \tfrac{1}{2}\rho(s+1,n-1)$$

If $x = \Delta s$, $t = n\epsilon$

$$= \rho(s,n-1) + \tfrac{1}{2}\left[\rho(s-1,n-1) - 2\rho(s,n-1) + \rho(s+1,n-1)\right]$$

or

$$\left[\rho(s,n) - \rho(s,n-1)\right] = \tfrac{1}{2}\Big[\big(\rho(s+1,n-1) - \rho(s,n-1)\big) - \big(\rho(s,n-1) - \rho(s-1,n-1)\big)\Big]$$

$$\epsilon \left.\frac{\partial \rho}{\partial t}\right|_{s,n-\frac{1}{2}} = \frac{1}{2}\left[\Delta \left.\frac{\partial \rho}{\partial x}\right|_{s+\frac{1}{2},n-1} - \Delta \left.\frac{\partial \rho}{\partial x}\right|_{s-\frac{1}{2},n-1}\right]$$

$$= \tfrac{1}{2}\Delta^2 \left.\frac{\partial^2 \rho}{\partial x^2}\right|_{s,n-1}$$

Thus

$$\boxed{\frac{\partial \rho}{\partial t} = \frac{\Delta^2}{2\epsilon}\frac{\partial^2 \rho}{\partial x^2}}$$

$$D = \Delta^2/2\epsilon$$

The probability distribution (and hence the density) obeys (1-dim) diffusion equation

If also $\rho \geq 0$

$\int \rho\, dx = 1$

$\rho(x,t=0) = \delta(x)$

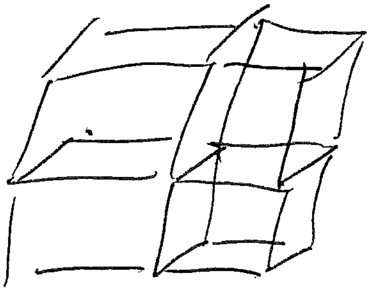
Then solution is

$$\boxed{\rho(x,t) = \frac{1}{\sqrt{4\pi D t}}\, e^{-x^2/4Dt}}$$

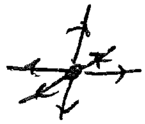
— and so we recover the normalized Gaussian

$$\sigma^2 = 2Dt = \Delta^2/\epsilon\; t$$

what about more dimensions?



e.g. cubic lattice in 3 dim



Now particle has 2d = 6 ways to go each with equal probability

$$\frac{\partial P}{\partial t} = \frac{\Delta^2}{2d\epsilon} \nabla^2 P$$

so $D = \frac{\Delta^2}{6\epsilon}$ in 3 dim

If we regard Δ as a mean free path, and Δ/ϵ as a mean velocity (between collisions), this is $\boxed{D = \frac{1}{6} L_{mf} \bar{c}}$ - in our crude model

(Differs by factor $\frac{1}{2}$ from formula in K+K)

In 3 dim, soln to $\frac{\partial P}{\partial t} = D \nabla^2 P$

$$\boxed{P(x,t) = \frac{1}{(4\pi D t)^{3/2}} e^{-\vec{x}^2/4Dt}}$$

peak reduced as distribution spreads

This is just the product of 3 independent distributions, for x_1, x_2, x_3

(spreading of ink drop)

width of distribution — (mean distance traveled)

$$\langle \vec{x}^2 \rangle = \tfrac{3}{2}(4Dt) = 6Dt$$

$$(= \Delta^2 t/\epsilon)$$

i.e. $\langle x_1^2 \rangle = \langle x_2^2 \rangle = \langle x_3^2 \rangle = \frac{1}{3}\Delta^2 t/\epsilon$

— since steps in a given direction 1/3 of the time

<u>Note</u> -- "average velocity" ~ $\frac{\langle x^2 \rangle}{t^2} = \frac{6D}{t} \to \infty$ as $t \to 0$

the "curve" traced out by randomly walking particle (in the formal limit of $\epsilon \to 0$ with D fixed) has no derivative, although it is continuous.

It is a "fractal" of dimension 2 (length of the curve ~ R^2, where R is radius of a circle that contains it)

Einstein (1905) noticed that $\langle x^2 \rangle = 6Dt$ can be applied to the Brownian motion of a small particle suspended in water. He also derived a formula for D, in terms of the mobility b of the suspended particle:

$$D = \tau b \quad (\text{"Einstein relation"}).$$

The mobility relates the force $\vec{F}$ applied to the particle and its drift velocity $\vec{v}$ (for "terminal" motion limited by frictional drag):

$$\vec{v} = b\vec{F}$$

Furthermore, the mobility of a sphere can be expressed in terms of the radius r of the particle and the viscosity η of the fluid (Stokes formula):

$$b = \frac{1}{6\pi\eta r}.$$

From observing the Brownian motion, one can measure $\langle x^2 \rangle / t$, hence D, and from Einstein's relation and the Stokes formula:

$$\frac{\langle x^2 \rangle}{t} = 6D = 6(k_B T)\, b = \frac{k_B T}{\pi \eta r}.$$

Einstein used this equation to estimate Boltzmann's constant k_B, and hence Avogadro's number

$$N_{\text{avo}} = R/k_B \quad \text{where } R \text{ is the gas constant}$$

($pV = R\bar{N}T$, where $\bar{N}$ is number in moles).

To derive the Einstein relation, note that an applied force produces a density gradient in equilibrium, where the diffusive flux matches and is opposite to the drift:

Total flux = 0 = Diffusive flux + drift flux

$$= -D\vec{\nabla}n + n\vec{v} = -D\vec{\nabla}n + nb\vec{F}$$

Furthermore, in equilibrium the density is proportional to the Boltzmann factor

$$n(\vec{x}) = \exp[-U(\vec{x})/\tau]$$

where $U(\vec{x})$ is the potential energy function, such that $\vec{F} = -\vec{\nabla}U$. Differentiating we find

$$\vec{\nabla}n = -\frac{1}{\tau}(\vec{\nabla}U)n = (\vec{F}/\tau)n$$

and plugging into the equation for the total flux:

$$0 = -D(\vec{F}/\tau)n + nb\vec{F} = (-D/\tau + b)n\vec{F} = 0$$

$$\Rightarrow \quad D = \tau b.$$

We can also derive the Einstein relation (up to a constant of order one) using our microscopic model of diffusion. Without any applied force, the suspended particle "forgets" its direction of motion in time ε, and moves with speed $V = \Delta/\varepsilon$; the diffusion constant is $D = \frac{\Delta^2}{2d\varepsilon} = \frac{1}{2d}V^2\varepsilon$ (in d spatial dimensions).

When the force <u>is</u> applied, the particle accelerates with $\vec{a} = \vec{F}/M$ (where M is its mass) in between successive times in which its direction of motion is "reset", hence acquiring <u>average</u> drift velocity

$$\vec{v} = \frac{1}{2}\vec{a}\varepsilon = \frac{1}{2}\vec{F}/M\,\varepsilon = b\vec{F} \quad \text{where} \quad b = \frac{\varepsilon}{2M},$$

and ε is the reset time. Writing $\varepsilon = \frac{(2d)D}{V^2}$, we have mobility

$$b = \varepsilon/2M = \frac{dD}{MV^2}.$$

The suspended particle is in equilibrium at temperature τ, hence (in between collisions)

$$\langle \tfrac{1}{2}MV^2 \rangle = d\left(\tfrac{1}{2}\tau\right)$$ by equipartition, or

$$\langle MV^2 \rangle = d\tau \Rightarrow \quad b = \frac{D}{\tau}.$$ This is the Einstein relation

(though the perfect agreement is somewhat fortuitous ---)

The Einstein relation is one of the earliest examples of a "fluctuation-dissipation relation." It relates the molecular motion responsible for erratic Brownian movement of a suspended particle ("fluctuation") to the drag when the particle is pulled through the fluid ("dissipation"); the connection between D and b relates molecular dynamics to a macroscopic response.

We already encountered another such relation: the Nyquist formula for Johnson noise. Compare:

$$\frac{\langle x^2 \rangle}{b} = 6\tau t \quad \text{and} \quad \frac{\langle V^2 \rangle}{R} = 4\tau(\Delta f)$$

In both formulas, the ratio of a measure of fluctuation to a measure of dissipation is controlled by the temperature.

What about the second law? Fluctuations in the thermal reservoir drive motion of a suspended particle, or current in a resistive circuit. But the motion/current do not produce useful work.

It's remarkable: Watching a pollen grain move under a microscope, and using a stop watch, you can determine Avogadros number.

$$\frac{\langle x^2 \rangle}{t} = 6\left(\frac{1}{6\pi\eta r}\right)\left(K_B T\right)$$

For $r = 1\ \mu m$, in water at $T = 300\,K$, particle moves $\langle x^2 \rangle^{\frac{1}{2}} \simeq 6\,\mu m$ in $t = 1$ minute.

After Einstein's prediction Jean Perrin (1909, Nobel Prize 1926) measured $N_{avo} \sim 6 \times 10^{23}$

Einstein himself, in another 1905 paper, estimated K_B from the black-body law:

$$J = \frac{\pi^2}{60}\,\frac{1}{\hbar^3 c^2}\left(K_B T\right)^4, \quad \text{finding } N_{avo} \simeq 6.17 \times 10^{23}.$$

That different estimates of N_{avo} yielded similar results reinforced the case for the reality of atoms.