1st quiz next Tue

come few minutes early to class

- put everything ~~off~~ desk except pen, pencil, or eraser
- no calculators
- 15 min

will post list of topics to know

Quick Review

Equilibrium macroscopic systems described by just a few macroscopic numbers, e.g. P, V, T

Criteria for equilibrium:

1. macroscopic time indep.
2. T same everywhere
3. P same everywhere unless grav, elect. fields, then P can vary
4. Fluxes are balanced when # of particles can vary chemical potential μ
5. no-relative macroscopic motion
6. properties independent of history, hardest to test

notion of internal microscopic motion scrambles history, e.g. random collisions in gas, liquid, random vibrations in solid

"ergodic": all possible ~~states~~ microscopic states eventually achieved

not obvious: wood
glass
alloys

quantum tunneling $\Rightarrow$ everything liquid over long enough times.

Review 2

For each kind of nonequilibrium, dissipation mechanisms act to restore equilibrium:

diff in temp $\Rightarrow$ heat conduction L^2/κ

diff in speeds (relative motion) $\Rightarrow$ viscous damping L^2/ν

diff in concentration $\Rightarrow$ particle diffusion L^2/D

diff in pressure $\Rightarrow$ relative motion L^2/ν

each mech has its own independent time scale, relaxation time τ

easiest to look up dissipation coefficients

$$\left.\begin{array}{ll} \text{thermal diffusivity} & \kappa \\ \text{kinematic viscosity} & \nu \\ \text{diffusion coeff} & D \end{array}\right\} \text{ all have units of } \frac{L^2}{T}$$

have to wait for longest relaxation time (usually many multiples) to reach equilibrium.

Class problem:

time to defrost Siberian mammoth

show slide

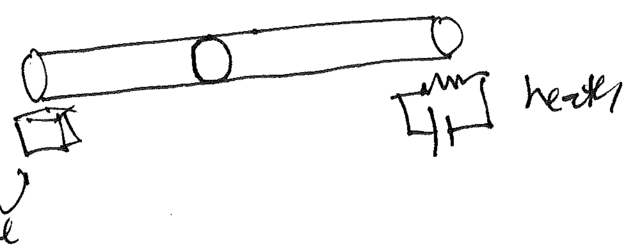
Small systems equilibrate quickly

100 nm blob of water

$$\tau_{thermal} = \frac{(10^{-7} m)^2}{2 \cdot 10^{-7} \frac{m}{s^2}} \simeq 10^{-7} s = 0.1 \mu s$$

so although most of universe non-equilibrium, small regions are in equil.

also explains why it is ok to talk about $T(t,x)$, T varying with time and space



although T strictly meaningful only for equil system, can apply to small region of system provided

$\Delta t > \tau$ local region equilibrates faster than overall dynamics

Why L^2 Scaling?
Why Does relaxation take so long?

Simple model of random collisions gives insight

Consider single He atom in middle of box of air (N_2)

assume:

(1) travels at constant speed v until it hits another molecule

(2) assume always travels same distance d before next collision

$d =$ mean free path

$\Delta t = d/v =$ collision time

for N_2 $\quad l \simeq 300\,nm >$ mean spacing $\approx$

$\simeq 40\times$ typical spacin

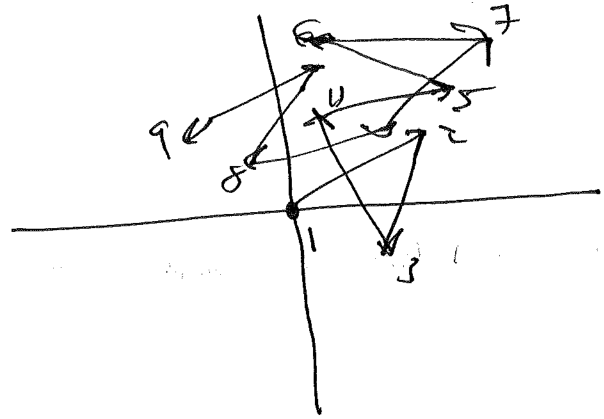
$\Delta t \simeq 3 \cdot 10^{-10} s \approx 0.3\,ns$

(3) assume each collision causes given particle to change direction randomly

Question: on average, how ~~...~~ far does particle get in time $T = N \Delta t$? $\quad N = \#$ of steps

Show MMA notebook

of random walk



note how plot looks like a long chain of links, our theory will apply to polymers

many repetitions suggest that, after N steps, particle has traveled distance $\sqrt{N}\, d$ from origin

compare with Nd if no collisions, travelling in straight line

more detailed analysis, with distribution of distance between collisions, gives same conclusion.

spectacular example: Sun has radius of $\simeq 2.2$ light-seconds
light you see started off as γ rays in core of Sun, took $\simeq 100{,}000$ years to diffuse to surface and escape!
core is dense, photons don't go far before colliding with p^+, e, etc...

1/20/11 (8)

Proof that $\langle L^2 \rangle \propto N$

Concept of <u>ensemble average</u>

$$\vec{X} = \vec{\Delta X}_1 + \vec{\Delta X}_2 + \cdots + \vec{\Delta X}_N = \sum_{i=1}^{N} \vec{\Delta X}_i$$

$|\vec{\Delta X}_i| = d$ all vector steps same distance

$$|\vec{X}|^2 = \vec{X}\cdot\vec{X} = (\vec{\Delta X}_1 + \vec{\Delta X}_2 + \cdots)\cdot(\vec{\Delta X}_1 + \vec{\Delta X}_2 + \cdots)$$

$$= \vec{\Delta X}_1^2 + \vec{\Delta X}_1\cdot\vec{\Delta X}_2 + \vec{\Delta X}_2^2 + \cdots + \vec{\Delta X}_2\cdot\vec{\Delta X}_1$$

$$= \sum_{i=1}^{N} \vec{\Delta X}_i^2 + 2\sum^{N}\sum_{i<j} \vec{\Delta X}_i\cdot\vec{\Delta X}_j$$

$$|X|^2 = Nd^2 + 2\sum\sum_{i<j} \vec{\Delta X}_i\cdot\vec{\Delta X}_j$$

now carry out ensemble average: repeat N steps from origin K diff times and record

$$\vec{\Delta X}_1^{(1)} \quad \vec{\Delta X}_1^{(2)} \quad \vec{\Delta X}_1^{(3)} \leftarrow \text{label of experiment}$$

$$\vec{\Delta X}_2^{(1)} \quad \vec{\Delta X}_2^{(2)} \quad \vec{\Delta X}_2^{(3)}$$

Define $\langle f \rangle$ = ensemble average

$$= \frac{1}{K}\sum_{s=1}^{K} f^{(k)}$$

← label f's value for k^{th} experiment starting in same way

$L^2 \propto N$ continued

Because $\langle \cdots \rangle$ is an average

$$\langle a+b \rangle = \langle a \rangle + \langle b \rangle$$

$$\langle cf \rangle = c \langle f \rangle \quad c \text{ some constant.}$$

Thus

$$\langle |x|^2 \rangle = \left\langle N d^2 + 2 \sum_{i<j} \vec{\Delta x}_i \cdot \vec{\Delta x}_j \right\rangle$$

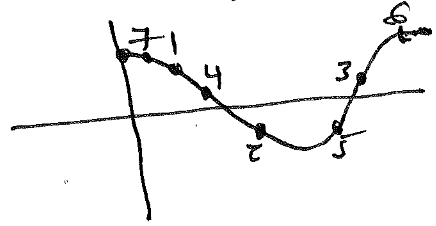
$$= \langle N d^2 \rangle + 2 \sum_{i<j} \langle \vec{\Delta x}_i \cdot \vec{\Delta x}_j \rangle$$

$$= N d^2 + 2 \sum_{i<j} \underbrace{\langle \cos(\theta_{ij}) \rangle}_{\text{tiny}} \rightarrow \frac{1}{K} \sum_{k=1}^{K} \cos(\theta_{ij}^{(k)})$$

becomes arbitrarily small for large K
try w/ Mathematica

$$\simeq N d^2 \quad \text{QED}$$

because random change in direction implies $\cos(\theta_{ij})$ will be averaged over all possible values of $0 \le \theta_{ij} < 2\pi$, plus and negative #s



so $\quad X_{rms} \propto \sqrt{N} \propto \sqrt{T} \Rightarrow T \propto X_{rms}^2$

L^2 scaling

$$\langle x^2 \rangle = \left(\frac{d^2}{\Delta t}\right) T$$

diffusion coeffiα $D = \frac{d^2}{\Delta t}$

Random walk is a big thing

Einstein used this idea to prove existence
of atoms <u>and</u> measure k and N_A accurately

$$\langle x^2 \rangle = \frac{kT}{3\pi \eta a} \cdot t$$

a = radius of little sphere
η = viscosity of fluid
t = observation time
k = Boltzmann's constant

experiments give
$R = N_A k$
so measuring k also
gives N_A

won Jean Perrin Physics Nobel in 1926

most cited paper of Einstein
big implications for biology: reliable processes in presence
of random collisions

path is fractal: infinite length, finite area

other ways to measure Avogadro's #?
Ben Franklin and tablespoon of oil