Lectures on Statistical Physics (A1)

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PART I. KINETIC THEORY.

§1. From certainties to probabilities.

— 1st year physics was deterministic: given initial positions and velocities of everything, from Newton's law could predict exact dynamics forever (modulo idealised models etc.)
So, in principle, we know how to describe classical, macroscopic world [NB: will learn from QM that this fails for microscopic world]

— What do we want to know about macroscopic many-particle systems, e.g. air in the room?
Practical measures: pressure, density, temperature (will learn shortly what this means)
Want to predict what will happen to these parameters as a function of some external influences (e.g. open window, turn on heating...)
Can we do this from Newton's laws?

— Air = many particles, flying around, colliding.
Simplest model: hard spheres, elastic collisions (billiard balls)
Say, we know all their positions and velocities at some $t=0$ (impossible even in principle — QM!)
Solve $\boxed{m\dot{\vec{v}} = \vec{F}}$ for each. Problem solved?

Three issues (apart from impossibility to do this):

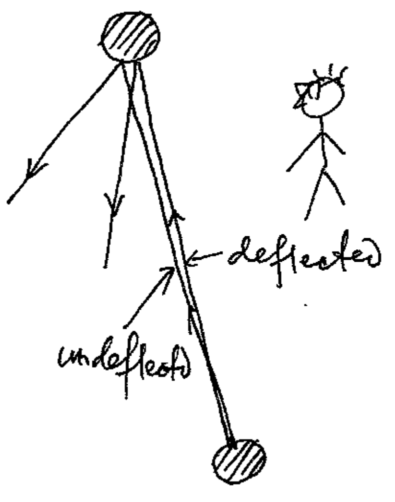
1) Too much information

$\sim 10^{28}$ particles in the room (Ex: estimate!)
So 1 data dump ($\vec{r}, \vec{v}$ for each particle at one time) takes about $5 \cdot 10^{17}$ Tb ($\sim 10^{8}$ yrs of Internet)
We can't process this — and don't need all this anyway

2) Sensitivity to initial conditions

Tiny external influences or imprecisions in initial conditions will result in completely wrong (different) solutions after just a few collisions.

Example. Consider a set of billiard balls. Suppose we are measuring their motion as they collide with each other. If someone enters the room, the deflection of balls due to his/her gravitational pull on the balls will completely alter trajectories after just ~ 10 collisions



Ex. Prove this!

Hint: consider all balls fixed, one moving and colliding with them.

Such systems are called chaotic, random. ["butterfly effect"]

3) Bulk properties is all we really care about.

So even if we did know where all the molecules are and how fast they are moving, we still have to develop a machinery for converting this information into some useful form.

So let us see what we really need to know. Q

The easiest thing to define is pressure (temperature is trickier — hold for it!)

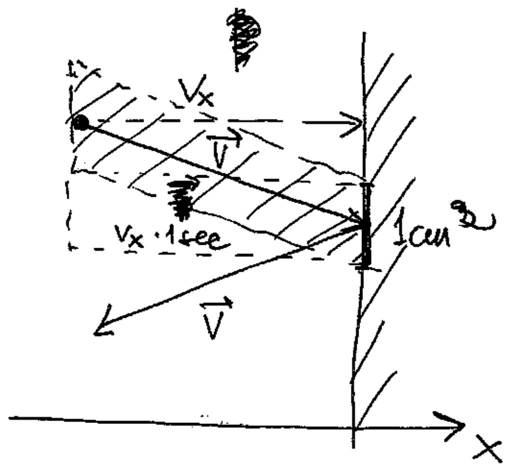
1.1. Pressure

[Pauli §24]

Pressure is force per unit area

force is momentum per unit time

Particles hit wall, bounce off — so their pressure on wall is momentum delivered to wall per unit time per unit area (of wall).



- Momentum delivered by one particle:

  $$2mv_x$$

- # of particles with v_x that hit $1\,cm^2$ of wall in 1sec = # of particles in shaded box

$$= \underbrace{1\,cm^2}_{\text{area}} \cdot \underbrace{v_x \cdot 1\,sec}_{\text{length}} \cdot n \cdot f(v_x)\,dv_x$$

n: overall # density of particles $[cm^{-3}]$ — Concentration

$f(v_x)\,dv_x$: fraction of particles with x-velocity in $[v_x, v_x+dx]$

$$dN(v_x) = v_x \cdot n\, f(v_x)\, dv_x$$

$dN(v_x)$: per unit time per unit area

So, pressure due just to the particles with $v_x \in [v_x, v_x + dv_x]$ is

$$dp = dN(v_x) \cdot 2mv_x = 2mv_x^2 \, n \, f(v_x) \, dv_x$$

Total pressure is the integral of this over all possible values of v_x:

$$p = \int\limits_{v_x > 0} dv_x \cdot 2mv_x^2 \, n \, f(v_x)$$

$v_x > 0$ ← only particles travelling towards the wall count.

Assume $f(v_x) = f(-v_x)$ (no preference between travelling towards or away from the wall – e.g. no mean flow in some specific direction; wall does not attract etc.). Then

$$p = mn \int_{-\infty}^{+\infty} dv_x \, v_x^2 f(v_x) = mn \underbrace{\langle v_x^2 \rangle}_{\text{average}}$$

NB: • We did not need to know <u>which</u> particles hit the wall [we will learn soon that for many systems this is in fact a meaningless question anyway as particles can be indistinguishable] — we just needed to know

1) particle mass
2) particle number density (concentration)
3) fraction of particles with particular velocity

So, what mattered, was the averages.

Let us then embrace the fact that motion is random/chaotic and that average properties of a large number of particles is what we need anyway. We will describe particle motion in terms of probabilities and our results will be statistical (this is why this course is called stat. physics)

For this, we will need a new mathematical machinery — theory of probability. [more in Steve Biller's course – here just the basic facts we will need]

[read BB Chapter 3 for a quick summary] $\boxed{\text{1.2 Probability}}$

- Random variable x can take values $x_1, x_2 \ldots$ [BB-3] with probabilities $P_1, P_2 \ldots$

So $\mathbb{P}\{x = x_i\} = P_i$

Normalisation: $\sum_i P_i = 1$

- Generalise to continuous random variables:

x can take values from some interval, say $[a, b]$

For any $x_0 \in [a,b]$, $\mathbb{P}\{x = x_0\} = 0$ because $[a,b]$ contains infinite # of points.

But instead of discrete probabilities P_i, we can define probability density function $f(x)$:

$$\mathbb{P}\{x \in [x_0, x_0+dx]\} = f(x_0)\,dx$$

[also known as p. distribution fn or pdf]

and, of course, $\int_a^b dx\, f(x) = 1$

This allows us to compute finite probabilities:

e.g. let $c \in [a,b]$. Then

$$\mathbb{P}\{x > c\} = \int_c^b dx\, f(x)$$

and averages (or means):

$$\langle x \rangle = \int_a^b dx\, x f(x) \qquad \left[\text{discrete: } \langle x \rangle = \sum_i x_i P_i\right]$$

$$\langle x^2 \rangle = \int_a^b dx\, x^2 f(x)$$

NB: If x is a physical quantity with some dimensions, $f(x)$ has dimensions inverse to it.

E.g. R.V. V_x – projection of particle velocity onto some direction x (e.g. $\perp$ wall)

$V_x \in (-\infty, +\infty)$

$f(V_x)dV_x$ – ~~[illegible]~~ probability for particle to have this velocity $\in [V_x, V_x + dV_x]$

↳ same as fraction of particles with such velocities (assume particle velocities random)

$$\int_{-\infty}^{+\infty} dV_x f(V_x) = 1$$

$$\langle V_x \rangle = \int_{-\infty}^{+\infty} dV_x\, V_x f(V_x) = 0 \text{ in our example}$$

(no mean velocity!)

$\langle v_x^2 \rangle = \int_{-\infty}^{+\infty} dv_x\, v_x^2 f(v_x)$ as in the calc. of pressure.

A few other facts :

- Joint pdf $f(x,y)$

$f(x_0,y_0)\,dx\,dy = \mathbb{P}\{x \in [x_0, x_0+dx] \text{ and } y \in [y_0, y_0+dx]\}$

so, if we want to describe a gas in 3D,
we need $f(v_x, v_y, v_z) \equiv f(\vec{v})$

$$\iiint f(v_x,v_y,v_z)\,dv_x\,dv_y\,dv_z = 1 \quad \text{or} \quad \int d^3\vec{v}\, f(\vec{v}) = 1$$

Then $f(v_x) = \iint f(v_x,v_y,v_z)\,dv_y\,dv_z$ Q

(if we care only about v_x, we must allow ~~always~~ v_y, v_z to take any values)

and $p = mn \iiint v_x^2 f(v_x,v_y,v_z)\,dv_x\,dv_y\,dv_z$

- In fact, particle positions are also random,
so we have $F(\vec{r}, \vec{v})$

$F(x,y,z,v_x,v_y,v_z)\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z =$ ~~[illegible]~~
fraction of particles in a cube $dx\,dy\,dz$ at position (x,y,z)
with velocities in the interval $(v_x, v_x+dv_x)\times(v_y, v_y+dv_y)\times(v_z, v_z+dv_z)$

It is conventional to normalise this space-dependent distribution not to 1, but to ~~particle density~~ # of particles

$$\int d^3\vec{r}\int d^3\vec{v}\; F(\vec{r},\vec{v}) = N$$

Then $\int d^3\vec{v}\, F(\vec{r},\vec{v}) = n(\vec{r})$ # density (distr. of particles in space, without regard to velocities) $\quad \int d^3\vec{r}\, n(\vec{r}) = N$

System is called homogeneous if $F(\vec{r},\vec{v}) = F(\vec{v})$.
indep. of $\vec{r}$

Then $\int d^3\vec{v}\, F(\vec{v}) = n = \dfrac{N}{V}$
indep. of $\vec{r}$

and $f(\vec{v}) = \frac{1}{n} F(\vec{v})$, so $\int d^3\vec{v}\, f(\vec{v}) = 1$

Note that $p = mn\int d^3\vec{v}\, v_x^2 f(\vec{v})$ implicitly assumed a homogeneous situation. More generally,

$$p(\vec{r}) = \int d^3\vec{v}\, m v_x^2 F(\vec{r},\vec{v})$$

- Probabilities of independent events multiply (*)

so, if x and y are indep. r.v.,

$$f(x,y) = f(x)\,f(y)$$

(*) Ex. Indep. events have an amazing property called C.L.T. Look it up!

For example, in gas of elastically colliding particles, one might argue that all components of velocity are distributed independently (we choose x, y, z arbitrarily and collisions conserve momentum in projection on each direction). Then

$$f(v_x, v_y, v_z) = f(v_x)\,f(v_y)\,f(v_z)$$

[Maxwell; we'll see conseq. of this form]

• Averaging operation is linear:

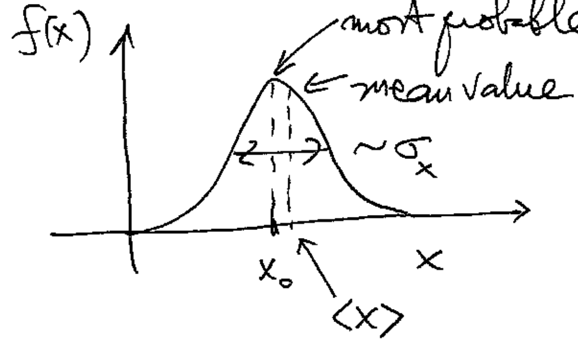
$$\langle ax+by+c\rangle = a\langle x\rangle + b\langle y\rangle + c$$

(simply because avg is an integral — summation is linear!)

For indep. r.v., $\langle xy\rangle = \langle x\rangle\langle y\rangle$

[follows from $f(x,y)=f(x)\,f(y)$]

• Deviations from mean



Measure departures from mean ("width" of pdf) by variance (or mean sq. deviation)

$$\sigma_x^2 \equiv \langle (x-\langle x\rangle)^2\rangle = \langle x^2\rangle - \langle x\rangle^2$$

Ex. Prove this.

Standard (or rms) deviation

$$\sigma_x = \sqrt{\sigma_x^2} = \sqrt{\langle x^2\rangle - \langle x\rangle^2}$$

• Isotropic distribution.

If we consider a situation where there are no preferred directions (particles of air in the room don't really feel gravity, e.g.), then

$$f(v_x, v_y, v_z) = f(v) \quad \text{fn only of } v=|\vec v| \text{ speed.}$$

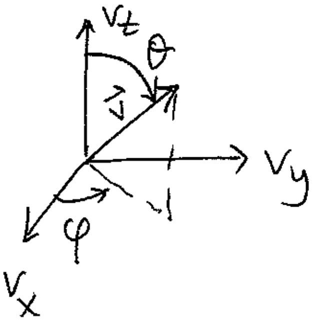
Then let's work out pdf of speed:

$$f(v_x,v_y,v_z)\,dv_x\,dv_y\,dv_z = f(v)\,\underbrace{v^2 dv \underbrace{\sin\theta}\, d\theta\, d\varphi}_{\text{polar coordinates in } v \text{ space}}$$

(end of L1.)

~~These are particular examples~~

So now $f(v)\,v^2 \sin\theta$ = prob. for particle velocity to be such that speed $\in [v, v+dv]$ and angles are in the intervals $[\theta, \theta+d\theta]$ and $[\varphi, \varphi+d\varphi]$.



This is a particular example of a more general operation, transformation of variables:

Let $u = u(x,y)$ (e.g.)
$v = v(x,y)$

Then $f(x,y)\,dx\,dy = \underbrace{f(x,y)\left|\frac{\partial(x,y)}{\partial(u,v)}\right|}_{\tilde{f}(u,v)} du\,dv$

Jacobian (change in the volume of an elemental cube)

transformed

So, $\tilde{f}(u,v) = f(x,y)\left|\frac{\partial(x,y)}{\partial(u,v)}\right|$ – pdf of u,v.

So, in our example, $\tilde{f}(v,\theta,\varphi) = f(v)\,v^2 \sin\theta$

$(v_x, v_y, v_z) \to (v, \theta, \varphi)$

(NB: distr. uniform in φ but not in θ!)

The distr. of speeds:

$$\tilde{f}(v) = \int d\theta \int d\varphi\, \tilde{f}(v,\theta,\varphi) = v^2 f(v) \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\varphi$$

$$= 4\pi v^2 f(v)$$

NB: $\int_0^{\infty} dv\, \tilde{f}(v) = 1$ (Ex. Convince yourself this is true)

Let us apply this to our calculation of pressure:

$$p = mn\langle v_x^2\rangle = \quad \text{assume isotropic} = f(v)$$

$$= mn\int d^3\vec{v}\; v_x^2 f(\vec{v}) =$$

$$= mn\int dv\, v^2 \int d\theta \sin\theta \int d\varphi\, f(v)\, v^2 \underbrace{\sin^2\theta \cos^2\varphi} =$$

$$= mn\,\frac{4\pi}{3}\int_0^\infty dv\, v^4 f(v)$$

$$= mn\,\frac{1}{3}\int_0^\infty dv\, v^2 \tilde{f}(v) = \frac{1}{3} mn\langle v^2\rangle$$

Ex. 1) Check this result

2) You can simplify integration a bit if you recall that we just arbitrarily called x direction x – it can just as well be z (or y – same result too)

In fact there is an even simpler way:

isotropy $\Rightarrow$ $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle$ (all direction are equal)

But $v^2 = v_x^2 + v_y^2 + v_z^2$

So $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = \frac{1}{3}\langle v^2\rangle$

and $p = \frac{1}{3} mn\langle v^2\rangle = \frac{1}{3} mv \int_0^\infty dv\, v^2 \tilde{f}(v)$ [BB-6]

Note that BB call $\tilde{f}(v) \to f(v)$ – distr. of speeds (and $f \to g$)

HW. Ex. For an isotropic distribution,

$\langle v_x v_y\rangle = ?$

$\langle v_x v_z\rangle = ?$

$\langle v_y v_z\rangle = ?$

(can calculate both directly and via symmetry arg.)