Key points from previous lecture

(1) how to extend Boltzmann machinery to classical systems with continuously varying labels like x, p, θ

(2) need to change from probability p_s for discrete state s to probability density $\mathcal{D}(q)$, which gives probability $\mathcal{D}(q)\,dq$ for system in equilibrium with reservoir of temp T to be ~~have~~ in particular state such that the quantity q lies in small range $q, q+dq$

(3) $\int_{-\infty}^{\infty} \mathcal{D}(q)\,dq = 1$ $\qquad \int_a^b \mathcal{D}(q)\,dq$ = prob for q to lie in interval $[a,b]$

(4) $$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x(q)\, e^{-\beta E(q)}\, dq}{\int_{-\infty}^{\infty} e^{-\beta E(q)}\, dq} \equiv \frac{1}{Z}\sum_s x_s p_s$$

$$\langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} \qquad Z = \int_{-\infty}^{\infty} e^{-\beta E(q)}\, dq$$

q is cont, variable

(5) applications to equipartition theorem with $E(q) = cq^2$) to classical electric dipole $E = -\vec{p}\cdot\vec{\mathcal{E}} = -p\mathcal{E}\cos\theta$ ← cont, variable

See my lecture ~~no~~ notes of 3/29 for more details

Applied ideas to ideal gas of non-interacting molecules of mass m at temperature T

$$\vec{E}(\vec{v}) = E(v_1, v_2, v_3) = \frac{1}{2}mv^2$$

Then velocity probability distribution $\mathcal{D}(\vec{v})$, which gives probability to observe molecule with velocity components in small ranges

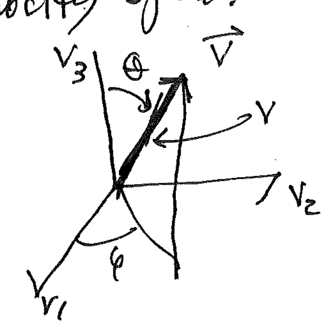
$$v_1, v_1+dv_1 \qquad v_2, v_2+dv_2 \quad v_3, v_3+dv_3$$

given by

$$\mathcal{D}(v_1,v_2,v_3) = \frac{e^{-\beta[\frac{1}{2}mv^2]}}{\int_{-\infty}^{\infty}dv_1\int_{-\infty}^{\infty}dv_2\int_{-\infty}^{\infty}dv_3\, e^{-\beta\frac{1}{2}mv^2}} = \frac{e^{-\beta[\frac{1}{2}mv^2]}}{\left(\int_{-\infty}^{\infty}dv_1\, e^{-\beta\frac{1}{2}mv_1^2}\right)\left(\int_{-\infty}^{\infty} v_2\right)\left(\int_{-\infty}^{\infty} v_3\right)}$$

$$\boxed{\mathcal{D}(v_1,v_2,v_3) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\beta mv^2/2}}$$

If we are not interested in orientation of velocity vector, just the speed v, we can switch to spherical coordinates in velocity space:



$$\vec{v} = (v_1, v_2, v_3) \longrightarrow (v, \theta, \varphi)$$

$$v^2 = v_1^2 + v_2^2 + v_3^2$$

$$v_1 = v\sin\theta\cos\varphi \quad v_2 = v\sin\theta\sin\varphi \quad v_3 = \cos\theta$$

$$dv_1\,dv_2\,dv_3 \to v^2\sin\theta\, dv\,d\theta\,d\varphi$$

$$1 = \underbrace{\int_{-\infty}^{\infty}}_{v_1}\underbrace{\int_{-\infty}^{\infty}}_{v_2}\underbrace{\int_{-\infty}^{\infty}}_{v_3}\mathcal{D}(v_1,v_2,v_3)\,dv_1\,dv_2\,dv_3 = \underbrace{\int_0^{\infty}}_{v}\underbrace{\int_0^{\pi}}_{\theta}\underbrace{\int_0^{2\pi}}_{\varphi}\mathcal{D}(v,\theta,\varphi)\cdot v^2\sin\theta\,dv\,d\theta\,d\varphi$$

If we evaluate the θ, φ integrals, we find:

$$1 = \int_0^\infty \underbrace{(4\pi v^2)\left[\frac{m}{2\pi kT}\right]^{3/2} e^{-\beta m v^2/2}}_{\text{this must be a prob. density}} dv$$

This tells us that

$$\boxed{\mathcal{D}(v) = \left(\frac{m}{2\pi kT}\right)^{3/2} \cdot 4\pi v^2 \cdot e^{-\beta m v^2/2}}$$

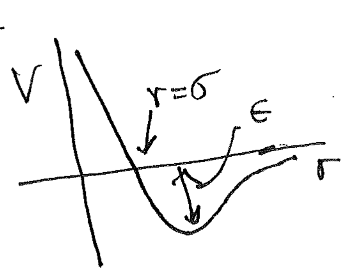
Maxwell speed distribution

is probability density for speed of molecule in equilibrium ideal gas. This is highly non-obvious result from classical mechanics point of view: if we throw a lot of small balls together and they start colliding with walls and with each other, speeds spread out until consistent with this expression.

Can get some intuition by looking at computer simulation of 2D gas consisting of point particles that collide elastically (no friction so energy is conserved during each collision)

Look at Java applets posted on Lectures webpage

(1) molecular dynamics $\quad m \frac{d\vec{x}_i}{dt} = \sum_j \vec{F}_{ij}$



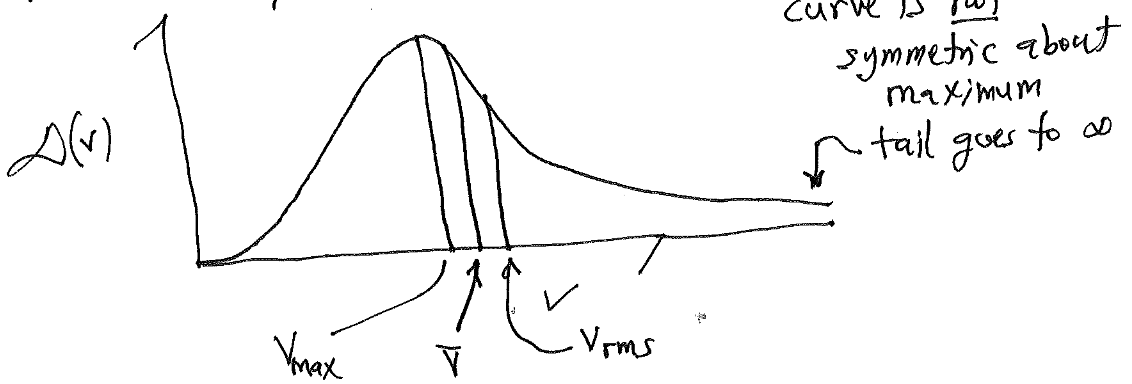
Lennard Jones potential $\quad V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

use toroidal geometry (periodic walls)

$$\frac{3}{2}kT = \left\langle \frac{1}{2} m v^2 \right\rangle \leftarrow \text{compute } T \text{ from } \vec{v}_i\text{'s}$$

<u>Brief class project:</u> a single He atom with mass m_{He} is thrown into container of N molecules with mass m_{N_2} and everything comes to equilibrium with temperature T. Write down expression for probability that He atom will have speed between $200 \frac{m}{s}$ and $400 \frac{m}{s}$.

Distribution has following shape



$$\frac{d\mathcal{D}(v)}{dv} = 0 \Rightarrow v_{max} = \left(\frac{2kT}{m}\right)^{1/2} \quad \approx 420 \tfrac{m}{s} \text{ for } N_2 \text{ at } T = 300K$$

$$\bar{v} = \int_0^\infty v\,\mathcal{D}(v)\,dv = \left(\frac{8kT}{\pi m}\right)^{1/2}$$

$$v_{rms} = \left[\int_0^\infty v^2 \mathcal{D}(v)\,dv\right]^{1/2} = \left(\frac{3kT}{m}\right)^{1/2}$$

consistent with equipartition $\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} kT$

$$v_{rms} : \bar{v} : v_{max} = \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} = 1.22 : 1.13 : 1$$

all rather close in value, for 10% accurate calculations, use any one

Comment (not needed for quizzes or exams, just for fun and insight):

high-speed tail of Maxwell distribution drops off rapidly with increasing speed v, NIntegrate can fail to give useful answer.

For example, in our classroom at room temperature, for what speed v_1 will only ten molecules be moving faster than v_1?

Need to use asymptotics, Problem B.5 on p. 387 of Schroeder

$$\int_x^\infty t^2 e^{-t^2} dt \simeq e^{-x^2} \cdot \frac{x}{2} + \frac{1}{4x} + O(x^{-3}) \quad x \gg 1$$

Then:
$$\frac{L_x L_y L_z}{22\ \ell/\text{mole}} \times \frac{6 \cdot 10^{23}\ \text{molecules}}{\text{mole}} \times \int_{v_1}^\infty \mathcal{D}(v)\,dv = 10$$

$L_x \sim 10\text{m}$, $L_y \sim 6\text{m}$, $L_z = 3\text{m}$, $22\ell = 22 \cdot 10^{-3}\text{m}^3$

$$10^{27} \frac{x}{2} \cdot e^{-x^2} = 10 \qquad \text{where } x = \frac{v_1}{v_{max}}$$

If $x \gg 1$, $\frac{x}{2}$ is large number multiplying reciprocal of a very ~~large~~ small number e^{-x^2} so $\frac{x}{2} e^{-x^2} \approx e^{-x^2}$ so $10^{27} e^{-x^2} \approx 10$

$$\Rightarrow x = \frac{v_1}{v_{max}} \simeq 8$$ i.e. almost no molecules moving faster than Mach 8

in particular, no particles moving relativistically, near speed of light

Important to evaluate average powers of v, v^n, for many kinetics problems. In homework, you show result:

$$\langle v^n \rangle = \int_0^\infty v^n \mathcal{D}(v)\,dv = \int_0^\infty v^n \left[\left(\frac{m}{2\pi kT}\right)^{3/2} \cdot 4\pi v^2 e^{-\beta m v^2/2}\right] dv$$

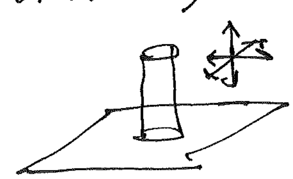
$$\boxed{\langle v^n \rangle = \frac{2}{\sqrt{\pi}}\left(\frac{2kT}{m}\right)^{n/2} \Gamma\left(\frac{n+3}{2}\right)}$$

holds even for ~~...~~ n a non-integer real number

E.g. $\langle v^2 \rangle = \frac{2}{\sqrt{\pi}}\left(\frac{2kT}{m}\right)^{2/2} \Gamma\left(\frac{5}{2}\right) = \frac{3kT}{m}$

since $\Gamma\left(\frac{5}{2}\right) = \frac{3}{2}\Gamma\left(\frac{3}{2}\right) = \frac{3}{4}\Gamma\left(\frac{1}{2}\right) = \frac{3\sqrt{\pi}}{4}$

We can finally go back to kinetic theory of Chapter 1 and do general case of isotropic gas in thermodynamic equilibrium with temperature T. For example, let's calculate flux of particles through tiny hole of area A whose diameter is smaller that a mean free path. Original argument looked like this:

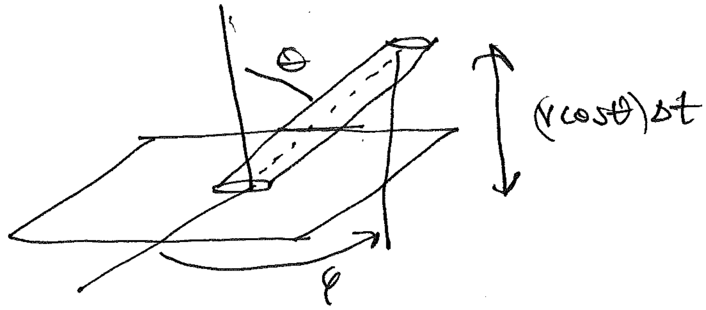


anisotropic gas
all speeds the same, v

$$\Delta N = \frac{1}{6} \cdot A \cdot (v\Delta t) \cdot \frac{N}{V}$$

$$\Rightarrow \Phi = \frac{1}{A}\frac{dN}{dt} = \frac{1}{6}\left(\frac{N}{V}\right) v \leftarrow \text{but what } v \text{ to use?}$$

v_{max}, $\bar{v}$, v_{rms}, v?



For isotropic gas velocities, we can repeat our argument from before:

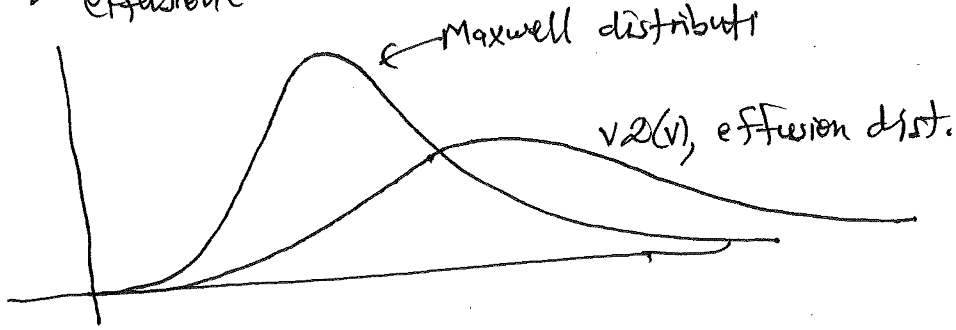
$$dN = \underbrace{A \cdot (v\cos\theta)\Delta t}_{dV} \times \frac{N}{V} \times \frac{\sin\theta \, d\theta \, d\varphi}{4\pi} \times \underbrace{\mathcal{D}(v)\,dv}$$

new factor, fraction of molecules with speed $v, v+dv$

$$d\Phi = \frac{dN}{A\Delta t} = n \cdot \frac{\sin\theta\cos\theta\, d\theta\, d\varphi}{4\pi} \cdot v\,\mathcal{D}(v)\,dv$$

This leads to unexpected insight: speed distribution of particles coming out of hole by effusion is not Maxwell distribution inside of gas:

$$\mathcal{D}_{effusion}(v) \propto v\,\mathcal{D}(v)\,dv$$



particles in effusion beam are hotter on average. In next homework assignment, you figure this out:

$$\frac{\langle E_{effusion}\rangle}{\langle E_{gas}\rangle} > 1 \quad = ?$$

Completing the calculation of the flux, we find

$$\Phi = \int_0^\infty dv \int_0^{\pi/2} d\theta \int_0^{2\pi} d\varphi \, d\Phi(\theta, \varphi, v)$$

$$= \frac{1}{4} n \bar{v} \quad \text{where} \quad \bar{v} = \int_0^\infty v \mathcal{D}(v)\, dv = \left(\frac{8kT}{m}\right)^{1/2}$$

so v in flux calculation is <u>not</u> v_{rms}, but the real average.

<u>For pressure calculation,</u> we would have

$$\underbrace{\Delta p}_{\substack{\text{change in}\\ \text{momentum}\\ \text{in time } \Delta t}} = A \cdot (v\cos\theta\, \Delta t) \times \left(\frac{N}{V}\right) \times \frac{\sin\theta\, d\theta\, d\varphi}{4\pi} \times 2mv\cos\theta \times \mathcal{D}(v)\,dv$$

leads to $\int_0^\infty v^2 \mathcal{D}(v)\, dv = v_{rms}^2$ ✓

<u>For energy calculation</u> · (cold plate problem),

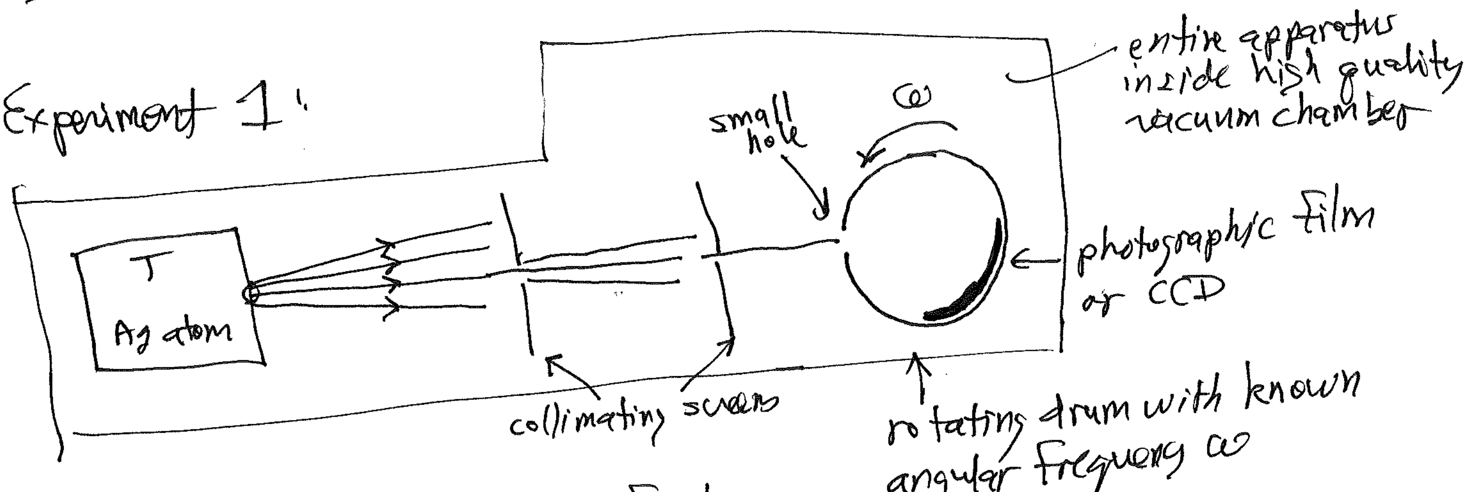
$$\Delta E = A \cdot v\cos\theta\, \Delta t \times \frac{N}{V} \times \frac{\sin\theta\, d\theta\, d\varphi}{4\pi} \times \frac{1}{2} m v^2 \times \mathcal{D}(v)\, dv$$

leads to integral $\int_0^\infty v^3 \mathcal{D}(v)\, dv$ ⇐ evaluate using gamma f^n^

3^rd^ moment of speed, not related to $\bar{v}$, v_{rms}, or v_{max}

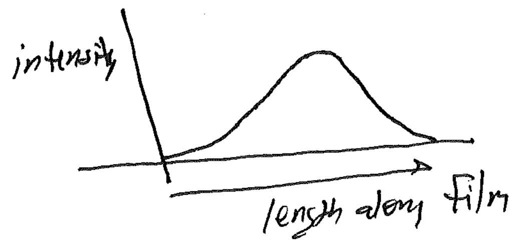
Effusion discussion gives idea of <u>how to</u> confirm the Maxwell speed distribution experimentally

Experiment 1:

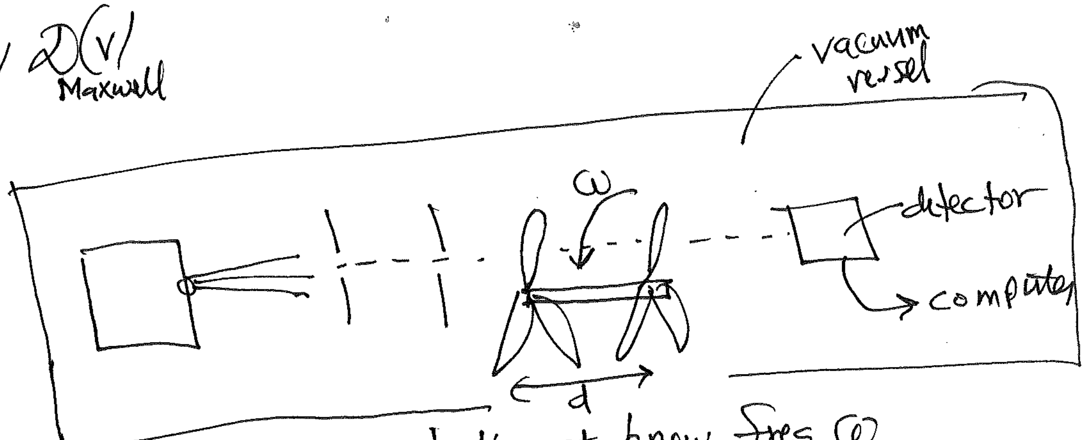


fastest particles will hit film first, then slower particles. Measuring degree of exposure will give $\mathcal{D}_{effusion}(v)$, compare with theory

$$c\, v\, \mathcal{D}_{Maxwell}(v)$$



Experiment 2:



use "chopper" to propellers on axis rotating at know freq ω only molecules moving in certain range of speeds $v_1 \le v \le v_2$ will not get blocked by second blade, so plot intensity $I(\omega)$, relate to $\mathcal{D}_{effusion}(v) \propto v\, \mathcal{D}_{Maxwell}(v)$.

What would 21st century exp't be? Doppler shift?

Maxwell distribution holds even for interacting colliding molecules!

General case, energy has form

$$E_i = \frac{1}{2}m\vec{v}_i^2 + \underbrace{V_{ext}(x_i, y_i, z_i)}_{\text{external grav. or electric field}} + \underbrace{\sum_{i \neq j} V_{mol}(\vec{x}_i - \vec{x}_j)}_{\text{pairwise interactions with other molecules}}$$

$$e^{-\beta E_i} = \underbrace{e^{-\frac{1}{2}mv_i^2 \beta}}_{\text{doesn't depend on locations}} \times \underbrace{e^{-\beta[V_{ext}(\vec{x}_i) + V_{int}(\vec{x}_1, \vec{x}_2, \dots)]}}_{\text{doesn't depend on velocities}}$$

So can integrate over all spatial coordinates and find <u>same</u> speed distribution $\mathcal{D}(v)dv$.

Harder to include effects of walls ...

Also implies that, for equilibrium atmosphere with constant temperature T, exponentially decreasing pressure and density, $\mathcal{D}(v)$ will be same at all heights.