Key points from previous lecture

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

(2) need to change from probability \( P_s \) for discrete states \( s \) to probability density \( \rho(\theta) \), which gives probability \( \rho(\theta) \, d\theta \) for system in equilibrium with reservoir of temp \( T \) to be in a particular state such that the quantity \( q \) lies in small range \( a, b + d\theta \)

(3) \[ \int_{-\infty}^{\infty} \rho(\theta) \, d\theta = 1 \]
\[ \int_{a}^{b} \rho(\theta) \, d\theta = \text{prob for } \theta \text{ to lie in interval } [a, b] \]

(4) \[ \langle x \rangle = \frac{\int_{-\infty}^{\infty} x(\theta) e^{-\beta E(\theta)} \, d\theta}{\int_{-\infty}^{\infty} e^{-\beta E(\theta)} \, d\theta} = \frac{1}{Z} \sum_{s} x_s \rho_s \]
\[ \langle E \rangle = -\frac{1}{Z} \frac{2\pi}{\beta} \varphi \]

(5) applications to equipartition theorem with \( E(\theta) = C(\theta) \)

See my lecture notes of 3/29 for more details
Applied ideas to ideal gas of non-interacting molecules of mass $m$ at temperature $T$

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

Then velocity probability distribution $\varphi(v)$, which gives probability to observe molecule with velocity components in small ranges $v_1, v_1 + dv_1, v_2, v_2 + dv_2, v_3, v_3 + dv_3$

given by

$$\varphi(v_1, v_2, v_3) = \frac{1}{\sqrt{2\pi} kT} e^{-\frac{m v^2}{2 kT}}$$

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

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

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

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

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

$$dv_1 dv_2 dv_3 \rightarrow v^2 \sin \theta \sin \phi \, dv \, d\theta \, d\phi$$

$$1 = \int \int \int \varphi(v_1, v_2, v_3) \, dv_1 \, dv_2 \, dv_3 = \int_0^\infty \int_0^{2\pi} \int_0^\pi \varphi(v, \theta, \phi) \cdot v^2 \sin \theta \, dv \, d\theta \, d\phi$$
If we evaluate the $\theta, \phi$ integrals, we find:

$$1 = \int_0^\infty \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\beta \frac{m}{2}} \frac{1}{4\pi \sigma^2} \, dv$$

This tells us that

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

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

$$m \frac{d\vec{x}_i}{dt} = \sum_j F_{ij}$$

Lennard-Jones potential

$$V(r) = 4\varepsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right\}$$

we toroidal geometry (periodic walls)

$$\frac{3}{2} kT = \left\langle \frac{1}{2} m v^2 \right\rangle$$

compute $T$ from $V$,
Brief class project: a single He atom with mass $m_{He}$ is thrown into a container of $N$ air 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

$\Delta(v)$

$V_{max}$ $V$ $V_{rms}$

curve is not symmetric about maximum, tail goes to $\infty$

$\frac{d2(v)}{dv} = 0 \Rightarrow V_{max} = \left(\frac{2kT}{m}\right)^{1/2}$

$\bar{V} = \int_{0}^{\infty} v \Delta(v) dv = \left(\frac{8kT}{m}\right)^{1/2}$

$V_{rms} = \left[\int_{0}^{\infty} v^2 \Delta(v) dv\right]^{1/2} = \left(\frac{3kT}{m}\right)^{1/2}$

consistent with equipartition

$\langle \frac{1}{2}mv^2 \rangle = \frac{3}{2} kT$

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

all rather close in value. For 10% accuracy 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 $V$, will only ten molecules be moving faster than $V$?

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

$$\int_{0}^{\infty} x^2 e^{-x^2/2} \, dx \approx \sqrt{\frac{2\pi}{1}} x^2 + \frac{1}{\sqrt{x}} + O(x^{-3/2})$$

Then:

$$\frac{L_x L_y L_z}{22 \text{ e/mole} \times 6.023 \text{ molecules}} \times \int_{0}^{\infty} 20(v) \, dv = 10$$

$L_x = 10 \text{ m}$, $L_y = 6 \text{ m}$, $L_z = 3 \text{ m}$, $22L = 22 \times 10^{-3} \text{ m}^3$

$$10^{27} \frac{x^2}{2} e^{-x^2} = 10 \quad \text{where} \quad x = \frac{V_i}{V_{max}}$$

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

$$\Rightarrow x = \frac{V_i}{V_{max}} \approx 8 \quad \text{i.e. almost no molecule moving faster than Mach 8}$$

in particular, no particle moving relativistically, near speed of light
Important to evaluate average power of $v, v^n$
for many kinetic problems. In homework, you show result:

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

\[
\langle v^n \rangle = \frac{2}{\sqrt{\pi}} \left( \frac{2\pi T}{m} \right)^{n/2} \pi \left( \frac{n+3}{2} \right)
\]

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

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

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

We can finally go back to kinetic theory of Chapter 4 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 than a mean free path. Original argument looked like this:

\[
\Delta N = \frac{1}{6} \cdot A \cdot (\sqrt{4T}) \cdot \frac{N}{V}
\]

\[
\Rightarrow \vec{F} = \frac{1}{A} \frac{\Delta N}{dt} = \frac{1}{6} \left( \frac{N}{V} \right) V \text{ but what } V \text{ to use?}
\]

$V_{\text{max}}, \bar{V}, V_{\text{rms}}, V^\dagger$
For isotropic gas velocities, we can repeat our argument from before:

\[
\frac{dN}{dV} = \frac{A \cdot (V \cos \theta) \cdot t}{N} \cdot \frac{N}{V} \cdot \frac{\sin \theta \cdot d\theta \cdot d\psi}{4\pi} \cdot f(v) \cdot dv
\]

\[
pf = \frac{dn}{A \cdot \Delta t} = n \cdot \frac{\sin \theta \cdot cos \theta \cdot d\theta \cdot d\psi \cdot v \cdot f(v) \cdot dv}{4\pi}
\]

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

\[
D_{\text{effusion}}(v) \propto v \cdot f(v) \cdot dv
\]

\[
\text{Maxwell distribution}
\]

\[
\text{v}_2 \sigma(v) \text{, effusion dist.}
\]

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

\[
\frac{\langle E_{\text{effusion}} \rangle}{\langle E_{\text{gas}} \rangle} > 1 \Rightarrow \frac{2}{2} = 2
\]
Completing the calculation of the flux, we find

\[ \Phi = \int_0^\infty \int_0^{\pi/2} \int_0^\infty \Phi(\theta, \phi, \nu) \, d\phi \, d\theta \, d\nu \]

\[ = \frac{1}{4} \nu \bar{V} \quad \text{where} \quad \bar{V} = \int_0^\infty \nu D(\nu) \, d\nu = \left( \frac{8\pi hT}{m} \right)^{1/2} \]

so \( \nu \) in flux calculation is not \( \nu_{rms} \), but the real average.

For pressure calculation, we would have

\[ \Delta P = A \cdot (V \cos \theta) \times \left( \frac{N}{V} \right) \times \frac{\sin \theta \, d\theta \, d\nu}{2\pi} \]

\[ \text{change in momenta in time } dt \]

\[ \text{leads to} \quad \int_0^\infty \nu^2 D(\nu) \, d\nu = \nu_{rms}^2 \]

For energy calculation. (cold plate problem)

\[ \Delta E = A \cdot V \cos \theta \cdot dt \times \left( \frac{N}{V} \right) \times \frac{\sin \theta \, d\theta \, d\nu}{2\pi} \times \left( \frac{1}{2} m \nu^2 \right) \times D(\nu) \, d\nu \]

\[ \text{leads to integral} \quad \int_0^\infty \nu^3 D(\nu) \, d\nu \quad \leftarrow \text{evaluate using Gamma function} \]

3rd moment of speed, not related to \( \bar{V}, \nu_{rms}, \) or \( \nu_{max} \).
Effusion discussion gives idea of how to confirm the Maxwell speed distribution experimentally.

**Experiment 1:**

Fastest particles will hit film first, then slower particles. Measuring degree of expulsion will give $D_{effusion}$ compare with theory $CV^2D(v)/Maxwell$.

**Experiment 2:**

Use "chopper" to propel on axis rotating at known freq $\omega$. Only molecules moving in certain range of speeds $v_1 < v \leq v_c$ will not get blocked by second blade, so plot intensity $I(\omega)$ relates to $D_{effusion}(v) \propto D_{Maxwell}(v)$.

What would 21st century exp't be? Doppler shift?
Maxwell distribution holds even for interacting colliding molecules!

General case, energy has form

\[ E_i = \frac{1}{2}mv_i^2 + V(x_i, y_i, z_i) + \sum_{i \neq j} V(x_i, x_j) \]

- external grav.
- pairwise interactions with or electric field
- other molecules

\[ e^{-\beta E_i} = e^{-\frac{1}{2}mv_i^2} \times e^{-\beta \left[ V_{\text{ext}}(x_i) + V_{\text{int}}(x_i, x_j) \ldots \right]} \]

- doesn't depend on location
- doesn't depend on velocities

So can integrate over all spatial coordinates and find same speed distribution \( \pi N \pi v \).

Harder to include effect of walls ...

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