Week 1

Perspectives on the Maxwell-Boltzmann Distribution

1.1 Background and Ideal Gas Distributions

3/28:
- Learning objectives for CHEM 263.

    - The time-dependent phenomena.
    - Reaction rate and rate laws.
    - Reaction mechanisms and reaction dynamics.
    - Surface chemistry and catalysis.
    - Experimental design and instruments.

- Before we move into the content of CHEM 263, a few important notes from CHEM 262.

- **Partition function** (for a system with N states): The following function of temperature. *Denoted by* $\boldsymbol{Q(T)}$. *Given by*

$$Q(T) = \sum_{n=1}^{N} e^{-E_n/k_{\mathrm{B}}T}$$

- **Observable**: A quantum mechanical operator.

- Consider a system described by the partition function Q. Let $|i\rangle$ denote the state with energy E_i, and let A be an observable. Then the expected value of the observable A is given by

$$\langle A \rangle = \frac{1}{Q} \sum_{|i\rangle} \langle i|A|i\rangle \, e^{-E_i/k_{\mathrm{B}}T}$$

    - "This fundamental law is the summit of statistical mechanics, and the entire subject is either the slide-down from this summit, as the principle is applied to various cases, or the climb-up to where the fundamental law is derived and the concepts of thermal equilibrium and temperature T clarified" Richard Feynman, Statistical Mechanics.

- Now onto the CHEM 263 content.

- Tian duplicates the derivation of the ideal gas law given on Labalme (2021b, pp. 18–19).

    - Note that if M is the molar mass, m is the mass of a single molecule, N_{A} is Avogadro's number, N is the number of particles present, and n is the number of moles present, then since $N/N_{\mathrm{A}} = n$ and $M/N_{\mathrm{A}} = m$, we have that

$$M = \frac{Nm}{n}$$
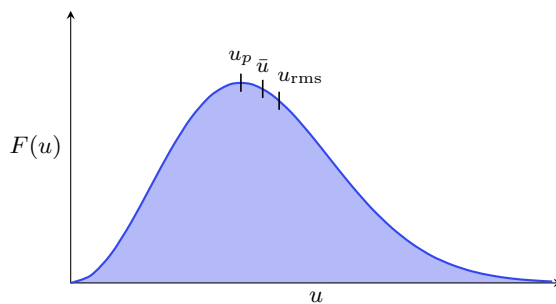
- Important values of molecular speed u.

Figure 1.1: Important values of molecular speed.

- **Maxwell Speed Distribution Function**: The following normalized function, which gives the probability that a particle in an ideal gas will have a given speed. *Denoted by $f(u)$. Given by*

$$f(u) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} u^2 \exp\left(-\frac{Mu^2}{2RT} \right)$$

- **Most probable speed**: The speed that a particle in an ideal gas is most likely to have. *Denoted by u_p. Given by*

$$u_p = \sqrt{\frac{2RT}{M}}$$

- **Mean speed**: The average speed of all of the particles in an ideal gas. *Denoted by $\bar{u}$. Given by*

$$\bar{u} = \sqrt{\frac{8RT}{\pi M}}$$

- **Root mean squared speed**: The square root of the average of the speeds squared. *Denoted by u_{rms}. Given by*

$$u_{\mathrm{rms}} = \left\langle u^2 \right\rangle^{1/2} = \sqrt{\frac{3RT}{M}}$$

- The distributions of the molecular speed and velocity components are different.

    - While speed follows the Maxwell-Boltzmann distribution, velocity follows (on each Cartesian axis) a Gaussian distribution centered at zero.
    - At higher temperatures, both distributions "flatten out," but maintain their shape.

- Deriving the distribution of the velocity component.

    - The velocity components are independent.
    - Let

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

    be the distribution of speed with velocity components between $u_x, u_x + \mathrm{d}u_x$, $u_y, u_y + \mathrm{d}u_y$, and $u_z, u_z + \mathrm{d}u_z$, where $f(u_i)$ is the probability distribution of components i.

        ■ Note that $h(u)$ is *not* the speed distribution with velocity components between $u, u + \mathrm{d}u$.

– Clever step: Note that the logarithmic form of the above equation leads to

$$\ln h(u) = \ln f(u_x) + \ln f(u_y) + \ln f(u_z)$$

$$\left(\frac{\partial \ln h}{\partial u_x}\right)_{u_y,u_z} = \frac{\mathrm{d} \ln h}{\mathrm{d} u}\left(\frac{\partial u}{\partial u_x}\right)_{u_y,u_z}$$

$$= \frac{u_x}{u}\frac{\mathrm{d} \ln h}{\mathrm{d} u}$$

where we evaluate $\partial u/\partial u_x$ by using the generalized Pythagorean theorem definition of u.

– Additionally, we have that

$$\left(\frac{\partial \ln h}{\partial u_x}\right)_{u_y,u_z} = \frac{\mathrm{d} \ln f(u_x)}{\mathrm{d} u_x}$$

since the $\ln f(u_i)$ $(i \neq x)$ terms are constant with respect to changes in u_x.

– Thus, combining the last two results, we have that

$$\frac{\mathrm{d} \ln h(u)}{u \, \mathrm{d} u} = \frac{\mathrm{d} \ln f(u_x)}{u_x \, \mathrm{d} u_x}$$

– It follows since the gas is isotropic that

$$\frac{\mathrm{d} \ln h(u)}{u \, \mathrm{d} u} = \frac{\mathrm{d} \ln f(u_x)}{u_x \, \mathrm{d} u_x} = \frac{\mathrm{d} \ln f(u_y)}{u_y \, \mathrm{d} u_y} = \frac{\mathrm{d} \ln f(u_z)}{u_z \, \mathrm{d} u_z}$$

– But since the three speed components are independent of each other, the above term is constant.

– It follows if we call the constant -2γ, then

$$\frac{\mathrm{d} \ln f(u_i)}{u_i \, \mathrm{d} u_i} = -2\gamma$$

$$f(u_i) = A\mathrm{e}^{-\gamma u_i^2}$$

for $i = x, y, z$.

– We will pick up with solving for A and γ in the next lecture.

1.2 Velocity vs. Speed

3/30: • Exam preferences.

– Asks for midterm preferences. People prefer a take-home exam.
– Asks for final preferences. Probably a 2-hour test?

• Continuing with the derivation for the distribution of the velocity component.

– Note that we choose -2γ because we know we're gonna have to integrate and we want the final form to be as simple as possible. For instance,

$$\frac{\mathrm{d} \ln f(u_i)}{u_i \, \mathrm{d} u_i} = \frac{\mathrm{d} \ln f(u_i)}{\frac{1}{2}\,\mathrm{d} u_i^2}$$

should help rationalize the 2.

– Solving for A.

■ We apply the normalization requirement.

$$
\begin{aligned}
1 &= \int_{-\infty}^{\infty} f(u_i)\,\mathrm{d}u_i \\
&= A \int_{-\infty}^{\infty} \mathrm{e}^{-\gamma u_i^2}\,\mathrm{d}u_i \\
&= 2A \int_{0}^{\infty} \mathrm{e}^{-\gamma u_i^2}\,\mathrm{d}u_i \\
&= 2A \sqrt{\frac{\pi}{4\gamma}} \\
A &= \sqrt{\frac{\gamma}{\pi}}
\end{aligned}
$$

■ Thus, for $i = x, y, z$, we have

$$
f(u_i) = \sqrt{\frac{\gamma}{\pi}}\mathrm{e}^{-\gamma u_i^2}
$$

– Solving for γ.

　　■ We know from the previous lecture that

$$
\begin{aligned}
\frac{1}{3}m\left\langle u^2 \right\rangle &= RT \\
\left\langle u^2 \right\rangle &= \frac{3RT}{M} = \frac{3k_{\mathrm{B}}T}{m} \\
\left\langle u_x^2 \right\rangle &= \frac{RT}{M}
\end{aligned}
$$

　　■ But we also have by definition that (taking u_x in particular because γ is the same in the equations for u_x, u_y, u_z)

$$
\left\langle u_x^2 \right\rangle = \int_{-\infty}^{\infty} u_x^2 f(u_x)\,\mathrm{d}u_x
$$

　　■ Thus, we have that

$$
\begin{aligned}
\frac{RT}{M} &= \int_{-\infty}^{\infty} u_x^2 f(u_x)\,\mathrm{d}u_x \\
&= \sqrt{\frac{\gamma}{\pi}} \int_{-\infty}^{\infty} u_x^2 \mathrm{e}^{-\gamma u_x^2}\,\mathrm{d}u_x \\
&= 2\sqrt{\frac{\gamma}{\pi}} \int_{0}^{\infty} u_x^2 \mathrm{e}^{-\gamma u_x^2}\,\mathrm{d}u_x \\
&= 2\sqrt{\frac{\gamma}{\pi}} \cdot \frac{1}{4\gamma}\sqrt{\frac{\pi}{\gamma}} \\
&= \frac{1}{2\gamma} \\
\gamma &= \frac{M}{2RT}
\end{aligned}
$$

– It follows that

$$
f(u_i) = \sqrt{\frac{M}{2\pi RT}}\mathrm{e}^{-Mu_i^2/2RT} = \sqrt{\frac{m}{2\pi k_{\mathrm{B}}T}}\mathrm{e}^{-mu_i^2/2k_{\mathrm{B}}T}
$$

• Now we can compute other speeds, such as the average velocity $\langle u_x \rangle$.

– Evaluating the odd integrand gives us $\langle u_x \rangle = 0$, as expected.

- As per the Gaussian distribution, if the temperature increases or mass decreases, the distribution of speeds broadens and flattens.

- **Doppler effect**: The change in frequency of a wave in relation to an observer who is moving relative to the wave source. *Also known as* **Doppler shift**.

  - Example: The change of pitch heard when a vehicle sounding a horn approaches and recedes from an observer. Compared to the emitted frequency, the received frequency is higher during the approach, identical at the instant of passing by, and lower during the recession.

- An application of the velocity distribution: The Doppler effect and spectral line broadening.

  - Radiation emitted from a gas will be spread out due to the motion of the molecules.
  - The frequency ν detected by the observer and the frequency ν_0 emitted by the emitter are related by
  $$\nu \approx \nu_0 \left(1 + \frac{u_x}{c}\right)$$
  - Algebraic rearrangement gives us
  $$u_x = \frac{c(\nu - \nu_0)}{\nu_0}$$
  - Doppler-broadened spectral lineshape.
  $$I(\nu) \propto e^{-mc^2(\nu-\nu_0)^2/2\nu_0 k_B T}$$
  - Thus, the variance of the spectral line is
  $$\sigma^2 = \frac{\nu_0^2 k_B T}{mc^2} = \frac{\nu_0^2 R T}{Mc^2}$$
  - The result is that if gas particles are at rest, the emission line spectrum will have very narrow lines. If the gas particles are moving, the lines are broadened.
    - ■ This is why so much spectroscopy is done at super-low temperatures and with heavier molecules! In particular, because Doppler broadening blurs results.

- We know that the average velocity is zero. But we can also consider the average velocity in the positive direction.

  - We calculate
  $$\langle u_x + \rangle = \int_0^\infty u_x f(u_x) \, \mathrm{d}u_x$$
  $$= \sqrt{\frac{m}{2\pi k_B T}} \int_0^\infty u_x e^{-mu_x^2/2k_B T}$$
  $$= \sqrt{\frac{m}{2\pi k_B T}} \cdot \frac{2k_B T}{2m}$$
  $$= \sqrt{\frac{m}{2\pi k_B T}}$$
  - This will be one-fourth the average speed from Figure 1.1, though.

- Moving from velocity to speed: Deriving the Maxwell-Boltzmann Speed Distribution.

  - Define
  $$F(u) \, \mathrm{d}u \approx f(u_x) \, \mathrm{d}u_x \, f(u_y) \, \mathrm{d}u_y \, f(u_z) \, \mathrm{d}u_z$$
    - ■ This function gives us the velocity of each particle in the velocity space. But the speed of each particle is just it's distance from the origin.

– We have that

$$F(u)\,\mathrm{d}u \approx \left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} \mathrm{e}^{-m(u_x^2+u_y^2+u_z^2)/2k_\mathrm{B} T}\,\mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$$

from where we can convert to spherical coordinates using $u^2 = u_x^2 + u_y^2 + u_z^2$ and $4\pi u^2\,\mathrm{d}u = \mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$ to get our final result.

$$F(u)\,\mathrm{d}u = 4\pi\left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} u^2 \mathrm{e}^{-mu^2/2k_\mathrm{B} T}\,\mathrm{d}u$$

– Note that we invoke the equals sign only at the end because speed is inherently spherical in the velocity space; any use of Cartesian infinitesimals must by definition be an approximation at best.

- Some important differences.

    – $h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$ is the distribution of molecular speeds with velocity components (in Cartesian coordinates) between $u_x, u_x + \mathrm{d}u_x$, $u_y, u_y + \mathrm{d}u_y$, and $u_z, u_z + \mathrm{d}u_z$.

    – $f(u_x) = \sqrt{M/2\pi RT}\mathrm{e}^{-Mu_x^2/2RT}$ is the distribution of molecular speed componentwise in Cartesian coordinates, and has a Gaussian distribution.

    – $F(u) = 4\pi\left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} u^2 \mathrm{e}^{-mu^2/2k_\mathrm{B} T}$ is the distribution of molecular speed, and has a Maxwell-Boltzmann distribution as per spherical coordinates.

- Maxwell-Boltzmann speed distribution of noble gases.

    – Heavier Noble gases have more "flattened" M-B distributions.

- Different metrics of M-B speed distribution.

    – We can, from the above formula, calculate the average speed $\langle u \rangle$, the root mean square speed $\langle u^2 \rangle$, and the most probable speed by taking a derivative and setting it equal to zero.

    – We get

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi M}} \qquad u_\mathrm{rms} = \sqrt{\frac{3RT}{M}} \qquad u_\mathrm{mp} = \sqrt{\frac{2k_\mathrm{B} T}{m}}$$

1.3 Energy Distribution and Collision Frequency

4/1:
- The final exam is 50 minutes on the last day of class.

- We can also express the M-B distribution in terms of kinetic energy.

    – We know that energy $\varepsilon = \frac{1}{2}mu^2$, so $u = \sqrt{2\varepsilon/m}$ and thus $\mathrm{d}u = \mathrm{d}\varepsilon/\sqrt{2m\varepsilon}$.

    – This allows us to write

$$F(\varepsilon)\,\mathrm{d}\varepsilon = 4\pi\left(\frac{m}{2\pi k_\mathrm{B} T}\right)^{3/2} \cdot \frac{2\varepsilon}{m} \cdot \mathrm{e}^{-\varepsilon/k_\mathrm{B} T}\frac{\mathrm{d}\varepsilon}{\sqrt{2m\varepsilon}}$$

$$= \frac{2\pi}{(\pi k_\mathrm{B} T)^{3/2}}\varepsilon^{1/2}\mathrm{e}^{-\varepsilon/k_\mathrm{B} T}\,\mathrm{d}\varepsilon$$

    – Thus, we can calculate that

$$\langle \varepsilon \rangle = \int_0^\infty \varepsilon f(\varepsilon)\,\mathrm{d}\varepsilon$$

$$= \frac{3}{2}k_\mathrm{B} T$$

as expected.

(a) Molecular speed distribution.

(b) Stretching the molecular speed distribution.

(c) Comparing the energy and speed distributions.
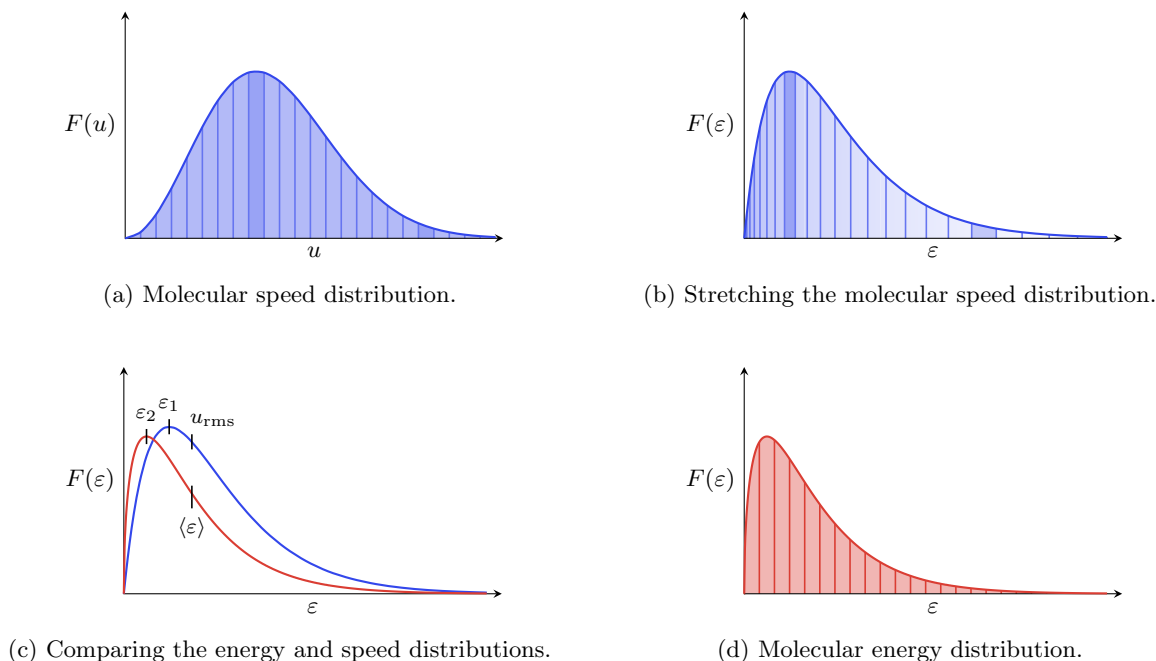
(d) Molecular energy distribution.

Figure 1.2: Relating molecular speed and molecular energy.

- Aside: Understanding the probability distribution $F(u)\,\mathrm{d}u$ and the relation between $F(u)\,\mathrm{d}u$ and $F(\varepsilon)\,\mathrm{d}\varepsilon$.

    - $F(u)$ is a probability distribution. Thus, its graph (see Figure 1.2a) indicates the number density of particles we'd expect to find at a given velocity u by the vertical height of the curve. Importantly, if we imagine filling in the area under the curve with each particle at its u-position and evenly spaced in the F direction, eventually we'd get a continuous color under the curve (as in Figure 1.2a; the darkened regions are illustrated as such for the sole purpose of contrast with Figure 1.2b, as discussed below).

    - We note that $\varepsilon = \frac{1}{2}mu^2$ is a stretching operation. This means that as u increases, ε increases faster. For example, as u increases $1, 2, 3, 4$, ε increases proportionally by $1, 4, 9, 16$. Thus, we can approximate $F(\varepsilon)$ by stretching the graph of $F(u)$ horizontally by greater and greater amounts (see Figure 1.2b).

    - An important consequence of this is that the particles moving within a certain range of velocities have a larger range of energies (compare the darkly shaded blocks of Figures 1.2a and 1.2b, as well as the general increase in spacing of the vertical lines).

    - However, when we approximate by stretching, we ignore some of the other changes in the equation. For instance, when we sketch the actual energy distribution, its most probable energy $\varepsilon_{\mathrm{mp}} = \varepsilon_2$ has a lower value than that predicted by just stretching the graph of the speed distribution (which we denote in Figure 1.2c by $\varepsilon_1 = \frac{1}{2}mu_{\mathrm{mp}}^2$). All in one equation,

$$\varepsilon_{\mathrm{mp}} \neq \frac{1}{2}mu_{\mathrm{mp}}^2$$

    - Additionally, note that the actual curve (Figure 1.2d) has even density beneath it.

- Calculating the most probable kinetic energy.

$$\frac{\mathrm{d}F}{\mathrm{d}\varepsilon} = \frac{2\pi}{(\pi k_\mathrm{B}T)^{3/2}} \left[\frac{\varepsilon^{-1/2}\mathrm{e}^{-\varepsilon/k_\mathrm{B}T}}{2} - \frac{\mathrm{e}^{-\varepsilon/k_\mathrm{B}T}\cdot\varepsilon^{1/2}}{k_\mathrm{B}T} \right]$$

$$0 = \frac{2\pi\mathrm{e}^{-\varepsilon/k_\mathrm{B}T}}{(\pi k_\mathrm{B}T)^{3/2}} \left[\frac{1}{2\sqrt{\varepsilon}} - \frac{\sqrt{\varepsilon}}{k_\mathrm{B}T} \right]$$

$$\varepsilon_\mathrm{mp} = \frac{k_\mathrm{B}T}{2}$$

  - The most probable energy calculated from the most probable speed via $\frac{1}{2}mu_\mathrm{mp}^2$ is $k_\mathrm{B}T$, so the actual value is one-half the predicted value (notice how $\varepsilon_2 = \frac{1}{2}\varepsilon_1$).

- Since $\langle\varepsilon\rangle = \langle\frac{1}{2}mu^2\rangle$, $\langle\varepsilon\rangle$ is related to the root mean square speed.

  - This relates $u_\mathrm{rms}^2 = 3k_\mathrm{B}T/m$ to $\langle\varepsilon\rangle = 3k_\mathrm{B}T/2$ by a factor of $m/2$.
  - This linear relation appears in Figure 1.2c, where u_rms and $\langle\varepsilon\rangle$ occur in the same place and differ only by a vertical stretch factor $(m/2)$.

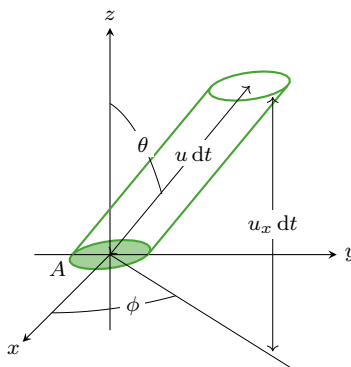- Calculating the frequency of collisions.

Figure 1.3: Collision frequency cylinder.

  - Construct a cylinder to enclose all those molecules that will strike the area A at an angle θ with speed u in the time interval $\mathrm{d}t$.
  - Its volume is $V = Au\cos\theta\,\mathrm{d}t$.
  - The number of molecules in the cylinder is ρV, where ρ is the number density.
  - The fraction of molecules that have a speed between $u, u + \mathrm{d}u$ is $F(u)\,\mathrm{d}u$.
  - The fraction travelling within a solid angle bounded by $\theta, \theta + \mathrm{d}\theta$ and $\phi, \phi + \mathrm{d}\phi$ is $\sin\theta\,\mathrm{d}\theta\cdot\mathrm{d}\phi\,/4\pi$, where 4π represents a complete solid angle.
  - The number $\mathrm{d}N_\mathrm{coll}$ of molecules colliding with the area A from the specified direction in the time interval $\mathrm{d}t$ is

$$\mathrm{d}N_\mathrm{coll} = \rho(Au\,\mathrm{d}t)\cos\theta\cdot F(u)\,\mathrm{d}u\cdot\frac{\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}{4\pi}$$

  - The number of collisions per unit time per unit area with the wall by molecules whose speeds are in the range $u, u + \mathrm{d}u$ and whose direction lies within the solid angle $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ is

$$\mathrm{d}z_\mathrm{coll} = \frac{1}{A}\frac{\mathrm{d}N_\mathrm{coll}}{\mathrm{d}t} = \frac{\rho}{4\pi}uF(u)\,\mathrm{d}u\cdot\cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

- If we integrate over all possible speeds and directions, then we obtain

$$z_{\text{coll}} = \frac{\rho}{4\pi} \int_0^\infty uF(u)\, \mathrm{d}u \int_0^{\pi/2} \cos\theta \sin\theta\, \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi$$
$$= \frac{\rho \langle u \rangle}{4}$$

- Deriving the pressure through the collision frequency.

  - We have

$$\mathrm{d}P = (2mu\cos\theta)\, \mathrm{d}z_{\text{coll}}$$
$$= (2mu\cos\theta)\frac{\rho}{4\pi}uF(u)\, \mathrm{d}u \cos\theta \sin\theta\, \mathrm{d}\theta\, \mathrm{d}\phi$$
$$= \rho \left(\frac{m}{2\pi k_{\text{B}}T}\right)^{3/2} (2mu\cos\theta)u^3 \mathrm{e}^{-mu^2/2k_{\text{B}}T}\, \mathrm{d}u \cos\theta \sin\theta\, \mathrm{d}\phi$$

  - Thus, since

$$\int_0^{\pi/2} \cos^2\theta \sin\theta\, \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi = \frac{2\pi}{3} \qquad 4\pi \left(\frac{m}{2\pi k_{\text{B}}T}\right)^{3/2} \int_0^\infty u^4 \mathrm{e}^{-mu^2/2k_{\text{B}}T}\, \mathrm{d}u = \langle u^2 \rangle$$

  we have that

$$P = \frac{1}{3}\rho m \langle u^2 \rangle = \frac{1}{3V}Nm \langle u^2 \rangle$$

1.4   Office Hours (Tian)

- Can you explain the whole $F(u)\, \mathrm{d}u$ differential notation for probability?

  - $F(u)$ is the probability function. $F(u)$ is the y axis of the individual points. Probability density.
  - $F(u)\, \mathrm{d}u$ is the infinitesimal probability at u, but only within an infinitely small range. It's an abbreviation/approximation for the tiny infinitesimal rectangle under the curve that we picture as we integrate.
  - $\int_0^\infty F(u)\, \mathrm{d}u = 1$ (summing all of the tiny probabilities) gets you to 1 for a normalized probability distribution.

- What is up with the relation between u_{rms} and $\langle \varepsilon \rangle$?

  - We have

$$\langle \varepsilon \rangle = \left\langle \frac{1}{2}mu^2 \right\rangle$$
$$= \frac{1}{2}m \langle u^2 \rangle$$
$$= \frac{1}{2}mu_{\text{rms}}^2$$
$$= \frac{m}{2} \cdot \frac{3k_{\text{B}}T}{m}$$
$$= \frac{3k_{\text{B}}T}{2}$$

- Post lecture notes before class? Write down what's on the lecture slides or listen?

  - He has been and will continue to post the slides the night before the lecture.

- When will HW 1 be posted?

- No homework this week.
- The first homework will be posted next Monday.
- He will post a homework every Monday that will be due the next Monday.

- When are gases isotropic?

  - A gas is isotropic unless there is a driving force.
  - For example, gas in a closed box is isotropic, but gas in a cylinder with a fan at one end is not isotropic (particles are more likely to move in one direction).

- What is the total solid angle geometrically?

  - Hard to visualize three dimensionally. You get 4π by doing the integrals for the components:

  $$4\pi = \int_{-\pi/2}^{\pi/2} \sin\theta \, d\theta \int_0^{2\pi} d\phi$$

- We don't need to memorize most of the derivations, but we do need to know the conclusions and the assumptions we need to get them.

  - We won't be asked to give a derivation unless we're given the full starting point.
  - The final can't have much heavy calculation on it because there's not that much time.
  - The midterm will be a online take-home exam with limited time (probably 2 hours).

- Not every topic in the remainder of McQuarrie and Simon (1997) will be covered; some sections will be skipped.

  - He will focus a lot on the practical applications. Once the student understands the basic principle, he wants us to be able to apply it to research and life.

1.5   Chapter 27: The Kinetic Theory of Gases

From McQuarrie and Simon (1997).

3/28:
- **Kinetic theory of gases**: A simple model of gases in which the molecules (pictured as hard spheres) are assumed to be in constant, incessant motion, colliding with each other and with the walls of the container.

- McQuarrie and Simon (1997) does the KMT derivation of the ideal gas law from Labalme (2021a). Some important notes follow.

  - McQuarrie and Simon (1997) emphasizes the importance of

  $$PV = \frac{1}{3}Nm \left\langle u^2 \right\rangle$$

  as a fundamental equation of KMT, as it relates a macroscopic property PV to a microscopic property $m \left\langle u^2 \right\rangle$.

  - In Chapter 17-18, we derived quantum mechanically, and then from the partition function, that the average translational energy $\langle E_{\text{trans}} \rangle$ for a single particle of an ideal gas is $\frac{3}{2}k_B T$. From classical mechanics, we also have that $\langle E_{\text{trans}} \rangle = \frac{1}{2}m \left\langle u^2 \right\rangle$. *This* is why we may let

  $$\frac{1}{2}m \left\langle u^2 \right\rangle = \frac{3}{2}k_B T$$

  recovering that the average translational kinetic energy of the molecules in a gas is directly proportional to the Kelvin temperature.

- **Isotropic** (entity): An object or substance that has the same properties in any direction.

  - For example, a homogeneous gas is isotropic, and this is what allows us to state that $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \langle u_z^2 \rangle$.

- McQuarrie and Simon (1997) derives

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

  - u_{rms} is an estimate of the average speed since $\langle u^2 \rangle \neq \langle u \rangle^2$ in general.

- McQuarrie and Simon (1997) states without proof that the speed of sound u_{sound} in a monatomic ideal gas is given by

$$u_{\text{sound}} = \sqrt{\frac{5RT}{3M}}$$

- Assumptions of the kinetic theory of gases.

  - Particles collide elastically with the wall.

    - Justified because although each collision will not be elastic (the particles in the wall are moving too), the average collision will be elastic.

  - Particles do not collide with each other.

    - Justified because "if the gas is in equilibrium, on the average, any collision that deflects the path of a molecule... will be balanced by a collision that replaces the molecule" (McQuarrie & Simon, 1997, p. 1015).

- Note that we can do the kinetic derivation at many levels of rigor, but more rigorous derivations offer results that differ only by constant factors on the order of unity.

- Deriving a theoretical equation for the distribution of the *components* of molecular velocities.

  - Let $h(u_x, u_y, u_z)\, \mathrm{d}u_x\, \mathrm{d}u_y\, \mathrm{d}u_z$ be the fraction of molecules with velocity components between u_j and $u_j + \mathrm{d}u_j$ for $j = x, y, z$.

  - Assume that the each component of the velocity of a molecule is independent of the values of the other two components[1]. It follows statistically that

$$h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

    - Note that we use just one function f for the probability distribution in each direction because the gas is isotropic.

  - We can use the isotropic condition to an even greater degree. Indeed, it implies that any information conveyed by u_x is necessarily and sufficiently conveyed by u_y, u_z, and u. Thus, we may take

$$h(u) = h(u_x, u_y, u_z) = f(u_x)f(u_y)f(u_z)$$

  - It follows that

$$\frac{\partial \ln h(u)}{\partial u_x} = \frac{\partial}{\partial u_x}(\ln f(u_x) + \text{terms not involving } u_x) = \frac{\mathrm{d} \ln f(u_x)}{\mathrm{d}u_x}$$

---

[1]This can be proven.

– Since

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

$$\frac{\partial}{\partial u_x}\left(u^2\right) = \frac{\partial}{\partial u_x}\left(u_x^2 + u_y^2 + u_z^2\right)$$

$$2u\frac{\partial u}{\partial u_x} = 2u_x$$

$$\frac{\partial u}{\partial u_x} = \frac{u_x}{u}$$

we have that

$$\frac{\partial \ln h}{\partial u_x} = \frac{\mathrm{d}\ln h}{\mathrm{d}u}\frac{\partial u}{\partial u_x} = \frac{u_x}{u}\frac{\mathrm{d}\ln h}{\mathrm{d}u}$$

$$\frac{\mathrm{d}\ln h(u)}{u\,\mathrm{d}u} = \frac{\mathrm{d}\ln f(u_x)}{u_x\,\mathrm{d}u_x}$$

which generalizes to

$$\frac{\mathrm{d}\ln h(u)}{u\,\mathrm{d}u} = \frac{\mathrm{d}\ln f(u_x)}{u_x\,\mathrm{d}u_x} = \frac{\mathrm{d}\ln f(u_y)}{u_y\,\mathrm{d}u_y} = \frac{\mathrm{d}\ln f(u_z)}{u_z\,\mathrm{d}u_z}$$

– Since u_x, u_y, u_z are independent, we know that the above equation is equal to a constant, which we may call $-\gamma$. It follows that for any $j = x, y, z$, we have that

$$\frac{\mathrm{d}\ln f(u_j)}{u_j\,\mathrm{d}u_j} = -\gamma$$

$$\frac{1}{f}\frac{\mathrm{d}f}{\mathrm{d}u_j} = -\gamma u_j$$

$$\int \frac{\mathrm{d}f}{f} = \int -\gamma u_j\,\mathrm{d}u_j$$

$$\ln f = -\frac{\gamma}{2}u_j^2 + C$$

$$f(u_j) = A\mathrm{e}^{-\gamma u_j^2}$$

where we have incorporated the $1/2$ into γ.

– To determine A and γ, we let arbitrarily let $j = x$. Since f is a continuous probability distribution, we may apply the normalization requirement.

$$1 = \int_{-\infty}^{\infty} f(u_x)\,\mathrm{d}u_x$$

$$= 2A\int_0^{\infty} \mathrm{e}^{-\gamma u_x^2}\,\mathrm{d}u_x$$

$$= 2A\sqrt{\frac{\pi}{4\gamma}}$$

$$A = \sqrt{\frac{\gamma}{\pi}}$$

– Additionally, since we have that $\left\langle u_x^2 \right\rangle = \frac{1}{3}\left\langle u^2 \right\rangle$ and $\left\langle u^2 \right\rangle = 3RT/M$, we know that $\left\langle u_x^2 \right\rangle = RT/M$.

This combined with the definition of $\langle u_x^2 \rangle$ as a continuous probability distribution yields

$$
\begin{aligned}
\frac{RT}{M} &= \langle u_x^2 \rangle \\
&= \int_{-\infty}^{\infty} u_x^2 f(u_x) \, \mathrm{d}u_x \\
&= 2\sqrt{\frac{\gamma}{\pi}} \int_0^{\infty} u_x^2 \mathrm{e}^{-\gamma u_x^2} \, \mathrm{d}u_x \\
&= 2\sqrt{\frac{\gamma}{\pi}} \cdot \frac{1}{4\gamma} \sqrt{\frac{\pi}{\gamma}} \\
&= \frac{1}{2\gamma} \\
\gamma &= \frac{M}{2RT}
\end{aligned}
$$

- Therefore,

$$
f(u_x) = \sqrt{\frac{M}{2\pi RT}} \mathrm{e}^{-Mu_x^2/2RT}
$$

- It is common to rewrite the above in terms of molecular quantities m and k_B.

- It follows that as temperature increases, more molecules are likely to be found with higher component velocity values.

- We can use the above result to show that

$$
\langle u_x \rangle = \int_{-\infty}^{\infty} u_x f(u_x) \, \mathrm{d}u_x = 0
$$

- We can also calculate that $\langle u_x^2 \rangle = RT/M$ and $m \langle u_x \rangle^2 /2 = k_B T/2$ from the above result[2].

  - An important consequence is that the total kinetic energy is divided equally into the x-, y-, and z-components.

- **Doppler broadening**: The broadening of spectral lines due to the distribution of molecular velocities.

  - Ideally, spectral lines will be very narrow.
  - However, due to the Doppler effect, if an atom or molecule emits radiation of frequency ν_0 while moving away or toward the observer with speed u_x, then the observed frequency will be

$$
\nu \approx \nu_0 \left(1 + \frac{u_x}{c} \right)
$$

  - Indeed, "if one observes the radiation emitted from a gas at temperature T, then it is found that the spectral line at ν_0 will be spread out by the Maxwell distribution of u_x of the molecule emitting the radiation" (McQuarrie & Simon, 1997, p. 1021).
  - It follows by the definition of $f(u_x)$ and the above that

$$
I(\nu) \propto \mathrm{e}^{-mc^2(\nu-\nu_0)^2/2\nu_0^2 k_B T}
$$

  i.e., that $I(\nu)$ is of the form of a Gaussian centered at ν_0 with variance $\sigma^2 = \nu_0^2 k_B T/mc^2$.

- Deriving **Maxwell-Boltzmann distribution**.

---

[2]See the equipartition of energy theorem from Labalme (2021b).

– Let the probability that a molecule has speed between u and $u + \mathrm{d}u$ be defined by a continuous probability distribution $F(u)\,\mathrm{d}u$. In particular, we have from the above isotropic condition that

$$F(u)\,\mathrm{d}u = f(u_x)\,\mathrm{d}u_x\,f(u_y)\,\mathrm{d}u_y\,f(u_z)\,\mathrm{d}u_z$$

$$= \left(\frac{m}{2\pi k_B T}\right)^{3/2} \mathrm{e}^{-m(u_x^2+u_y^2+u_z^2)/2k_B T}\,\mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$$

– Considering F over a **velocity space**, we realize that we may express the probability distribution F as a function of u via $u^2 = u_x^2 + u_y^2 + u_z^2$ and the differential volume element in every direction over the sphere of equal velocities (a sphere by the isotropic condition) by $4\pi u^2\,\mathrm{d}u = \mathrm{d}u_x\,\mathrm{d}u_y\,\mathrm{d}u_z$.

– Thus, the Maxwell-Boltzmann distribution in terms of speed is

$$F(u)\,\mathrm{d}u = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} u^2 \mathrm{e}^{-mu^2/2k_B T}\,\mathrm{d}u$$

- **Maxwell-Boltzmann distribution**: The distribution of molecular speeds.

- **Velocity space**: A rectangular coordinate system in which the distances along the axes are u_x, u_y, u_z.

- The above integral as well as some other variations occur commonly in the study of kinetics.

$$\int_0^\infty x^{2n}\mathrm{e}^{-\alpha x^2}\,\mathrm{d}x = \frac{1 \cdot 3 \cdot 5 \cdots (2n-1)}{2^{n+1}\alpha^n}\left(\frac{\pi}{\alpha}\right)^{1/2} \qquad n \geq 1$$

$$\int_0^\infty x^{2n+1}\mathrm{e}^{-\alpha x^2}\,\mathrm{d}x = \frac{n!}{2\alpha^{n+1}} \qquad n \geq 0$$

$$\int_0^\infty x^{n/2}\mathrm{e}^{-\alpha x}\,\mathrm{d}x = \frac{n(n-2)(n-4)\cdots(1)}{(2\alpha)^{(n+1)/2}}\left(\frac{\pi}{\alpha}\right)^{1/2} \qquad n \text{ odd}$$

$$= \frac{(n/2)!}{\alpha^{(n+2)/2}} \qquad n \text{ even}$$

Table 1.1: Common integrals in the kinetic theory of gases.

- We may use the above result to calculate that

$$\langle u \rangle = \sqrt{\frac{8RT}{\pi m}}$$

which only differs from u_{rms} by a factor of 0.92.

- **Most probable speed**: The most probable speed of a gas molecule in a sample that obeys the Maxwell-Boltzmann distribution. *Denoted by $\boldsymbol{u}_{\mathrm{mp}}$. Given by*

$$u_{\mathrm{mp}} = \sqrt{\frac{2RT}{M}}$$

– Derived by setting $\mathrm{d}F/\mathrm{d}u = 0$.

- We may also express the Maxwell-Boltzmann distribution in terms of energy via $u = \sqrt{2\varepsilon/m}$ and $\mathrm{d}u = \mathrm{d}\varepsilon / \sqrt{2m\varepsilon}$ to give

$$F(\varepsilon)\,\mathrm{d}\varepsilon = \frac{2\pi}{(\pi k_B T)^{3/2}}\sqrt{\varepsilon}\mathrm{e}^{-\varepsilon/k_B T}\,\mathrm{d}\varepsilon$$

- We can also confirm our previously calculated values for $\langle u^2 \rangle$ and $\langle \varepsilon \rangle$.

4/6:   - Deriving an expression for the frequency of collisions that the molecules of a gas make with the walls of its container (refer to Figure 1.3 throughout the following).

- Note that this quantity is central to the theory of rates of surface reactions.
- McQuarrie and Simon (1997) gets to the following equation as in class.

$$\mathrm{d}z_{\mathrm{coll}} = \frac{1}{A}\frac{\mathrm{d}N_{\mathrm{coll}}}{\mathrm{d}t} = \frac{\rho}{4\pi}uF(u)\,\mathrm{d}u \cdot \cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

- Note that the above equation is of the form $u^3\mathrm{e}^{-mu^2/2k_{\mathrm{B}}T}$ whereas M-B distribution is of the form $u^2\mathrm{e}^{-mu^2/2k_{\mathrm{B}}T}$.
  - ■ Thus, the above equation peaks at higher values of u.
  - ■ This reflects the fact that molecules traveling at a higher speed (than average) are more likely to strike the wall in a given window of time.
- McQuarrie and Simon (1997) finishes the derivation to obtain the equation for z_{coll} and notes that Problems 27-49 through 27-52 develop its applications to effusion rate theory.

- Note that we can calculate the number density ρ from pressure and temperature data via the ideal gas law as follows.

$$\rho = \frac{N}{V} = \frac{N_{\mathrm{A}}n}{V} = \frac{N_{\mathrm{A}}P}{RT}$$

- (Re)deriving $P = \rho m\langle u^2\rangle/3$ from a collision frequency perspective.

  - If θ is the angular deviation in the particle's path from the normal to the wall, then the component of momentum of a particle of mass m moving with speed u that lies perpendicular to the wall is $mu\cos\theta$.
  - This particles change in momentum upon colliding elastically with the wall is thus $2mu\cos\theta$.
  - Since pressure is the force per unit area and force is the change in momentum per unit time, the pressure is equal to the product of the change in momentum per collision and the frequency (number per unit time) of collisions per unit area. Mathematically, the infinitesimal pressure applied by just the molecules with speeds between u and $u + \mathrm{d}u$ that lie within the solid angle $\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$ is

$$\mathrm{d}P = (2mu\cos\theta)\,\mathrm{d}z_{\mathrm{coll}}$$
$$= \rho\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2}(2mu\cos\theta)u^3\mathrm{e}^{-mu^2/2k_{\mathrm{B}}T}\,\mathrm{d}u\cos\theta\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi$$

  - It follows since

$$\int_0^{\pi/2}\cos^2\theta\sin\theta\,\mathrm{d}\theta\int_0^{2\pi}\mathrm{d}\phi = \frac{2\pi}{3} \qquad 4\pi\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2}\int_0^{\infty}u^4\mathrm{e}^{-mu^2/2k_{\mathrm{B}}T}\,\mathrm{d}u = \langle u^2\rangle$$

    that

$$P = \rho m \cdot \frac{\langle u^2\rangle}{2\pi}\cdot\frac{2\pi}{3} = \frac{1}{3}\rho m\langle u^2\rangle$$

4/10:
- McQuarrie and Simon (1997) discusses Kusch and coworker's experimental verification of the M-B distribution, which used a beam of potassium atoms and a rotating velocity selector.

  - Kusch was awarded the Nobel prize in physics in 1955.

- We now discuss the frequency of collisions between the molecules in a gas.

- We first consider the frequency of collisions of a single gas-phase molecule.

- Assumptions.

  - The molecules are hard spheres of diameter d.

- All molecules other than the one in question are stationary; we will account for their motion at the end of the derivation.

- **Collision cylinder**: A cylinder of diameter $2d$ that the molecule in question sweeps out as it travels along.

  - The molecule in question will collide with any molecule whose center lies within this cylinder.
  - See Figure 2.1.

- **Collision cross section**: The target of effective radius d presented by each hard sphere molecule. *Denoted by $\boldsymbol{\sigma}$. Given by*

$$\sigma = \pi d^2$$

Gas	d (pm)	σ (nm^2)
He	210	0.140
Ar	370	0.430
Xe	490	0.750
H$_2$	270	0.230
N$_2$	380	0.450
O$_2$	360	0.410
Cl$_2$	540	0.920
CH$_4$	410	0.530
C$_2$H$_4$	430	0.580

Table 1.2: Collision diameters and collision cross sections.

  - See Table 1.2 for some example values.

- Calculating the number of collisions $\mathrm{d}N_{\mathrm{coll}}$ the moving molecule makes in the time $\mathrm{d}t$.

  - The volume of the collision cylinder is the product of its cross section σ and its length $\langle u \rangle \, \mathrm{d}t$.
  - Whenever the center of another molecule lies within this cylinder, a collision will occur.
  - Thus, since $\sigma \langle u \rangle \, \mathrm{d}t$ represents a small volume within the overall volume the gas occupies, the expected number of collisions $\mathrm{d}N_{\mathrm{coll}}$ would be equal to the number of molecules expected to lie in the volume $\sigma \langle u \rangle \, \mathrm{d}t$.
  - If the N molecules can be expected to be evenly distributed throughout the volume V with number density $\rho = N/V$, then we have that

$$\mathrm{d}N_{\mathrm{coll}} = \rho \sigma \langle u \rangle \, \mathrm{d}t$$

  - We must now undue the one assumption that cannot stay: That all other molecules are stationary.
  - To do this, we treat the motion of the two bodies by the reduced mass.

- **Collision frequency**: The expected number of collisions per unit time. *Denoted by $\boldsymbol{Z_A}$. Given by*

$$z_A = \frac{\mathrm{d}N_{\mathrm{coll}}}{\mathrm{d}t} = \rho \sigma \langle u_r \rangle = \rho \sigma \sqrt{\frac{8 k_{\mathrm{B}} T}{\pi \mu}}$$

$$= \sqrt{2} \rho \sigma \langle u \rangle = \sqrt{2} \rho \sigma \sqrt{\frac{8 k_{\mathrm{B}} T}{\pi m}}$$