Chapter 27

Kinetic Theory of Gases

27.1 Background and Ideal Gas Distributions

- 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

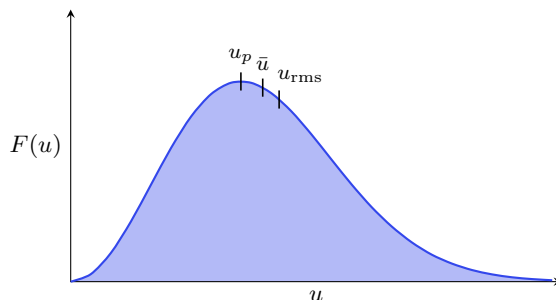$$M = \frac{Nm}{n}$$

- Important values of molecular speed u.

Figure 27.1: 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.

27.2 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.

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

$$= A \int_{-\infty}^{\infty} \mathrm{e}^{-\gamma u_i^2} \, \mathrm{d} u_i$$

$$= 2A \int_{0}^{\infty} \mathrm{e}^{-\gamma u_i^2} \, \mathrm{d} u_i$$

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

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

- ■ Thus, for $i = x, y, z$, we have
$$f(u_i) = \sqrt{\frac{\gamma}{\pi}} e^{-\gamma u_i^2}$$

  - – Solving for γ.
    - ■ We know from the previous lecture that
$$\frac{1}{3} m \langle u^2 \rangle = RT$$
$$\langle u^2 \rangle = \frac{3RT}{M} = \frac{3k_{\mathrm{B}}T}{m}$$
$$\langle u_x^2 \rangle = \frac{RT}{M}$$

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

    - ■ Thus, we have that
$$\frac{RT}{M} = \int_{-\infty}^{\infty} u_x^2 f(u_x) \, \mathrm{d}u_x$$
$$= \sqrt{\frac{\gamma}{\pi}} \int_{-\infty}^{\infty} u_x^2 e^{-\gamma u_x^2} \, \mathrm{d}u_x$$
$$= 2\sqrt{\frac{\gamma}{\pi}} \int_{0}^{\infty} u_x^2 e^{-\gamma u_x^2} \, \mathrm{d}u_x$$
$$= 2\sqrt{\frac{\gamma}{\pi}} \cdot \frac{1}{4\gamma} \sqrt{\frac{\pi}{\gamma}}$$
$$= \frac{1}{2\gamma}$$
$$\gamma = \frac{M}{2RT}$$

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

- • 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

$$\sigma^2 = \frac{\nu_0^2 k_B T}{mc^2} = \frac{\nu_0^2 RT}{Mc^2}$$

– 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

$$\langle u_x+ \rangle = \int_0^\infty u_x f(u_x)\, du_x$$
$$= \sqrt{\frac{m}{2\pi k_B T}} \int_0^\infty u_x e^{-mu_x^2/2k_B T}$$
$$= \sqrt{\frac{m}{2\pi k_B T}} \cdot \frac{2k_B T}{2m}$$
$$= \sqrt{\frac{m}{2\pi k_B T}}$$

– This will be one-fourth the average speed from Figure 27.1, though.

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

– Define
$$F(u)\, du \approx f(u_x)\, du_x\, f(u_y)\, du_y\, f(u_z)\, du_z$$

■ 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

$$F(u)\, du \approx \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(u_x^2+u_y^2+u_z^2)/2k_B T}\, du_x\, du_y\, du_z$$

from where we can convert to spherical coordinates using $u^2 = u_x^2 + u_y^2 + u_z^2$ and $4\pi u^2\, du = du_x\, du_y\, du_z$ to get our final result.

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

– 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

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

27.3 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.

- 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 27.2a) 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 27.2a; the darkened regions are illustrated as such for the sole purpose of contrast with Figure 27.2b, 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 27.2b).

(a) Molecular speed distribution.

(b) Stretching the molecular speed distribution.

(c) Comparing the energy and speed distributions.

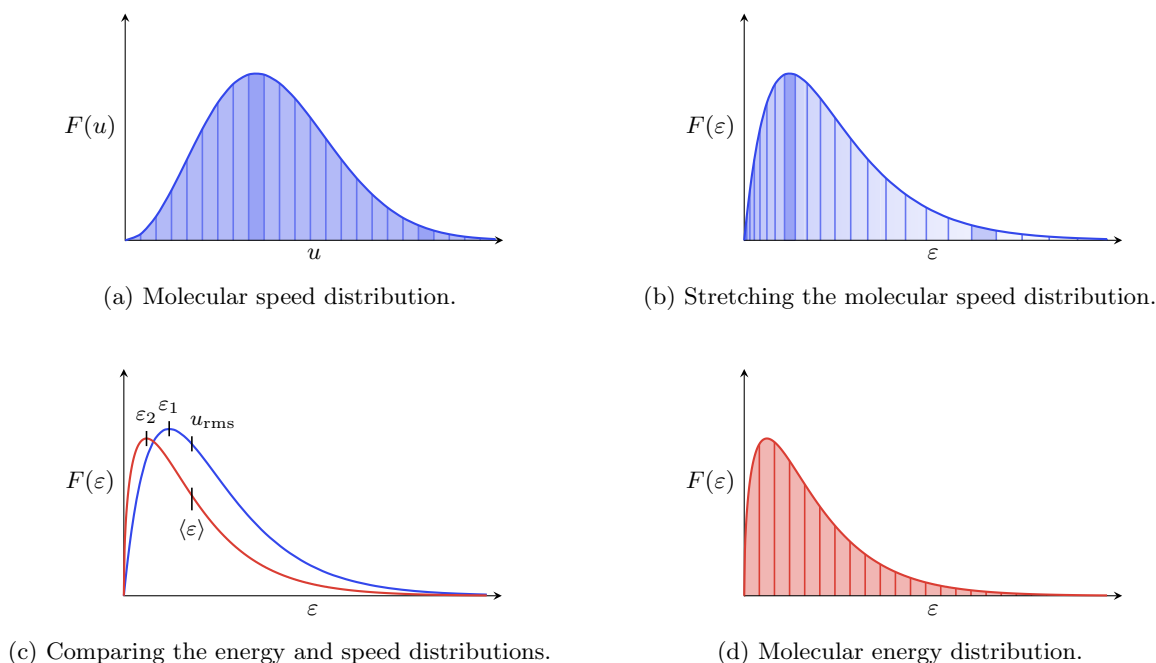
(d) Molecular energy distribution.

Figure 27.2: Relating molecular speed and molecular energy.

- 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 27.2a and 27.2b, 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 $\varepsilon_{\text{mp}} = \varepsilon_2$ has a lower value than that predicted by just stretching the graph of the speed distribution (which we denote in Figure 27.2c by $\varepsilon_1 = \frac{1}{2}mu_{\text{mp}}^2$). All in one equation,

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

- Additionally, note that the actual curve (Figure 27.2d) has even density beneath it.

• Calculating the most probable kinetic energy.

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

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

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

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

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

- This relates $u_{\text{rms}}^2 = 3k_{\text{B}}T/m$ to $\langle \varepsilon \rangle = 3k_{\text{B}}T/2$ by a factor of $m/2$.

- This linear relation appears in Figure 27.2c, where u_{rms} and $\langle \varepsilon \rangle$ occur in the same place and differ only by a vertical stretch factor $(m/2)$.
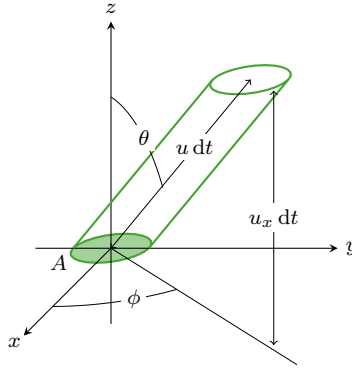
- Calculating the frequency of collisions.

Figure 27.3: 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

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

- Deriving the pressure through the collision frequency.

  - We have

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

  - Thus, since

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

  we have that

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

27.4 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 $\left\langle E_{\text{trans}} \right\rangle$ for a single particle of an ideal gas is $\frac{3}{2}k_B T$. From classical mechanics, we also have that $\left\langle E_{\text{trans}} \right\rangle = \frac{1}{2}m\left\langle u^2 \right\rangle$. *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 $\left\langle u_x^2 \right\rangle = \left\langle u_y^2 \right\rangle = \left\langle u_z^2 \right\rangle$.

- McQuarrie and Simon (1997) derives

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

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

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

- Since

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

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.

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[1]This can be proven.

- 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 $\langle u_x^2 \rangle = \frac{1}{3}\langle u^2 \rangle$ and $\langle u^2 \rangle = 3RT/M$, we know that $\langle u_x^2 \rangle = RT/M$. This combined with the definition of $\langle u_x^2 \rangle$ as a continuous probability distribution yields

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

- 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

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

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

– 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

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

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**.

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

  $$F(u) \, du = f(u_x) \, du_x \, f(u_y) \, du_y \, f(u_z) \, du_z$$
  $$= \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(u_x^2+u_y^2+u_z^2)/2k_B T} \, du_x \, du_y \, du_z$$

  – 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 $4\pi u^2 \, du = du_x \, du_y \, du_z$.

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

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

- **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.

- 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 $\boldsymbol{u}_{\text{mp}}$. Given by*

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

  – Derived by setting $dF/du = 0$.

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

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

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

- McQuarrie and Simon (1997) does a higher-level derivation of the ideal gas law that is rather analogous to the one done in class (i.e., via its flux perspective).

- McQuarrie and Simon (1997) discusses a simple and Nobel-prize winning experiment that verified the Maxwell-Boltzmann distribution.