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 (2021, 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

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

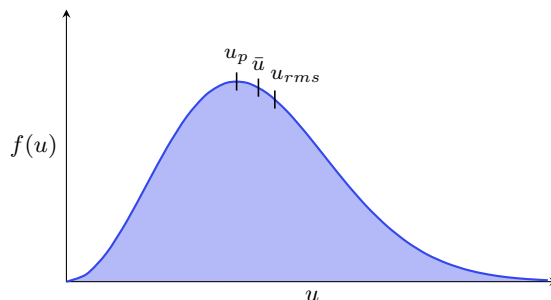- Important values of molecular speed u.

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 $\boldsymbol{f(u)}$. 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 $\boldsymbol{u_p}$. Given by*

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

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

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

- 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 that

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

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

for $i = x, y, z$.

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