Physical Chemistry

Lecture 3
Kinetic Theory of Gases

Model of gases

- A material that consists of many particles
  - Supported by many experiments
- The macroscopic parameters manifest the microscopic interactions
  - Force of collision → pressure
  - Energy → temperature
- Simple application of Newtonian physics
  - Molecules act as particles

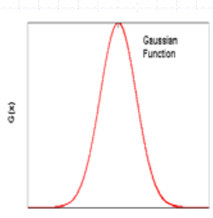
Number density

- The number of molecules per volume, $n^* = N/V$, determines many properties
- For purposes of simple theory, calculate n^* with the ideal-gas law
  - $n^* = PL/RT$
  - $L = 6.0221367 \times 10^{23}$

Distributions of properties

- Not all molecular properties are uniform across a sample
  - Particular example, molecular speed
- Must be able to describe the macroscopic effects in terms of the distribution
- Mathematically described by a distribution function, F(v)
- Calculate properties as averages

Normal probability distribution in one dimension



- Random processes determine G(x)
- Normal probability distribution or gaussian distribution
  - $A \exp(-(x-x_0)^2/2\sigma^2)$
- A determined so that area under G(x) is 1:

$$\int_{-\infty}^{+\infty} G(x)\,dx = 1$$

Estimating average values of random variables

- Use distribution to determine averages of functions of the independent variable
- Examples:

$$\langle x \rangle = \int_{-\infty}^{+\infty} xG(x)dx$$

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2G(x)dx$$

$$\langle x^n \rangle = \int_{-\infty}^{+\infty} x^nG(x)dx$$

Speed distribution function in one dimension

- $f(v_x)$ is determined by the Boltzmann factor
  - $f(v_x) = A \exp(-E/kT) = A \exp(-mv_x^2/2kT)$
- Assumes molecule has only kinetic energy
- Normalization over all speeds ($0<v<\infty$) gives $A = (2m/\pi kT/)^{1/2}$

Average values of functions of the speed in one dimension

- $<v_x> = (2kT/\pi m)^{1/2}$
- $<v_x^2> = kT/m$
- $<v_x^3> = (8k^3T^3/\pi m^3)^{1/2}$

Probability distributions in three dimensions

- $F(v) = f(v_x)f(v_y)f(v_z)$
- Because of the independence of the variables
  - $<v_x^2> = <v_y^2> = <v_z^2>$
  - Root-mean-square speed
    - $u = (<v^2>)^{1/2} = (<v_x^2>+<v_y^2>+<v_z^2>)^{1/2}$
    - $u = (3kT/m)^{1/2}$
  - Average kinetic energy per unit volume
    - K.E. = $n*m<v^2>/2 = 3n*kT/2$
  - Average kinetic energy per molecule
    - K.E. = $3kT/2$

Pressure and molecular collisions

- Pressure is the force imparted per unit area to the walls of a container
  - P = force/area
- Force measures momentum transfer during collisions with the wall
  - $F_{collision} = dp_x/dt = m\,(dv_x/dt) = 2m|v_x|/\Delta t$
  - F_{total} = Area $n*m<v_x^2>$
  - $P = n*m<v_x^2> = n*m(kT/m) = n*kT$
  - Or $P = RT/V_m$, the ideal-gas law
- The simple kinetic theory leads to the ideal-gas relationship

Knudsen flow

- Collision frequency
  - z = number of collisions per unit time per unit area
  - $z = (n*/2) <|v_z|>$
  - Calculate average to give
    - $z = n*(kT/2\pi m)^{1/2}$
- If the area is a hole, z is the number of molecules passing through the hole of area A per unit time – Knudsen flow
- Can measure low vapor pressure above a solid accurately by measuring weight loss as a function of time

Knudsen flow

- Generally measure by weight loss over time
- Simple formula

$$\mu = \frac{1}{A}\left(\frac{\Delta W}{\Delta t}\right)$$

- Use ideal-gas law to measure of pressure

$$P = \left(\frac{2\pi RT}{M}\right)^{1/2} \mu$$

Kinetic theory summary

- Connects macroscopic parameters with averages over distribution of microscopic parameters
- Uses simple physical model
- Leads to simple equations like the ideal-gas law
- Predicts average kinetic energy
- Allows measurement of properties like vapor pressure of a solid