Physical Chemistry

Lecture 1

Distributions and averages

Characteristics of macroscopic materials

- Large numbers of particles
- Distribution of properties
  - Example: speed
  - Describe with a distribution function, F(v)
    - Normalized: $\int_0^\infty F(v)dv = 1$
    - Average of a function of speed

$$< f(v) > = \int_0^\infty F(v) f(v) dv$$

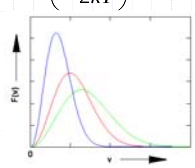
Boltzmann's distribution

- Speed distribution function, F(v)
- Consider only kinetic energy

$$F(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right)$$

- This is normalized

$$\int_0^\infty F(v)dv = 1$$



Calculating average molecular properties

- Use the distribution function

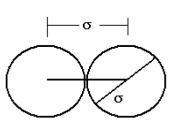
$$\overline{f(v)} = \int_0^\infty f(v)F(v)dv$$

- Example: average speed

$$\bar{v} = \int_0^\infty vF(v)dv = \sqrt{\frac{8kT}{\pi m}}$$

Molecular collisions

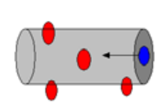
- Collisions dominate effects that depend on close proximity of molecules
- "Hard-sphere" model



Collisions of a molecule

- Determined by the number of molecules in the space ($N = n^* V$)
- Collision frequency

$$\bar{z}_{AA} = n^* \pi\sigma^2 \bar{v}_{rel} = \sqrt{2}\, n^* \pi\sigma^2 \bar{v}$$



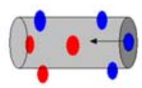
- Mean-free path

$$\lambda = \frac{\bar{v}}{\bar{z}_{AA}} = \frac{1}{\sqrt{2}\,\pi\sigma^2 n^*} = \frac{kT}{\sqrt{2}\,P\pi\sigma^2}$$

Collisions of unlike molecules

- Three different kinds of collision
- Collision frequencies per molecule

$$\bar{z}_{AA} = n_A^* \pi\sigma^2 \bar{v}_{rel} = \sqrt{2}\, n_A^* \pi\sigma^2 \bar{v}$$



$$\bar{z}_{A:B} = \pi\sigma_{AB}^2 \bar{v}_{AB} n_B^*$$

$$\bar{z}_{B:A} = \pi\sigma_{AB}^2 \bar{v}_{AB} n_A^*$$

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$$

Total collisions in a mixture

- Often must know the total number of collisions per unit time

$$Z_{AA} = \bar{z}_A \frac{n_A^*}{2} = \frac{\pi\sigma_A^2 \bar{v}_A}{\sqrt{2}} n_A^{*2}$$

$$Z_{AB} = \bar{z}_{A:B} n_A^* = \pi\sigma_{AB}^2 \bar{v}_{AB} n_A^* n_B^*$$

$$Z_{AB} = \bar{z}_{B:A} n_B^* = \pi\sigma_{AB}^2 \bar{v}_{AB} n_A^* n_B^*$$

Summary

- Simple kinetic theory allows calculation of various average properties
- Calculate average properties with the distribution function
- Collision frequency important for properties that depend on the molecules being in close proximity
- Mixtures have multiple kinds of collisions