Physical Chemistry
Lecture 1
Distributions and averages

Characteristics of macroscopic materials
- Large numbers of particles, \( N \)
- Distribution of properties: \( F(v) = n(v)/N \)
  - 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 at dynamic equilibrium
- 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
  \[
  < f(v) > = \int_0^\infty F(v)f(v)dv
  \]
- Example: average speed
  \[
  < v > = \int_0^\infty vF(v)dv = \frac{8kT}{\pi m}
  \]

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
  \[
  < z_{coll} > = n^* m d^2 < v_{rel} > = \sqrt{2} n^* m d^2 < v >
  \]
- Mean-free path
  \[
  \lambda = \frac{< v >}{< z_{coll} >} = \frac{1}{\sqrt{2} m d^2 n^*} = \frac{kT}{\sqrt{2} \ p m d^2}
  \]
Collisions of unlike molecules

- Three different kinds of collision
- Collision frequencies per molecule

\[
< z_{AA} > = n_A^* \pi d_A^2 < v_{rel} >
= \sqrt{2} n_A^* \pi d_A^2 < v >
\]

\[
< z_{AB} > = \pi d_{AB}^2 < v_{AB} > n_B^* d_{AB} = \frac{d_A + d_B}{2}
\]

\[
< z_{BB} > = \pi d_{BB}^2 < v_{BB} > n_B^* d_{BB}
\]

Total collisions in a mixture

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

\[
Z_{AA} = < z_{AA} > \frac{n_A^*}{2} = \frac{\pi d_A^2 < v >}{\sqrt{2}} n_A^2
\]

\[
Z_{AB} = < z_{A:B} > n_A^* = \pi d_{AB}^2 < v_{AB} > n_A^* n_B^*
\]

\[
Z_{BB} = < z_{B:B} > n_B^* = \pi d_{BB}^2 < v_{BB} > n_A^* n_B^*
\]

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