## Introductory Gas Kinetic Theory

- Approach to understanding gas properties - both equilibrium and nonequilibrium (rates) by examining
  - translational **motions** of molecules and
  - their interactions, called **collisions**
- In most systems of interest, there are large number of molecules present
  - SATP ~3×10^{19} molec/cm^3 or in $V=(10\mu m)^3$ we have 30×10^9 molecules >> human population
  - each molecule in constant state of motion and with different velocities
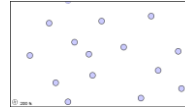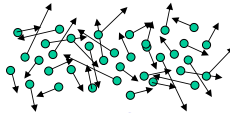
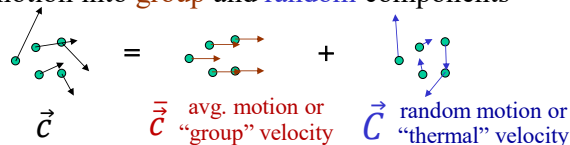 - **too many molecules to follow them all individually** $\Rightarrow$**use statistical approach**

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Random (Statistical) Motion

- Break motion into group and random components

$$\vec{c} = \vec{\bar{c}} + \vec{C}$$

$\vec{\bar{c}}$ avg. motion or "group" velocity

$\vec{C}$ random motion or "thermal" velocity

- Random motion is free motion of molecules, until a "collision" with another molecule or surface
  - free motion means molecule moves in straight line between collisions
  - significant time spent in free/straight-line motion; this is why gas is different from liquid/solid
  - why? – related to large spacing between molec. $d\sim3\text{Å}=3\times10^{-8}$ cm; $\Delta_{avg}\sim n^{-1/3}$ @SATP=3×10^{-7} cm

    $\Delta/d \sim O(10)$ *later will show mean free path $\lambda>>\Delta>>d$*

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Summary: Gas Kinetic Theory

- Examines properties of statistical motion of all molecules, not trying to follow each one

  – valid only for large numbers of molecules

- Assumes molecules spend most of their time moving in straight lines between collisions

- But molecules do interact
 – *need models to describe molecular interactions*

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Molecular Models

- How do molecules interact ("collide")?
  – through force fields
    - attractive: electrostatic, e.g., $- \leftrightarrow +$ (, gravity, …)
    - repulsive: electrostatic, e.g, $- \leftrightarrow -$ (,Pauli exclusion,…)
- Simplifications to force models, often assume
  1) only **elastic collisions**,
     no internal energy changes
  2) **spherically symmetric** force fields
    - only function of separation (r), not θ, ϕ
    - not strictly true, e.g., polar molecule like H_2O
      (but rotations tend to average out directionality)
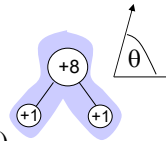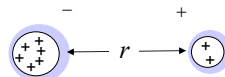
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Intermolecular Potentials

- Model **short range attractive** intermolecular forces of **neutral** molecules with electrostatic potentials

$$V_{attr}(r) = -\sum_{\alpha=1}^{\infty} \frac{B_\alpha}{r^\alpha}$$

$$F = -\frac{dV}{dr} = \sum_{\alpha=1}^{\infty} \alpha \frac{B_\alpha}{r^{\alpha+1}}$$

charged

- $\alpha=1$ monopole-monopole (Coulomb)
- $\alpha=2$ monopole-dipole (e^- - H_2O)
- $\alpha=3$ dipole-dipole (H_2O – H_2O)
- $\alpha=4$ dipole-quadrupole
- $\alpha=6$ dipole-induced dipole
  - induced dipole - induced dipole
- $\alpha\to\infty$ essentially no attraction
  - (F=0 until r~0)

- Model **repulsive terms**
  - primarily due to electron fields overlapping
    - strong electrostatic repulsion at short distance, along with Pauli exclusion principle
  - can also use power laws, high α for short distance

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Example Intermolecular Potentials

- **Lennard-Jones** potentials
  - simple two term models, can capture basic trends
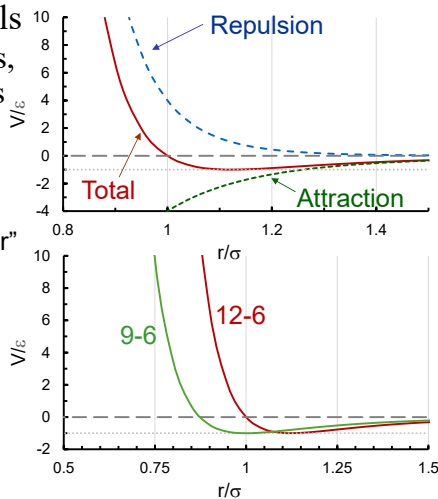
repulsion   attraction

LJ 12-6
$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right]$$

"well-depth"   LJ "diameter"

separation distance

LJ 9-6
$$V(r) = \varepsilon\left[2\left(\frac{\sigma}{r}\right)^9 - 3\left(\frac{\sigma}{r}\right)^6\right]$$

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Example Intermolecular Potentials

- **Rigid/Hard Sphere** model
  - also known as elastic **billiard ball** model
  - assumes no attraction and infinite repulsion potential when $r \leq r_{crit}$
  - simplest model, analytically tractable
  - can still provide useful results

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