# CE 530 Molecular Simulation

## Lecture 2

## Physical quantities; Hard-sphere MD

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# Physical Quantities in Molecular Simulation

- State variables
  - *each variable has an associated "conjugate" variable*
    - temperature, energy (kT,E)
    - pressure, volume (P,V)
    - chemical potential, number of molecules (μ,N)
  - *specification of state requires fixing one of each pair*
  - *the dependent variable can be measured by the simulation*
- Configuration variables
  - *position, orientation, momentum of each atom or molecule*
  - *energy, forces and torques*
  - *time*
- Properties
  - *transport coefficients, free energies, structural quantities, etc.*
- Molecular model parameters
  - *characteristic energy, size, charge*

# Dimensions and Units 1. Magnitudes

- Typical simulation size very small
  - *100 - 1000 atoms*
- Important extensive quantities small in magnitude
  - *when expressed in macroscopic units*
- Small numbers are inconvenient
- Two ways to magnify them
  - *work with atomic-scale units*
    - ps, amu, nm or Å
  - *make dimensionless with characteristic values*
    - model values of size, energy, mass

| Symbol | Definition | Value |
|---|---|---|
| ***1. Constants*** | | |
| $k$ | Boltzmann's constant | $1.3806\times10^{-23}$ J/(molec·K) |
| $N_0$ | Avagadro's number | $6.022\times10^{23}$ |
| ***2. Simulation Variables*** | | |
| $N$ | Number of molecules | $\sim 10^3$ |
| $V$ | Simulation cell volume | $\sim 10^{-24}$ m$^3$ |
| $m$ | Molecular mass | $\sim 10^{-25}$ kg/molec |
| $\rho$ | Number density | $\sim 10^{27}$ molec/m$^3$ |
| $E$ | Energy (total) | $\sim 10^{-20}$ J/molec |
| $t$ | time | $\sim 10^{-12}$ s |
| ***3. Model Variables*** | | |
| $\sigma$ | Size variable | $\sim 5\times10^{-10}$ m |
| $\epsilon$ | Energy variable | $\sim 10^{-21}$ J/molec |
| $r_b$ | Bond distance | $\sim 10^{-10}$ m |
| $k_v$ | Vibrational spring constant | $\sim 10^3$ J/m$^2$ |

# Dimensions and Units 2. Scaling

- Scaling by model parameters
  - *Size $\sigma$*
  - *Energy $\varepsilon$*
  - *Mass m*
- Choose values for one atom/ molecule pair potential arbitrarily
- Other model parameters given in terms of reference values
  - *e.g., $\varepsilon_2/\varepsilon_1 = 1.2$*
- Physical magnitudes less transparent
- Sometimes convenient to scale coordinates differently

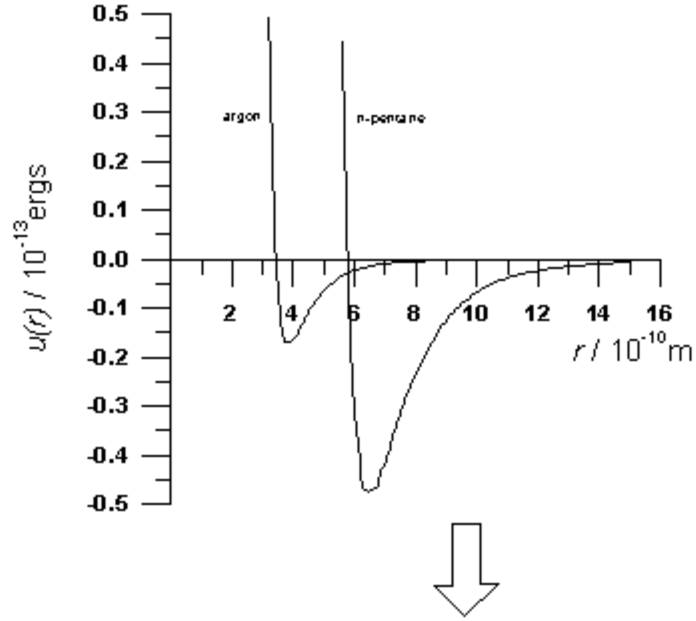
| Symbol | Meaning | Definition |
|---|---|---|
| $r^*$ | dimensionless distance | $r/\sigma$ |
| $E^*$ | dimensionless energy | $E/\epsilon$ |
| $T^*$ | dimensionless temperature | $kT/\epsilon$ |
| $U^*$ | dimensionless internal energy | $U/\epsilon$ |
| $t^*$ | dimensionless time | $t/[\sigma(m/\epsilon)^{0.5}]$ |
| $v^*$ | dimensionless velocity | $v/(\epsilon/m)^{0.5}$ |
| $F^*$ | dimensionless force | $F\sigma/\epsilon$ |
| $P^*$ | dimensionless pressure | $P\sigma^3/\epsilon$ |
| $D^*$ | dimensionless self diffusion coefficient | $D/[\sigma(\epsilon/m)^{0.5}]$ |

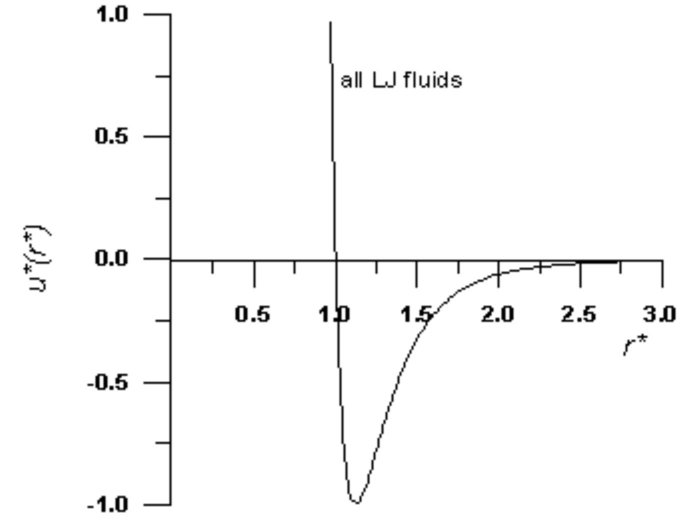
# Dimensions and Units 3. Corresponding States

- Lennard-Jones potential in dimensionless form

$$u^*(r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right]$$

- Parameter independent!
- Dimensionless properties must also be parameter independent
  - *convenient to report properties in this form, e.g. P*(ρ*,T*)*
  - *select model values to get actual values of properties*
  - *Basis of corresponding states*
- Equivalent to selecting unit value for parameters



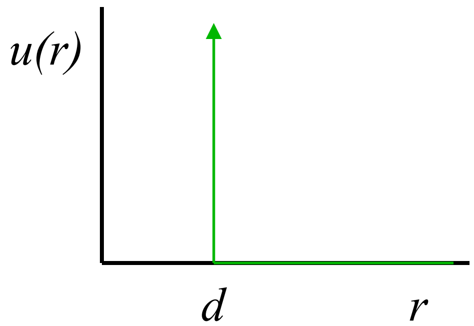



# Dimensions and Units 4. Corresponding States Example

- Want pressure for methane at 0.0183 mol/cm$^3$ and 167 K
- LJ model parameters are $\sigma$ = 0.3790 nm, $\varepsilon/k$ = 142.1 K
- Dimensionless state parameters
  - $\rho^* = \rho\sigma^3 = (0.0183 \text{ mol/cm}^3)(3.790 \times 10^{-8} \text{ cm})^3(6.022 \times 10^{23}$ molecules/mole$) = 0.6$
  - $T^* = T/(\varepsilon/k) = (167 \text{ K})/(142.1 \text{ K}) = 1.174$
- From LJ equation of state
  - $P^* = P\sigma^3/\varepsilon = 0.146$
- Corresponding to a pressure
  - $P = 0.146\ (142.1 \text{ K})(13.8 \text{ MPa-Å}^3\text{/molecule})/(3.790\text{Å})^3 = 5.3 \text{ MPa}$
  - 53 bars

# Dimensions and Units 5.
# Hard Potentials

- Special case
  - $u(r) = 0, r > d$
  - $u(r) = \infty, r < d$

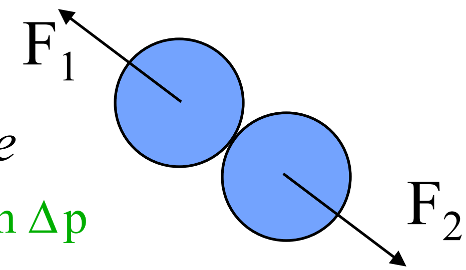



- No characteristic energy!
- Temperature (kT) provide the only characteristic energy
- All dimensionless properties (*e.g.*, $Pd^3/kT$), independent of temperature!

# Hard Sphere Molecular Dynamics

- Prototype of a molecular simulation
  - *basis for discussion*
- Introduce features common to all simulations
  - *dimensions and units*
  - *atom looping*
  - *boundary conditions*
  - *averaging and error estimation*
  - *initialization*
- For later consideration:
  - *integrators for soft potentials*
  - *Monte Carlo methods*

# Hard Sphere Dynamics




## ○ Impulsive, pairwise collisions

- *infinite force exerted over an infinitesimal time*

  impulse = force × time = finite change in momentum $\Delta$p

- *force directed along line joining centers of atoms*
- *magnitude of impulse governed by conservation of energy*

$$\left.\begin{aligned}\vec{p}_1^{\,new} &= \vec{p}_1^{\,old} + \Delta\vec{p} \\ \vec{p}_2^{\,new} &= \vec{p}_2^{\,old} - \Delta\vec{p}\end{aligned}\right\}\text{conservation of momentum}$$

$$\frac{1}{m_1}\left|\vec{p}_1^{\,new}\right|^2 + \frac{1}{m_2}\left|\vec{p}_2^{\,new}\right|^2 = \frac{1}{m_1}\left|\vec{p}_1^{\,old}\right|^2 + \frac{1}{m_2}\left|\vec{p}_2^{\,old}\right|^2 \quad \text{conservation of energy}$$

- *thus* $$\Delta p_{[xy]} = m_R \frac{\vec{v}_{12}\cdot\vec{r}_{12}}{\sigma^2} r_{12[xy]}$$

$$\vec{r}_{12} \equiv \vec{r}_2 - \vec{r}_1$$

$$\vec{v}_{12} \equiv \vec{v}_2 - \vec{v}_1$$

$$m_R = \frac{2m_1 m_2}{m_1 + m_2} \quad \text{reduced mass}$$

consider glancing collision

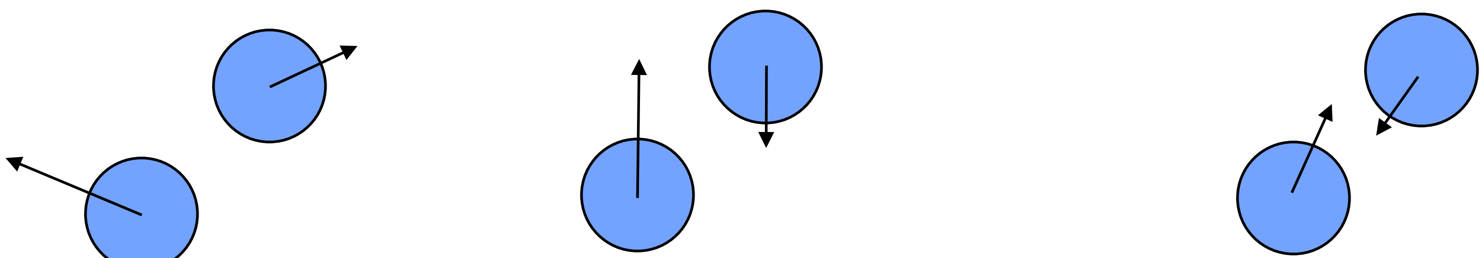
consider head-on collision

# Hard Sphere Kinematics

- Free flight between collisions
  - $\vec{r}(t+\Delta t) = \vec{r}(t) + \vec{v}(t)\Delta t$
- Collision time for any pair solved analytically
  - *Find Δt such that* $\left|\vec{r}_2(t+\Delta t) - \vec{r}_1(t+\Delta t)\right|^2 = \sigma^2$
  - *leads to quadratic equation*

$$\vec{v}_{12}^2(\Delta t)^2 + 2(\vec{v}_{12}\cdot\vec{r}_{12})(\Delta t) + (\vec{r}_{12}^2 - \sigma^2) = 0$$

  - *three cases*



separating

$\vec{v}_{12}\cdot\vec{r}_{12} > 0$

approaching, but miss

$\vec{v}_{12}\cdot\vec{r}_{12} < 0$

$\left(\vec{v}_{12}\cdot\vec{r}_{12}\right)^2 - \vec{v}_{12}^2(\vec{r}_{12}^2 - \sigma^2) < 0$

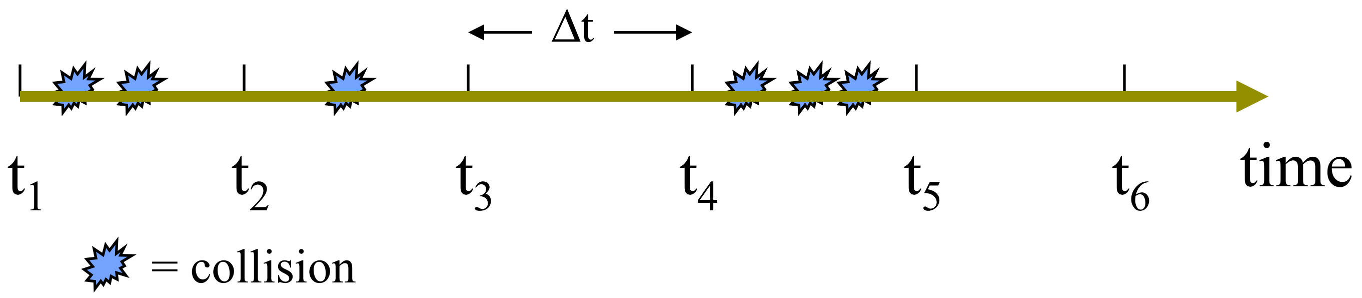
approaching, and hit

$\vec{v}_{12}\cdot\vec{r}_{12} < 0$

$\left(\vec{v}_{12}\cdot\vec{r}_{12}\right)^2 - \vec{v}_{12}^2(\vec{r}_{12}^2 - \sigma^2) > 0$

# Integration Strategy

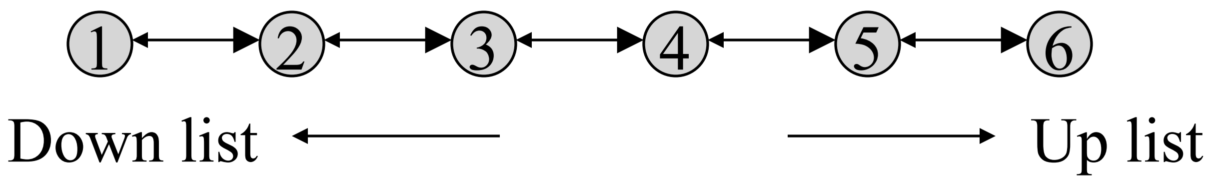
- Choose a time interval, $\Delta t$; do the following to advance the system across this interval, bringing the system to time $t_{n+1} = t_n + \Delta t$
  - *Loop over all pairs* ij, *computing collision time* $t_{ij}$
  - *Identify minimum* $t_{ij}^{min}$ *as next colliding pair*
  - *If* $t_{ij}^{min} < t_{n+1}$, *advance all spheres to positions at* $t_{ij}^{min}$
  - *Perform collision dynamics on colliding pair*
  - *Identify next colliding pair, repeat until* $t_{ij}^{min} < t_{n+1}$, *then advance to* $t_{n+1}$.
  - *Accumulate averages, repeat for next time interval*



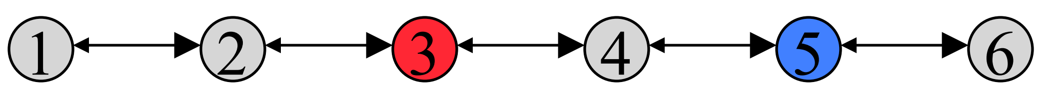

- Click here for applet highlighting collision pairs

# Ordering the Atoms

- Atoms are placed in an arbitrary order
- Each atom links to the next one up and next one down the list



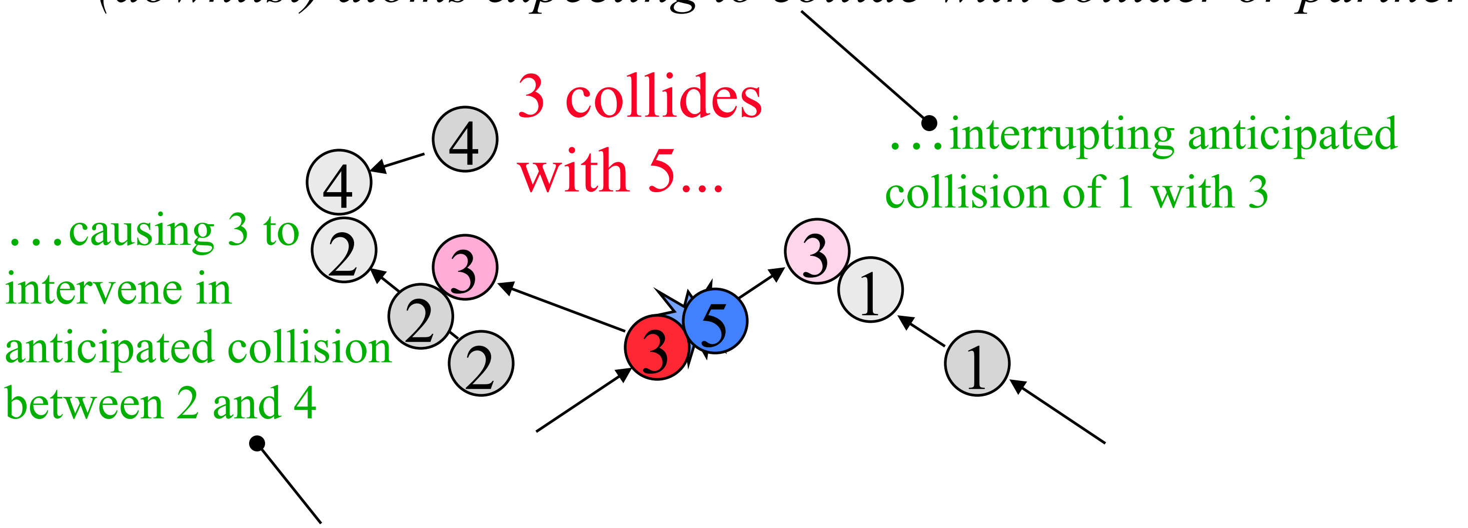

- Atom looks only up list to find collision partner
  - *collisions with down-list atoms monitored by down-list atoms*
- Example
  - *atoms 3 and 5 next to collide*




| | | | | | | |
|---|---|---|---|---|---|---|
| partner | 3 | 4 | 5 | 5 | 6 | null |
| time | 1.2 | 0.7 | 0.1 | 0.5 | 1.5 | null |

# Collision Update Requirements

- No need to re-identify **all** collisions with each step
- Upon collision, must update (check all atoms up-list of)
  - *collider*
  - *partner*
  - *(downlist) atoms expecting to collide with collider or partner*




- Also check if downlist atoms of collider or partner will now collide with either of them next