ME 517: Micro- and Nanoscale Processes

Lecture 29: Molecular Dynamics - II

Steven T. Wereley
Mechanical Engineering
Purdue University
West Lafayette, IN USA

Spring 2014

PURDUE UNIVERSITY

ME/CHE 517
Project 2
Due: at final exam

The goal of this project is to study a simplified version of molecular dynamics. We will consider the model problem of two Argon atoms interacting along the line separating the center of the two atoms (see figure below). Use a numerical integration scheme (Runge-Kutta, trapezoidal, etc.) to study what happens as the two atoms interact. We will use the Lennard-Jones interaction potential as a good model for how the atoms exert forces on each other.

Consider the following specific cases:

1. Separate the two molecules by a large distance (at least on atomic length scales). Allow time to pass.
    a. What is the final state?
    b. How close do the atoms get to one another?
    c. If you add some damping what is the final state?
2. Consider driving the left atom with a time dependent force F(t).
    a. What sort of behaviors do you observe as you vary the frequency and amplitude of F(t)? You may want to add a small amount of damping to converge to a final solution.
    b. Can you equate these behaviors to behaviors different phases of matter?
3. Compute the "density" of your Argon atom system under various conditions. This will require making liberal assumptions. How do these density calculations compare to Argon's macroscopic physical properties?

Prepare a report describing the equations used, the numerical integration scheme, the specific goals above and the conclusions you reached. Be sure to cite appropriate sources. Use convincing figures.

Particles near a wall

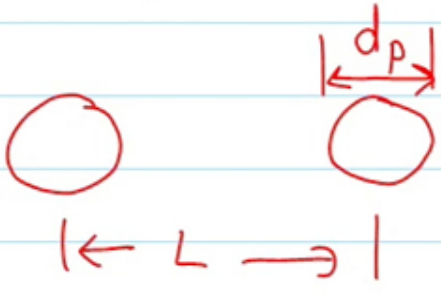
μ $\quad F_D = \lambda F_{D,SPNS}$ $\quad$ where $\lambda_\perp = 1 + \frac{9}{8}\frac{r_0}{\ell}$

$\lambda_\parallel = 1 + \frac{9}{16}\frac{r_0}{\ell}$

7/8

All single particle expressions assumed 1 particle in an unbounded medium.

→ simplify to



$L \gg d_p$

$L \geq 10 d_p$

Vol concentration $< 0.1\%$

Molecular Interaction Forces: Lennard-Jones 6-12 Potential

$$V_{ij}(r) = 4\varepsilon\left[c_{ij}\left(\frac{r}{\sigma}\right)^{-12} - d_{ij}\left(\frac{r}{\sigma}\right)^{-6}\right]$$

$$F_{ij}(r) = -\frac{\partial V_{ij}}{\partial r} = \frac{48\varepsilon}{\sigma}\left[c_{ij}\left(\frac{r}{\sigma}\right)^{-13} - \frac{d_{ij}}{2}\left(\frac{r}{\sigma}\right)^{-7}\right]$$

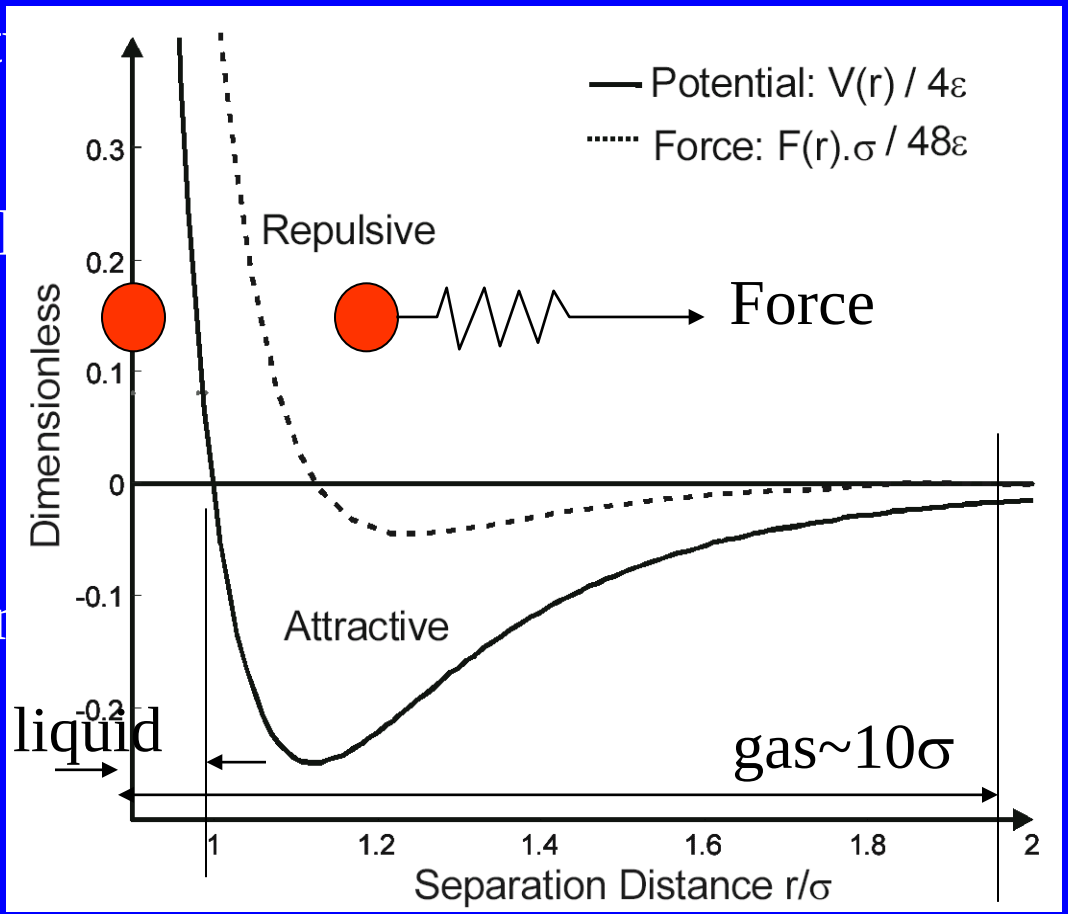
V_{ij}=potential energy between t molecules i and j

F_{ij}=force between two molecul i and j

c_{ij} and d_{ij} are parameters for chosen molecules

ε,σ are characteristic energy ar length scales respectively

r is the separation distance



Lennard Jones Constants

Fluid	ε/K *(K)*	σ *(nm)*
Air	97	0.362
N_2	91.5	0.368
CO_2	190	0.400
O_2	113	0.343
Ar	124	0.342

Phases	*Intermolecular Forces*	*Ratio of Thermal Vibration Amplitude Compared to* σ	*Approach Needed*
Solid	Strong	« 1	Quantum
Liquid	Moderate	~ 1	Quantum/classical
Gas	Weak	» 1	Classical

Molecular Dynamics Governing Equations

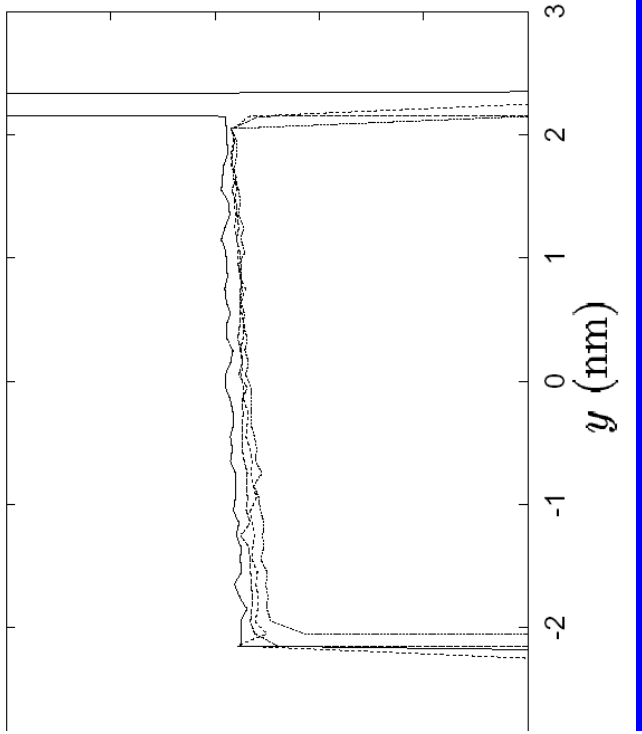
$$m\frac{d^2\mathbf{r}_i}{dt^2} = \sum_{j\neq i}\frac{\partial V_{ij}}{\partial \mathbf{r_i}} - \frac{m}{\tau}\frac{d\mathbf{r_i}}{dt} + \eta_i \qquad \tau = \sqrt{\frac{\sigma^2 m}{\varepsilon}}$$

- where $\mathbf{r_i}$ is the position vector, V_{ij} is the potential energy between any two molecules, τ is characteristic time scale, m is atomic mass
- Last two terms on RHS couple the particle dynamics with thermodynamics
  - Velocity term governs heat exchange with reservoir
  - η_i term is a Gaussian stochastic force with variance $2mk_b/\tau$
- For liquid argon, $\tau=2.2^{-12}$ sec
- Evolve the position of every molecule forward in time using Newton's 2nd Law

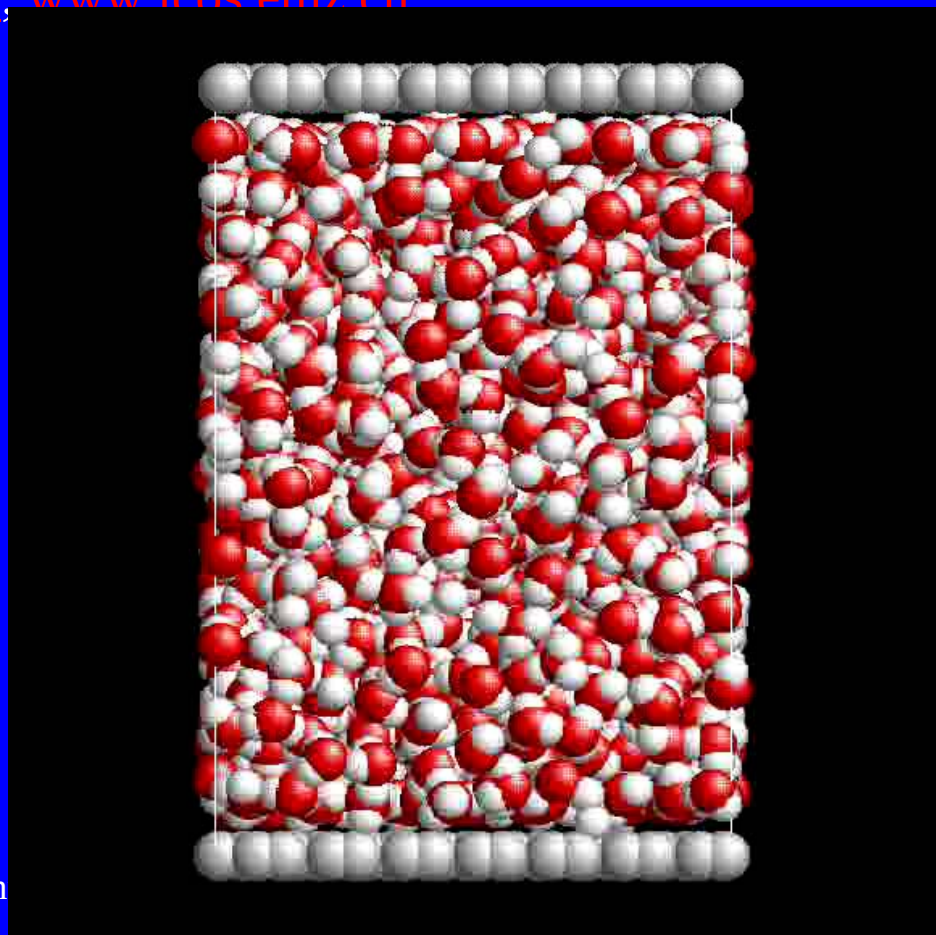
MD: Water Flow between Graphite Sheets

- ETH-Zurich simulated flows in and around CNTs and graphite sheets (Nanotech 2003)
- Exploring validity of no-slip assumption
- www.fisica.uniud.it/~ercolessi/md/; www.ices.ethz.ch

U=100m/s

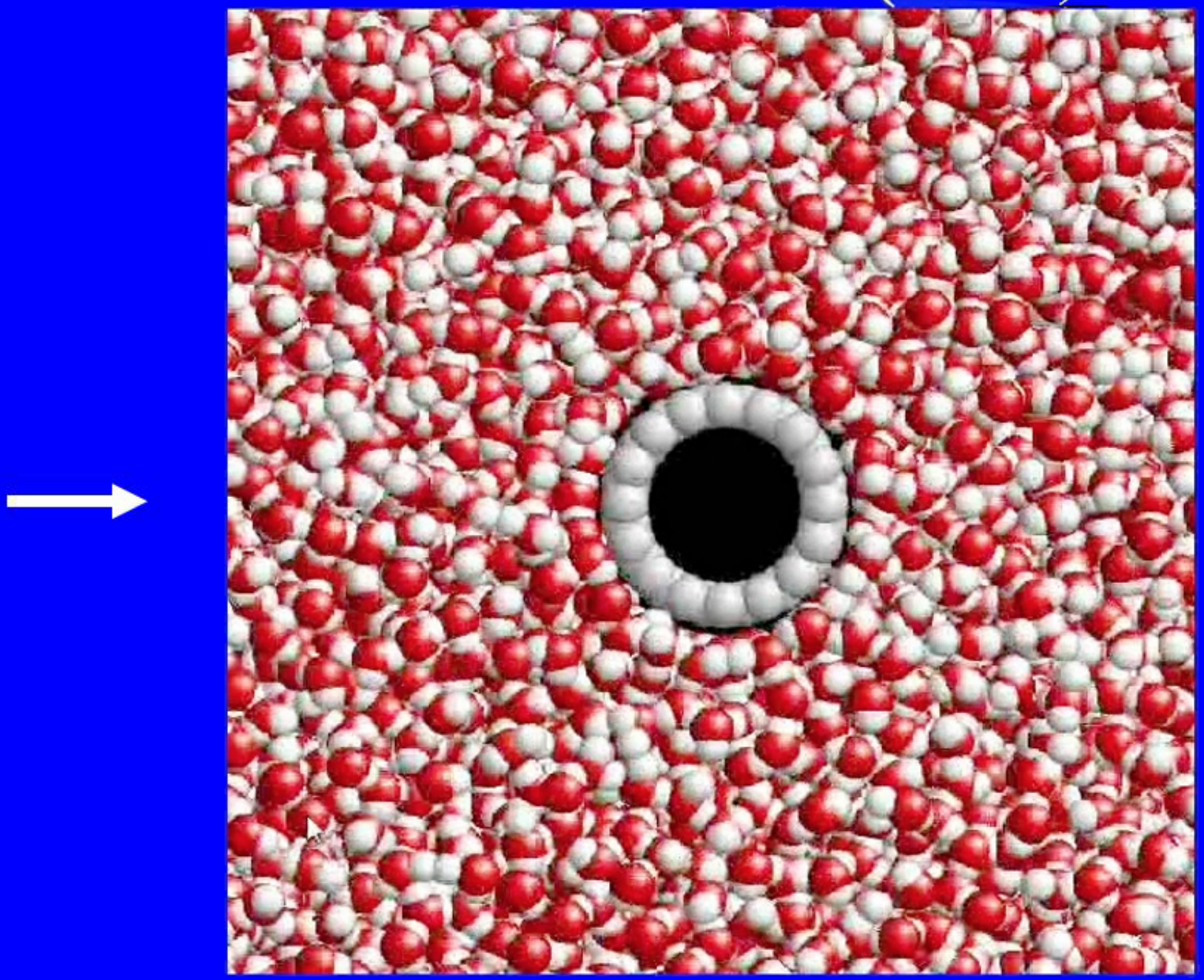


Slip lengths of 14-63 nm
→No-slip violated

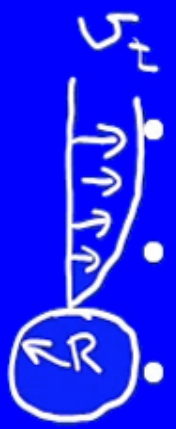


oscale Ph

Flow Around CNTs (ETHZ)



Flow Around CNTs (ETHZ)



- Flow agrees quite well with continuum theory
- Slip length less than a single molecular diameter
- Considerable variations in fluid density near CNT