ME 517: Micro- and Nanoscale Processes

Lecture 28: Molecular Dynamics - I

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Molecular Interaction Forces: Lennard-Jones 6-12 Potential

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

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

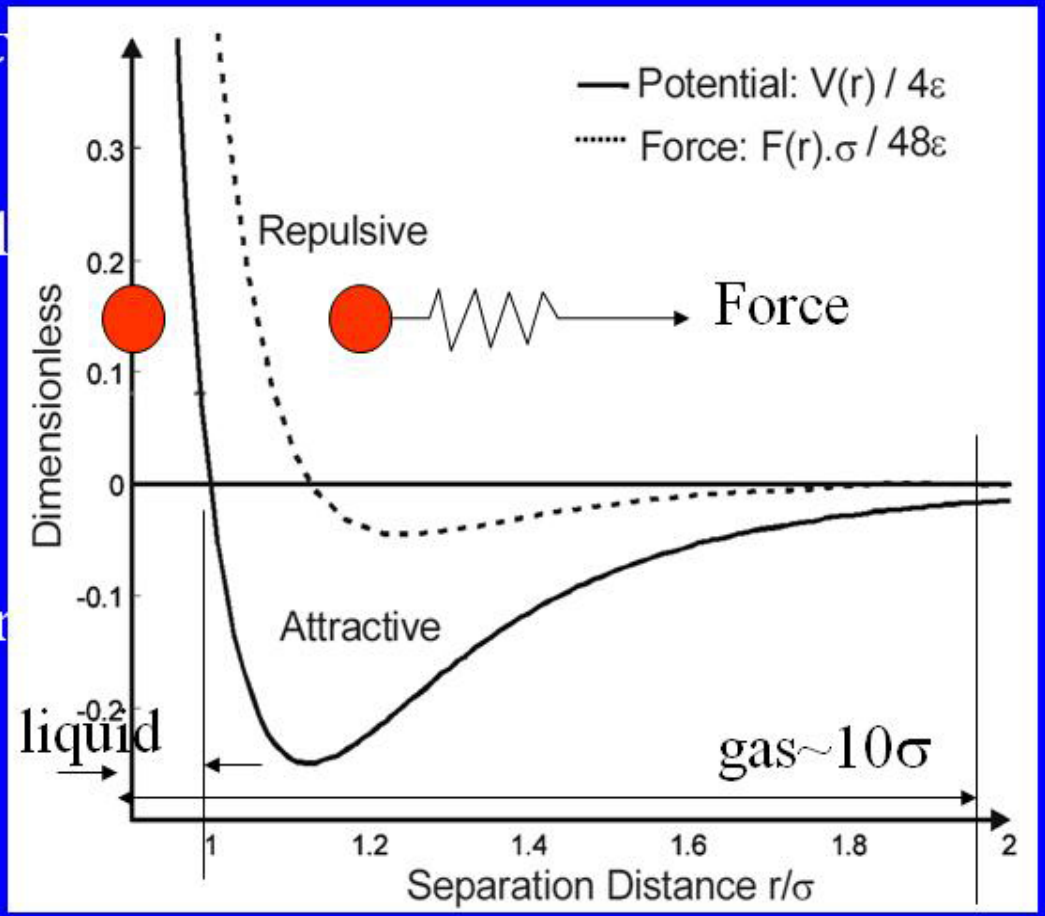
V_{ij}=potential energy between t molecules i and j

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

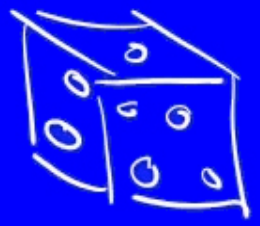
Fluid	ε/K *(K)*	σ *(nm)*
Air	97	0.362
N_2	91.5	0.368
CO_2	190	0.400
O_2	113	0.343
Ar	124	0.342

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

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

$$\tau = \sqrt{\frac{\sigma^2 m}{\varepsilon}}$$

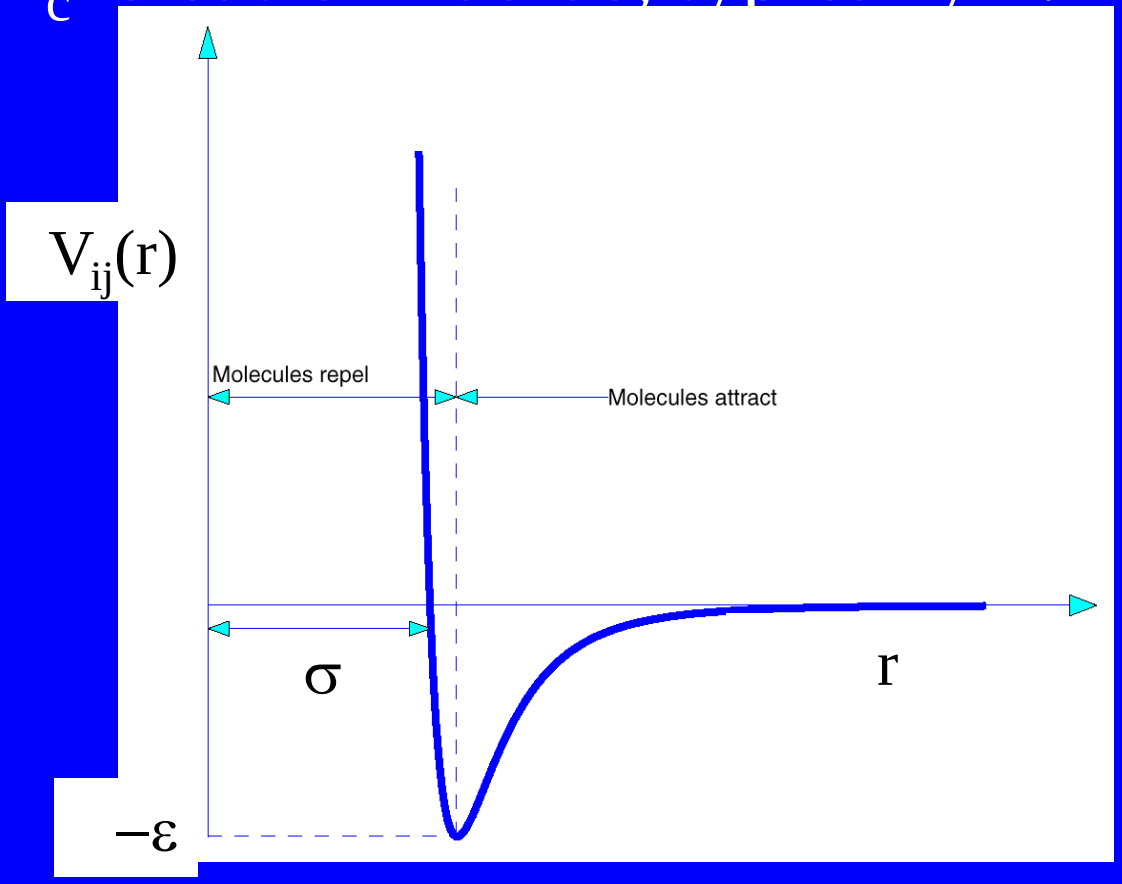


- where $\mathbf{r}_i$ is the position vector, V_{ij} is the potential energy between any two molecules, τ is characteristic time scale, m is atomic mass
- Last two terms on RHS couple the particle dynamics with thermodynamics
  - Velocity term governs heat exchange with reservoir
  - η_i term is a Gaussian 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

Shifted Lennard-Jones Potential

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

- r_c is cut-off radius, typically $2.2\sigma < r_c < 2.5\sigma$



Lennard-Jones Potential

- Works reasonably well for electrically neutral, non-polarizable, spherical molecules
- Dynamics for immiscible liquids ($d_{12}=d_{21}$)
  - $d_{12}=0$ implies pure short-range repulsion
  - $d_{12}=1$ implies symmetric interaction → single species
  - $d_{12}>1$ implies enhanced attraction
- Dynamics of wall boundaries can be simulated with same L-J approach but different constants
- Complicated molecules require complicated potentials, e.g. polymer chains can have a potential between all monomers plus a strongly attractive potential when all monomers in neighboring molecules line up

Temporal Evolution

- Equations of motions can be integrated forward in time by typical predictor-corrector scheme
  - typical time step size $\Delta t=0.005\tau$
  - for liquid Ar, $\Delta t=1.1e\text{-}14$ sec
- Another commonly used discretization called Verlet integration rule is

$$\boldsymbol{r}^{n+1} = 2\boldsymbol{r}^{n} - \boldsymbol{r}^{n-1} + \Delta t^2 \boldsymbol{a}(t) + \mathcal{O}(\Delta t^4)$$

Imposing External Forces

- Most flows driven by some external force
  - e.g. vibrating wall, pressure gradient, body force
- Need some way to couple in those forces
- Eulerian velocity computed as time average of N_i molecules according to

$$\boldsymbol{v}(\boldsymbol{x}) = \frac{1}{N_i} < \sum_j \frac{d\boldsymbol{x}_j}{dt} >$$

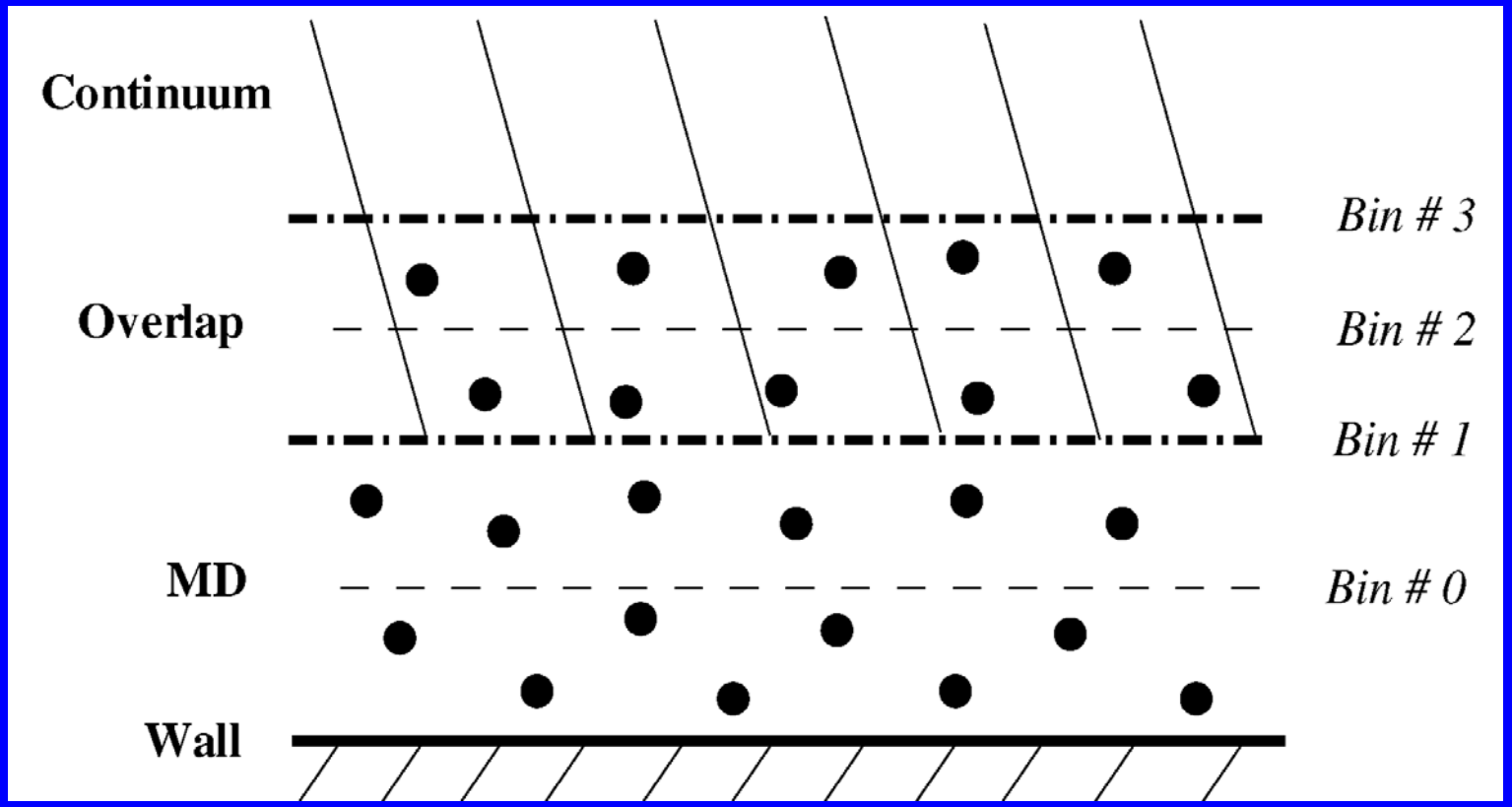
$$\tau(\boldsymbol{x}) = \frac{1}{V_i} < \sum_j \left[\frac{d\boldsymbol{x}_j}{dt} - \boldsymbol{v}(\boldsymbol{x})\right]\left[\frac{d\boldsymbol{x}_j}{dt} - \boldsymbol{v}(\boldsymbol{x})\right] + \sum_{j<i} \boldsymbol{r}_{ij}\boldsymbol{f}_{ij} >$$

Computational Complexity

- Have to sum over all pairs of molecules so order N^2
- Cut-off distance reduces computational complexity somewhat
- Pairs of interacting molecules stored in *Verlet list*
  - For each molecule a=1,2,…N create a list of neighbors that are within a distance r_c+r_s where r_c is the cut-off distance and r_s is called a *skin thickness*
  - r_s is chosen such that in a time interval of S~20 Δt, no molecules from outside the skin enter the interaction range of molecule a
- Computational intensity reduced somewhat to (order N) + S^{-1} (order N^2)

MD/Continuum Approach

- Occasionally desirable to combine MD and Continuum approach (e.g. N-S)
  - For example external flow over a body

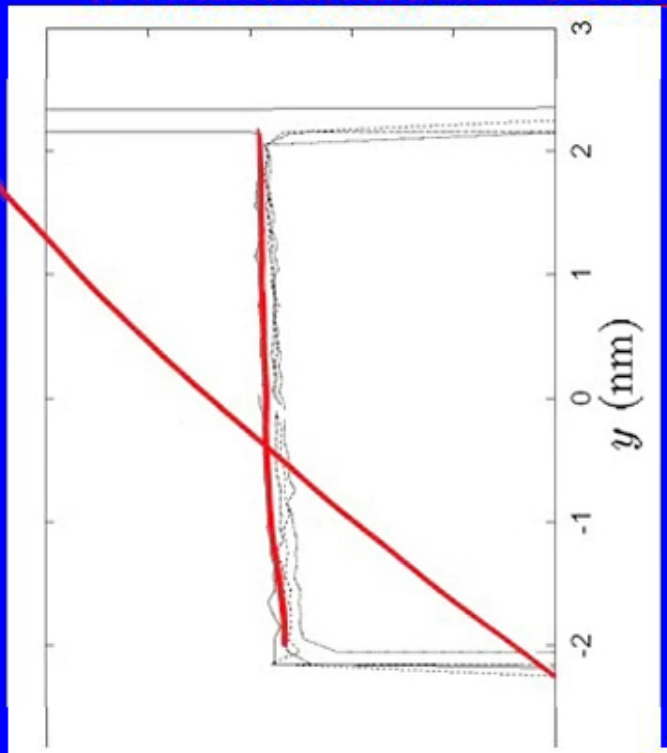


Karniadakis and Beskok, 2002

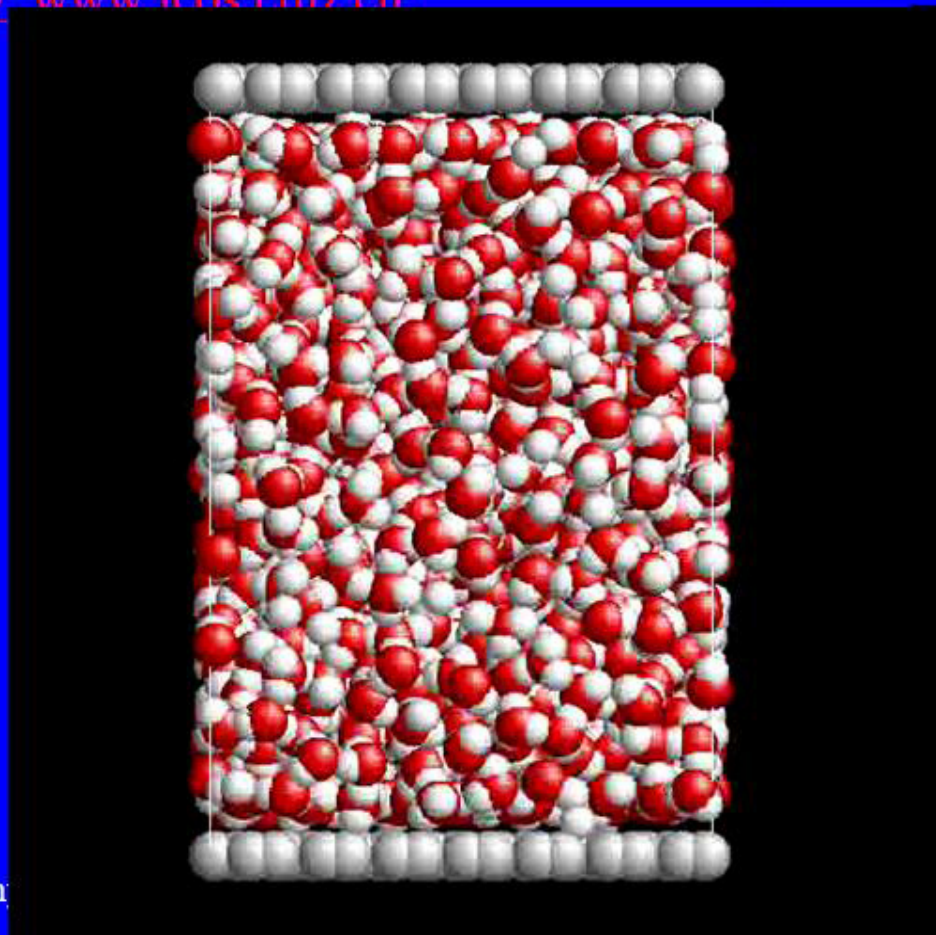
MD: Water Flow between Graphite Sheets

- 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.icos.ethz.ch

U=100m/s

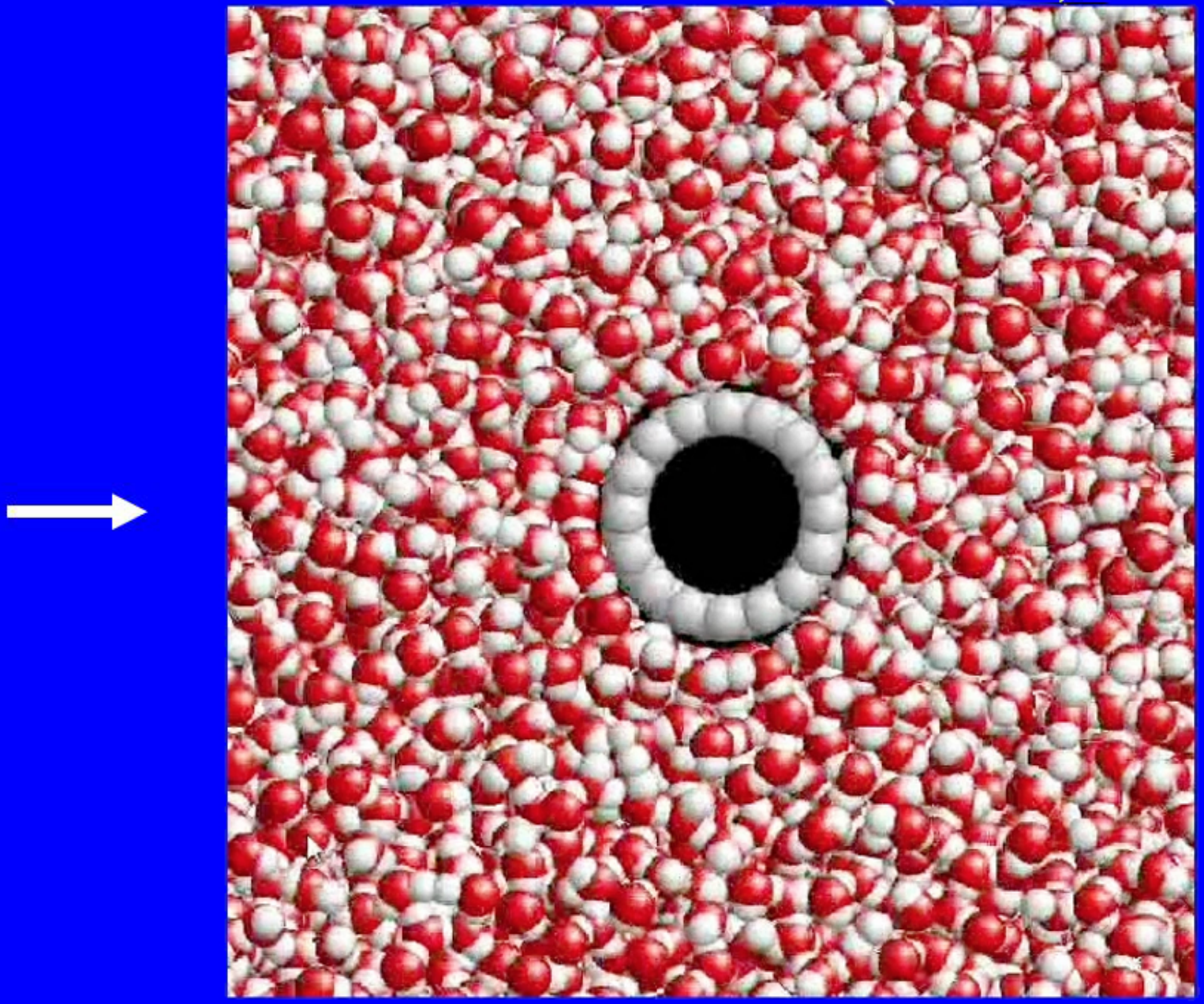


Slip lengths of 14-63 nm
→No-slip violated



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