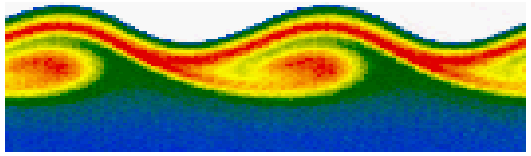
The use of Molecular Simulations in the study of Micro/Nano Fluidics: A Case Study

German Drazer

The Benjamin Levich Institute



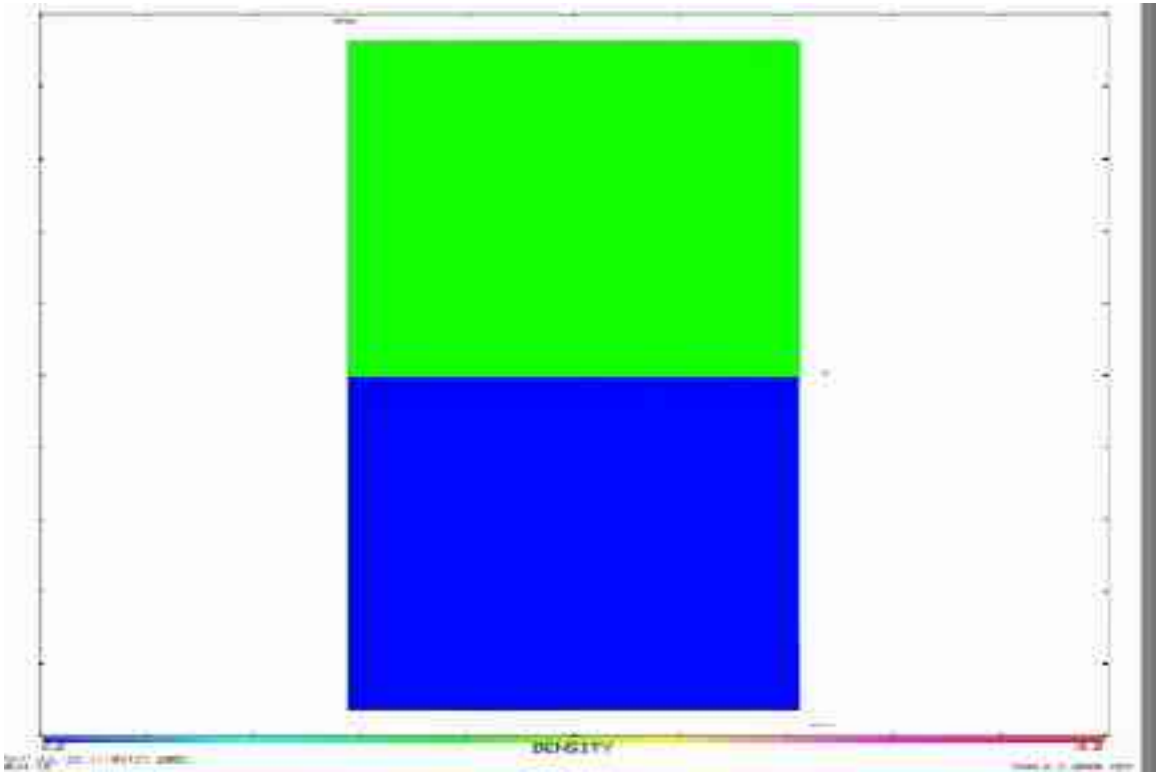
the City College of New York

Molecular Simulations

State-of-the-Art

Nanohydrodynamics simulations: An atomistic view of the Rayleigh–Taylor instability

Kai Kadau *†, Timothy C. Germann†, Nicolas G. Hadjiconstantinou§, Peter S. Lomdahl†, Guy Dimonte‡, Brad Lee Holian†, and Berni J. Alder¶



100,589,840 atoms!
1600 CPUs!
250,000 Time Steps!

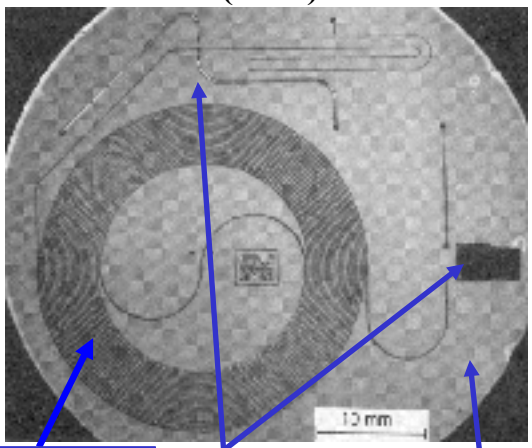
1000 x 1000 x 1000
100nm x 100nm x 100nm
NanoHydrodynamics

Microfluidic Devices

Micro-Fabrication

Gas Chromatograph

S. C. Terry, J. H. Jerman & J. B. Angell (1977)



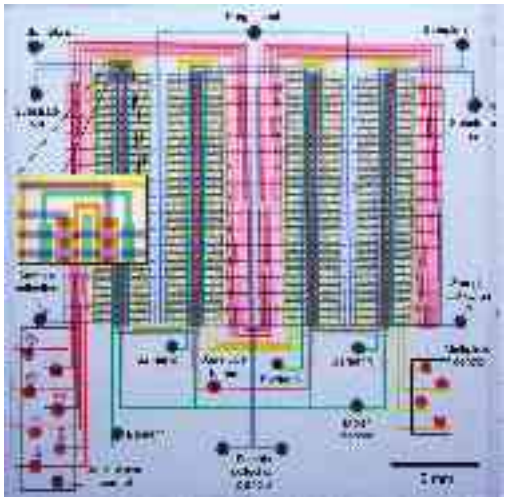
1.5 m Separation Column !

Detection & Injection Systems

Silicon Wafer

Large Scale Intergation

T. Thorsen, S. J. Maerkl & S. R. Quake (2003)

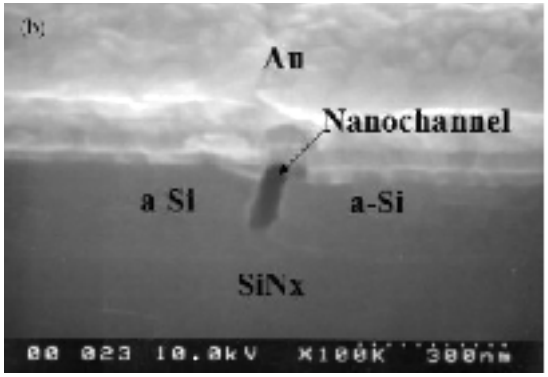


> 2,000 Valves

~ 256 Reactions

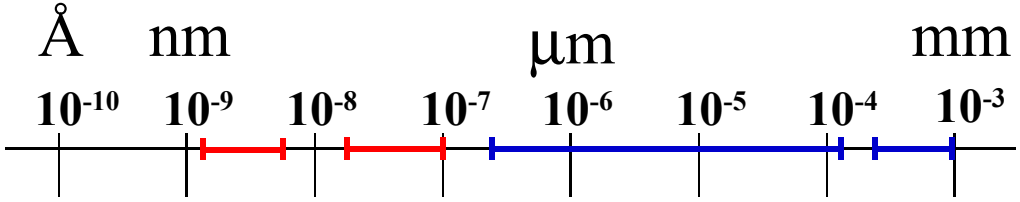
Nanochannel Fabrication Techniques

C. Lee, E. H. Yang, N. V. Myung & T. George (2003)



50nm x 100nm x **10mm!!**

Working Length Scales



Molecular Simulations

Micro-Fabrication

MS 60's | MS 00's | MS-MF 10's | MF 00's | MF 70's

Microfluidic Devices:
Challenges & Opportunities


news feature

Honey, I shrunk the lab

Take a lab full of test tubes, flasks and stirrers, and cram it onto a silicon chip — that's the dream of microfluidics

Lab-on-a-chip **devices or** ***μTAS***

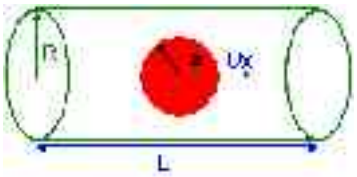
Portability	**High Throughput**	**Great Sensitivity**
Reduced Volumes	**Real Time Analysis**	**…**

Basic Problem:

Transport of colloidal particles through nanometer size channels

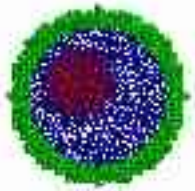
From *mm* to *nm*

Re↓ Pe↓ S/V↑ N↓



Molecular Simulations

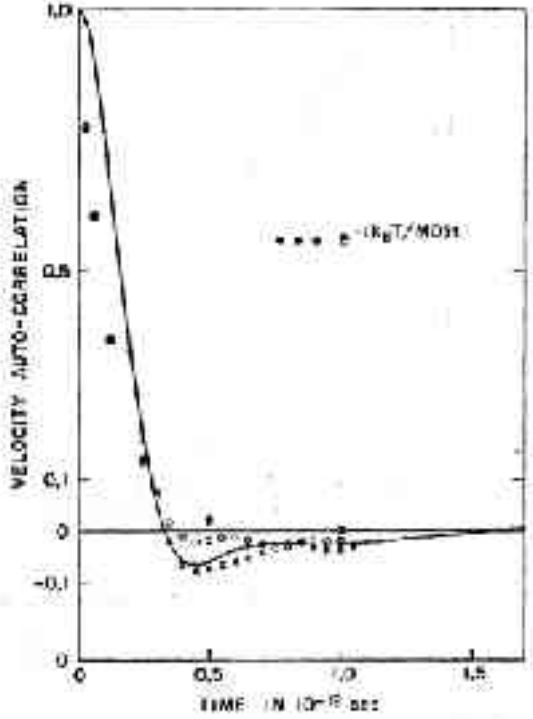
Atomistic Description of the System



Macroscopic Properties

Statistical Mechanics

Structure + Dynamic properties

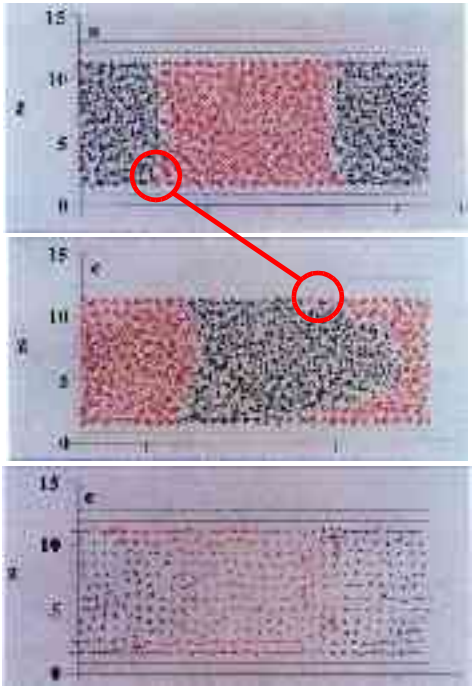


"Correlations in the motion of atoms in liquid argon", A. Rahman, Phys. Rev. 136A, 405 (1964)

Microscopic

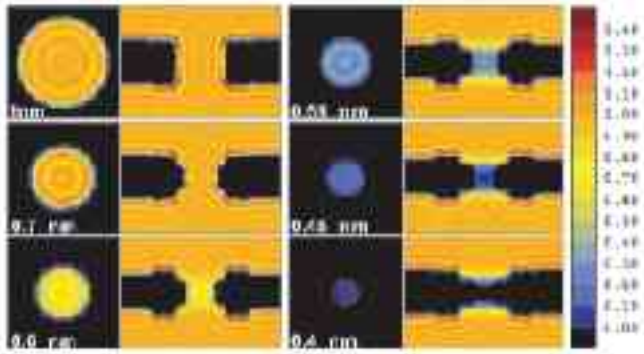
Macroscopic

No-Slip BC
Contact Line Motion

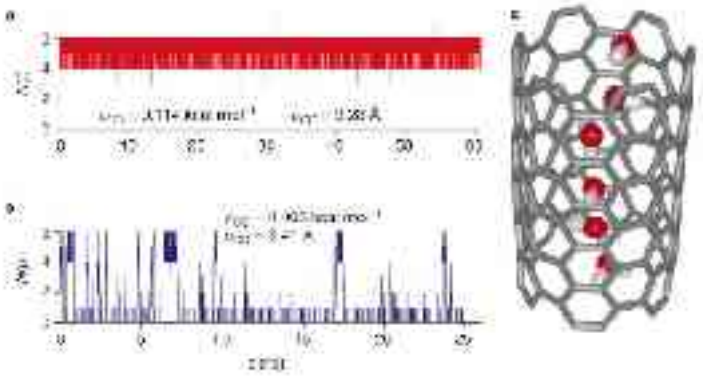


"Molecular Dynamics of Poiseuille flow and moving contact lines", J. Koplik, J. R. Banavar and J. F. Willemsen, Phys. Rev. Lett 60, 1282 (1988)

Behavior at Nanoscales



"Liquid–vapor oscillations of water in hydrophobic nanopores", O. Beckstein and M. S. P. Sansom, Proc. Nat. Acad. Sci. 100, 7063 (2003).



"Water conduction through the hydrophobic channel of a carbon nanotube" G. Hummer, J. C. Rasaiah & J. P. Noworyta,

Nature 414, 188 (2001)

Molecular Simulations

Intermolecular interactions - Possible Models

Heuristic Approach

(Hard Spheres, Lattice-Gases, Dissipative Particle Dynamics …)

"In nature the behavior of fluids depends very little on the nature on the individual particles… We have invented a type of imaginary particle that is especially simple for us to simulate. The flow of this particles on a large enough scale is very similar to the flow of natural fluids."

Richard P. Feynman

First-Principles to Phenomenological Models

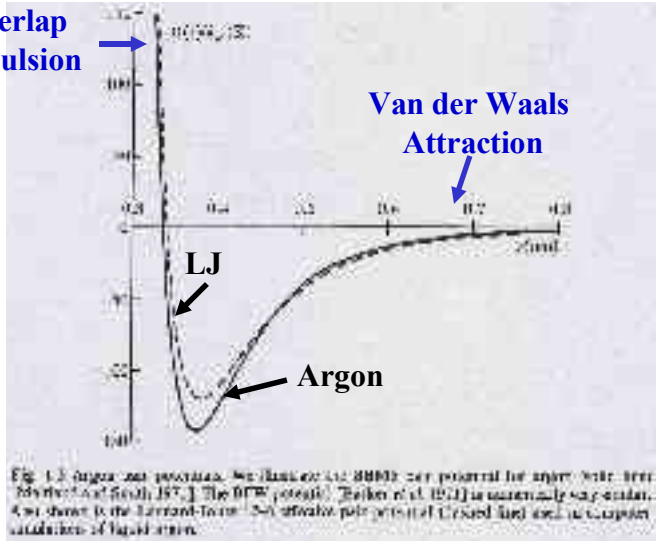
- ***Full*** Quantum Many-Body Problem!
- *"Ab-Initio"* Calculations (N ~ 10^2-10^3; Picoseconds)

  (Density Funtional Theory; Car-Parinello; Bohr-Oppenheimer)
- Interatomic Potentials;

  (Multipole expansions; Triplets!?)
- Phenomenological (Pair) Potentials (N ~ 10^6-10^8; Nanoseconds)

  (Dispersion Forces; Overlap Repulsion; Electrostatic Interactions; Chemical Bonds;)

Lennard-Jones Fluid



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

- "Effective" potential
- Non-Polar Materials
- Pair-wise additive interactions
- Classical Description
  (Hamilton / Newton)

Short-Range vs. Long-Range Interactions

$V(r) \propto (1/r)^{\nu}$

ν vs. D

$R^{D-\nu}$

Electrostatic Interactions: $\nu=1$ **Long-Range**

Dispersion Interactions: $\nu=6$ **Short-Range**

Interaction Cut-off $r \sim 2.5\,\sigma$

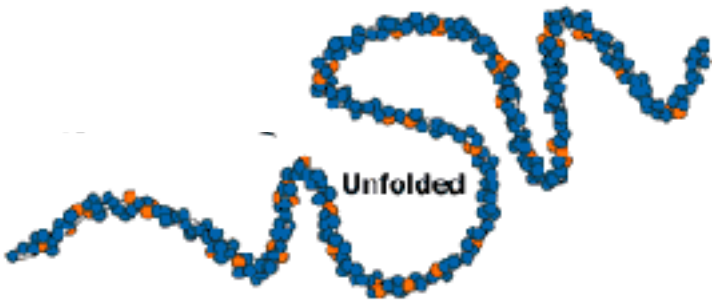
Monte-Carlo Simulations

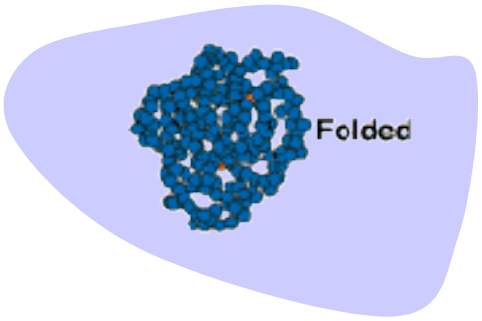
Equilibrium Static Properties

From Genomics To Proteomics

Protein Folding

PHE -VAL -ASN-GLN -HIS -LEU -CYS- GLY- ASP -HIS -LEU-
VAL- GLU- ALA -LEU- TYR -LEU- VAL- CYS- GLY- GLU-
ARG -GLY- PHE -PHE -TYR - THR -PRO -LYS -THR





- Sampling of the Phase Space
  Most of the cases are high energy

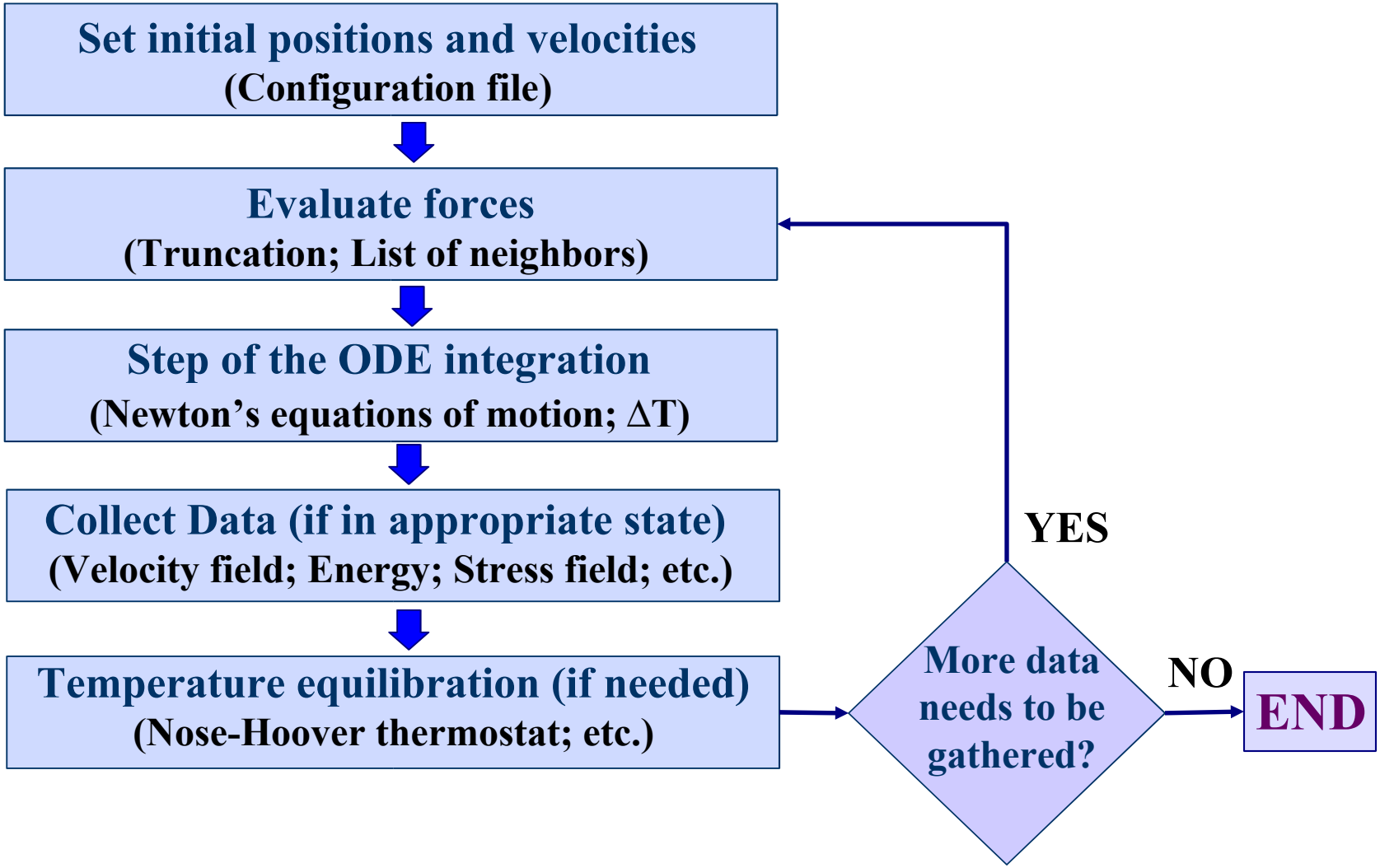
- "Smart" Trajectory in Phase Space
  Importance Sampling

- Complex Energy Landscapes
  Energy Minimization Techniques

Molecular Dynamics Simulations

Equilibrium & Non-Equilibrium Dynamics

Molecular Dynamics Code:



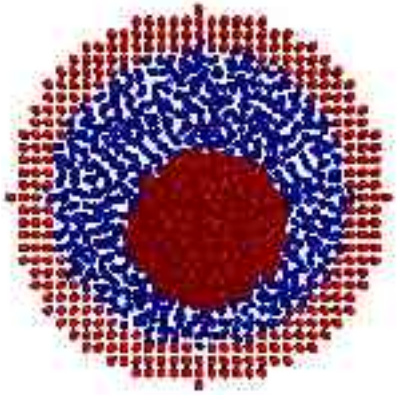
Generalized Lennard-Jones Potential

MD Simulations for Non-Polar Molecules

Tube Wall Molecules

Solid Particle Molecules

Fluid Molecules



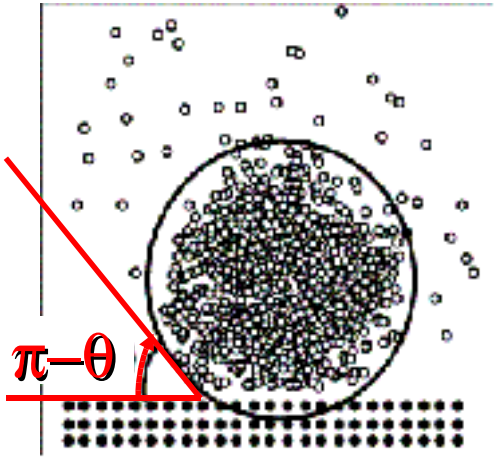
$$V_{LJ}(r)=4\varepsilon\left[\left(\frac{r}{\sigma}\right)^{-12}-\left(\frac{r}{\sigma}\right)^{-6}\right]$$

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

σ ~ Size of a fluid or solid molecule~ 0.3 nm.

ε ~ Attraction Strength ~ 120 K k_B.

$A^{\bullet\bullet}$ = Fluid-Solid attraction



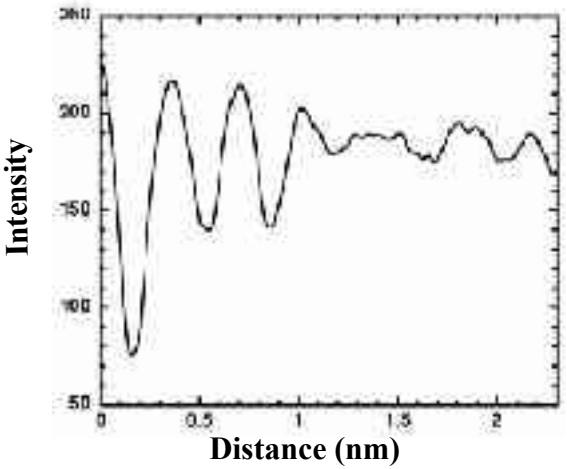
$$\text{Cos}(\theta) \approx -1+2A^{\bullet\bullet}$$

$A^{\bullet\bullet} \to 1$	$A^{\bullet\bullet} \to 0$
$\theta \to 0$	$\theta \to \pi$
Perfect Wetting	**Non-Wetting**

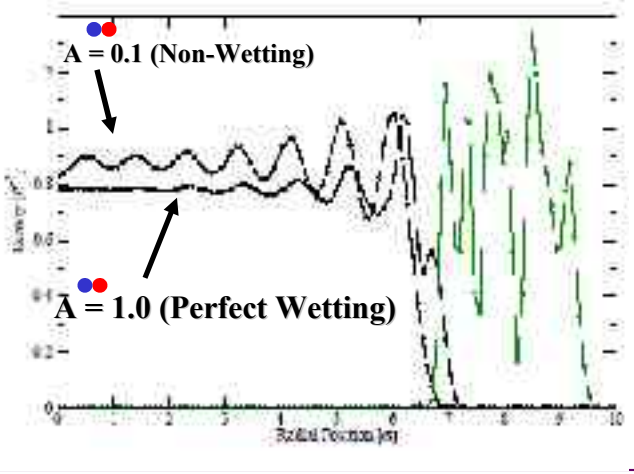
Large Slip Effect at a Nonwetting Fluid-Solid Interface, J.L. Barrat & L. Bocquet, Phys. Rev. Lett. 1999

Behavior at Small Scales

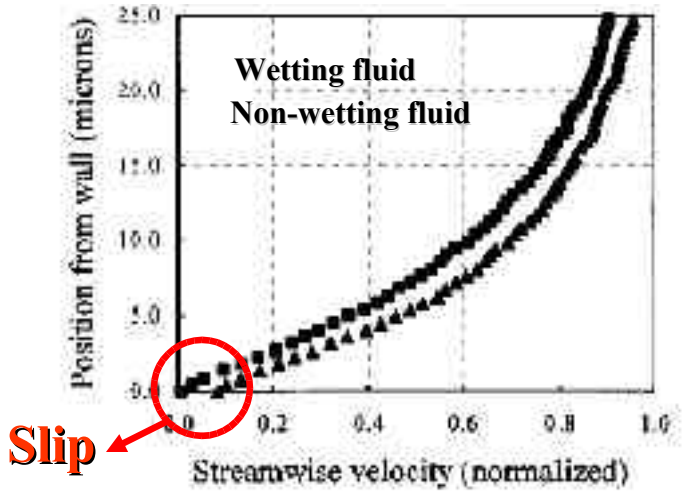
Equilibrium Simulations
Molecular Layering



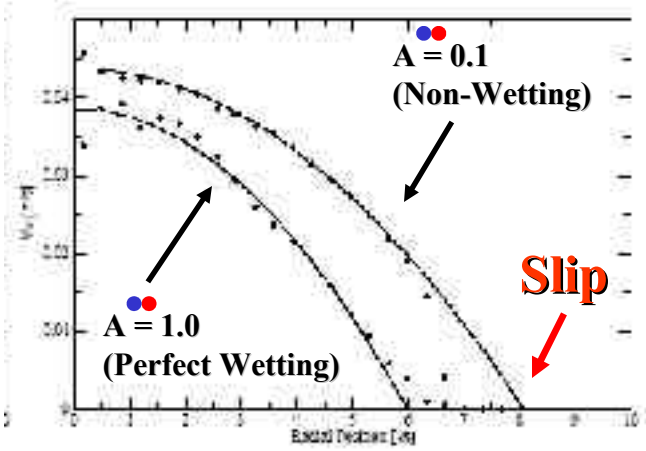
Ordering in a Fluid Inert Gas Confined by Flat Surfaces, Stephen E. Donnelly, Robert C. Birtcher, Charles W. Allen, Ian Morrison, Kazuo Furuya, Minghui Song, Kazutaka Mitsuishi, Ulrich Dahmen, Science, Vol 296, 507 (2002)



Non-Equilibrium Simulations
No-Slip Boundary Conditions

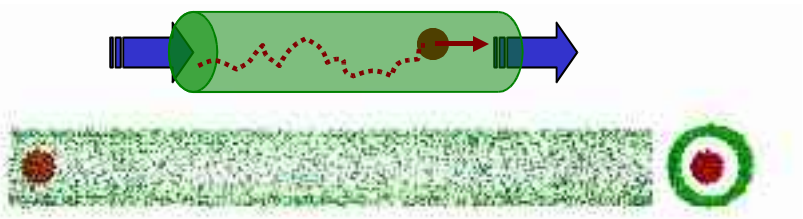


Apparent fluid slip at hydrophobic microchannel walls Derek C. Tretheway and Carl D. Meinhart, Phys. Fluids, Vol. 14, L9 (2002)



Motion of a Nanometer Particle at Short Times

Dependence on the Relative Size

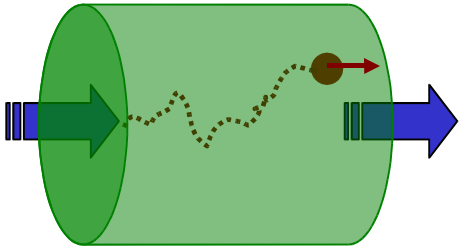


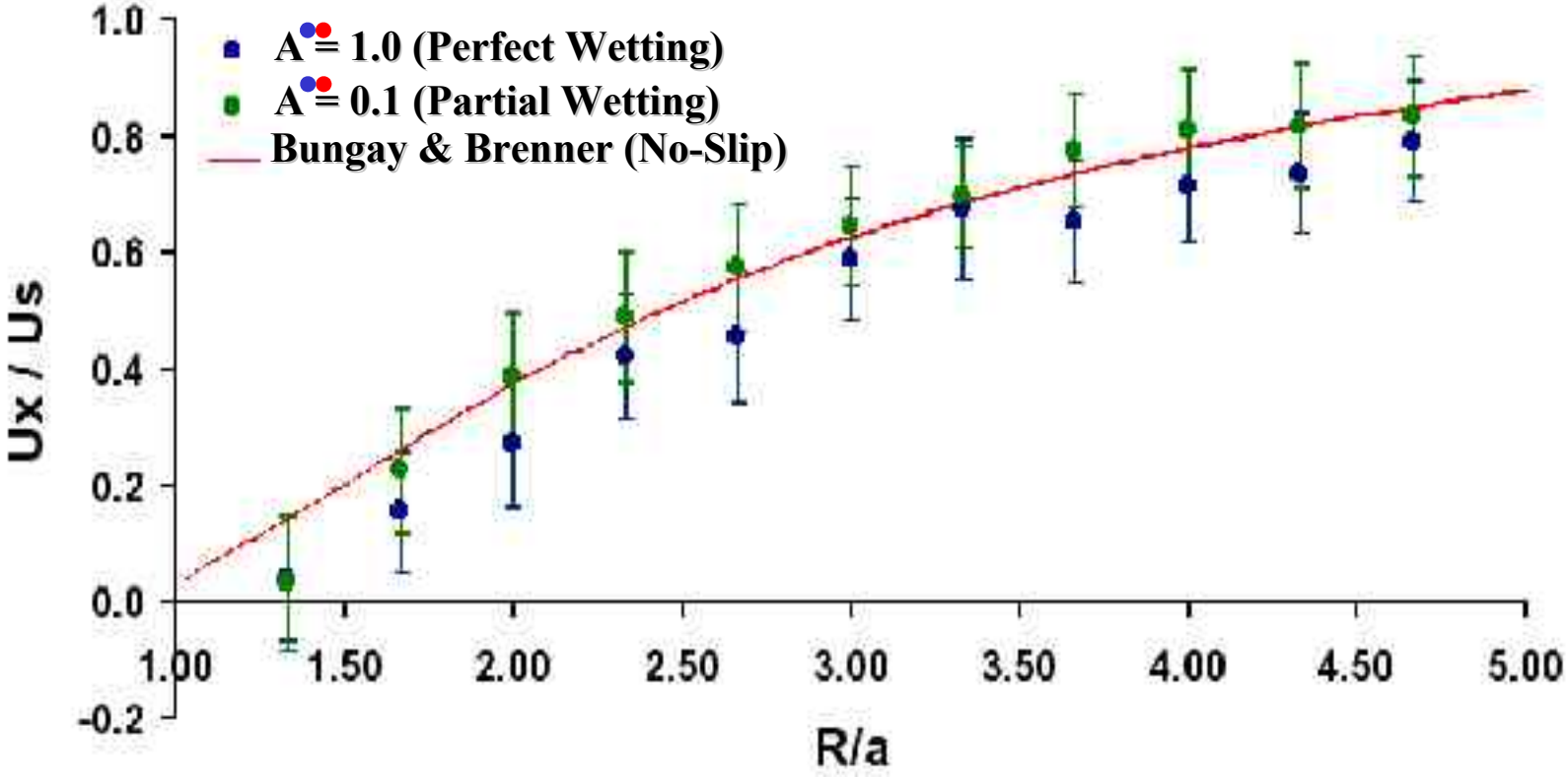
$1 < (R/a) < 5$

$R \sim 7\sigma\text{-}24\sigma \sim 2 - 8$ nm

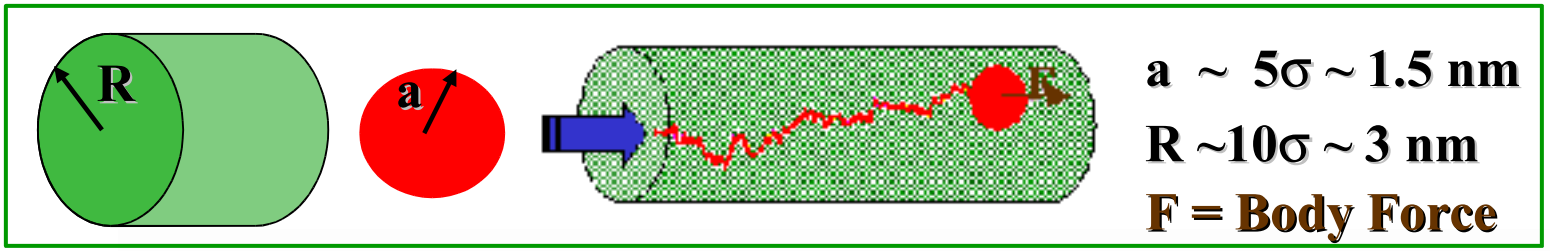
$a \sim 5\sigma \sim 1.5$ nm

F = Body Force





Motion of a Nanometer Particle at Long Times



$A_{\bullet\bullet} = 1.0$
Complete Wetting

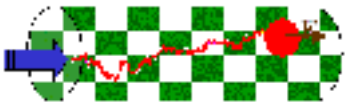
$A_{\bullet\bullet} = 0.3$
Partial Wetting

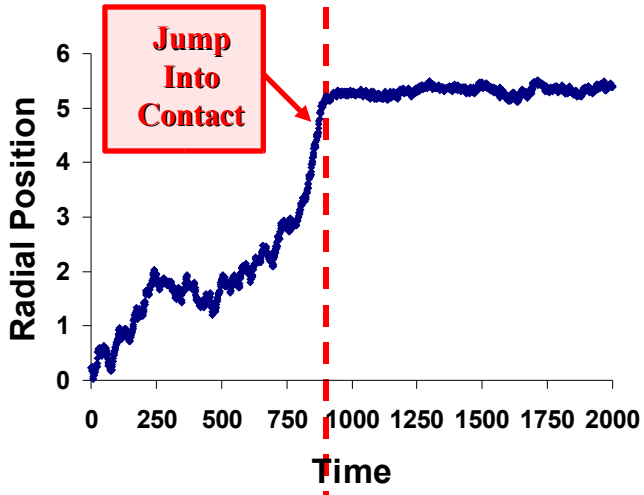
Motion before/after Adsorption

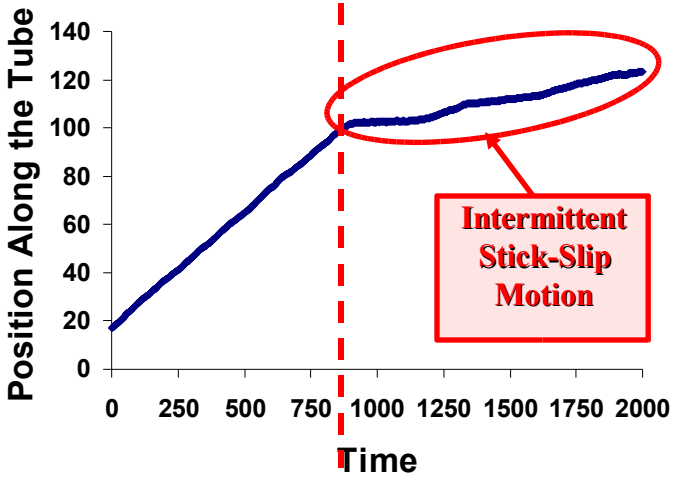
a ~ 5σ ~1.5 nm

R ~10σ ~3 nm

$A^{\bullet\bullet}$ = 0.3



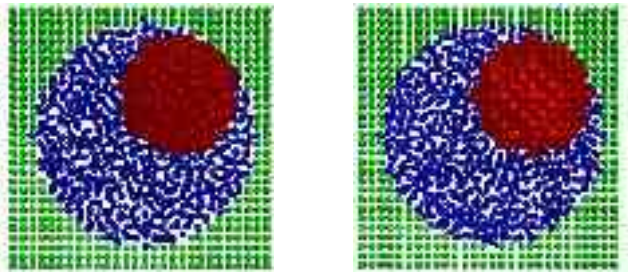




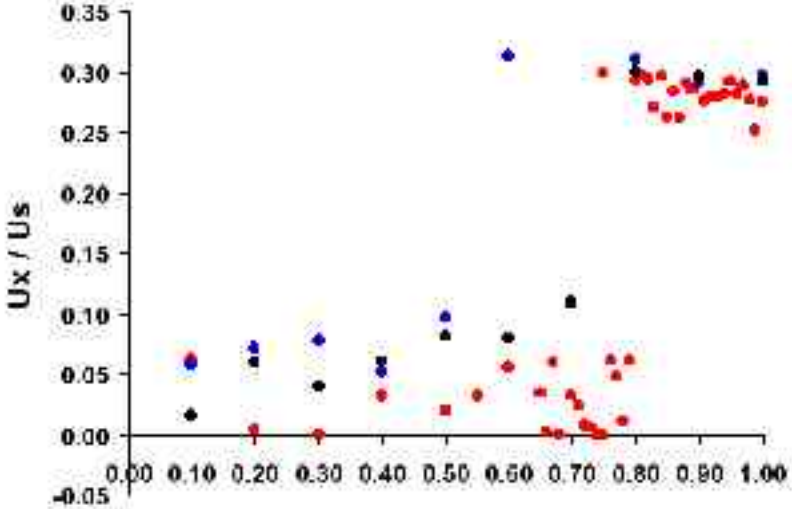
The Colloidal Particle displaces all fluid molecules!!

Slip

Stick



Wetting-Controlled Separation of Nanoparticles



Adsorption phenomena:

Adsorption ← $A^{\bullet\bullet}$ ~ 0.75 → No-Adsorption

Is this Transition Real !?

Some Limitations in Molecular Dynamics Simulations

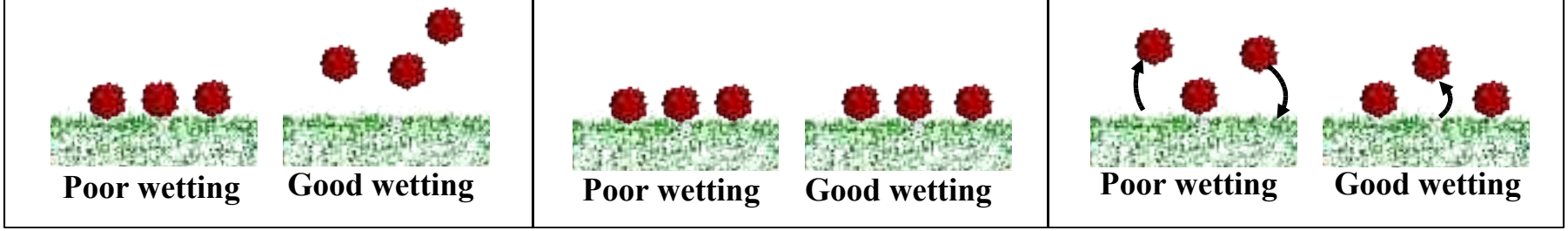
Times Scales are small

$\Delta t \approx 1$ fs $\rightarrow 10^8$ iterations = 0.1 μs!!

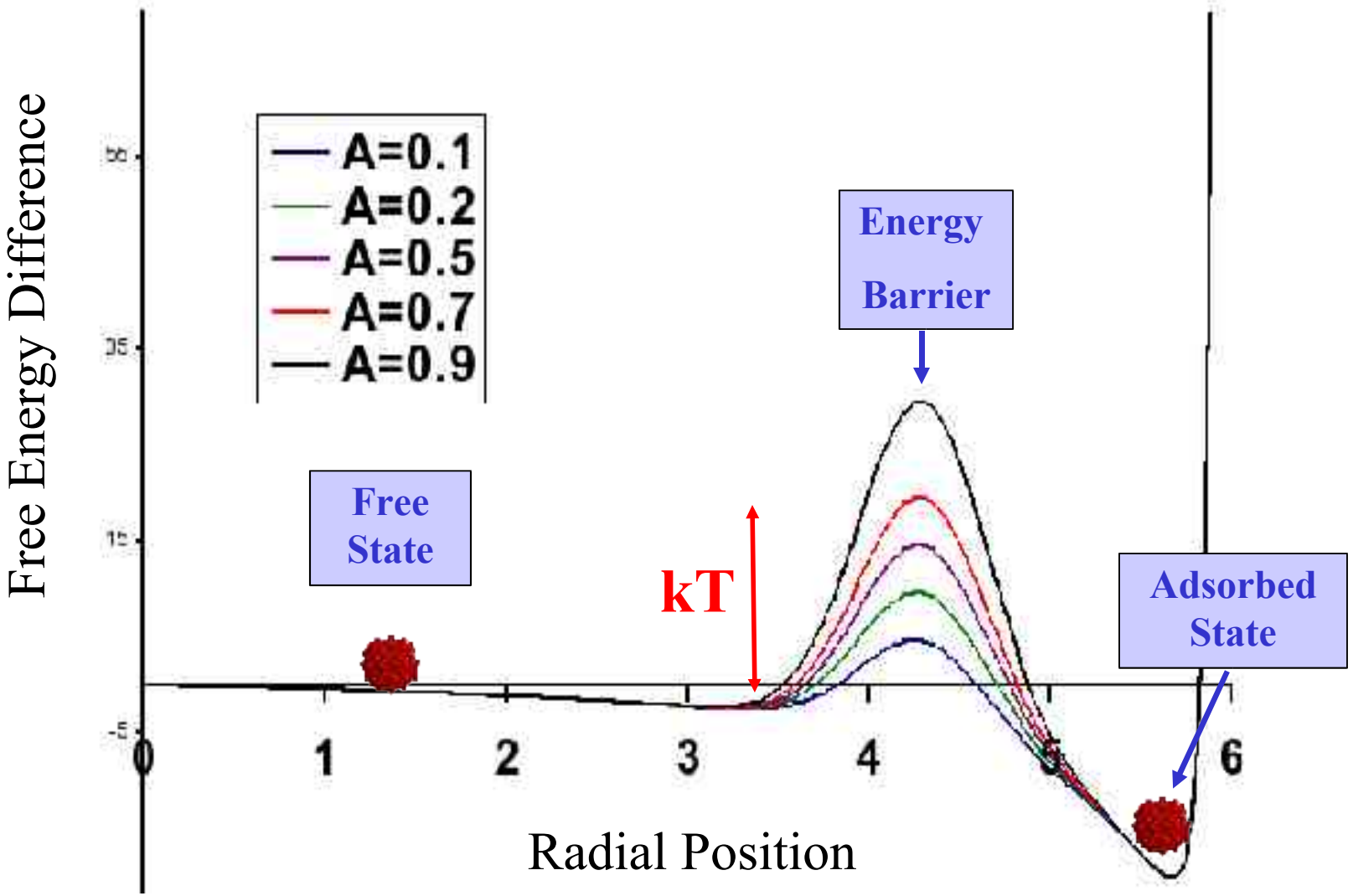
What happens at longer times? (1ms ~ 10⁶ longer)

Multi-scale approach!

What happens at time scales of milliseconds?



Free Energy Differences Landscape

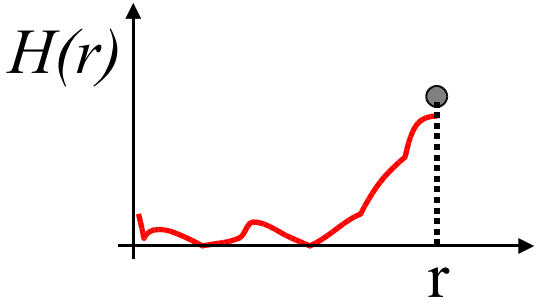


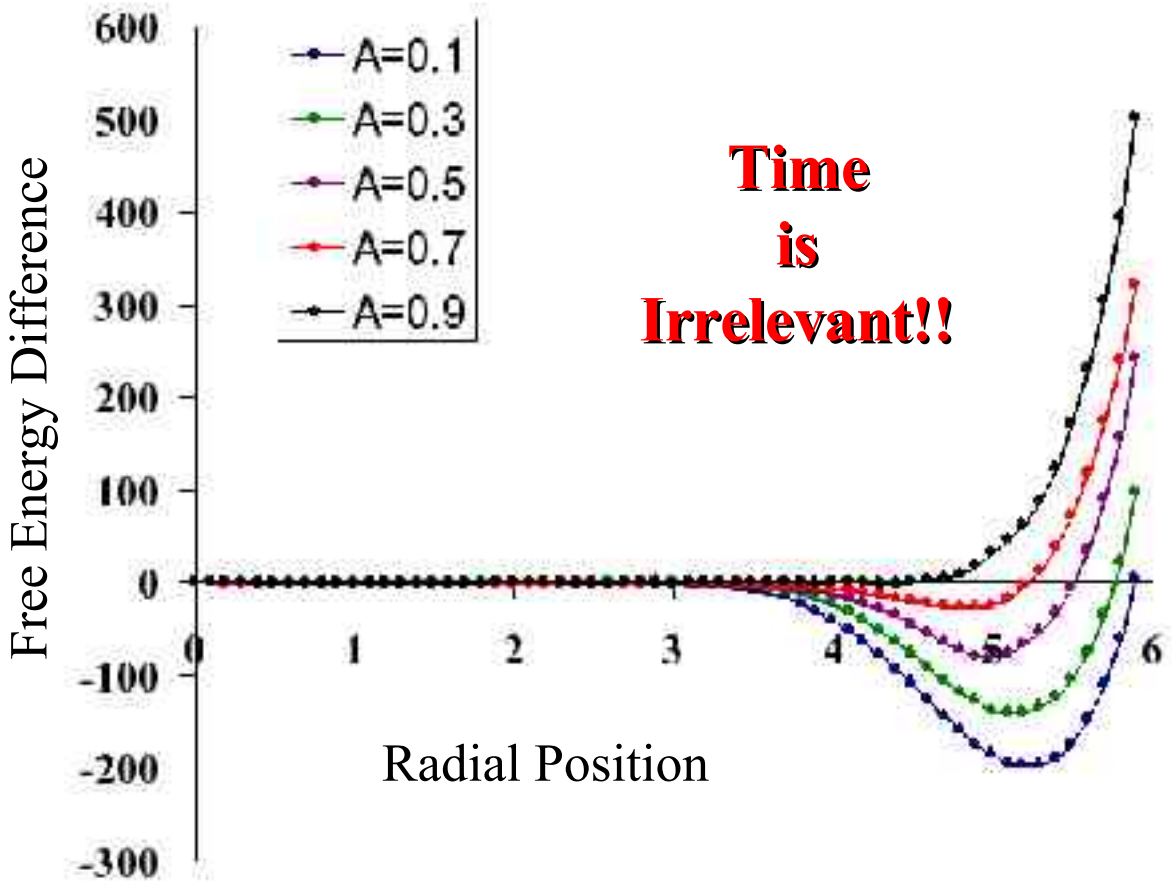
Free Energy Differences Landscape

Atomic Force Apparatus

$$\Delta H = W$$

$$H(r) = \int_{r}^{\infty} dH = \int_{r}^{\infty} \vec{F}\, dr$$





Multi-Scale Approach

Molecular Dynamics Simulations

Newton Equation

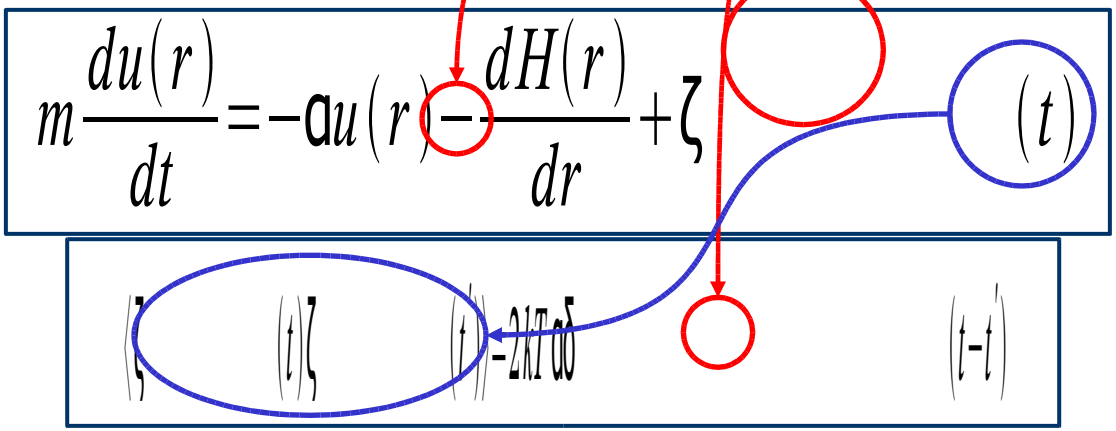
Drag Force ③ $F_D = \alpha U$

Diffusion Coefficient ⑧ D_m

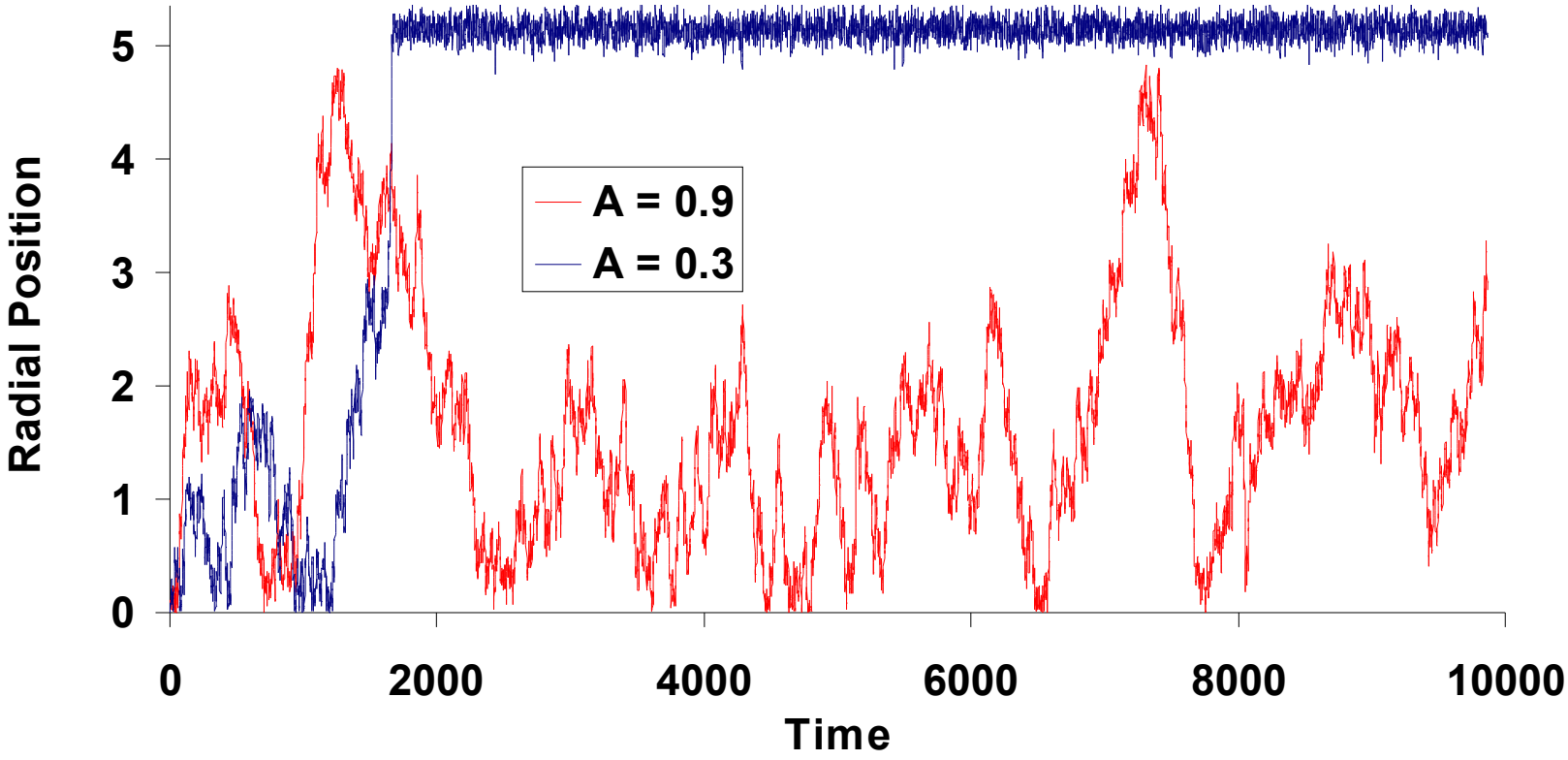
Free Energy Differences ③ H(r)

Brownian Dynamics Simulations

Langevin Equation



Brownian Dynamics Simulations



Time Step $\Delta t \sim 1$ ps
Computationally $T_{BD} \sim T_{MD} / 10^4$
Milliseconds!

Molecular Simulations

Computer Power + Theoretical Developments

Improve Sampling Methods

Improve Interaction Potentials

Develop novel Multi-Scale methods

Help Design Materials from MS

J.J. de Pablo, On the Structure of Molecular Modeling, Challenges for the Chemical Sciences in the 21st Century, National Research Council, www.nap.org