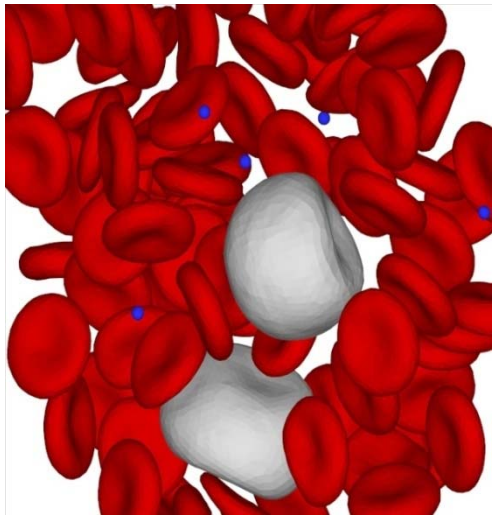
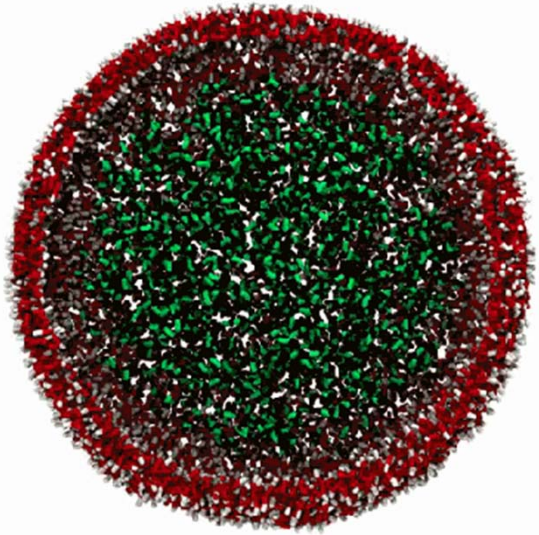
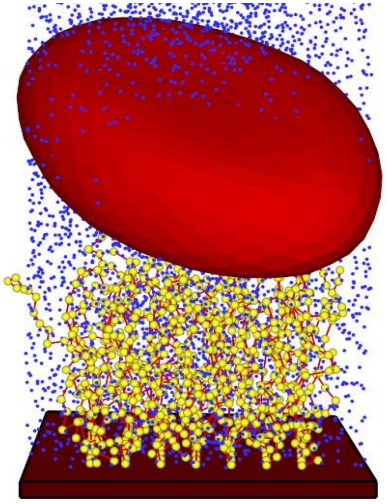
Dissipative Particle Dynamics: Foundation, Evolution and Applications

Lecture 1: Dissipative Particle Dynamics – An Overview

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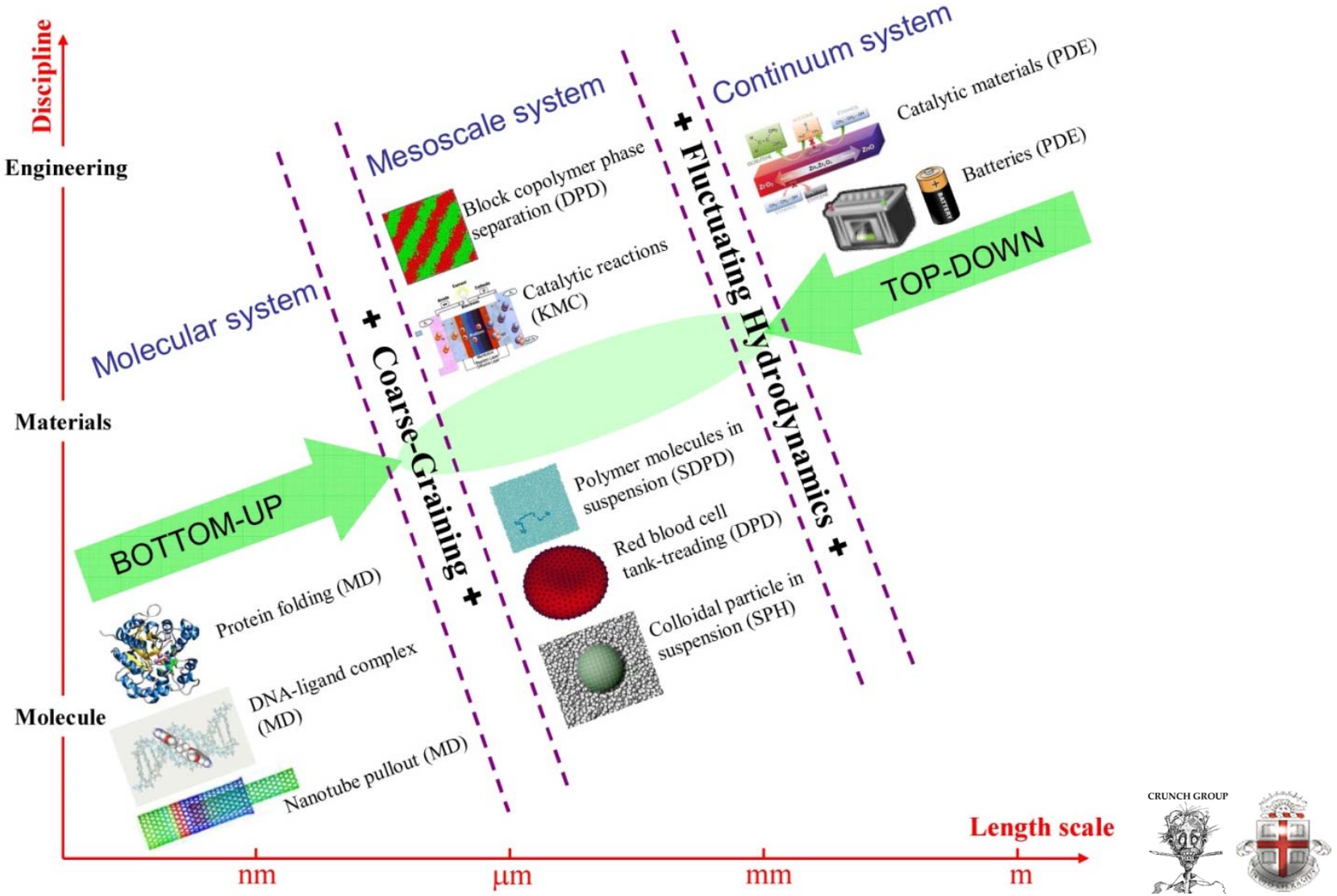
The CRUNCH group: www.cfm.brown.edu/crunch

Outline

- Numerical Modeling Methods
- DPD Framework
- DPD Applications
- DPD Software / Packages
- Open Issues

Mesoscale Phenomena and Models

Due to wide range of characteristic lengths - times, several simulation methods that describe length and time scales have been developed:



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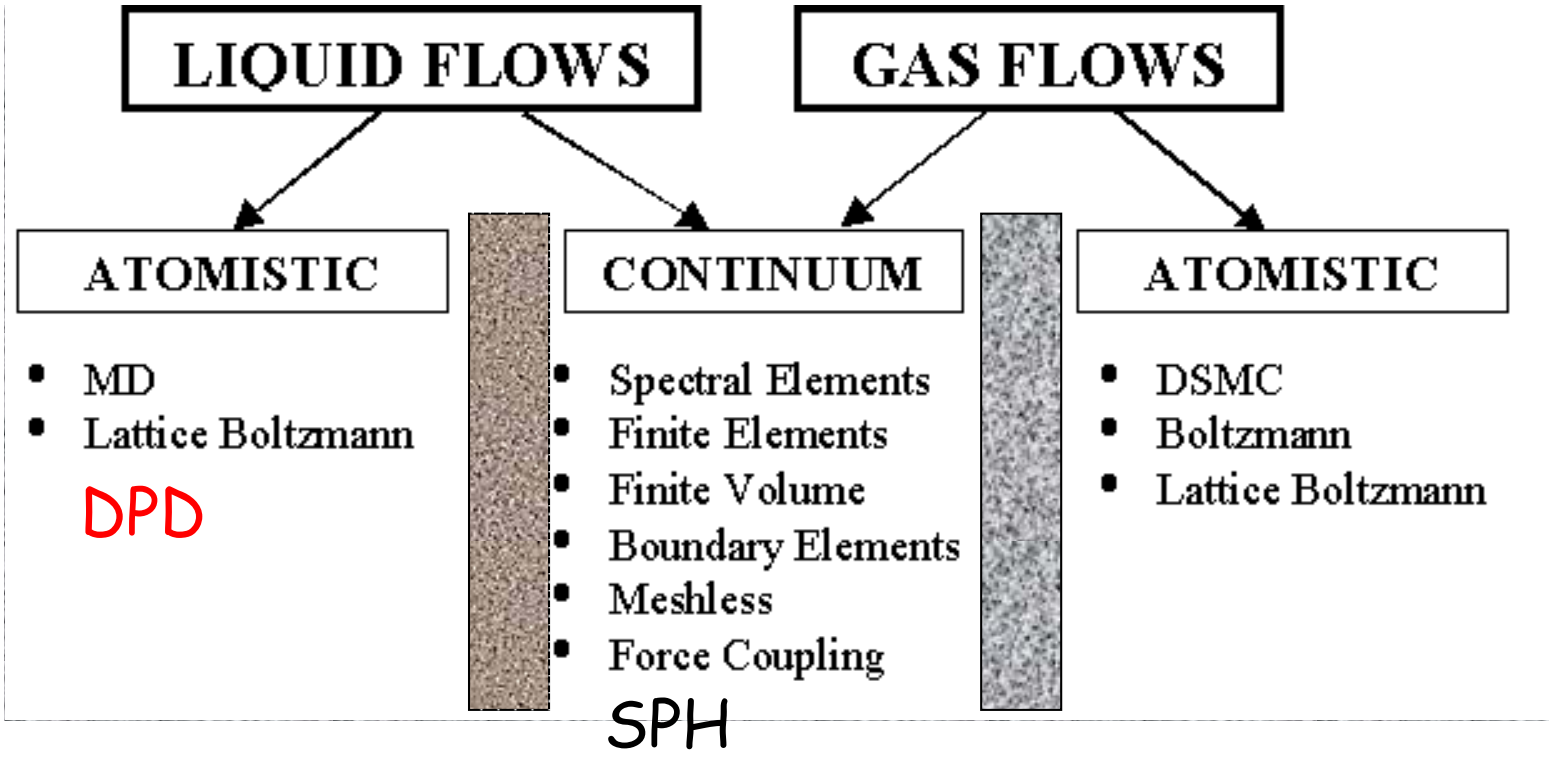
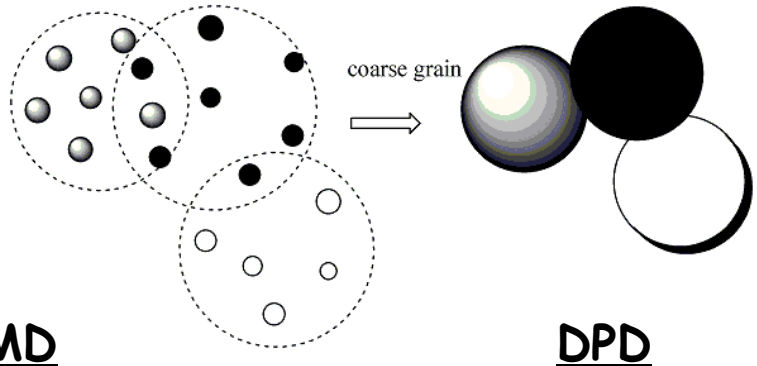
Numerical Modeling Methods



Dissipative Particle Dynamics (DPD)



MD

- MICROscopic level approach
- atomistic approach is often problematic because larger time/length scales are involved

DPD

- set of point particles that move off-lattice through prescribed forces
- each particle is a collection of molecules
- MESOscopic scales
- momentum-conserving Brownian dynamics

Navier-Stokes

- continuum fluid mechanics
- MACROscopic modeling

Ref on Theory: Lei, Caswell & Karniadakis, Phys. Rev. E, 2010

Dissipative Particle Dynamics: History

Babyhood (1992-1995)

- Original formulation (Hoogerbrugge & Koelman, 1992)

  New scheme for mesoscopic simulations of complex fluids

Youth (1995-2003)

- Correction of fluctuation-dissipation relation (Español & Warren, 1995)
- Important contributions to the DPD methodology
  - Polymer (Groot & Warren, 1997)
  - Charged system (Groot, 2003)
  - Others

Golden Era (2003-now)

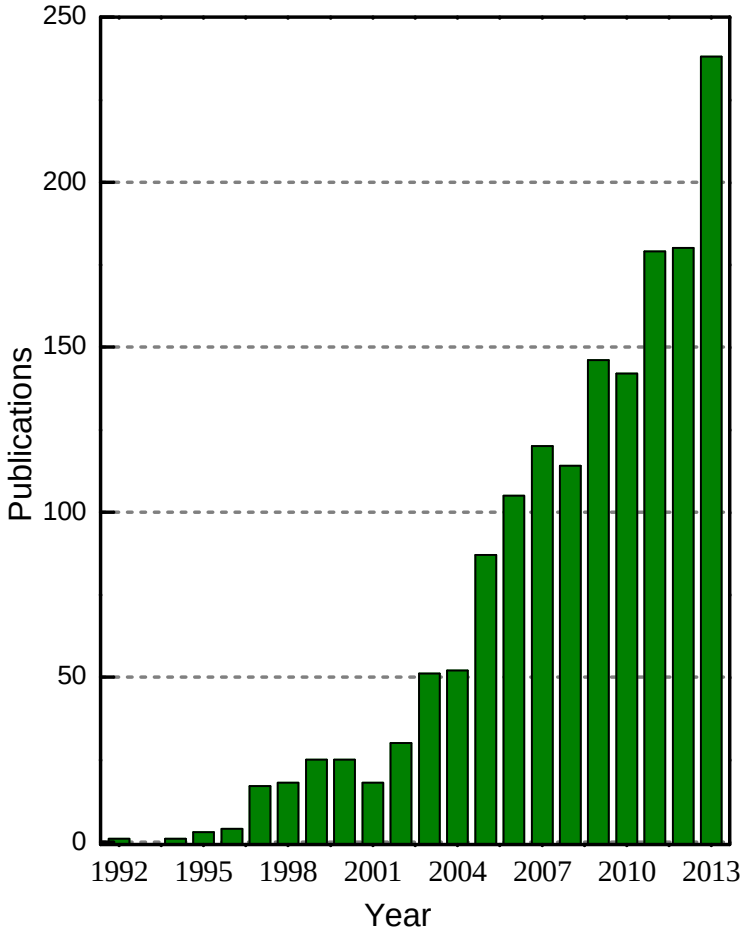
- Often used for amphiphilic systems, polymers, colloids, lipid bilayer membranes, fluids.
- What remains: Coarse-graining limits; handshaking, etc.

Dissipative Particle Dynamics: History

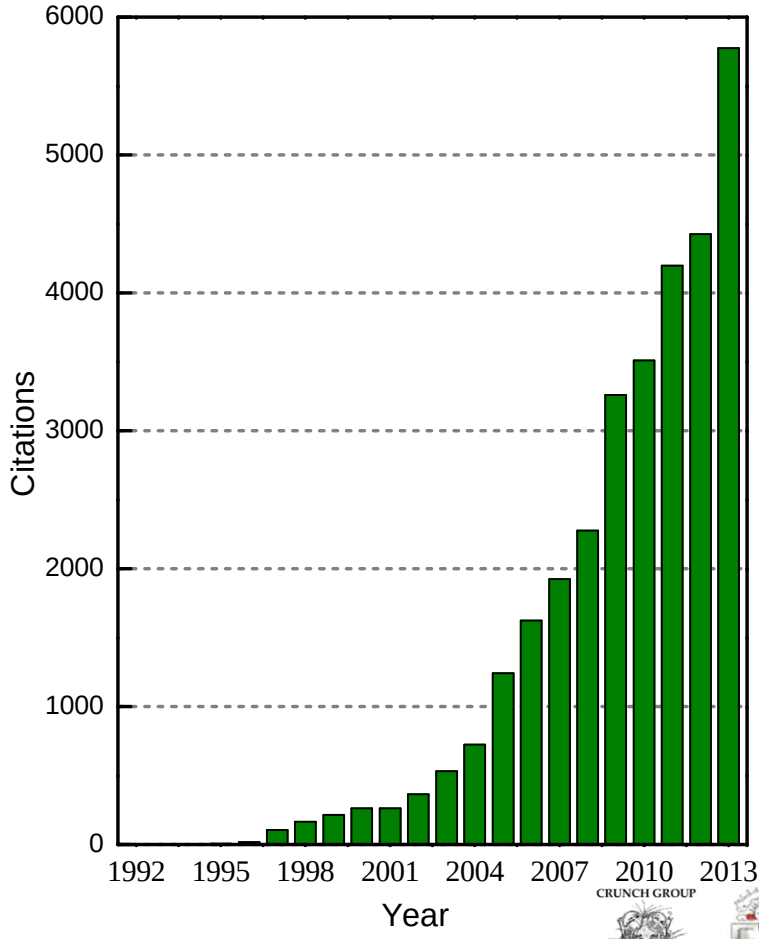
Searched for topic: ("Dissipative Particle Dynamics")

(from Web of Science Core Collection)

Published items in each year



Citations in each year



Dissipative Particle Dynamics (DPD)

- Particles in DPD represent clusters of molecules and interact through simple pair-wise forces

$$\vec{F}_{\mathrm{i}} = \sum_{j \neq i} \left(\vec{F}_{\mathrm{ij}}^{\,\mathrm{C}} + \vec{F}_{\mathrm{ij}}^{\,\mathrm{D}} + \vec{F}_{\mathrm{ij}}^{\,\mathrm{R}} \Big/ \sqrt{\mathrm{dt}} \right)$$

- DPD system is thermally equilibrated through a thermostat defined by forces $\vec{F}^{\,D}, \vec{F}^{\,R}$
- The time evolution equations are given by:

$$d\vec{r}_i = \vec{v}_i dt \qquad d\vec{v}_i = \vec{F}_i dt$$

Hoogerbrugge & Koelman, Europhys. Lett., 1992

Pairwise Interactions

Forces exerted by particle J on particle I:

$$\vec{F}_{ij}^{C} = F_{ij}^{(c)}(r_{ij})\vec{e}_{ij}$$

$$\vec{F}_{ij}^{D} = -\gamma\omega^{D}(r_{ij})(\vec{v}_{ij}\cdot\vec{e}_{ij})\vec{e}_{ij}$$

$$\vec{F}_{ij}^{R} = \sigma\omega^{R}(r_{ij})\xi_{ij}\vec{e}_{ij}$$

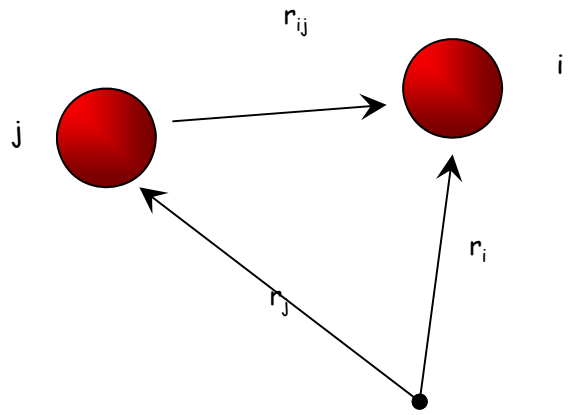
Fluctuation-dissipation relation:

$\sigma^2 = 2\gamma k_B T$ $\omega^D = [\omega^R]^2$

Conservative
fluid / system dependent

Dissipative
frictional force, represents viscous resistance within the fluid – accounts for energy loss

Random
stochastic part, makes up for lost degrees of freedom eliminated after the coarse-graining



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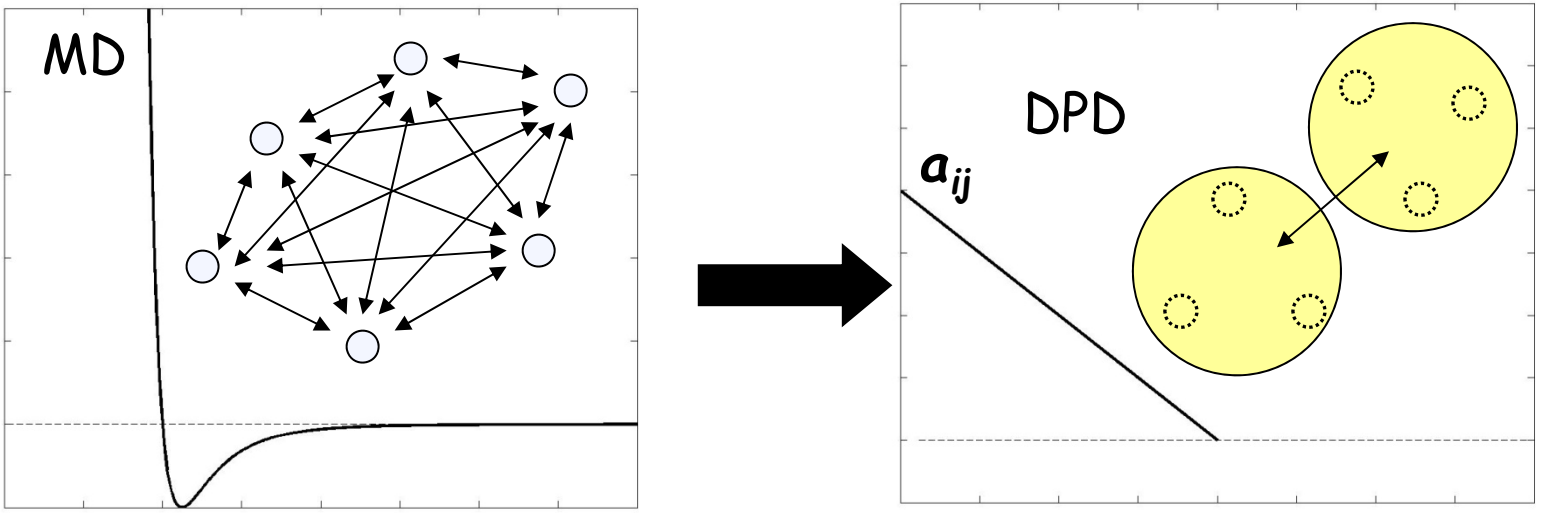
Conservative Force



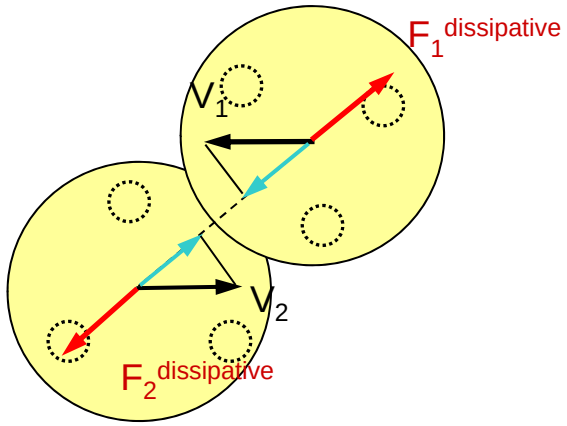
Soft repulsive force

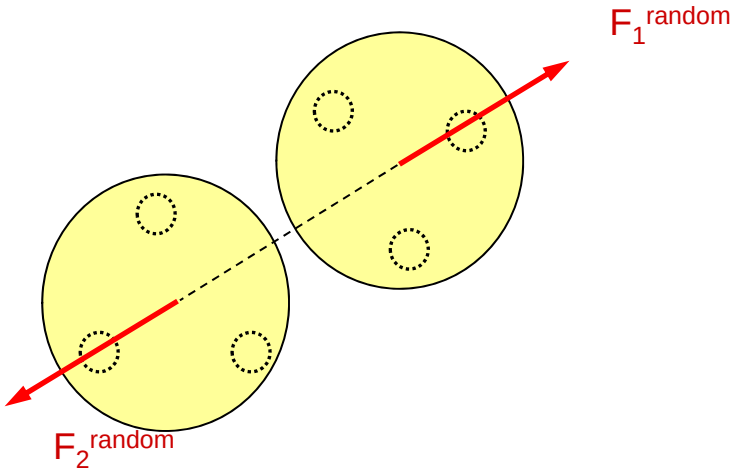
$$\vec{F}_{ij}^{\,C}\left(r_{ij}\right)=\begin{cases} a_{ij}\left(1-\dfrac{r_{ij}}{r_c}\right)\vec{e}_{ij} & r_{ij}<r_c \\ 0 & r_{ij}\geq r_c \end{cases}$$

determines strength of soft repulsion

- Soft potentials were obtained by averaging the molecular field over the rapidly fluctuating motions of atoms during short time intervals.
- This approach leads to an effective potential similar to one, used in DPD.

Dissipative and Random Forces





- Dissipative (friction) forces reduce the relative velocity of the pair of particles
- Random forces compensate for eliminated degrees of freedom
- **Dissipative and random forces form DPD thermostat**
- The magnitude of dissipative and random forces are defined by fluctuation-dissipation theorem.

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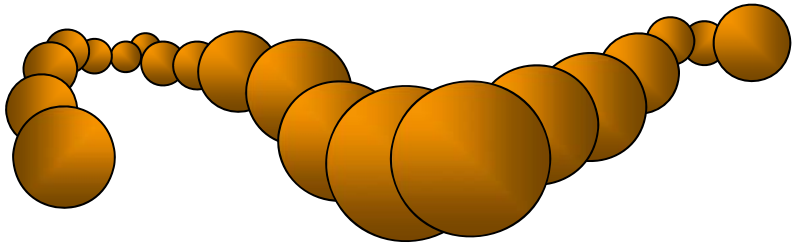
DPD intramolecular terms

- Lennard-Jones Repulsion

$$U_{\mathrm{LJ}} = 4\epsilon[(\frac{L}{r_{ij}})^{12} - (\frac{L}{r_{ij}})^{6} + \frac{1}{4}]$$



- Stiff (Fraenkel) / Hookean Spring

$$U_{\mathrm{STIFF}} = \frac{\kappa}{2}(|\vec{r}_i - \vec{r}_{i-1}| - r_{\mathrm{eq}})^2, \qquad \text{where} \quad i = 2, 3, 4, ..., M$$

- Finitely-Extensible Non-linear Elastic (FENE) Spring

$$U_{\mathrm{FENE}} = -\frac{\kappa}{2} r_{\max}^2 log[1 - \frac{|\vec{r}_i - \vec{r}_{i-1}|^2}{r_{\max}^2}], \qquad \text{where} \quad i = 2, 3, 4, ..., M$$

- Marko-Siggia/WormLike Chain (WLC)…

$$F_{\mathrm{WLC}} = \frac{k_{\mathrm{B}}T}{\lambda \mathrm{p}}\left[\frac{1}{4(1-R)^2} - \frac{1}{4} + R\right], \quad R = \frac{|\vec{r}_i - \vec{r}_{i-1}|}{L_{\mathrm{spring}}} = \frac{r}{L_{\mathrm{spring}}}$$

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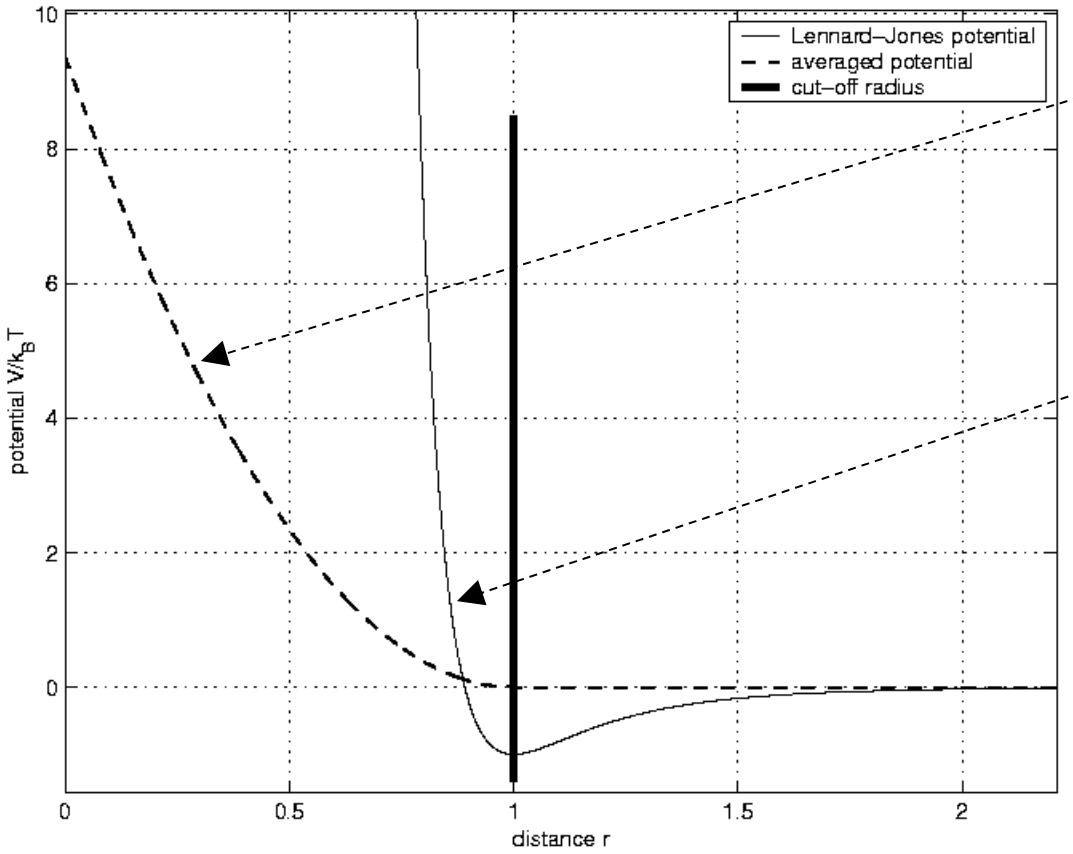
Mixing Soft-Hard Potentials

Motivation for 2 different time-steps (Δt,δt): Subcycling

Symeonidis & Karniadakis, J. Comput. Phys., 2006



Solvent
(soft repulsive)

Polymer
Lennard-Jones
(hard repulsive)

Forrest & Suter, J. Chem. Phys., 1995

idea of pre-averaging - in the spirit of conservative forces in DPD solvent

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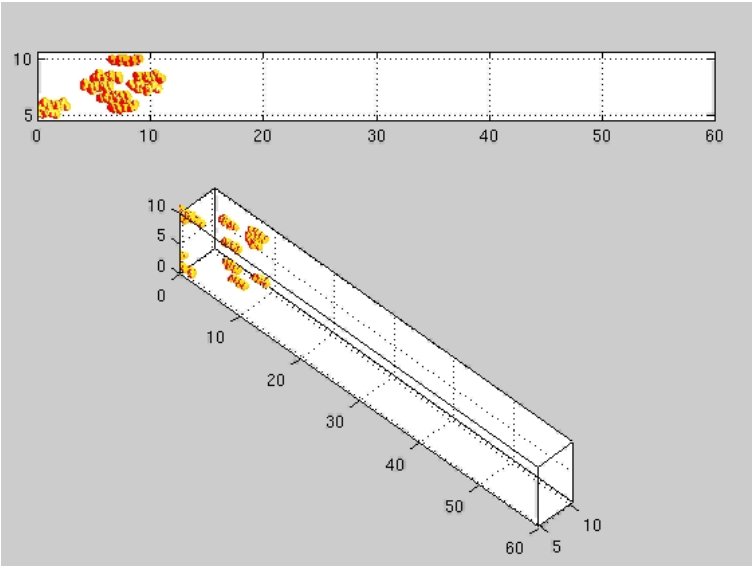
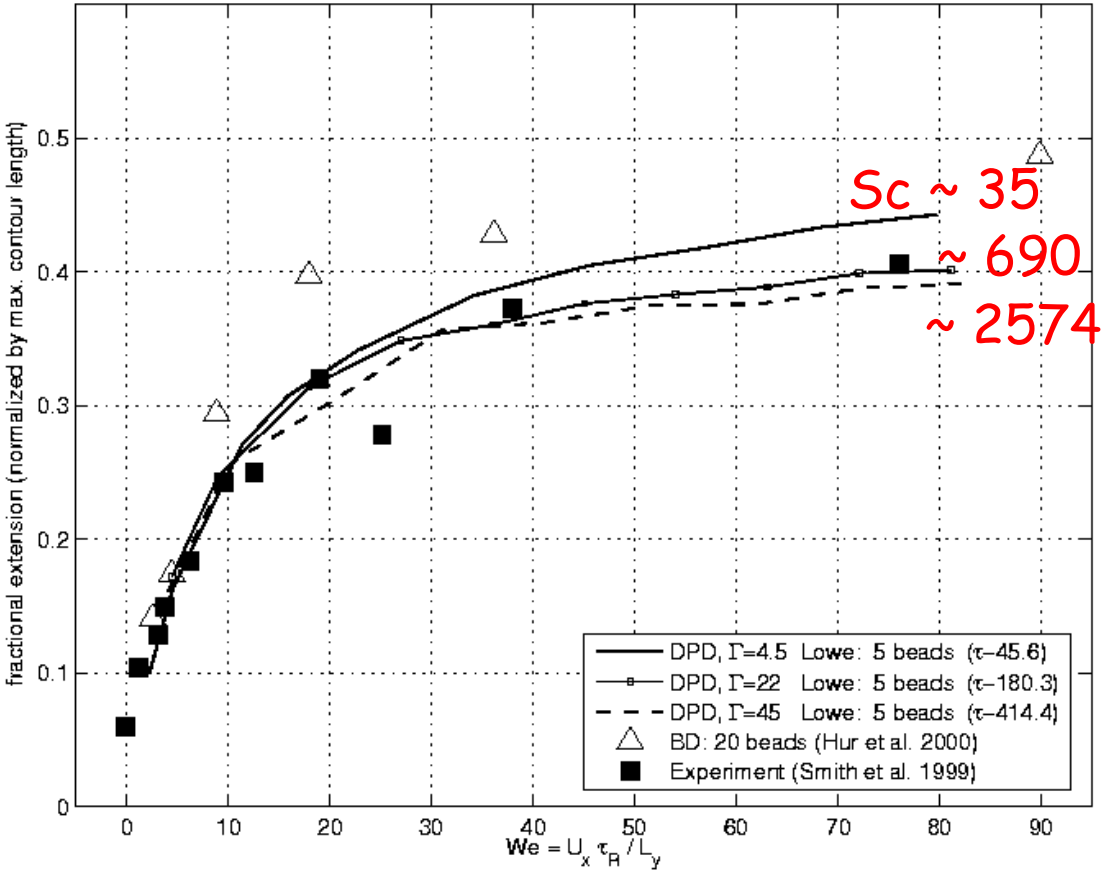
DNA Chains in Pressure-Driven Flow





Symeonidis, Caswell & Karniadakis, PRL, 2005

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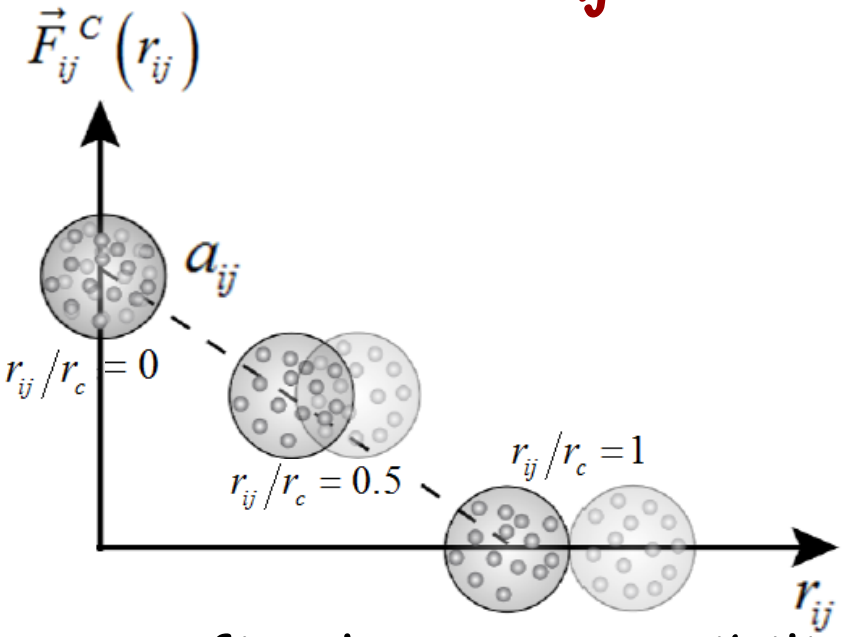
DPD repulsive parameter a_{ij}

$$\vec{F}_{ij}^{\,C}(r_{ij}) = \begin{cases} a_{ij}\left(1-\dfrac{r_{ij}}{r_c}\right)\vec{e}_{ij} & r_{ij} < r_c \\ 0 & r_{ij} \geq r_c \end{cases}$$

repulsive parameter



The repulsive parameter a_{ij} is set to fix the compressibility of the system to the real system

System pressure is calculated from virial theorem

$$P = \rho k_B T + \frac{1}{3V}\left\langle \sum_{j>i} (r_i - r_j)\cdot F_i \right\rangle$$

[Groot & Warren (1997)]

$$= \rho k_B T + \frac{2\pi}{3}\rho^2 \int_0^{r_c} r f^C(r) g(r) r^2 dr$$

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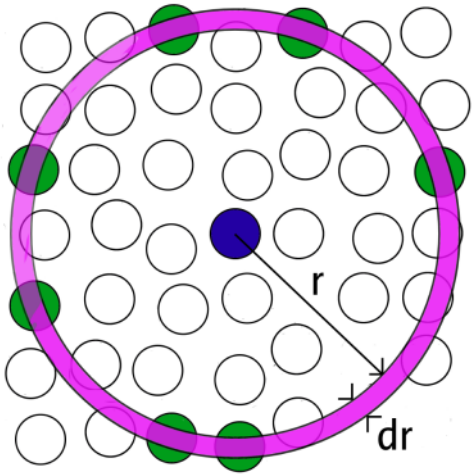
DPD repulsive parameter a_{ij}

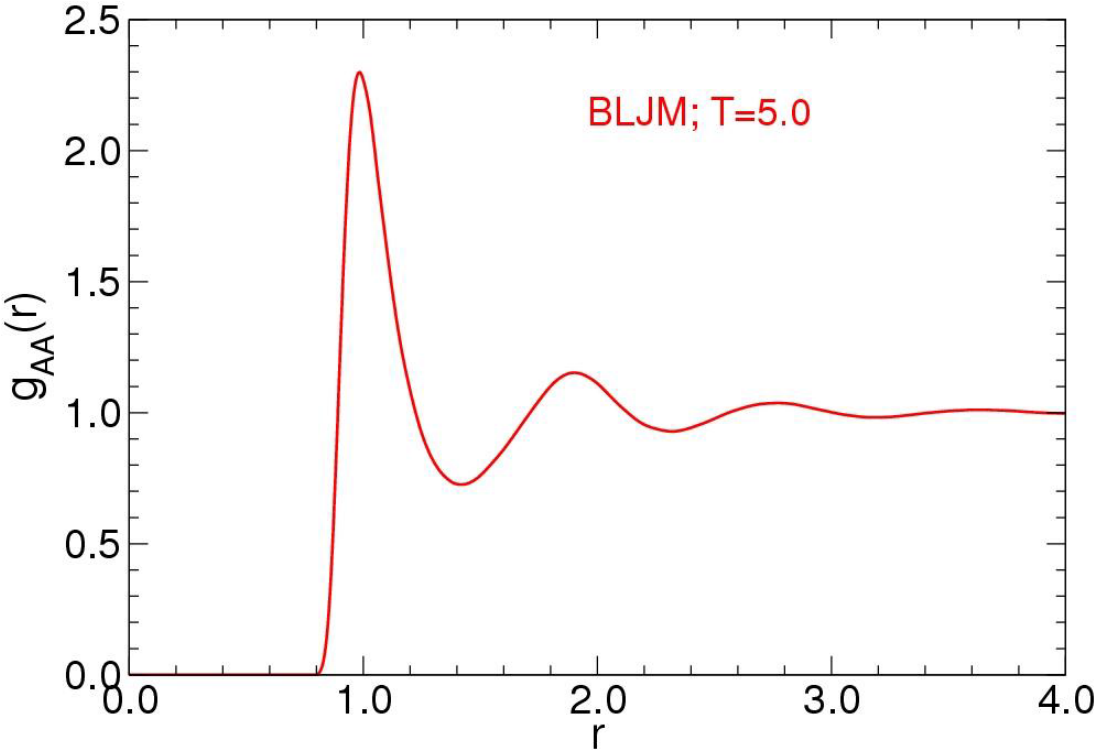
Radial Distribution Function *g*(*r*): describe how density varies as a function of distance from a reference particle.

$$g(r) = 4\pi r^2 \rho dr$$

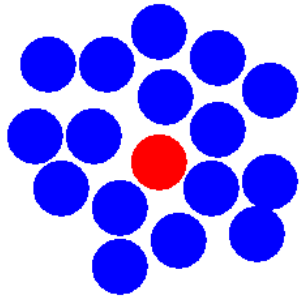
look for neighbors of a reference particle:

$$g(r) = \frac{1}{N^2} \sum_{i,j=1}^{N} \left\langle \delta\left(\left|\mathbf{r}_{ij}\right| - r\right)\right\rangle$$





g(*r*) for a simple liquid
(binary Lennard-Jones mixture)



DPD repulsive parameter a_{ij}

System pressure

$$P = \rho k_B T + \frac{2\pi}{3}\rho^2 \int_0^{r_c} r f^C(r) g(r) r^2 dr$$

For a soft potential with range r_c at high density

$$\frac{P}{\rho k_B T} = 1 + \frac{2\pi}{3k_B T}\rho \int_0^{r_c} r f^C(r) r^2 dr = 1 + \frac{\alpha}{k_B T}\rho$$

$$P = \rho k_B T + \alpha \rho^2$$

The standard soft potential gives by matching with atomistic or experimental results

$$\alpha \sim 0.1 a_{ij} r_c^4$$

Note: If ρ is too high or $k_B T$ too low the DPD fluid will freeze making the method useless.

DPD repulsive parameter a_{ij}

The dimensionless compressibility is

$$\kappa^{-1} = \frac{1}{k_B T}\frac{\partial p}{\partial \rho} = \frac{1}{k_B T}\frac{\partial p}{\partial n}\frac{\partial n}{\partial \rho}$$

For a (high density) DPD fluid from the equation of state

$$\kappa^{-1} = 1 + 0.2\frac{a_{ij}\rho}{k_B T}$$

For water $\kappa^{-1} \sim 16$, so in DPD

$$a_{ij} = 75\frac{k_B T}{\rho r_c^{\,4}}$$

[Groot & Warren (1997)]

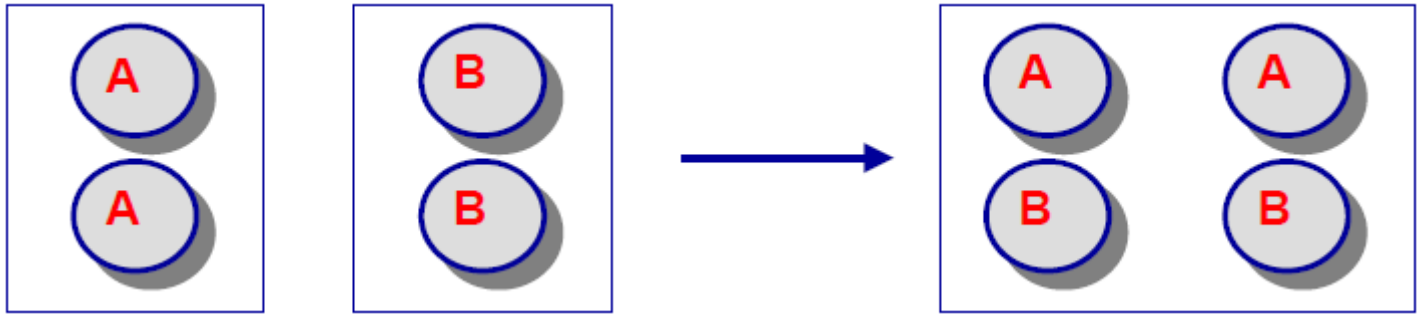
Due to the purely repulsive force: no liquid-vapor coexistence.

DPD repulsive parameter a_{ij}

DPD can be used to simulate liquid-liquid and liquid-solid interfaces.

It is similar to Flory-Huggins theory of polymers.

Free energy of mixing Flory-Huggins theory



$$\frac{F}{k_B T} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi \phi_A \phi_B$$

entropic term

enthalpic term

Flory, J. Chem. Phys., 1942

Huggins, J. Chem. Phys., 1941

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DPD repulsive parameter a_{ij}

Free energy density of a sing component in DPD:

$$\frac{f_V}{k_B T} = \rho \ln \rho - \rho + \frac{\alpha a \rho^2}{k_B T}$$

For a two component system of chains one expect

$$\frac{f_V}{k_B T} = \frac{\rho_A}{N_A} \ln \rho_A + \frac{\rho_B}{N_B} \ln \rho_B - \frac{\rho_A}{N_A} - \frac{\rho_B}{N_B} + \frac{\alpha(a_{AA}\rho_A^2 + 2a_{AB}\rho_A\rho_B + a_{BB}\rho_B^2)}{k_B T}$$

Choose $a_{AA} = a_{BB}$ and assume that $\rho_A + \rho_B$ is constant

$$\frac{f_V}{(\rho_A + \rho_B) k_B T} \approx \frac{x}{N_A} \ln x + \frac{(1-x)}{N_B} \ln(1-x) + \chi x(1-x)$$

Flory-Huggins parameter

$$\chi = \frac{2\alpha(a_{AB} - a_{AA})(\rho_A + \rho_B)}{k_B T}$$

DPD repulsive parameter

Groot & Warren, J. Chem. Phys., 1997

Integration algorithms for DPD

Idea: integrate the equations of motion step by step

$r(t)$, $v(t) \rightarrow r(t + \delta t)$, $v(t + \delta t) \rightarrow r(t + 2\delta t)$, $v(t + 2\delta t) \rightarrow$

At each step, we need to:

- compute forces acting on particles
- update the particles' positions and velocities

All the integration algorithms assume the positions, velocities and accelerations can be approximated by Taylor expansion:

$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{a(t)}{2}\delta t^2 + \cdots$$

$$v(t+\delta t) = v(t) + a(t)\delta t + \frac{b(t)}{2}\delta t^2 + \cdots$$

$$a(t+\delta t) = a(t) + b(t)\delta t + \cdots$$

Verlet Algorithm

To derive the Verlet algorithm one can write

$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{a(t)}{2}\delta t^2 + \cdots$$

$$r(t-\delta t) = r(t) - v(t)\delta t + \frac{a(t)}{2}\delta t^2 + \cdots$$

Summing these two equations, one obtains

$$\boxed{r(t+\delta t) = 2r(t) - r(t-\delta t) + a(t)\delta t^2}$$

It uses positions and accelerations at time t and positions from time $t-\delta t$ to calculate new positions at time $t+\delta t$.

The velocities are computed from the positions by using

$$\boxed{v(t) = \frac{r(t+\delta t) - r(t-\delta t)}{2\delta t}}$$

Verlet Algorithm

Algorithm

$$r(t+\delta t) = 2r(t) - r(t-\delta t) + a(t)\delta t^2$$

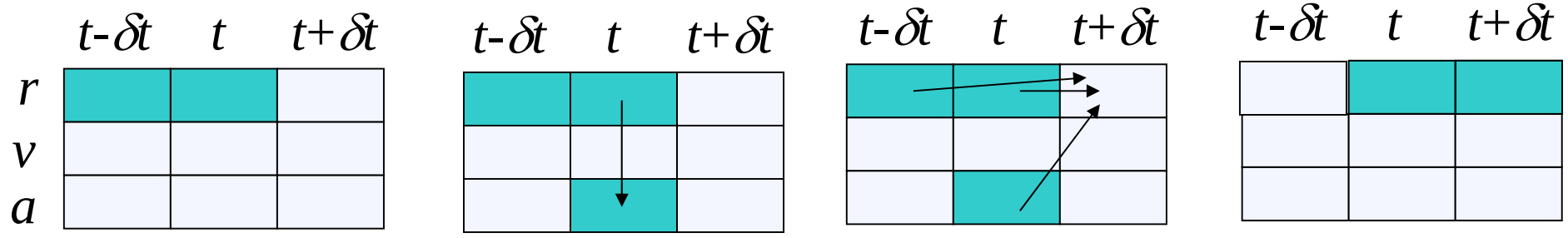
$$v(t) = \frac{r(t+\delta t) - r(t-\delta t)}{2\delta t}$$

Basic Verlet: velocity is not directly generated

Numerically inaccurate

Implemented in stages

- given current position and position at end of previous time step
- compute force at the current position
- compute new position from present and previous positions and present force
- advance to next time step, repeat



Velocity Verlet Algorithm

Algorithm

$$r(t+\delta t) = r(t) + v(t)\delta t + \frac{a(t)}{2}\delta t^2$$

$$v(t+\delta t) = v(t) + \frac{a(t)+a(t+\delta t)}{2}\delta t$$

$$v(t+\frac{\delta t}{2}) = v(t+\frac{\delta t}{2}) + \frac{a(t+\delta t)}{2}\delta t$$

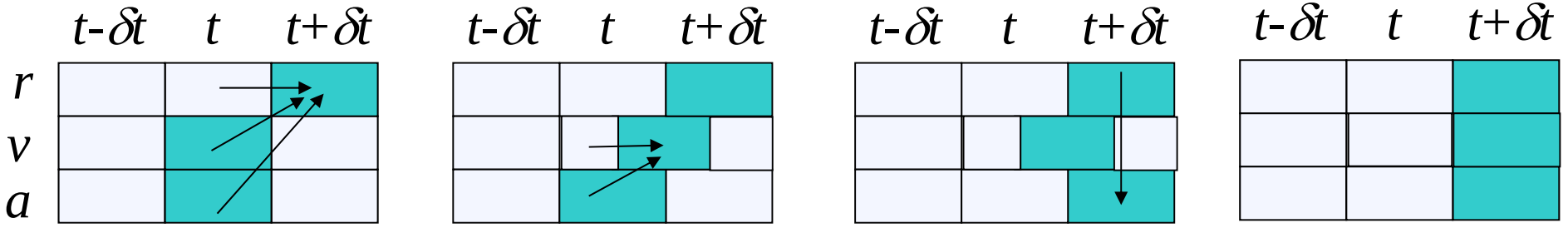
$$v(t+\frac{\delta t}{2}) = v(t) + \frac{a(t)}{2}\delta t$$

Implemented in stages

- compute position at new time
- compute velocity at half step
- compute new force at new position
- compute velocity at full step

Positions, velocities and accelerations at time $t+\delta t$ are obtained from the same quantities at time t.

Numerically accurate



Modified Velocity Verlet Algorithm for DPD

DPD force depend on velocity

$$\mathbf{r}_i(t+\Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \tfrac{1}{2}(\Delta t)^2 \mathbf{f}_i(t)$$

$$\tilde{\mathbf{v}}_i(t+\Delta t) = \mathbf{v}_i(t) + \lambda \Delta t \mathbf{f}_i(t)$$

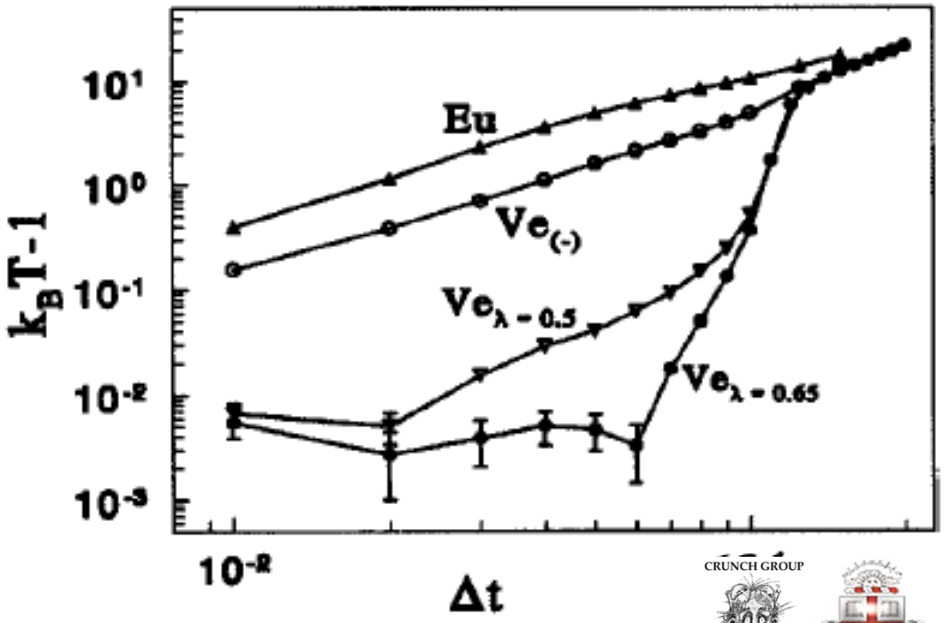
$$\mathbf{f}_i(t+\Delta t) = \mathbf{f}_i(\mathbf{r}(t+\Delta t), \tilde{\mathbf{v}}(t+\Delta t))$$

$$\mathbf{v}_i(t+\Delta t) = \mathbf{v}_i(t) + \tfrac{1}{2}\Delta t(\mathbf{f}_i(t) + \mathbf{f}_i(t+\Delta t))$$

Optimum value:

$$\lambda = 0.65$$

For this value the timestep can be increased to 0.06 without significant loss of temperature control



Groot & Warren, J. Chem. Phys., 1997

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DPD: Coarse-graining of MD

- The mass of the DPD particle is N_m times the mass of MD particle.

$$M = mN_m$$

- The cut-off radius can be found by equating mass densities of MD and DPD systems.

$$R_c = \left(\frac{N_m \rho^*_{\mathrm{DPD}}}{\rho_{\mathrm{MD}}}\right)^{\frac{1}{3}} \sigma$$

- The DPD conservative force coefficient *a* is found by equating the dimensionless compressibility of the systems.

$$a = k_B T \frac{\kappa^{-1} N_m - 1}{2\alpha \rho_{DPD}}$$

- The time scale is determined by insisting that the shear viscosities of the DPD and MD fluids are the same.

$$\tau_{\mathrm{DPD}} = \frac{\nu^*_{\mathrm{DPD}}}{\nu_{\mathrm{MD}}} \left(\frac{R_c}{\sigma}\right)^2 \tau$$

- The variables marked with the symbol "*" have the same numerical values as in DPD but they have units of MD.

Groot & Warren, J. Chem. Phys., 1997

Keaveny, Pivkin, Maxey & Karniadakis, J. Chem. Phys., 2005

Boundary Conditions in DPD

DPD simulations in confined geometry: imposition of boundary conditions.

Soft repulsion between DPD particles needs extra effort to impose accurately no-slip/partial-slip wall boundary condition.

- Modifying periodic boundary conditions
  - Lees-Edwards method [Boek et al. (1996)]
  - Reverse Poiseuille flow [Backer et al. (2005)]
- Freezing regions of the fluid to create rigid wall / body
  - for example, in particulate flow [Hoogerbrugge & Koelman (1992)]
- Combine different particle-layers with proper reflections
  - Specular reflection [Revenga et al. (1999)]
  - Bounce-back reflection [Visser et al. (2005)]
  - Maxwellian reflection [Revenga et al. (1998)]

Boundary conditions in DPD

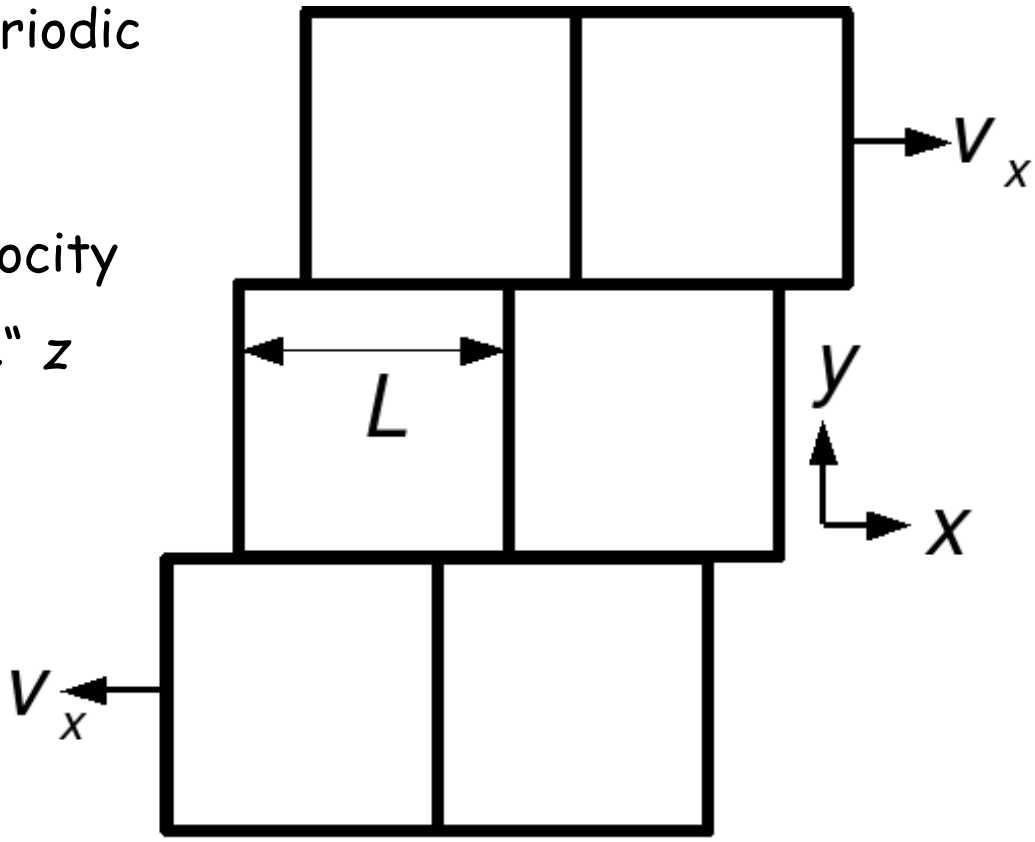
Lees-Edwards boundary condition

- no walls, instead modified periodic boundary conditions
- shear flow in *x* direction, velocity gradient in *y* direction, "free" *z* direction
- shear rate:

$$\dot{\gamma} = 2\mathrm{v}_x / L$$

- linear shear profile:

$$\mathrm{v}(y) = \dot{\gamma}(y - L/2)$$

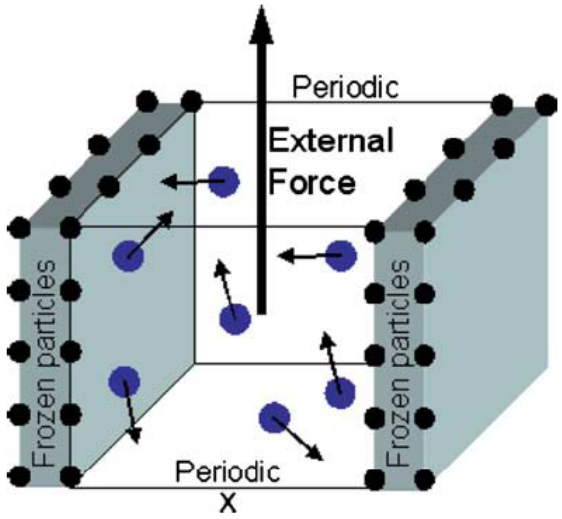


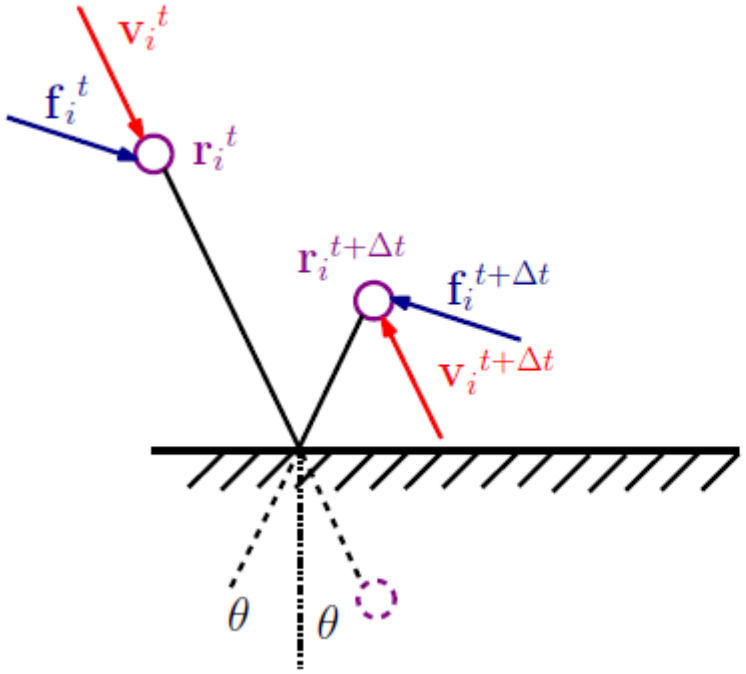
Lees & Edwards. J. Phys. C, 1972.

Boundary conditions in DPD

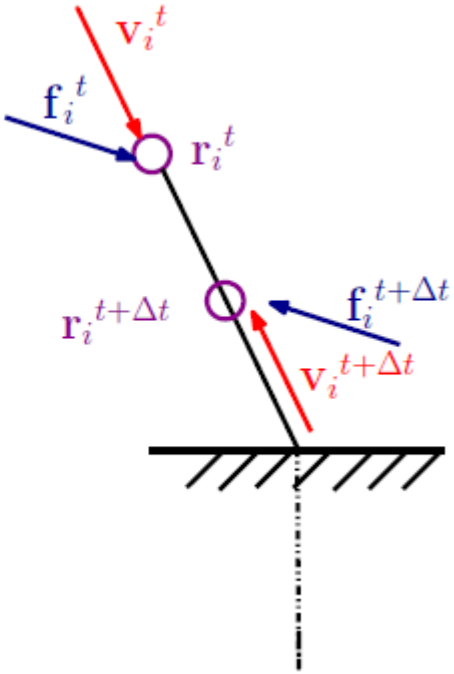
Frozen wall boundary condition

- Fluid in between parallel walls
- Walls are simulated by freezing DPD particles
- Flow induced by external body force





Bounce forward reflection



Bounce back reflection

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Shear viscosity

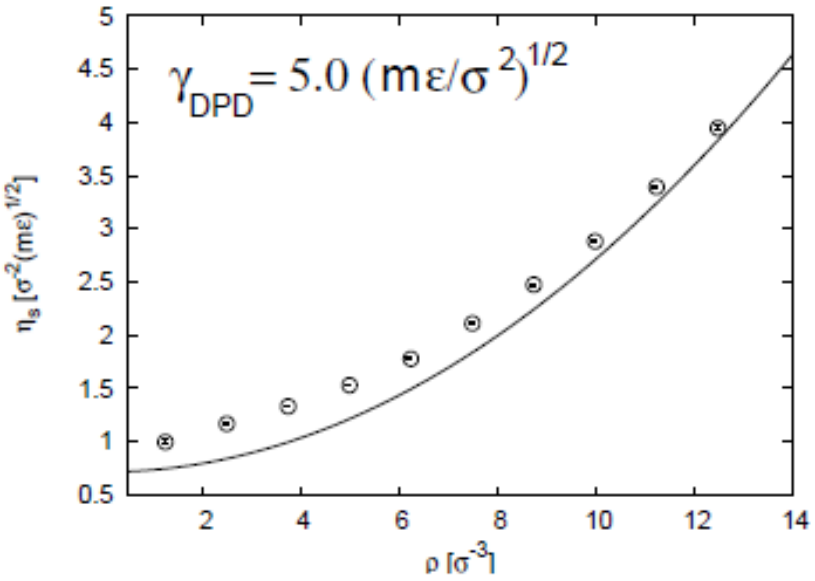
Shear viscosity in DPD is a function of several parameters.

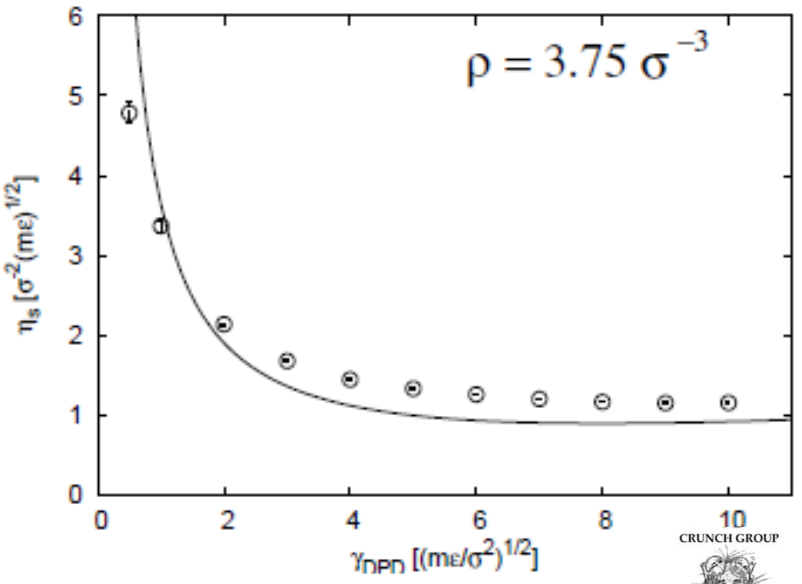
An approximation [Groot & Warren (1997)] is given by

$$\eta = \frac{45}{2\pi}\frac{(k_B T)^2}{\sigma^2 r_c^3} + \frac{\pi}{1575}\frac{\rho^2 \sigma^2 r_c^5}{k_B T}$$

More sophisticated theory in [Marsh et al (1997)].

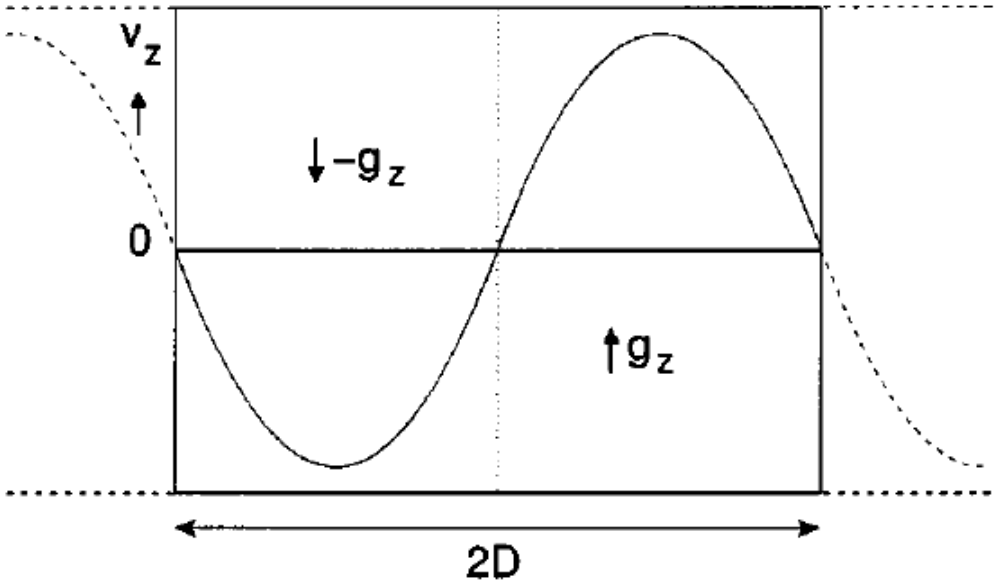
Simulation results:





Shear viscosity

Reverse Poiseuille flow



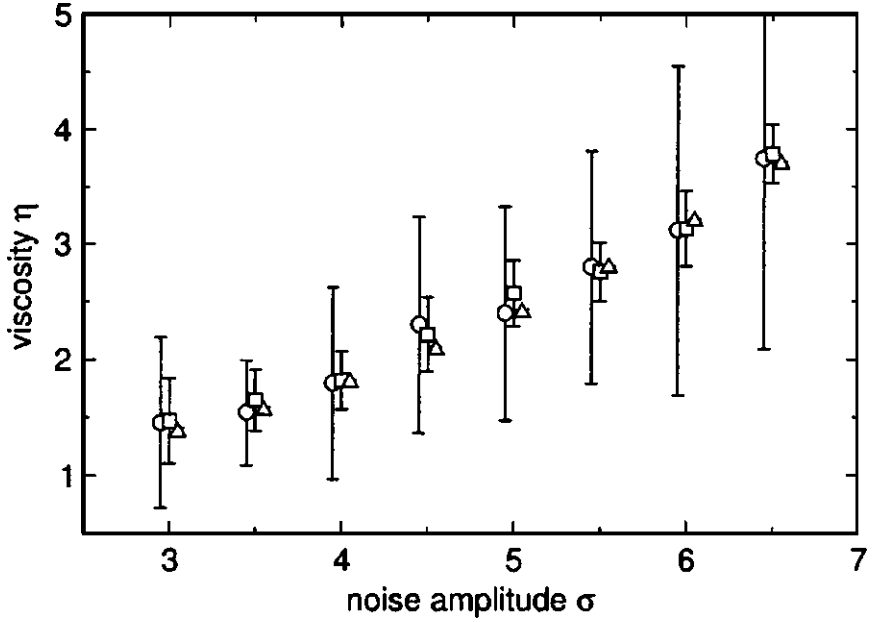
Shear stress:

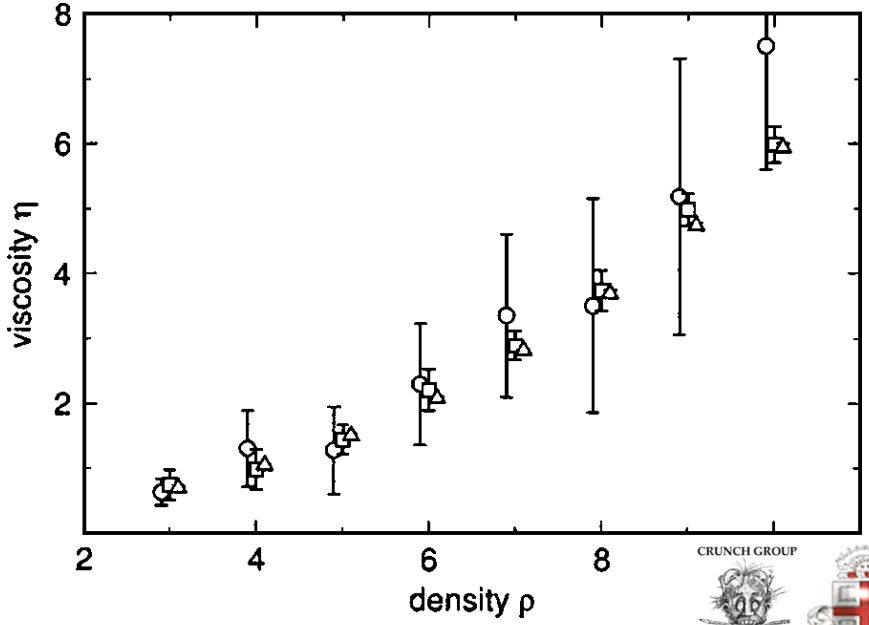
$$\tau_{xz} = \rho g_z (x - \tfrac{1}{2}D)$$

Velocity:

$$v_z = \frac{\rho g_z}{2\eta}(xD - x^2)$$

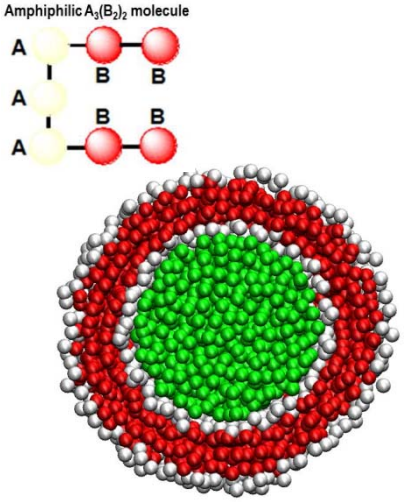
Simulation results:



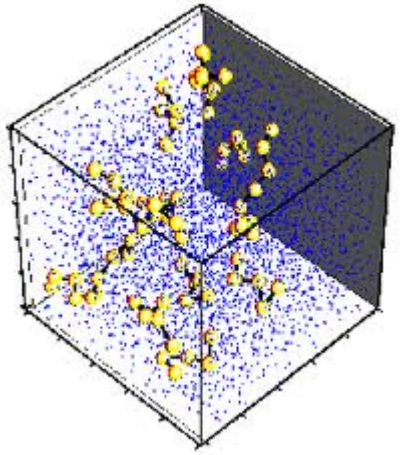


Backer, Lowe, Hoefsloot & Ledema, J. Chem. Phys., 2005

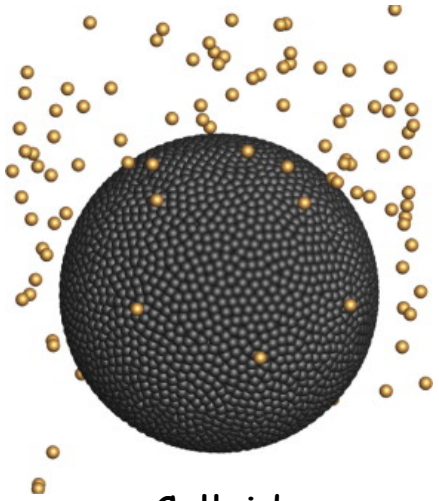
Applications



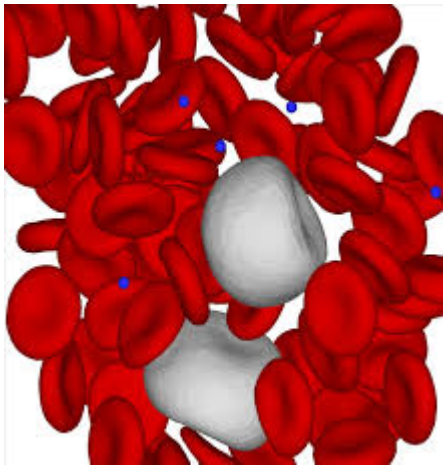
Polymer self-assembly



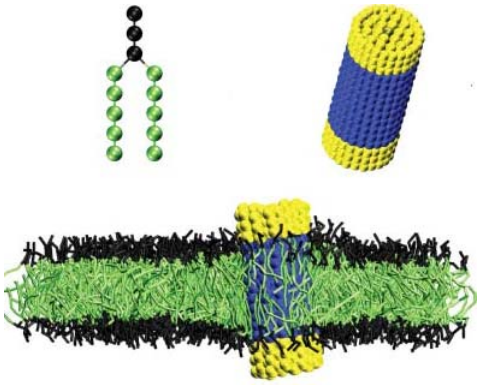
DNA



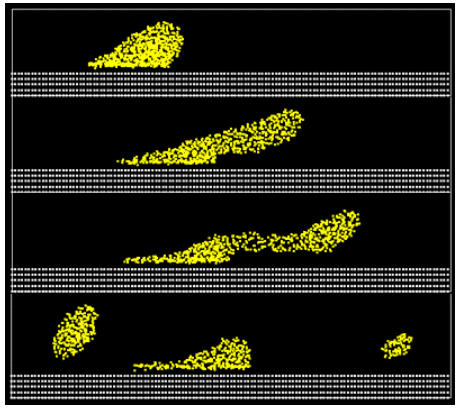
Colloids



Blood

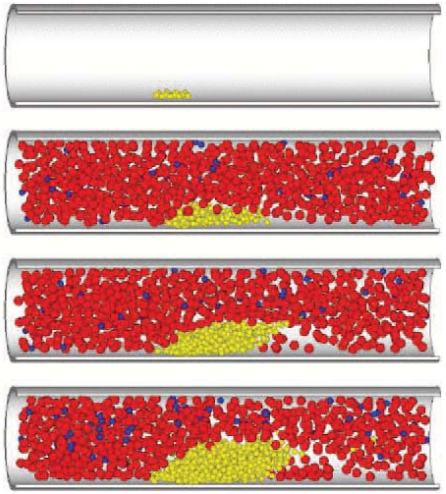


Membrane



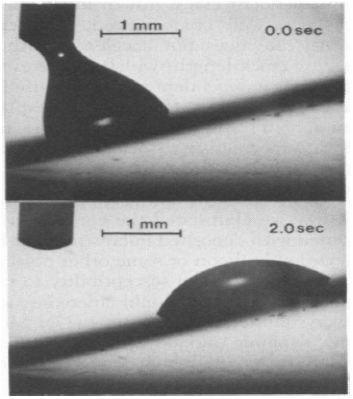
Droplet

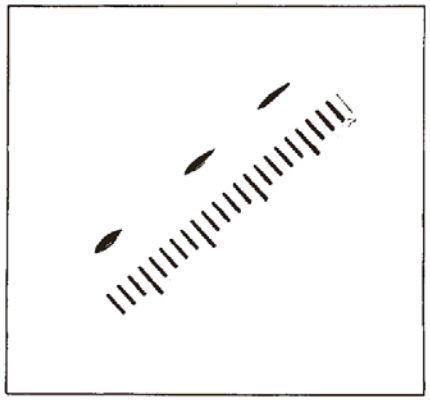
Surfactant



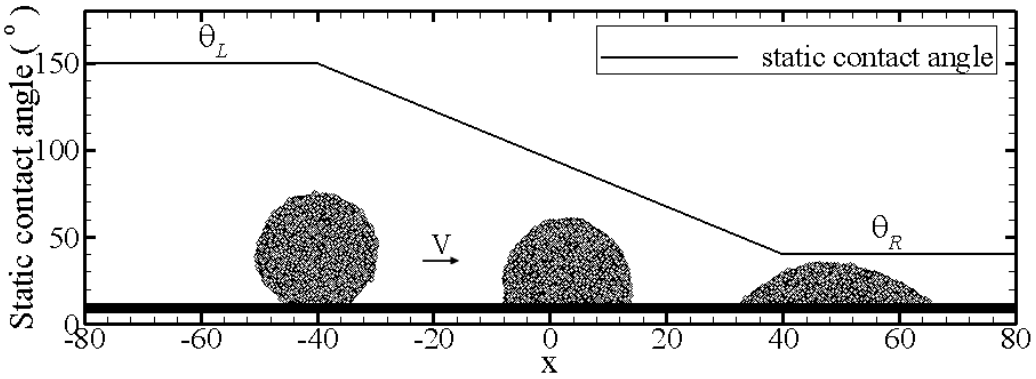
Platelets

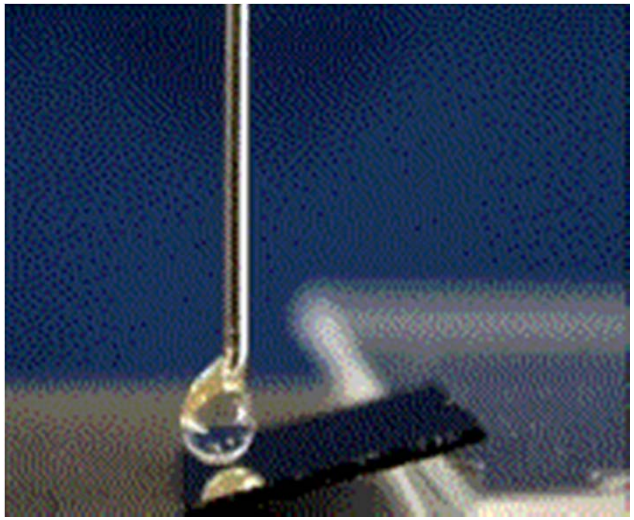
Application 1 – Droplet uphill motion



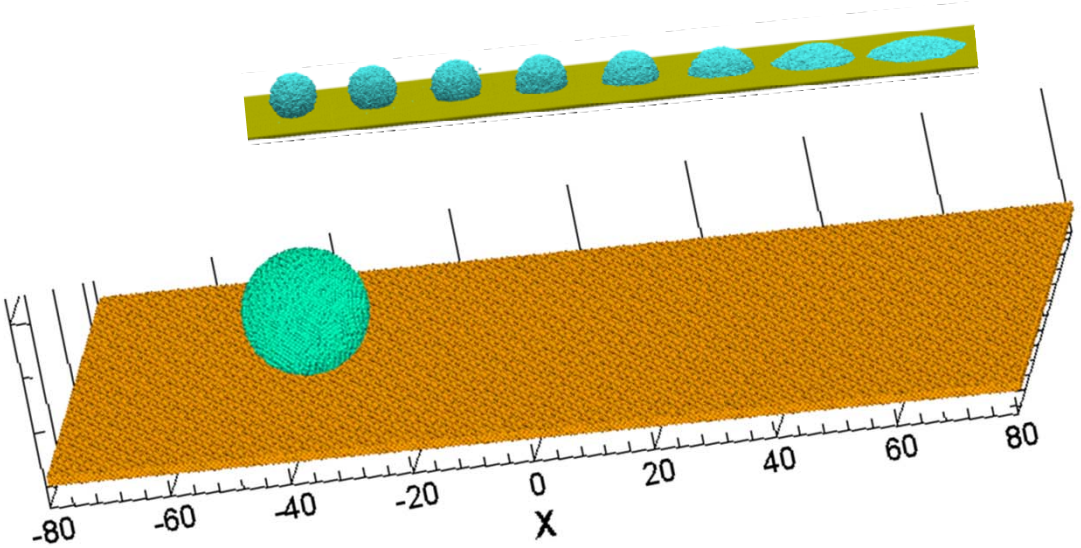


Chaudhury, et al. Science, 1992. Bain, et al. Nature, 1994.





From the website of LSST of ETH Zürich



Li, Hu, Wang, Ma & Zhou, Phys. Fluids, 2013

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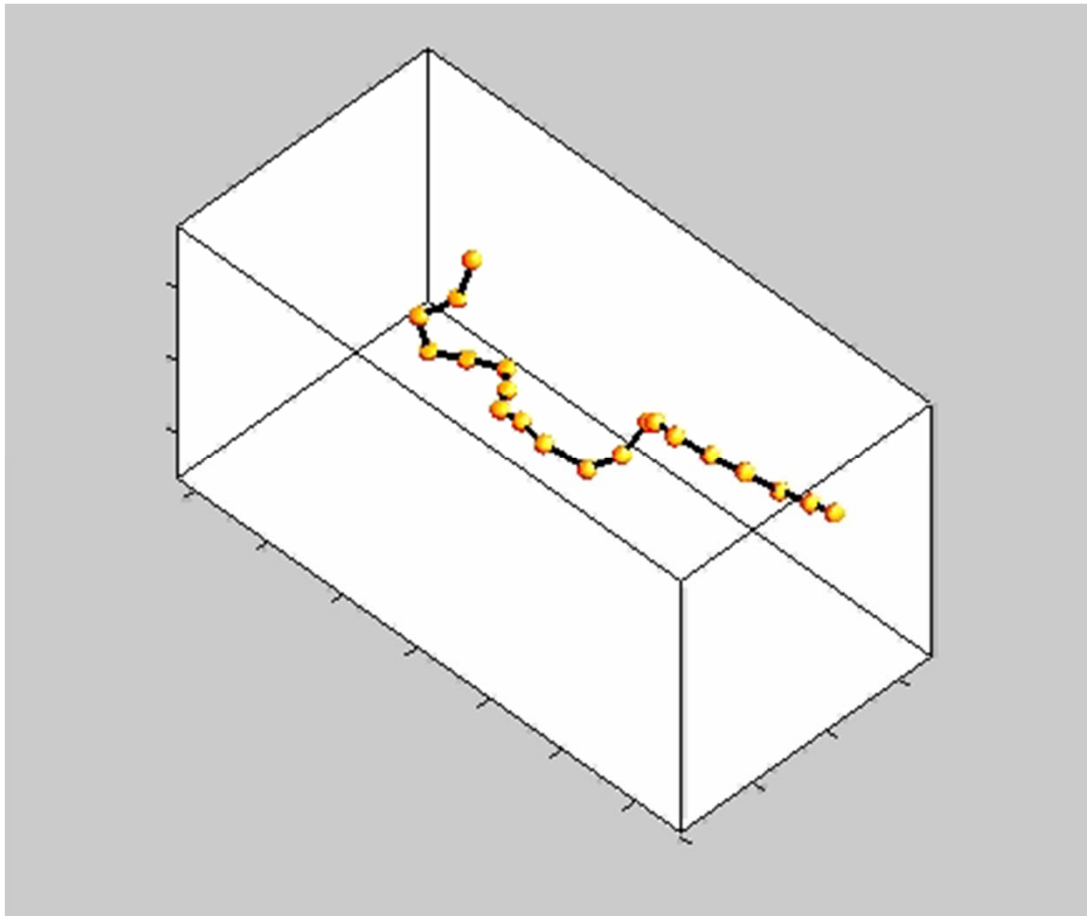
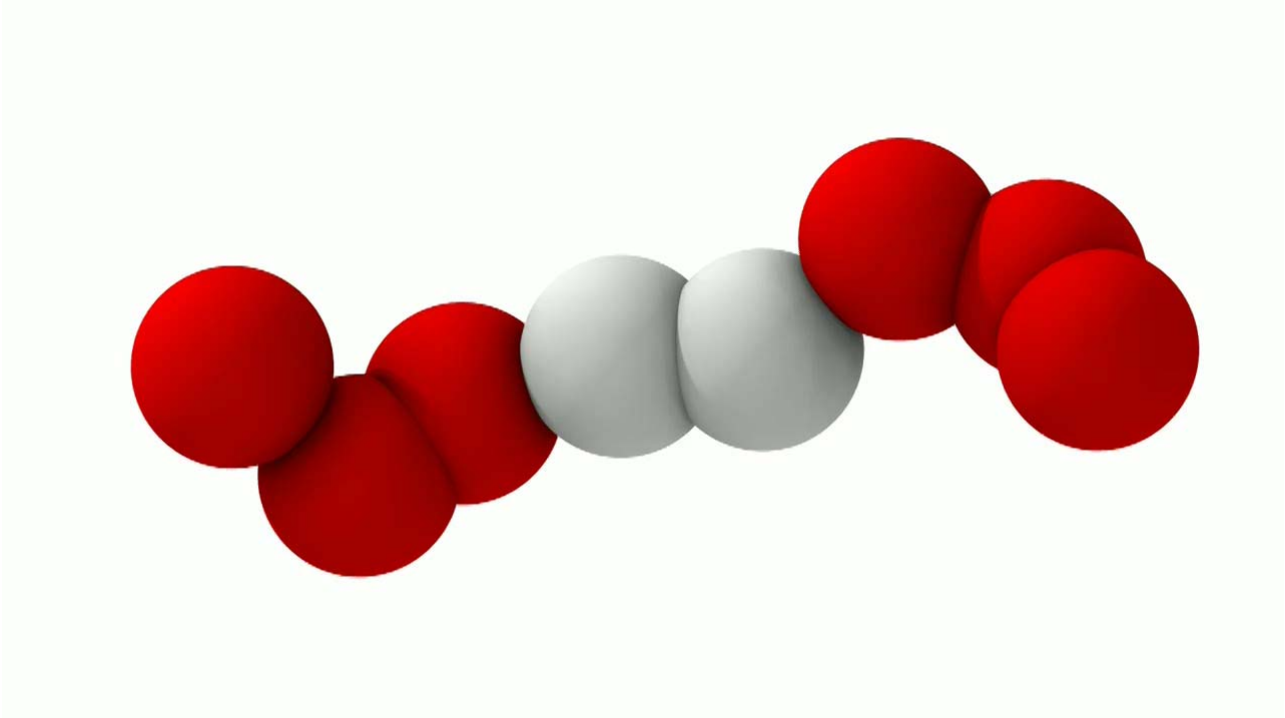
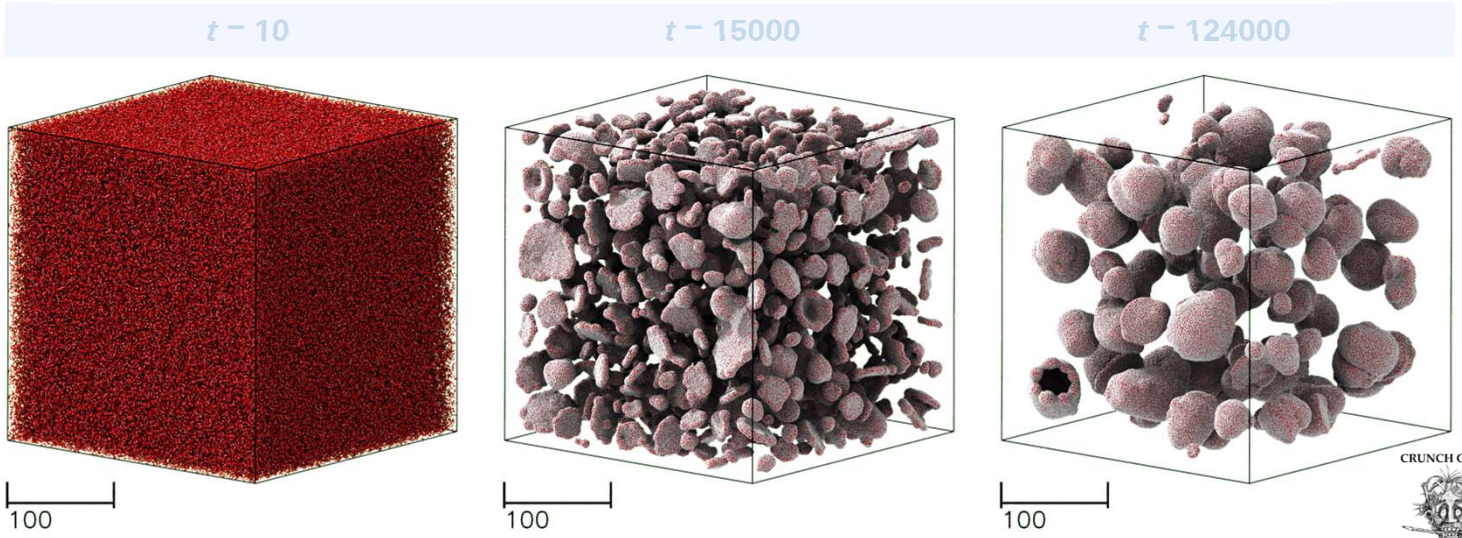
Application 2 – DNA in shear flow



Symeonidis, Caswell & Karniadakis, PRL, 2005

Application 3 – Amphiphilic self-assembly





Tang & Karniadakis, Comput. Phys. Commun, 2014

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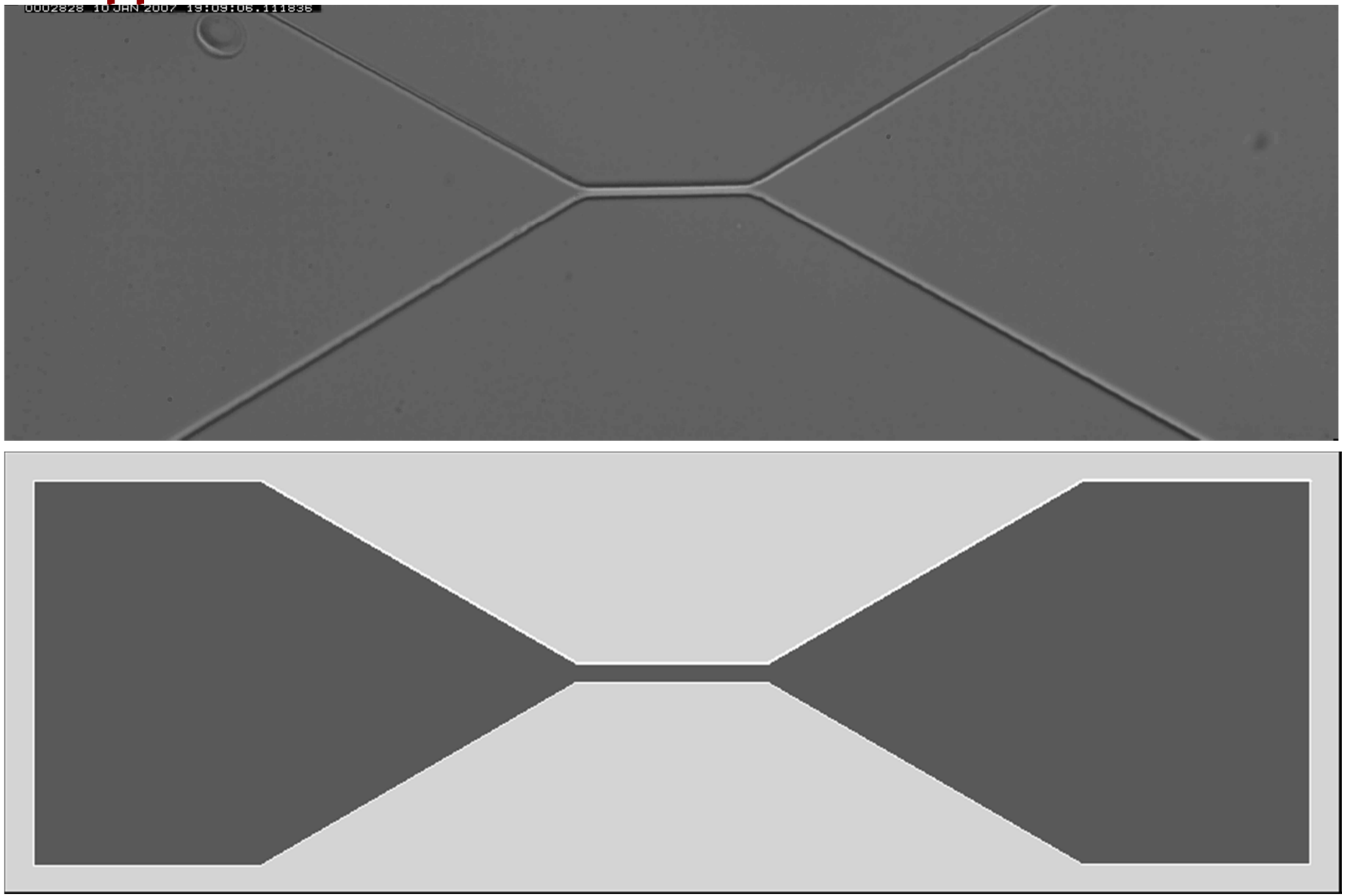
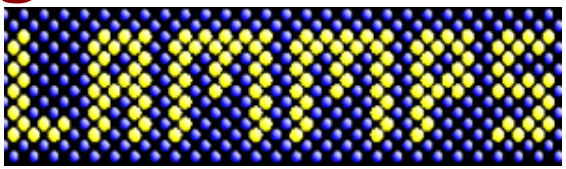
Application 4 – Red blood cell in microchannel



Quinn, Pivkin, Wong, Chiam, Dao, Karniadakis & Suresh, ABE, 2011

DPD Sofware/Package

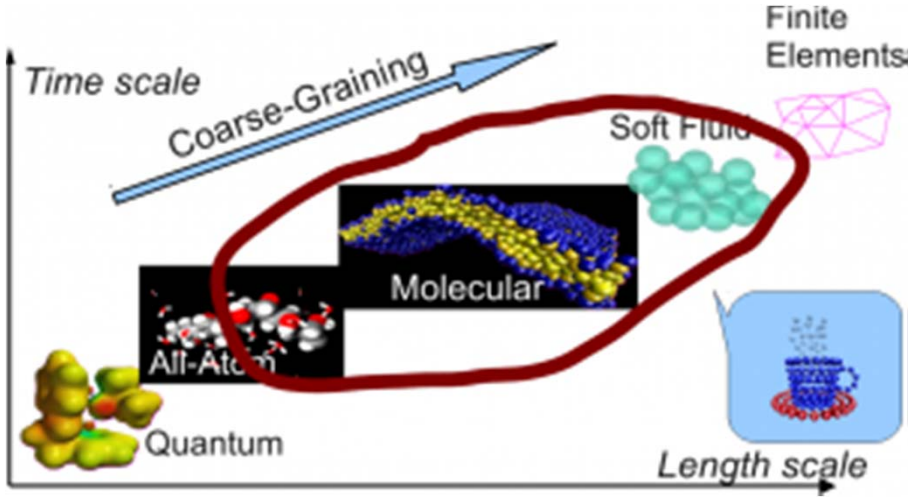
LAMMPS: http://lammps.sandia.gov/



- Highly parallelized
- Distributed-memory MPI
- GPU and OpenMP support for many code features
- Highly portable C++
- Open-source distribution

ESPResSo: http://espressomd.org/

- Extensible
- Open-source
- Parallelized
- Portable



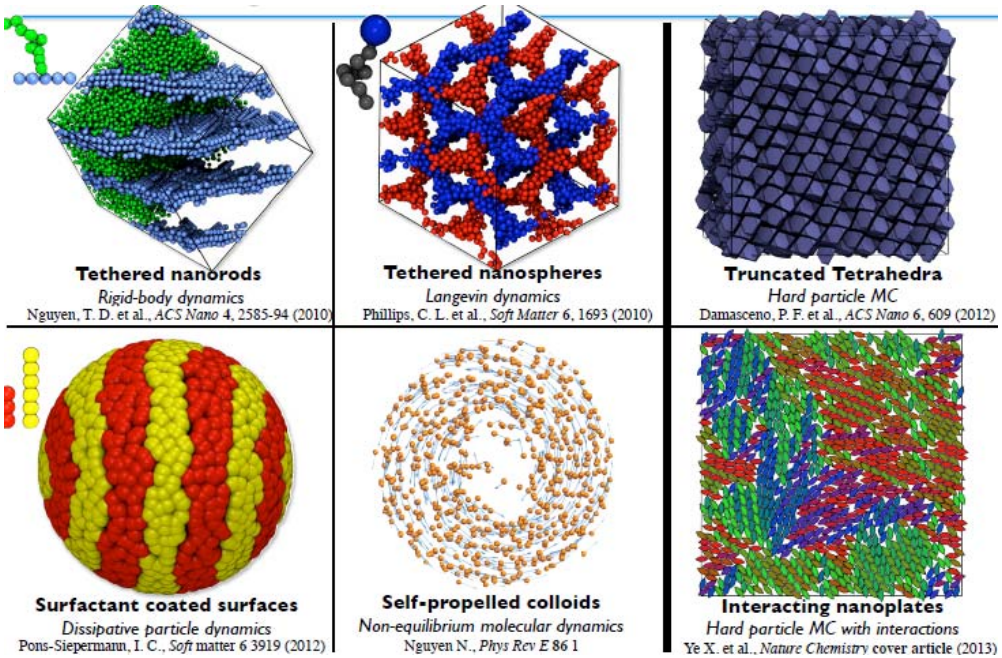
Length and time scales where ESPResSo works best

DPD Sofware/Package

HOOMD-blue: http://codeblue.umich.edu/hoomd-blue/

HOOMD-blue

- Fast GPU performance
- Scalable
- Flexible



DPDmacs: http://www.apmaths.uwo.ca/~mkarttu/dpdmacs.shtml

- Compatible with Gromacs

MyDPD: http://multiscalelab.org/mydpd

- Simple, serial but functional

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Open Issues

- Handshaking is still a problem (MD-DPD-NS)
- Coarse graining has its limits…
- Complex dynamics requires stochastic closures.
- Error/Uncertainty quantification needed.
- New verification & validation procedures are required for MSM.
- MSM should motivate new parallel computational paradigms.

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