SAND2013-8150P

6: Coarse-grained Techniques

Computation Rheology via LAMMPS Short Course

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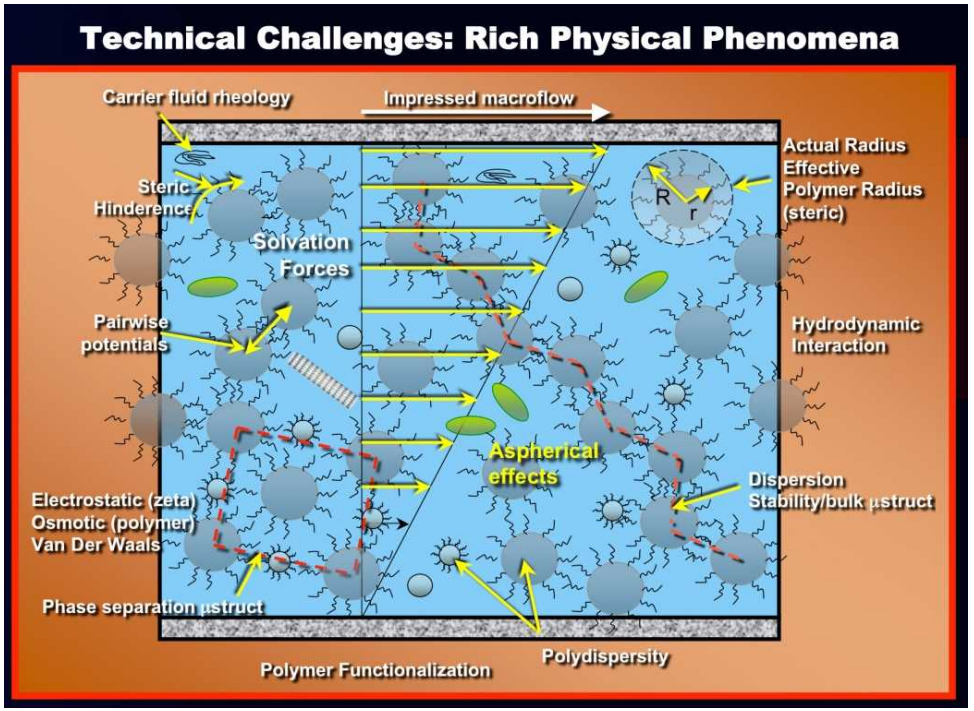
Coarse-graining Overview

- What is it?
  - A reduction in the number of things to keep track of
- When do we do it? What are the assumptions?
  - Some dynamics are so small/fast as to be irrelevant on larger scales (relaxation is quick) and tracking everything is cost prohibitive
    - So, ignore small/fast stuff
    - Or, average over small/fast stuff
- Specific Examples
  - Bead-spring polymers; Colloids – DLVO theory
  - Granular – Hertz Contact
  - Navier-Stokes

Computational Rheology of Complex Fluids

- Physical System
  - Colloids: $d \sim 10 - 1000\ nm$
  - Concentration: $\phi \sim 0.5$
  - Rate: $\dot{\gamma} \sim 100\ s^{-1}$
- Simulation Size and Run Time
  - Some rules of thumb
    - $> \sim O(10^4)$ particles
      - $L \sim O(0.1 - 10\ mm)$
    - Strain $\sim O(10)$ box units
      - $v_s \sim O(1 - 100\ mm/s)$
      - $T \sim O(0.1 - 1\ s)$



- Physical phenomena to model
  - Dimensionless #'s, e.g., Peclet Number, Pe
  - Length and time scales

Dimensionless Numbers and Characteristic Times

Physical parameters	$a = 10nm$	$a = 1\mu m$
$M \approx \frac{4}{3}\pi a^3 \times 10^{-12}\frac{g}{\mu m^3}$	$4.19 \times 10^{-18} g$	$4.19 \times 10^{-12} g$
$\frac{\xi_E}{\xi_S} \approx 1.6 \times 10^2 a$	≈ 1.6	$\approx 1.6 \times 10^2$
$\xi_S = 6\pi\eta a \approx 1.9 \times 10^{-5} a$	$\approx 1.9 \times 10^{-7}\frac{g}{s}$	$\approx 1.9 \times 10^{-5}\frac{g}{s}$
$D_{col} \approx \frac{k_B T}{6\pi\eta a} \approx \frac{0.2}{a}$	$\approx 20\frac{\mu m^2}{s}$	$\approx 0.2\frac{\mu m^2}{s}$
Hydrodynamic numbers	$a = 10nm$	$a = 1\mu m$
$Pe = \frac{v_S a}{D_{col}} \approx 5 v_S a^2$	≈ 0.005	≈ 50
$Re = \frac{v_S a}{\nu} \approx 10^{-6} v_S a$	$\approx 10^{-7}$	$\approx 10^{-5}$
$Kn = \frac{\lambda_{free}}{a} \approx \frac{0.3}{a} \times 10^{-3}$	≈ 0.03	≈ 0.0003
$Ma = \frac{v_S}{c_s} \approx 6.76 \times 10^{-10} v_S$	$\approx 6.8 \times 10^{-10}$	$\approx 6.8 \times 10^{-10}$
Time-scales	$a = 10nm$	$a = 1\mu m$
$\tau_D = \frac{a^2}{D_{col}} \approx 5a^3$	$\approx 5 \times 10^{-6} s$	$\approx 5\ s$
$t_S = \frac{a}{v_S} = \frac{\tau_\nu}{Re} = \frac{\tau_D}{Pe}$	$= 0.001\ s$	$= 0.1\ s$
$\tau_\nu = \frac{a^2}{\nu} \approx 10^{-6} a^2$	$\approx 10^{-10} s$	$\approx 10^{-6} s$
$\tau_B = \frac{M}{\xi_S} = \frac{2}{9}\tau_\nu$	$\approx 2.2 \times 10^{-11} s$	$\approx 2.2 \times 10^{-7} s$
$t_{cs} = \frac{a}{c_s} \approx 6.7 \times 10^{-10} a$	$\approx 6.7 \times 10^{-12} s$	$\approx 6.7 \times 10^{-10} s$

- Note: *Re, Pe,* τ_D, t_s
- Also, note: τ_ν, timescale for momentum to diffuse in fluid over length *a*
  - Propagation length grows as $\sqrt{t}$
    - Colloid inertia: $\tau_\nu/\tau_B \sim 1$
    - SD and the like imply $\tau_\nu = 0$
  - Compressibility: $\tau_\nu/t_{cs} \sim a c_s/\nu \sim 1$
- Low Pe: Suspension Stability/Self Assembly
  - $\tau_D = d^2/D_{col} \sim O(10^{-6} - 1\ s)$
    - Scales as a^3

Radius, a = 0.01μm (10nm) and 1μm in water at standard temperature and pressure pressure, moving at a velocity v_S = 10μm/s. Colloid assumed neutrally buoyant.
From Padding and Louis (2006) cond-mat/0603391

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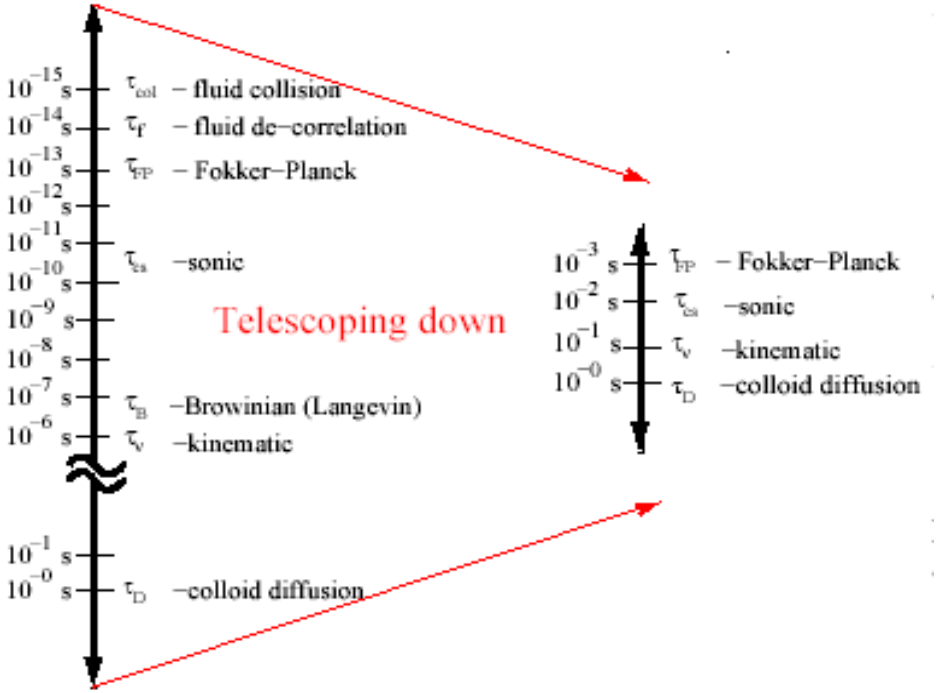
Length and Time Scales

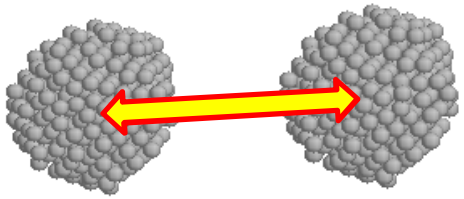
- Large systems & long times
  - N > O(10^4) colloids
  - T ~ O(10^7)δt_{coll}
- Can we resolve the relevant phenomena?
- Options?
  - Ignore certain phenomena
  - Collapse ("telescope") timescales
  - Coarse-grain



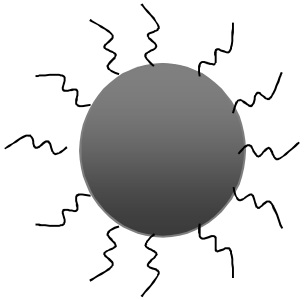
Time scales for 1 μm colloid in water.
From Padding and Louis (2006) cond-mat/0603391

Coarse-graining

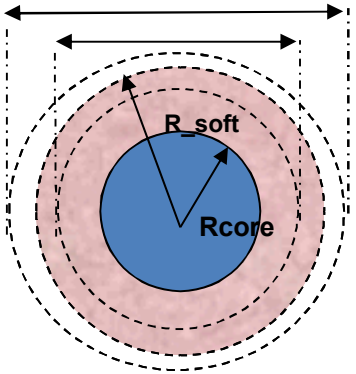
Particles



All atom representation of colloids

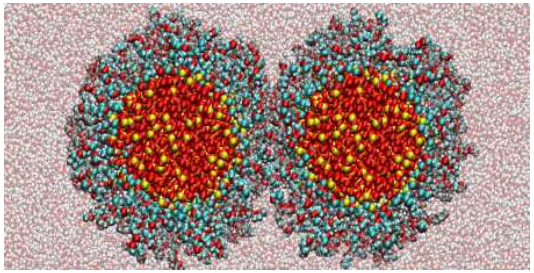


Integration to Hammaker's Equation for colloid



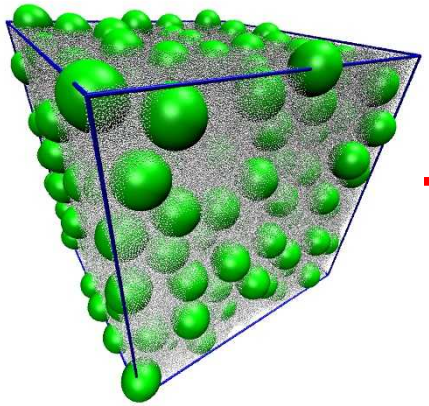
- Polymer layer parameters (osmotic and steric/structural effects)
- Structural constants (polymer and hard core)

Solvent



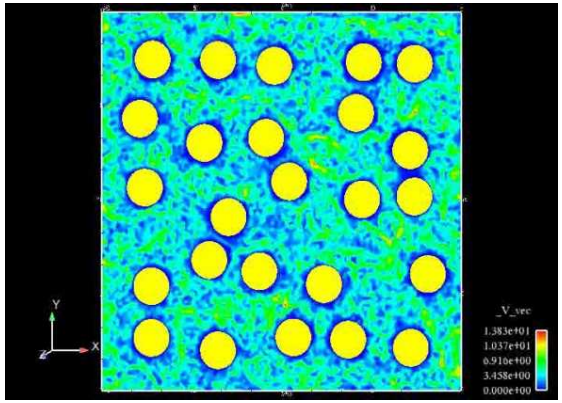
All atom Molecular Dynamics

(Lane et al.)



SRD/DPD: dual particle approach

(In 't Veld et al.)



Continuum: FEM

Colloid Dynamics

- Generalized Langevin Equation (with interactions)

$$m\frac{d\mathbf{v}_i}{dt} = \int_0^t \Gamma_i(t-t')\frac{d\mathbf{v}_i}{dt'}dt' + \mathbf{F}_i^B(t) + \sum_j \mathbf{F}_{ij}^{eff}(r_{ij})$$

- Approaches to hydrodynamics

  $\Gamma \sim 6\pi\mu a\delta(t\text{-}t')$

  – Ignore colloid particle inertia
    - Small Stokes number, $St = Re_p\rho_d/\rho_f$, or large friction $\mu = \rho_f\nu$
    - Smolukowski limit

Mazur and Oppenheim (1970)
Deutch and Oppenheim (1971)
Murphy and Aguirre (1972)

- Effective Interaction Potentials

$$\mathbf{F}_{ij}^{eff} = -\nabla V^{eff}\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right)$$

- Fluctuation Dissipation

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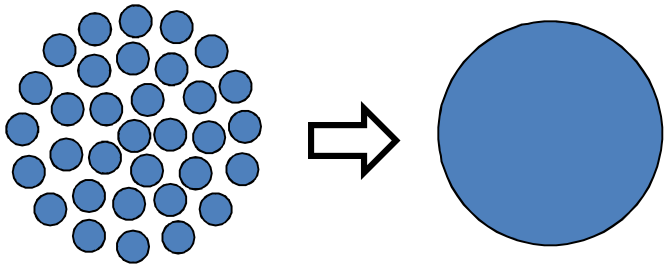
Effective Potentials in LAMMPS

- Colloid Package
  - DLVO: van der Waals attraction + electrostatic repulsion
    - `pair_colloid`
    - `pair_yukawa/colloid`
    - `pair_hybrid overlay`
- Numerically Calculated
  - `pair_table`
- Granular Package
  - Hertzian Contact Mechanics and Coulomb friction: Noncolloidal Particles
    - `pair_hertz_history` …

Colloid Interactions

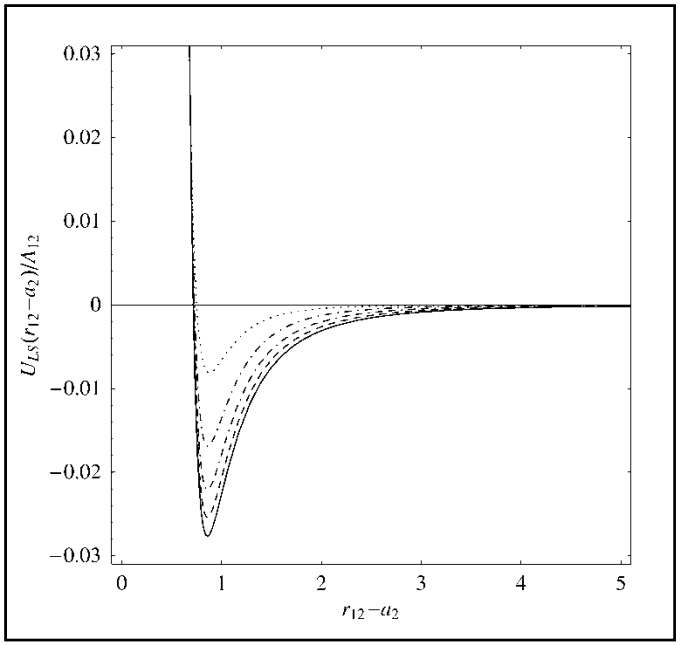


$$U_A = -\frac{A_{12}}{6}\left[\frac{2a_1a_2}{r_{12}^2-(a_1+a_2)^2}+\frac{2a_1a_2}{r_{12}^2-(a_1-a_2)^2}+\ln\left(\frac{r_{12}^2-(a_1+a_2)^2}{r_{12}^2-(a_1-a_2)^2}\right)\right]$$

$$U_R = \frac{A_{12}}{37800}\frac{\sigma^6}{r_{12}}\left[\frac{r_{12}^2-7r_{12}(a_1+a_2)+6\left(a_1^2+7a_1a_2+a_2^2\right)}{(r_{12}-a_1-a_2)^7}+\frac{r_{12}^2+7r_{12}(a_1+a_2)+6\left(a_1^2+7a_1a_2+a_2^2\right)}{(r_{12}+a_1+a_2)^7}-\frac{r_{12}^2+7r_{12}(a_1-a_2)+6\left(a_1^2-7a_1a_2+a_2^2\right)}{(r_{12}+a_1-a_2)^7}-\frac{r_{12}^2-7r_{12}(a_1-a_2)+6\left(a_1^2-7a_1a_2+a_2^2\right)}{(r_{12}-a_1+a_2)^7}\right]$$

$$U = U_A + U_R, \qquad r_{12} < r_c$$

- Integrated Lennard-Jones potential[1]
  - Repulsive "soft-sphere"
    - $a_1 = a_2 = 5\sigma$
    - $A_{12} = 1$
    - $r_c = r_{min} = 30^{-1/6}\sigma$



[1]R. Everaers and M.R. Ejtehadi, Phys. Rev. E ***67***, 41710 (2003)

Interactions Between Granular Particles

- Visco-Elastic Normal *Contact* Force
  - No-tension (repulsive only) "spring-dashpot"
  - No particle-particle adhesion
- Coulomb Friction *Tangential* Contact Force

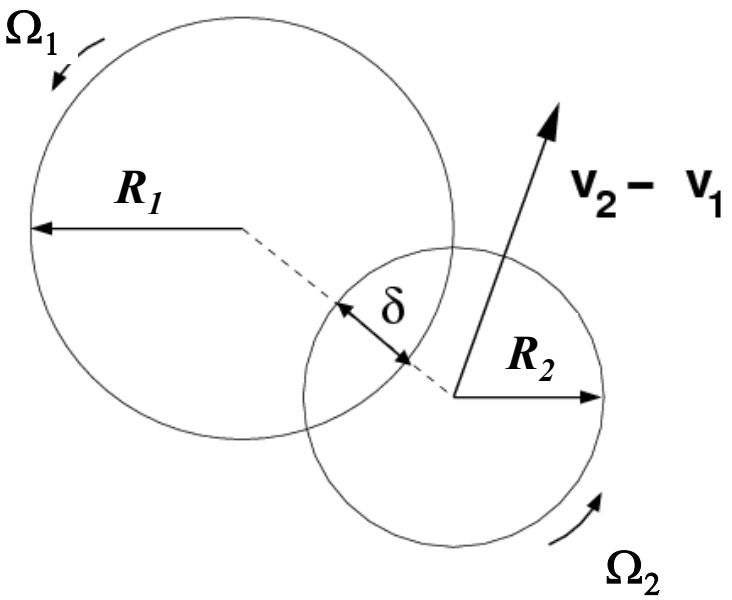
$$F_n = f(\delta / R)(k_n \delta - \frac{m}{2} \varsigma_n v_n)$$

$$F_t = f(\delta / R)(-k_t \Delta s_t - \frac{m}{2} \varsigma_t v_t)$$

$f(x) = \sqrt{x}$ Hertzian springs

Δs_t Elastic tangential displacement

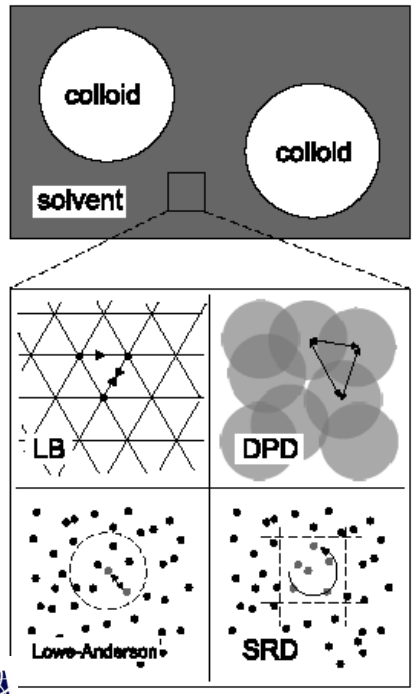
$F_t \leq \mu F_n$ Coulomb Failure Criterion

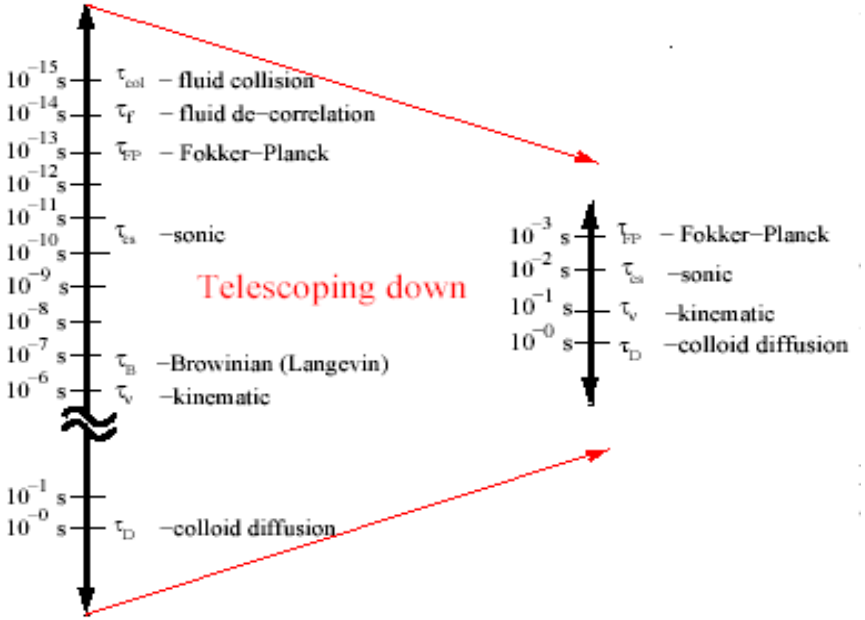


Brilliantov et al. (2000)

Capturing Hydrodynamics

- Methods to treat hydrodynamics
  - Particle-based, "explicit solvent" methods
    - Atomistic solvent (e.g. LJ solvent)
    - "Approximate" coarse-grained solvent
      - DPD solvent
      - SRD/LB solvent treated as ideal fluid particles with a mass
  - Continuum, "implicit solvent" methods
    - BD – Stokes drag, FLD, etc.
    - SD/BEM
    - Solve continuum Navier-Stokes equations numerically





Time scales for 1 μm colloid in water.
From Padding and Louis (2006) cond-mat/0603391

Hydrodynamic Models in LAMMPS

- Stochastic Techniques (Low Pe)
  - Brownian Dynamics (with intertia)
    - `fix_langevin`
  - FLD (with and without inertia)
    - `pair_lubricate (pair_lubricateU)`
    - `pair_brownian`
    - `pair_hybrid overlay`
  - Generalized Langevin Equation
  - DPD
  - Multi-Particle Collision Dynamics (SRD)
  - Lattice-Boltzmann

Case Study: Langevin Eqn. + Interactions

- Brownian Dynamics Simulations
  - Markov assumption

$$m\frac{d\mathbf{v}_i}{dt} = -\mathbf{R}\cdot\mathbf{v}_i + \sum_{j\neq i}\mathbf{F}_{ij}^{colloid}\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) + \mathbf{F}_i^B(t)$$

$$\left\langle \mathbf{F}_i^B(t)\right\rangle = 0; \left\langle \mathbf{F}_i^B(t)\mathbf{F}_j^B(t')\right\rangle = 2\mathbf{R}_{FU}k_BT\delta_{ij}\delta(t-t')$$

  - $\mathbf{F}^B$ assumed Gaussian distributed and self similar
  - Colloid inertia is often neglected (we don't)
- Can we obtain a Generalized Langevin version?
  - This is a constitutive we may be able to measure

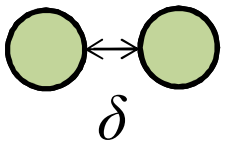
Simple Hydrodynamic Interactions

- Steady state (quasistatic) incompressible Newtonian fluid flow
  - Stokesian Dynamics
    - PME
      - » *O(NlogN)*
  - Fast Lubrication Dynamics
    - *O(N)*

$$R = (I - \mathcal{R})^{-1} R_{1B} + R_{lub}$$

Isotropic Constant
(mean-field mobility)

$$R = R_0 + R_\delta$$

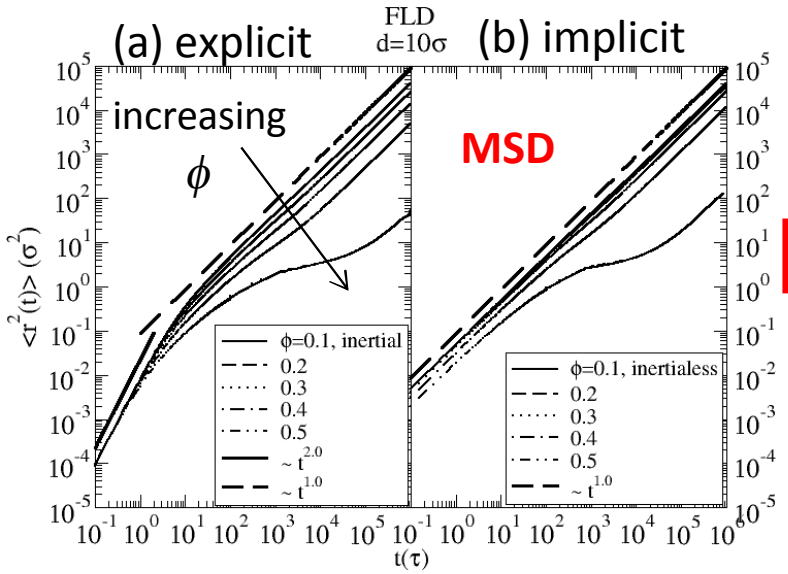


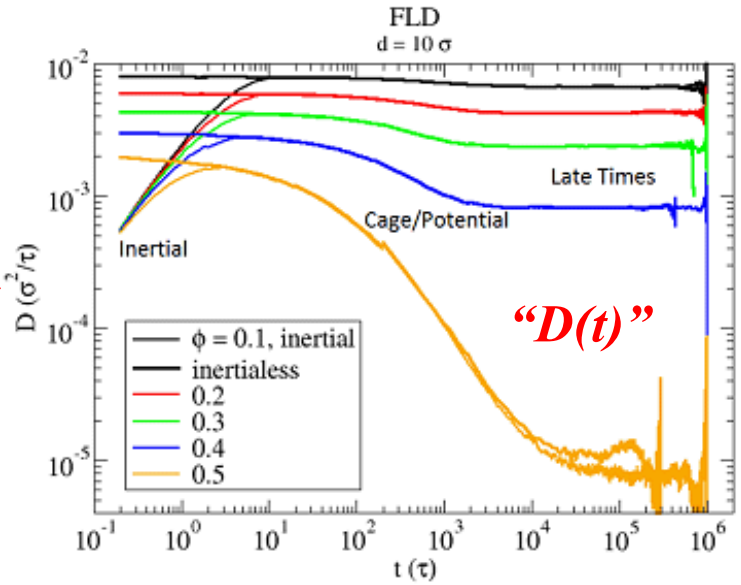
$$\mathbf{R}_0 = 3\pi\mu d(1+2.16\phi)\mathbf{I}$$

δ^{-1} or $\delta^{-1}+log(\delta^{-1})$

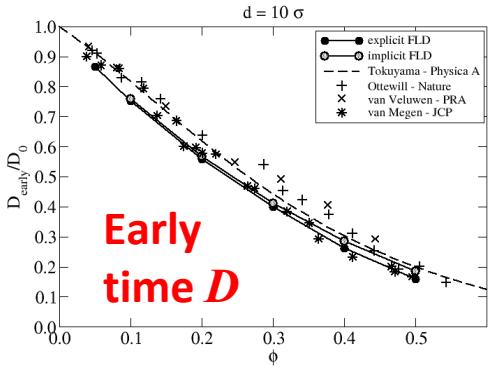
Kumar and Higdon, Phys Rev E, 82, 051401 (2010)
Ball and Melrose, Physica A, 247, 444-472 (1997)

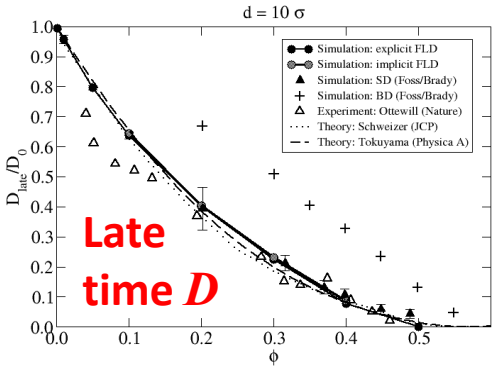
Simulation Results: MSD Validation





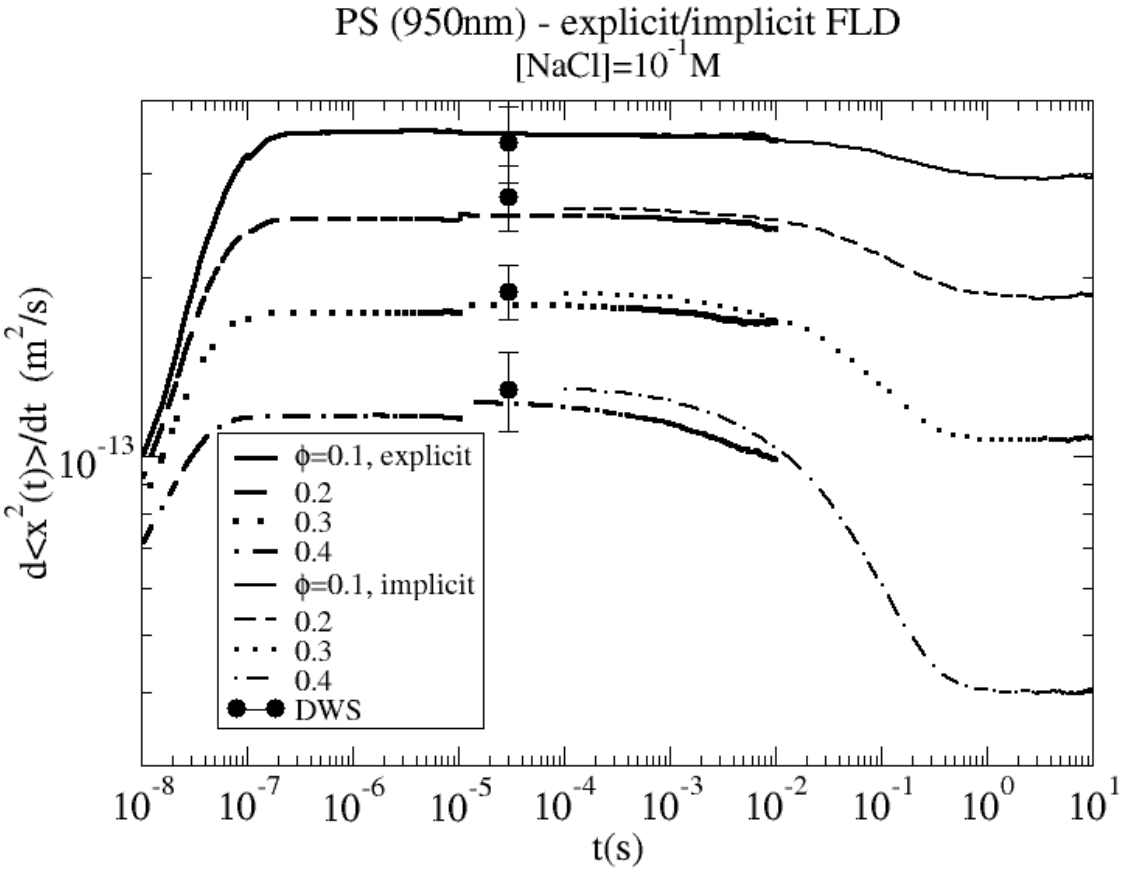
- $MSD = f(t) \neq Dt^{\alpha};\ \alpha \neq 1$
  - "Early" and "Late" time D compare well with experiments
  - Temptation
    - $D = D(t) \rightarrow MSD = D(t)t$





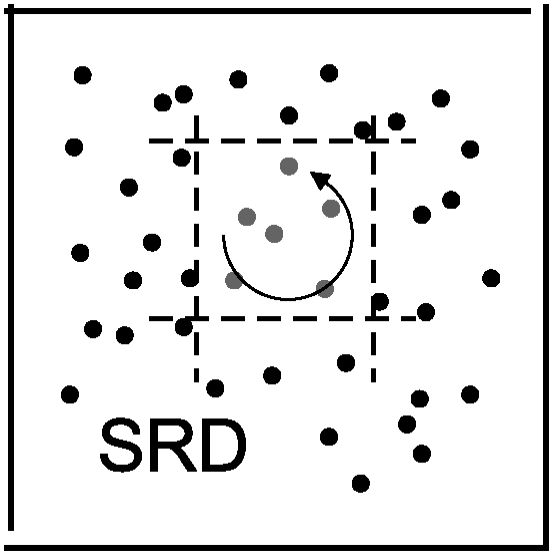
Combining Techniques

- FLD explicit and Implicit "seamlessly" overlap to give 9 orders of magnitude!
- Comparison to Experiment limited…



Stochastic Rotation Dynamics (SRD)

- Simulation domain divided up into cubic cells of side a
  - On average, M SRD particles with mass m_f are in the i^{th} cell, ξ_i, of volume Δx^3
- Two simulations steps
  - Particle streaming
    - particles move according to Forward Euler $v_i \Delta t$
  - Velocity update (coarse-grained collision)
    - Apply rotation about randomly chosen axis to fluctuating part of the velocity



$$\mathbf{v}_i(t+\tau) = \mathbf{u}(\xi_i(t+\tau)) + \omega(\xi_i(t+\tau))(\mathbf{v}_i(t) - \mathbf{u}(\xi_i(t+\tau)))$$

Padding and Louis (2006) http://arxiv.org/pdf/cond-mat/0603391v3.pdf
Gompper et al. (2008) http://arxiv.org/pdf/0808.2157.pdf

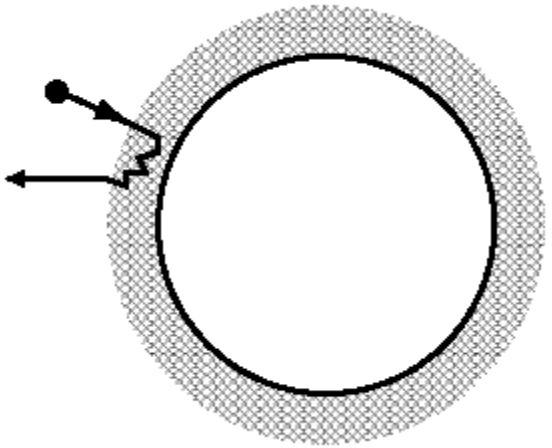
Coupling to Colloids

- To avoid finite size effects $a < R_c/2$
- SRD particles collide with colloids
  - Solvent coarse-grained so assume no-slip via stochastic rule
    - SRD particle receives a new random velocity magnitude

$$P(v_n) \propto v_n \exp(-\beta v_n^2)$$

$$P(v_t) \propto \exp(-\beta v_t^2)$$

    - Difference in new and old velocity is momentum transferred to colloid



- Can have general slip conditions or pair-interaction, $U(r_{coll}\text{-}r_{SRD})$

Selecting Parameters for LJ System

- Dynamics of interest

$$D_{coll} = \frac{1}{6\pi R}\left(\frac{k_B T}{\rho_f \nu_f}\right), \quad \nu_r = \nu_{bulk} / \nu_f$$

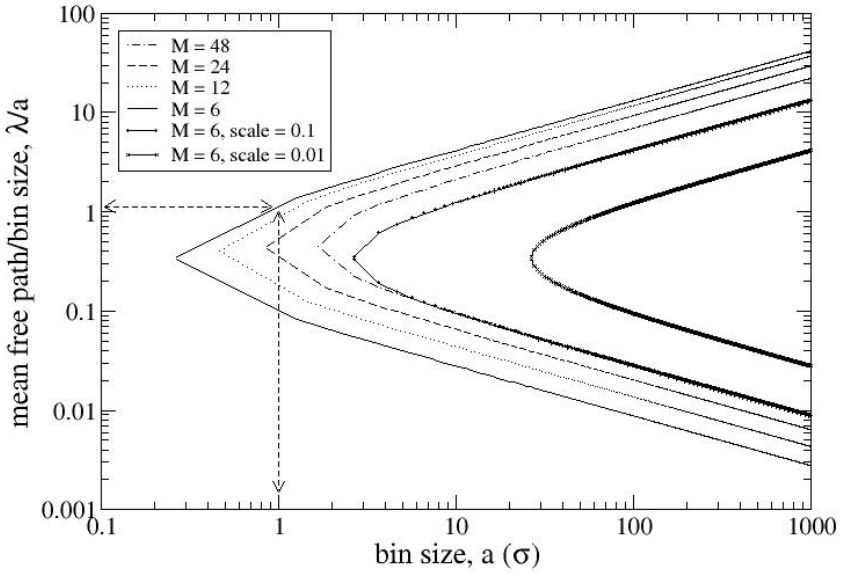
$$Pe = \frac{\tau_D}{t_s} = \frac{4R^2 / D_{coll}}{2R / u_s} = 12\pi u_s R^2 \left(\frac{\rho_f \nu_f}{k_B T}\right)$$

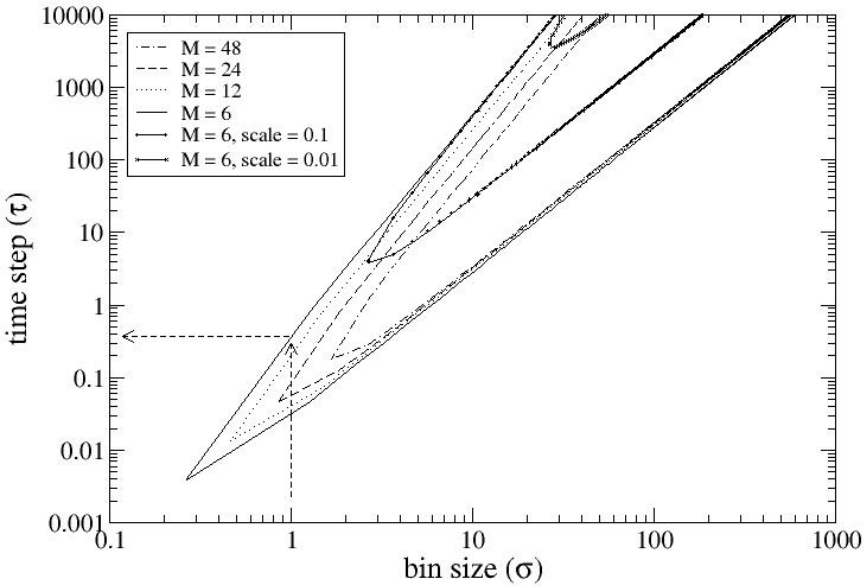
- Physical parameters: $\rho_f, \nu_f, k_B T, R, P$
- Computational parameters

$$\nu_f = \frac{\Delta x^2}{18\Delta t}\left(1 - \frac{1 - e^{-M}}{M}\right) + \frac{k_B T \Delta t}{4\rho_f \Delta x^3}\frac{M(M+2)}{M-1}$$

$$\lambda = \Delta t \sqrt{M k_B T / \rho_f \Delta x^3}, \quad \lambda << R$$

$$\rho_f = M m_f / \Delta x^3, \quad \frac{P}{k_B T} = \frac{M}{\Delta x^3}, \quad \Delta x < R/2$$





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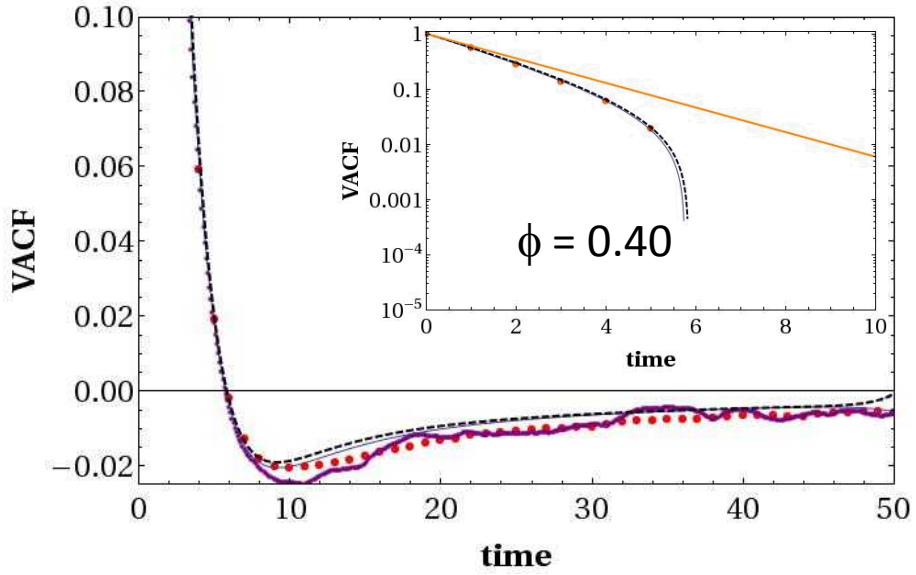
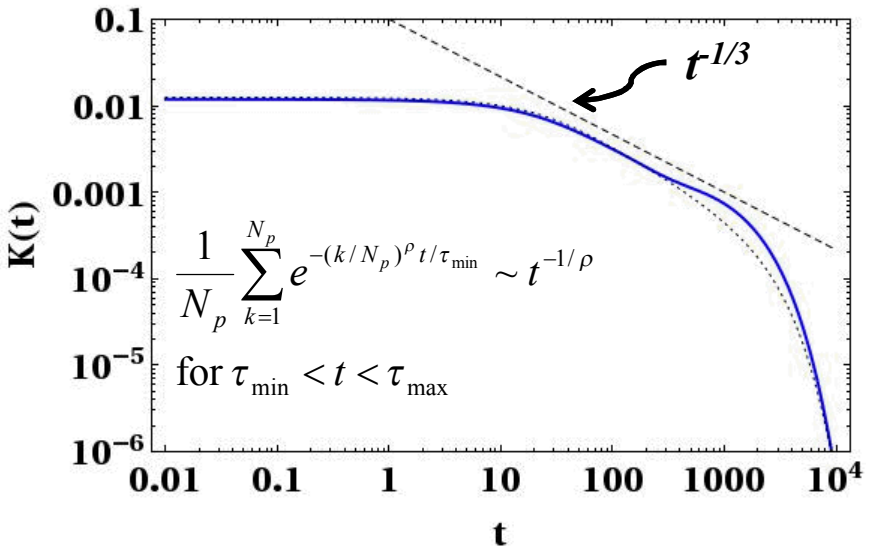
VACF and Memory Kernel





- **Or, fit VACF with**

$$f(t) = -A_N \sum_{i=0}^{N} c_i \lambda_i e^{-\lambda_i t} \qquad A_N = \frac{1}{\sum_{i=0}^{N} c_i / \lambda_i}$$

- **Which leads to**

$$m_i \frac{d\mathbf{v}_i(t)}{dt} = -\int_0^t K(t-t')\mathbf{v}_i(t')dt' + \mathbf{F}_i^R(t) \qquad K(t) \sim \delta(t) + \frac{1}{N}\sum_{k=1}^{N} e^{-(k/N)^{\rho} t/\tau_{coll}}$$

Summary: Langevin Equations to Generalized Diffusion Equations

- Brownian Dynamics Simulations
  - Markovian: Langevin with interactions

$$m\frac{d\mathbf{v}_i}{dt} = -\mathbf{R}\cdot\mathbf{v}_i + \sum_{j\neq i}\mathbf{F}_{ij}^{colloid}\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) + \mathbf{F}_i^B(t)$$

$$\left\langle \mathbf{F}_i^B(t)\right\rangle = 0; \left\langle \mathbf{F}_i^B(t)\mathbf{F}_j^B(t')\right\rangle = 2\mathbf{R}_{FU}k_BT\delta_{ij}\delta(t-t')$$

  - Non-Markovian: Generalized Langevin

$$m_i\frac{d\mathbf{v}_i(t)}{dt} = -\int_0^t K(t-t')\mathbf{v}_i(t')dt' + \mathbf{F}_i^R(t)$$

$$\left\langle \mathbf{F}_i^R(t)\right\rangle = 0; \left\langle \mathbf{F}_i^R(t)\mathbf{F}_j^R(t')\right\rangle = 2k_BT\delta_{ij}K(t-t')$$

$$K(t) \sim \delta(t) + \frac{1}{N}\sum_{k=1}^{N} e^{-(k/N)^{\rho}\, t/\tau_{coll}}$$

"Sticky" Particle Simulations: JKR Adhesion Theory for "Stiff" Spheres

- Modify contact normal force for attraction
- Modify sliding criterion
  - Amonton's Law

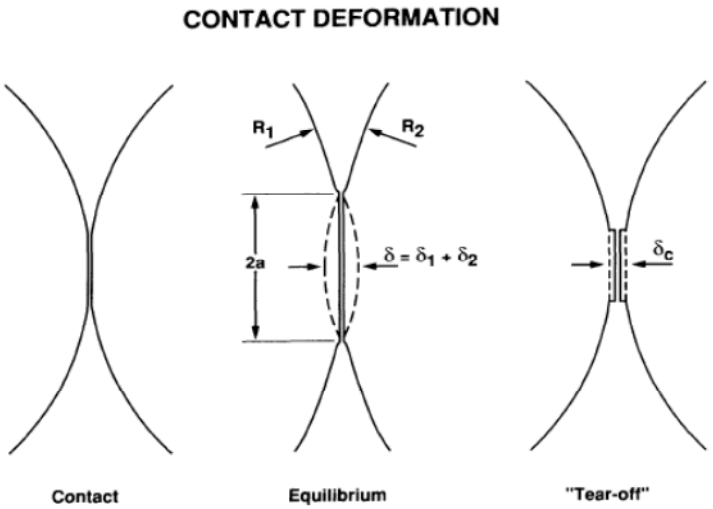
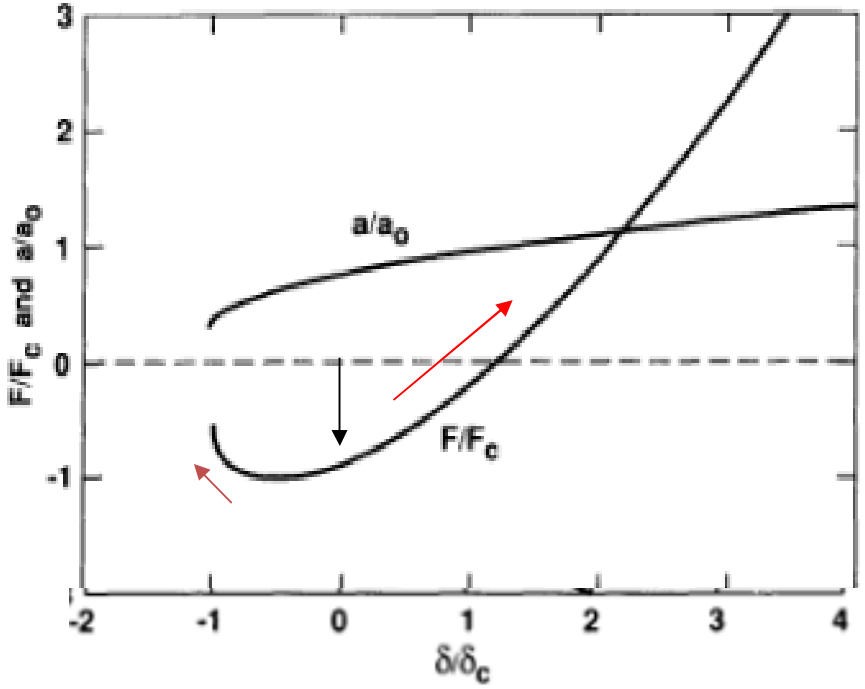


FIG. 2.—Schematic of the deformation during the collision process. At contact, a finite contact area is rapidly formed. This contact area grows in size during the compression and slowing down of the collision partners. Upon reversal of the collision process, the two grains will pull out a neck area, until they separate at a critical displacement, δ_c. See text for details.

From Chokshi, Tielens and Hollenbach (1993), ApJ



CHARACTERISTICS OF THE COLLISION PROCESS

Parameter	δ/δ_c	a/a_0	F/F_c	$U_T/F_c\,\delta_c$
Contact	0	$(2/3)^{2/3}$	$-8/9$	$-(8 \times 4^{2/3}/15)$
Equilibrium	$(4/3)^{2/3}$	1	0	$-(4 \times 6^{1/3})/5$
δ_{max} [a]	2.79	1.23	1.96	0
Tear-off	-1	$(1/6)^{2/3}$	$-5/9$	4/45

[a] Maximum compression, calculated assuming no initial velocity upon contact.

"Sticky" Particle Simulations: Bonded/Sintered Particle Model

- Constrain relative rotation for bonded pair
  - Rolling resistance
    - Torsion spring for contact moment and failure criterion
  - Twisting resistance
    - Torsion spring for twist moment and failure criterion

$$\mathbf{F}_i = \sum_j (F_n \mathbf{n} + F_t \mathbf{t}_S + \ldots)$$

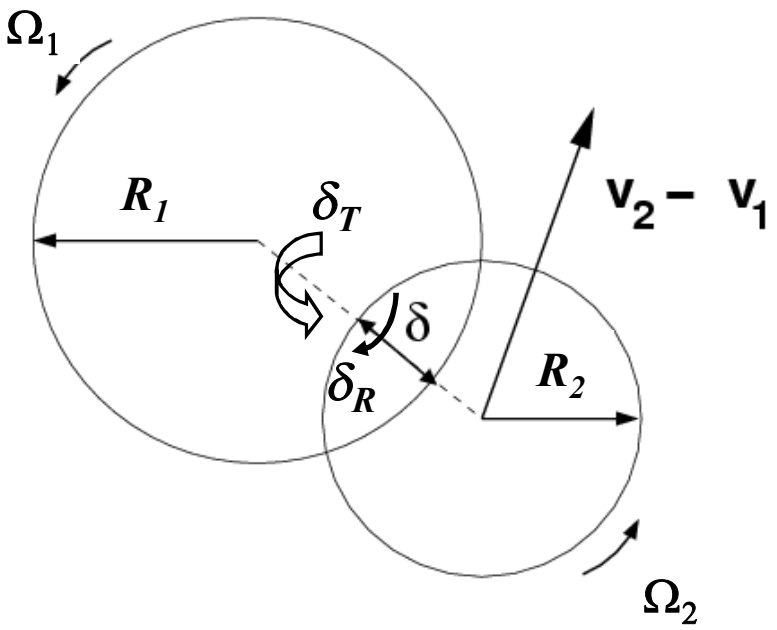
$$\mathbf{M}_i = \sum_j R_i F_t (\mathbf{n} \times \mathbf{t}_S) + M_R (\mathbf{t}_R \times \mathbf{n}) + M_T \mathbf{n}$$

$$M_R \le -k_R R_i \theta_c, \quad k_R = 4F_c (a/a_0)^{3/2}$$

$$M_T \le -\frac{2}{3}\mu a \left(F_n + 2F_c\right)$$

$$\mathbf{n} = \frac{\mathbf{r}_j - \mathbf{r}_i}{|\mathbf{r}_j - \mathbf{r}_i|}, \quad \mathbf{t}_S = \frac{\mathbf{v}_t}{|\mathbf{v}_t|}, \quad \mathbf{v}_t = \mathbf{v}_R - (\mathbf{v}_R \cdot \mathbf{n})\mathbf{n}$$

$$\mathbf{v}_R = (\mathbf{v}_i + \Omega_i \times R_i \mathbf{n}) - (\mathbf{v}_j + \Omega_j \times R_j \mathbf{n})$$



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7: Common Equilibrium Calculations

Computation Rheology via LAMMPS Short Course

85th Annual Society of Rheology Meeting

Montreal, Canada

Jeremy Lechman

Nanoscale and Reactive Processes Department

Sandia National Laboratories

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Observables and Ensemble Averages

- Variables in MD/partilce-based simulation
  - $\mathbf{r}(t) = (\mathbf{r}_1(t), \mathbf{r}_2(t), \ldots, \mathbf{r}_N(t))$; $\mathbf{p}(t) = (\mathbf{p}_1(t), \mathbf{p}_2(t), \ldots, \mathbf{p}_N(t))$
  - What we really are interested in is some (macroscopic) observable, $O = O(\mathbf{r}(t), \mathbf{p}(t))$
  - How to obtain?
    - Ensemble Average
      - Average over all possible values of $\mathbf{r}(t)$ and $\mathbf{p}(t)$; given $f^N(\mathbf{r}(t), \mathbf{p}(t))$

$$O(\mathbf{r}(t), \mathbf{p}(t)) = \langle O \rangle_{ens} = \int\int O(\mathbf{r}(t), \mathbf{p}(t)) f^N(\mathbf{r}(t), \mathbf{p}(t)) d\mathbf{r} d\mathbf{p}$$

    - In practice

$$O(\mathbf{r}(t), \mathbf{p}(t)) = \langle O \rangle_{time} = \lim_{t_{obs} \to \infty} \frac{1}{t_{obs}} \int_0^{t_{obs}} O(\mathbf{r}(t), \mathbf{p}(t)) dt$$

  - Note for Ergodic systems $\langle A \rangle_{time} = \langle A \rangle_{ens}$

Thermodynamic Averages

- Reported in LAMMPS Compute Thermo
  - Useful simulation diagnostic
- Temperature
  - Equipartition of energy

$$\langle \mathcal{K} \rangle = \left\langle \sum_{i=1}^{N} p_i^2 / 2m_i \right\rangle = \frac{3}{2} N k_B T$$

  - Instantaneous kinetic temperature

$$\mathcal{T}(t) = \frac{1}{3Nk_B} \sum_{i=1}^{N} p_i^2(t) / m_i$$

    - Not the thermodynamic temperature

Thermodynamics Averages

- Pressure
  - Virial equation

$$\mathcal{W} = \frac{1}{3}\sum_{i=1}^{N} \mathbf{r}_i \cdot \mathbf{f}_i$$

$$PV = Nk_B T + \langle \mathcal{W} \rangle$$

  - Instantaneous

$$\mathcal{P}(t) = \rho k_B \mathcal{T}(t) + \mathcal{W}(t)/V$$

    - Not the thermodynamic pressure
- Pressure or Stress Tensor

$$\sigma_{\alpha\beta} = \left\langle \frac{1}{V}\sum_{i=1}^{N}\left[\sum_{j\neq i}\frac{r_{ij}^{\alpha} f_{ij}^{\beta}}{2} + m_i v_i^{\alpha} v_j^{\beta}\right]\right\rangle$$

Fluctuations

- Particle simulations give more than averages
  - Statistical information is available too!
    - Fluctuations and (spatial/temporal) Correlations
- Fluctuations in (macro) observables are of interest

$$\delta A_{obs} = A_{obs} - \langle A \rangle_{ens}$$

  - Example: fluctuations in thermodynamic quantities
    - Specific heats
    - Coefficient of thermal expansion
    - Isothermal compressibility

Thermodynamic Fluctuations

- Specific Heat
  - See, e.g., Landau and Liftshitz (1980) *Statistical Physics*

$$\left\langle \delta E^2 \right\rangle = k_B T^2 C_V$$

  - In MD practice

$$\left\langle \delta E^2 \right\rangle = \left\langle \delta \mathcal{H}^2 \right\rangle_{NVT} = \left\langle \delta \mathcal{K}^2 \right\rangle_{NVT} + \left\langle \delta \mathcal{V}^2 \right\rangle_{NVT}$$

    - Recall from equipartition $\left\langle \delta \mathcal{K}^2 \right\rangle_{NVT} = \frac{3N}{2}\left(k_B T\right)^2$

$$\left\langle \delta \mathcal{V}^2 \right\rangle_{NVT} = k_B T^2 \left(C_V - \frac{3}{2} N k_B \right)$$

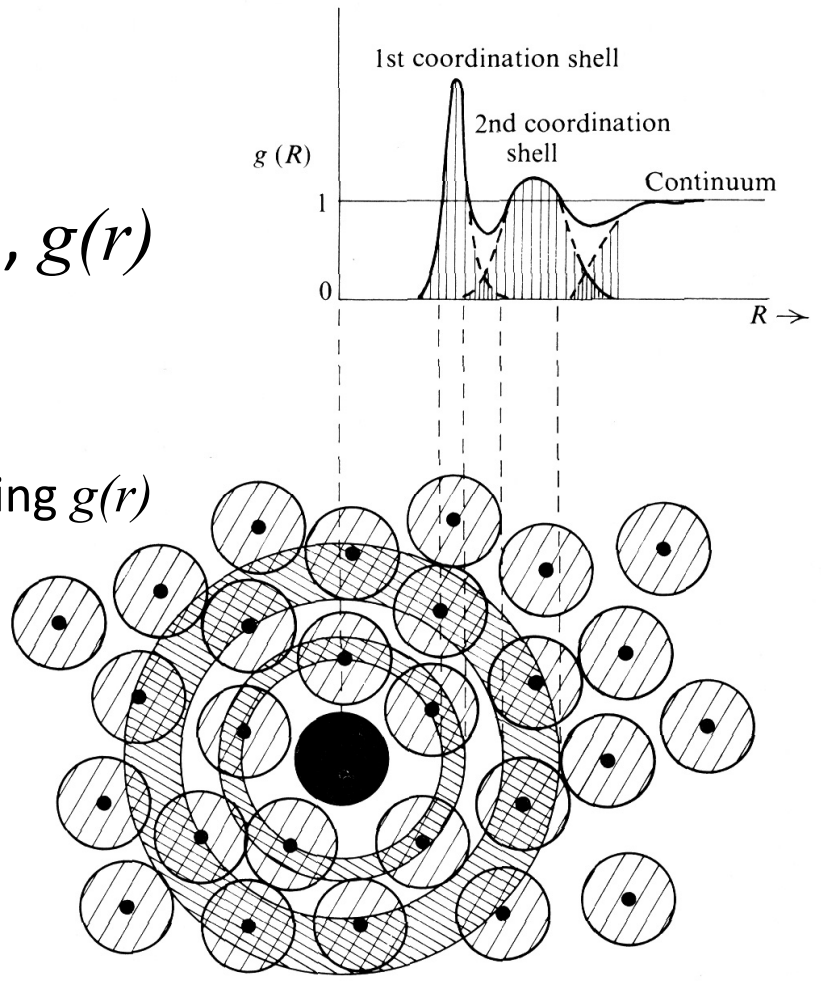
- Isothermal Compressibility $\left\langle \delta V^2 \right\rangle_{NPT} = V k_B T \beta_T$

Structural Quantities

- Correlation Functions
  - Pair correlation and Radial Distribution Function (RDF), $g(r)$
    - Usefulness
      - Ensemble average of any pair function may be expressed using $g(r)$
        - » Density, energy, pressure, chemical potential

$$\left\langle \frac{1}{N}\sum_{i}\sum_{j\neq i}\delta(r-r_j+r_i)\right\rangle = \rho g(r)$$

$$P = \rho k_B T + \frac{2\pi\rho^2}{3}\int \frac{dU(r)}{dr} g(r) r^3 dr$$



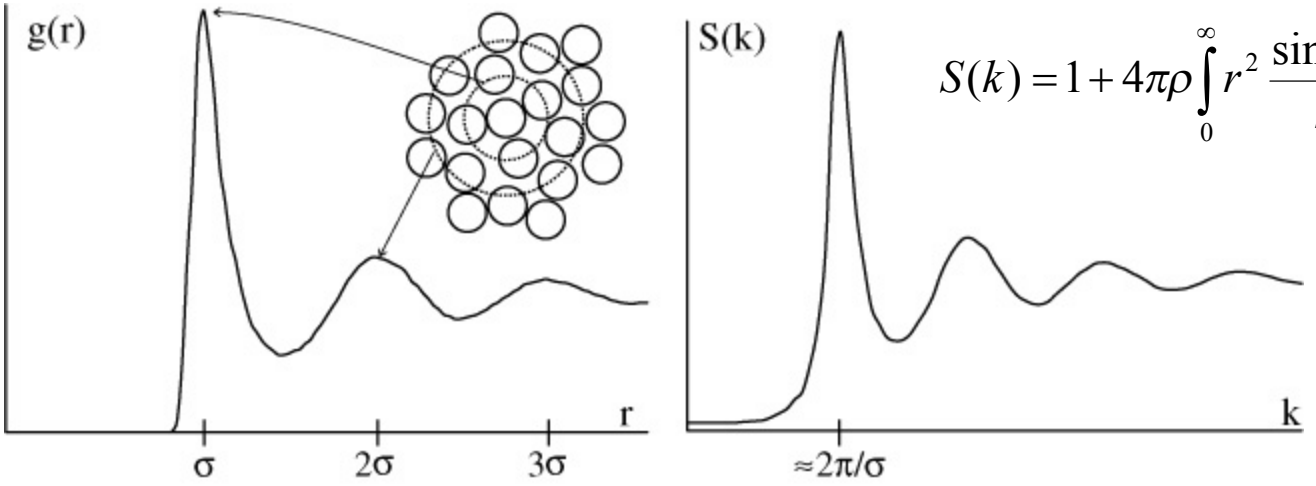
Typical fluid-like RDF

- Measurable via radiation-scattering

Structural Quantities (cont.)

– Structure Factor

$$S(k) = N^{-1}\left\langle \rho(k)\rho(-k)\right\rangle \qquad \rho(k) = \sum_{i=1}^{N} \exp\left[i\mathbf{k}\cdot\mathbf{r}_i\right]$$



$$S(k) = 1 + 4\pi\rho\int_0^\infty r^2 \frac{\sin(kr)}{kr} g(r)dr$$

– Intermediate Scattering Function

$$I(k,t) = N^{-1}\left\langle \rho(k,t)\rho(-k,0)\right\rangle$$

- Van Hove function

Temporal Correlation Functions

- Relation to transport coefficients
  - Linear Response Theory
    - Green-Kubo
      - Diffusion $$D = \frac{1}{3}\int_0^\infty \left\langle \mathbf{v}_i(t)\cdot\mathbf{v}_i(t')\right\rangle dt'$$
      - Shear Viscosity

$$\eta = \frac{V}{k_B T}\int_0^\infty \left\langle j_{\alpha\beta}(t)\cdot j_{\alpha\beta}(t')\right\rangle dt' \qquad j_{\alpha\beta}(t) = \frac{1}{V}\sum_{i=1}^{N}\left[\sum_{j\neq i}\frac{r_{ij}^{\alpha}(t) f_{ij}^{\beta}(t)}{2} + m_i v_i^{\alpha}(t) v_j^{\beta}(t)\right]$$

      - Bulk Viscosity
      - Thermal conductivity
- Others, e.g. orientation correlations, etc.
- Also useful in non-equilibrium settings

Einstein Relations

- Diffusion

$$2Dt = \frac{1}{3}\left\langle \left| \mathbf{r}_i(t) - \mathbf{r}_i(0) \right|^2 \right\rangle$$

- Viscosity

$$2\eta t = \frac{V}{k_B T}\left\langle \left(Q_{\alpha\beta}(t) - Q_{\alpha\beta}(0) \right)^2 \right\rangle$$

$$Q_{\alpha\beta} = \frac{1}{V}\sum_i r_i^{\alpha} p_i^{\beta}$$

9: Common Non-Equilibrium Calculations

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NNSA National Nuclear Security Administration

Sandia National Laboratories

Why NonEquilibrium MD (NEMD)?

- Classical Molecular Dynamics is a thermodynamic equilibrium technique
  - Newton's Equations of motion with pairwise central forces conserve energy
    - Microcanonical Ensemble
- What we are interested in is nonequilibrium properties
  - Transport: rheology

$$\boldsymbol{\sigma} = \eta\dot{\boldsymbol{\gamma}}$$

- Near equilibrium – fluctuations
  - Linear response
    - Effectively zero rate transport coefficients
    - Long-time for good statistics
- Far from equilibrium?
  - High rates, large gradients
  - Time dependent behavior

Equilibrium Steady States

- What happens when a constant force (through boundary conditions – applied gradient, or external field) is applied to Newton's Equations for particle dynamics?
  - For pairwise central forces, Newton's Equations yield Microcanonical Ensemble (NVE)
    - Thermodynamic equilibrium system
  - Constant force gives constant acceleration so kinetic energy (temperature) increases
- What to do?
  - Thermostat (on fluctuations about average) to balance energy input

$$k_B T = \frac{3(N-1)}{2} \left\langle \sum_i m_i (\mathbf{v}_i(t) - \mathbf{u}(r,t))^2 \right\rangle$$

Typical NEMD Techniques

- Non-Hamiltonian Systems – “perturb” equations of motion
  - SLLOD + Parrinello-Rahman
    - Shear flow
- Boundary Modifications
  - Lees-Edwards
    - Steady Couette Flow
  - Muller-Plathe
    - Shear or Heat flow
  - Deletion and insertion
    - Mass flow

Perturbations to Equations of Motion

- General Approach

$$\dot{\mathbf{q}} = \mathbf{p}/m + \mathbf{A}_{\mathbf{p}}(\mathbf{q},\mathbf{p}) \cdot \boldsymbol{\mathcal{F}}(t)$$

$$\dot{\mathbf{p}} = \mathbf{F} - \mathbf{A}_{\mathbf{q}}(\mathbf{q},\mathbf{p}) \cdot \boldsymbol{\mathcal{F}}(t)$$

- Shear
- Heat flow

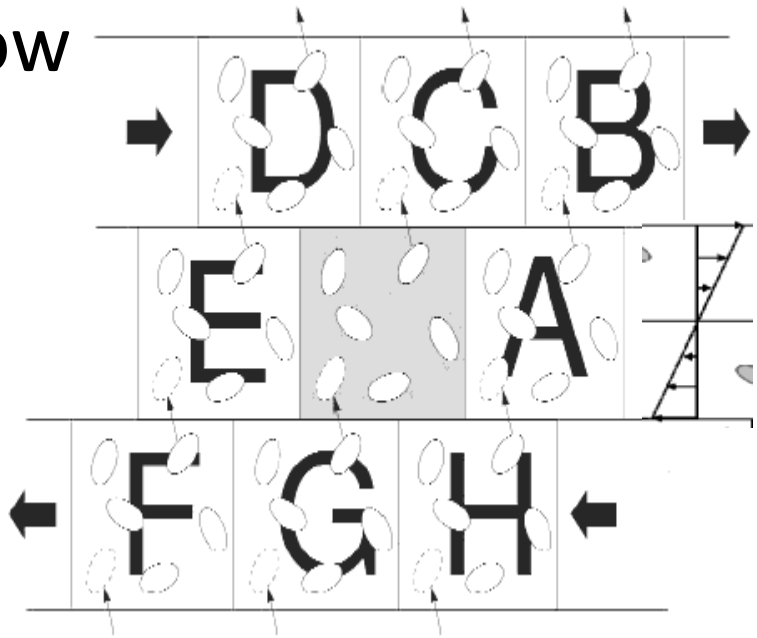
$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m_i$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \delta\varepsilon_i \boldsymbol{\mathcal{F}}(t) + \frac{1}{2}\sum_j \mathbf{F}_{ij}(\mathbf{r}_{ij} \cdot \boldsymbol{\mathcal{F}}(t)) - \frac{1}{2N}\sum_j \sum_k \mathbf{F}_{jk}(\mathbf{r}_{jk} \cdot \boldsymbol{\mathcal{F}}(t))$$

- Diffusion

Lees-Edwards Boundary Conditions

- Remap positions and velocities of particles crossing PBC
- Steady Shear (Couette) Flow
- Thermostat
  - E.g., Nose-Hoover
- No time dependent flow



SLLOD + Parinello-Rahman

- Apply Shear Perturbation to each particle
  - Deform Box/particle positions

$$\dot{\mathbf{q}}_i = \mathbf{p}_i / m_i + \mathbf{q}_i \cdot \nabla \mathbf{u}$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{p}_i \cdot \nabla \mathbf{u}$$

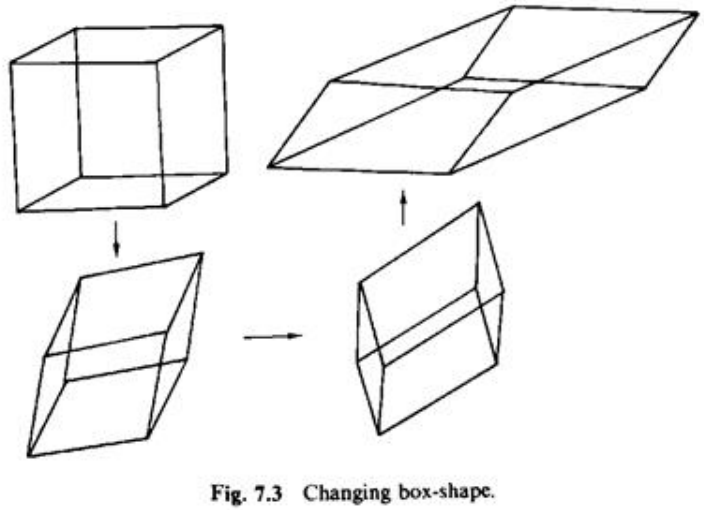
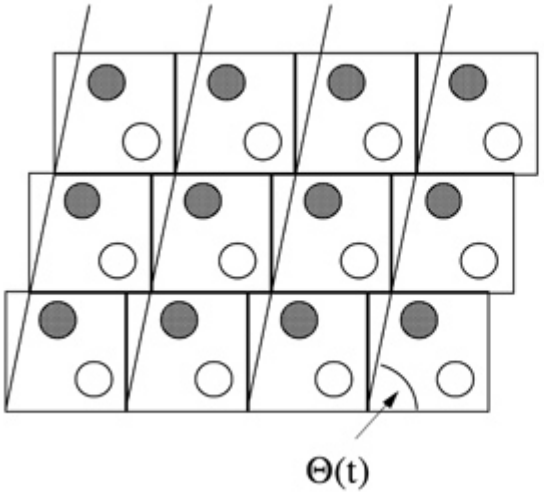
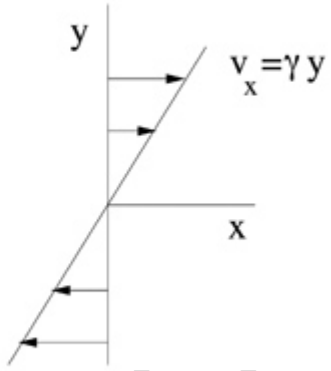


Fig. 7.3 Changing box-shape.

- Remap positions and/ velocities across PBC
- Thermostat!
  - E.g., Nose-Hoover





$$\nabla \mathbf{u}(\mathbf{r},t) = \begin{bmatrix} 0 & 0 \\ \gamma & 0 \end{bmatrix}$$

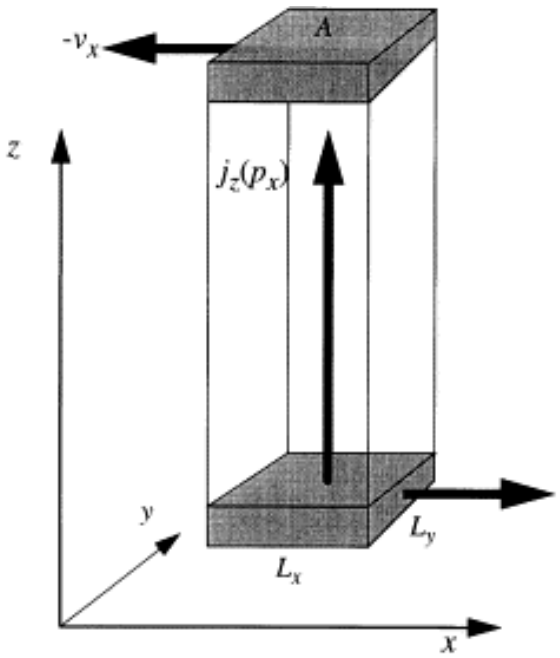
- Profile biased vs. profile unbiased

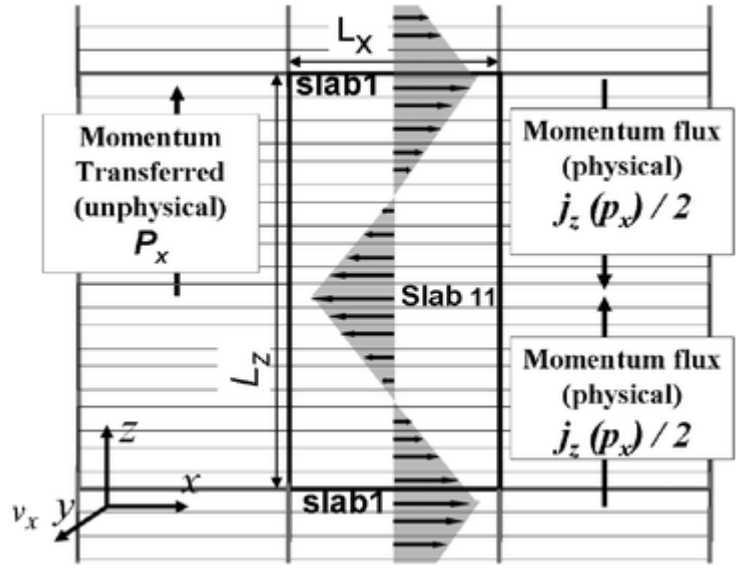
Muller-Plathe Approach

- Bin system in z
- Swap opposed velocities in top and bottom bins
  - Viscosity

$$j_z(p_x) = -\eta \frac{\partial v_x}{\partial z}$$

$$j_z(p_x) = \frac{P_{tot}}{2tL_xL_y}$$





  - Can swap “hot” and “cold” (largest difference in squared velocity magnitude) atoms for thermal conductivities

Additional NE Simulations

- Initial and boundary conditions
  - Phase changes
  - Concentration gradients
  - Evaporation
  - Shock