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85th Meeting of the Society of Rheology

6: Coarse-grained Applications

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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

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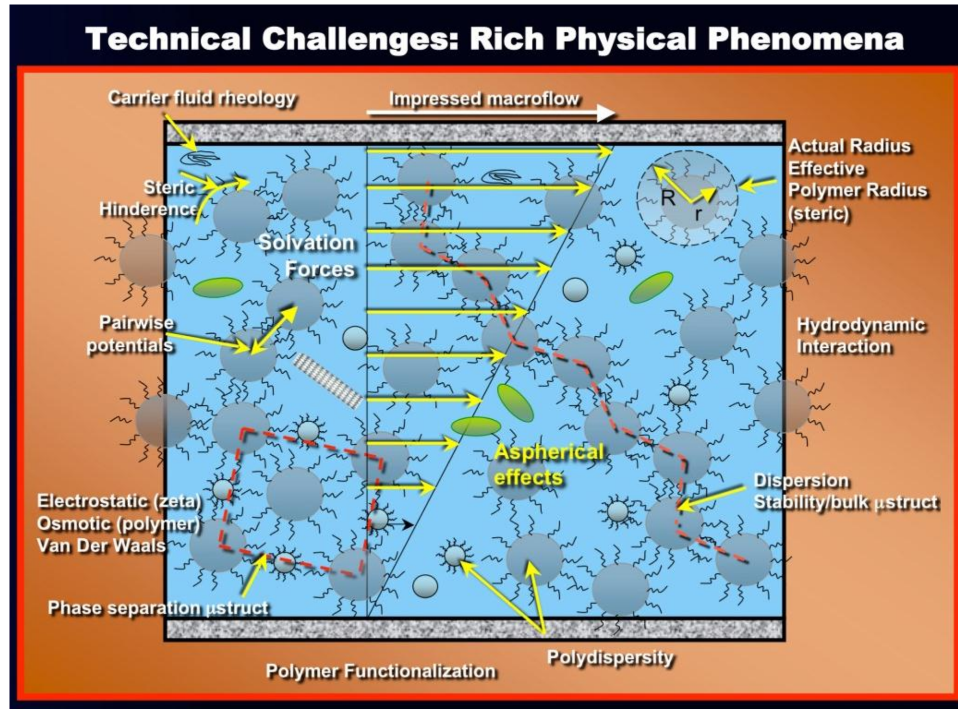
Computational Rheology of Complex Fluids

- Physical System
  - Colloids $d \sim 10 - 1000\ nm$, suspended in fluid
    - Concentration: $\phi \sim 0.5$
  - Shear 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	$a = 10nm$	$a = 1\mu m$
$M \approx \frac{4}{3}\pi a^3 \times 10^{-12} \frac{\mathrm{g}}{\mu\mathrm{m}^3}$	$4.19 \times 10^{-18}\mathrm{g}$	$4.19 \times 10^{-12}\mathrm{g}$
$\frac{\xi_E}{\xi_S} \approx 1.6 \times 10^2 a$	≈ 1.6	$\approx 1.6 \times 10^2$
$\xi_S = 6\pi\eta a \approx 1.9 \times 10^{-5} a$	$\approx 1.9 \times 10^{-7} \frac{\mathrm{g}}{\mathrm{s}}$	$\approx 1.9 \times 10^{-5} \frac{\mathrm{g}}{\mathrm{s}}$
$D_{\mathrm{col}} \approx \frac{k_B T}{6\pi\eta a} \approx \frac{0.2}{a}$	$\approx 20 \frac{\mu\mathrm{m}^2}{\mathrm{s}}$	$\approx 0.2 \frac{\mu\mathrm{m}^2}{\mathrm{s}}$

Hydrodynamic numbers	$a = 10nm$	$a = 1\mu m$
$\mathrm{Pe} = \frac{v_S a}{D_{\mathrm{col}}} \approx 5 v_S a^2$	≈ 0.005	≈ 50
$\mathrm{Re} = \frac{v_S a}{\nu} \approx 10^{-6} v_S a$	$\approx 10^{-7}$	$\approx 10^{-5}$
$\mathrm{Kn} = \frac{\lambda_{\mathrm{free}}}{a} \approx \frac{0.3}{a} \times 10^{-3}$	≈ 0.03	≈ 0.0003
$\mathrm{Ma} = \frac{v_S}{c_s} \approx 6.76 \times 10^{-10} v_S$	$\approx 6.8 \times 10^{-10}$	$\approx 6.8 \times 10^{-10}$

Time-scales	$a = 10nm$	$a = 1\mu m$
$\tau_D = \frac{a^2}{D_{\mathrm{col}}} \approx 5a^3$	$\approx 5 \times 10^{-6}\mathrm{s}$	$\approx 5\ \mathrm{s}$
$t_S = \frac{a}{v_S} = \frac{\tau_\nu}{Re} = \frac{\tau_D}{Pe}$	$= 0.001\ \mathrm{s}$	$= 0.1\ \mathrm{s}$
$\tau_\nu = \frac{a^2}{\nu} \approx 10^{-6} a^2$	$\approx 10^{-10}\mathrm{s}$	$\approx 10^{-6}\mathrm{s}$
$\tau_B = \frac{M}{\xi_S} = \frac{2}{9}\tau_\nu$	$\approx 2.2 \times 10^{-11}\mathrm{s}$	$\approx 2.2 \times 10^{-7}\mathrm{s}$
$t_{cs} = \frac{a}{c_s} \approx 6.7 \times 10^{-10} a$	$\approx 6.7 \times 10^{-12}\mathrm{s}$	$\approx 6.7 \times 10^{-10}\mathrm{s}$

- 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: $\tau_\nu/t_{cs} \sim ac_s/\nu \sim 1$
- 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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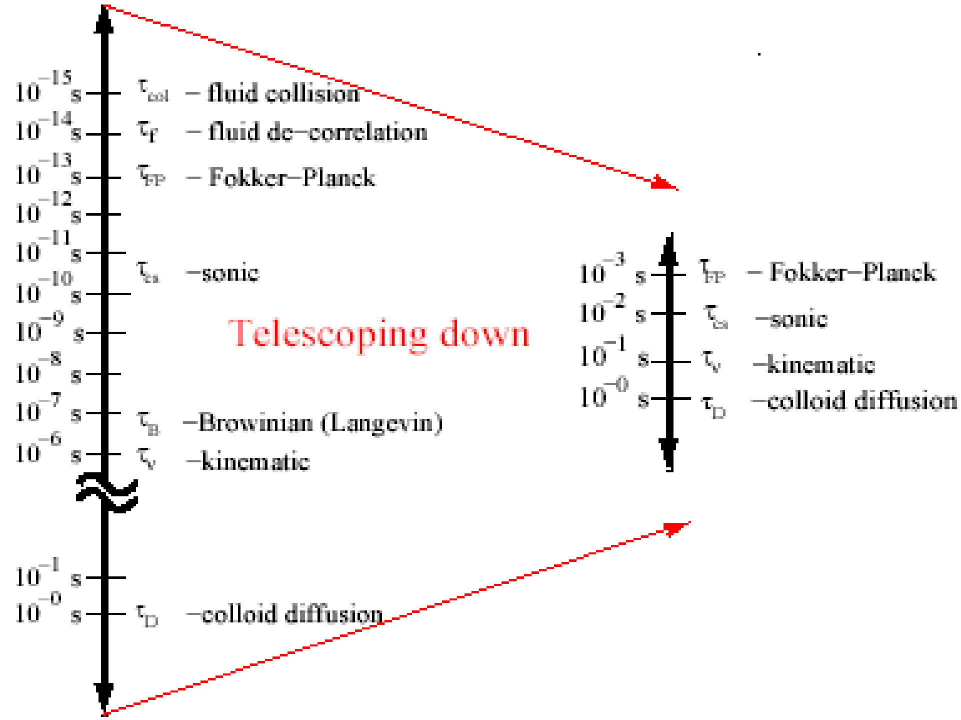
Length and Time Scales

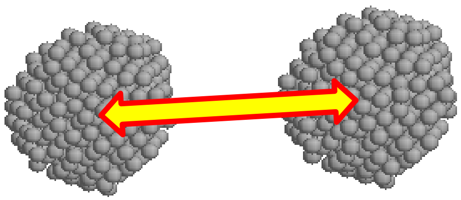
- Large systems & long times
  - $N > O(10^4)$ colloids
  - $T \sim O(10^7)\delta t_{coll}$
- Can we resolve the relevant phenomena?
- Options?
  - Ignore certain phenomena
  - Collapse ("telescope") timescales
  - Coarse-grain



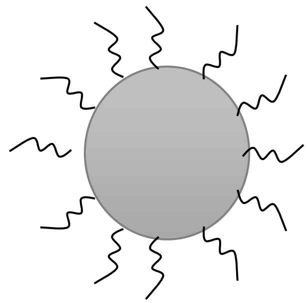
Time scales for 1 μm colloid in water.
From Padding and Louis (2006) cond-mat/0603391

Coarse-graining

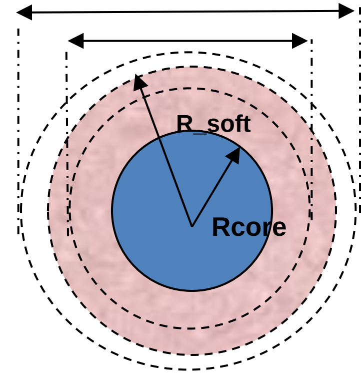
Particles



All atom representation of colloids

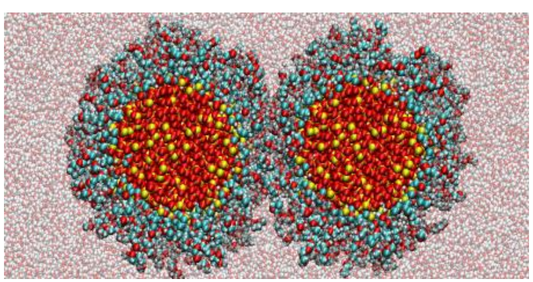


Integration to Hammaker's Equation for colloid



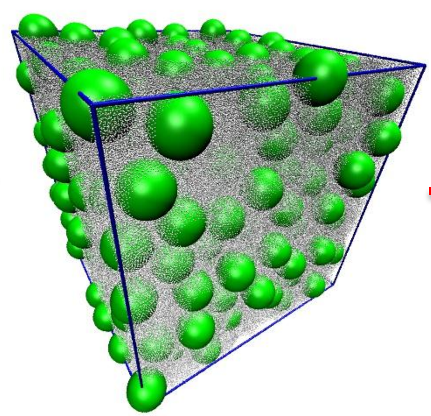
- **Polymer layer parameters (osmotic and steric/structural effects)**
- **Structural constants (polymer and hard core)**

Solvent



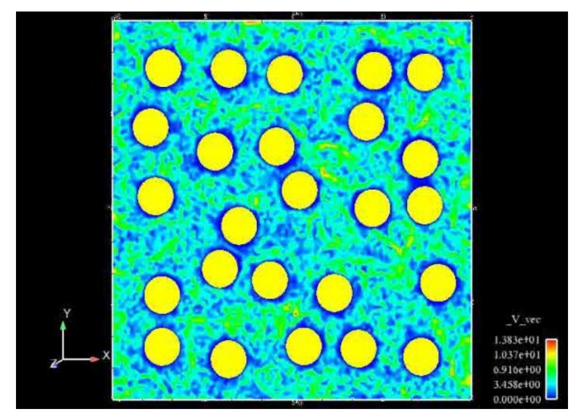
All atom Molecular Dynamics

(Lane et al.)



SRD/DPD: dual particle approach

(In 't Veld et al.)



Continuum: FEM

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Example: Colloid Dynamics

- Generalized Langevin Equation (with interactions)

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

- Approaches to hydrodynamics

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

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

  - Ignore colloid particle inertia
    - Small Stokes number, $St = Re_p\rho_c/\rho_f$, or large friction $\mu = \rho_f\nu$
    - Smolukowski limit
- 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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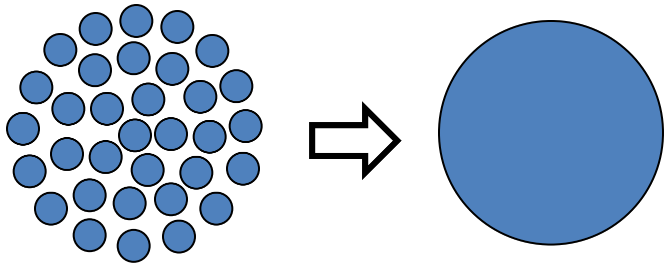
Effective Potentials in LAMMPS

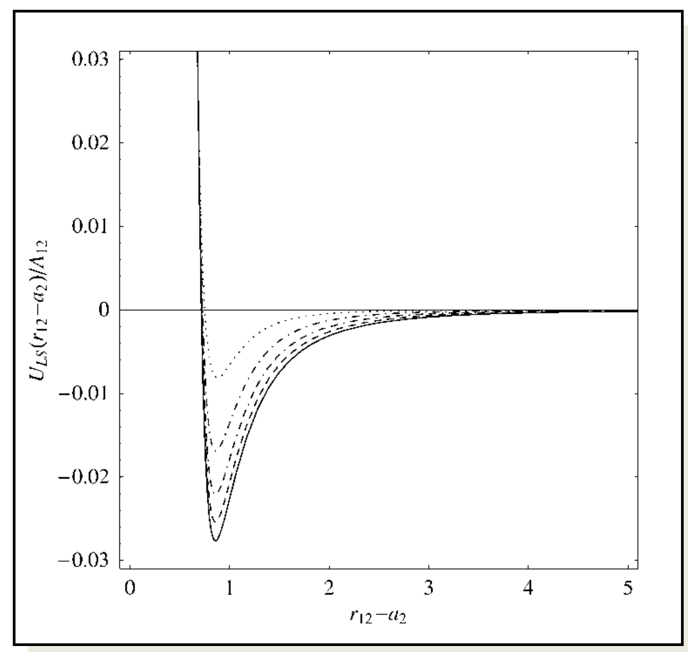
- Colloid Package
  - DLVO: van der Waals attraction + electrostatic repulsion
    - `pair_colloid`
    - `pair_yukawa/colloid`
    - `pair_hybrid overlay`
- Numerically Calculated
  - `pair_table`
- Granular Package
  - Hertzian Contact Mechanics and Coulomb friction: Noncolloidal Particles
    - `pair_hertz_history`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

Colloid Interactions



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

$$
\begin{aligned}
U_A &= -\frac{A_{12}}{6}\Bigg[\\
&\quad \frac{2a_1a_2}{r_{12}^2-(a_1+a_2)^2}+\frac{2a_1a_2}{r_{12}^2-(a_1-a_2)^2}+\ln\left(\frac{r_{12}^2-(a_1+a_2)^2}{r_{12}^2-(a_1-a_2)^2}\right)\Bigg] \\
U_R &= \frac{A_{12}}{37800}\frac{\sigma^6}{r_{12}}\Bigg[\\
&\quad \frac{r_{12}^2-7r_{12}(a_1+a_2)+6\left(a_1^2+7a_1a_2+a_2^2\right)}{(r_{12}-a_1-a_2)^7} \\
&\quad +\frac{r_{12}^2+7r_{12}(a_1+a_2)+6\left(a_1^2+7a_1a_2+a_2^2\right)}{(r_{12}+a_1+a_2)^7} \\
&\quad -\frac{r_{12}^2+7r_{12}(a_1-a_2)+6\left(a_1^2-7a_1a_2+a_2^2\right)}{(r_{12}+a_1-a_2)^7} \\
&\quad -\frac{r_{12}^2-7r_{12}(a_1-a_2)+6\left(a_1^2-7a_1a_2+a_2^2\right)}{(r_{12}-a_1+a_2)^7}\Bigg] \\
U &= U_A+U_R, \qquad r_{12}<r_c
\end{aligned}
$$



[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

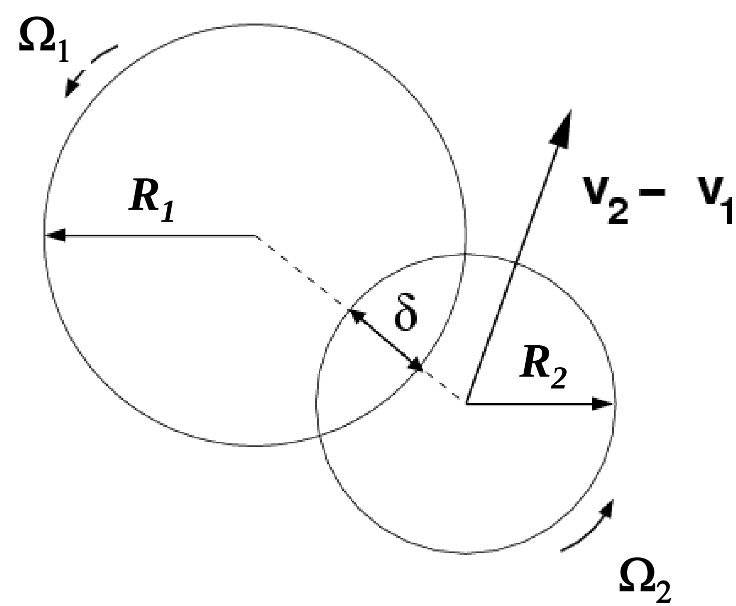
$$F_n = f(\delta / R)(k_n \delta - \frac{m}{2} \varsigma_n v_n)$$

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

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

Δs_t Elastic tangential displacement

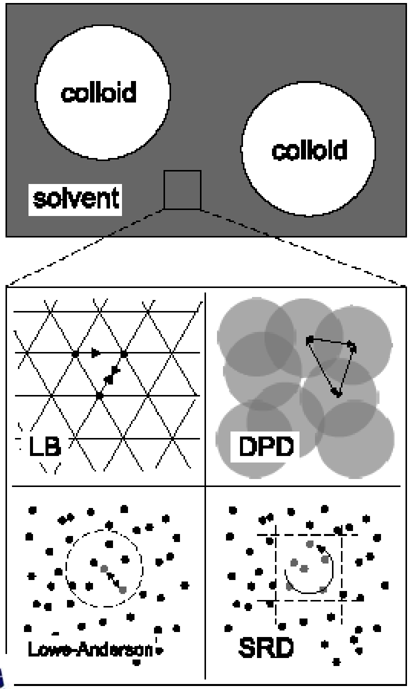
$F_t \le \mu F_n$ Coulomb Failure Criterion

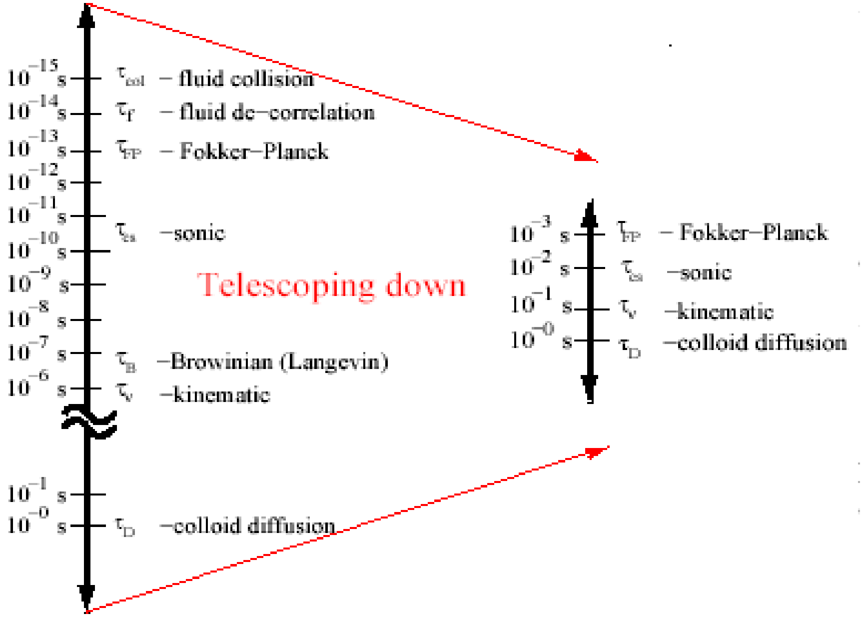


Brilliantov et al. (2000)

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

- Brownian Dynamics (with inertia)
  - `fix_langevin`
- FLD (with and without inertia)
  - `pair_lubricate (pair_lubricateU)`
  - `pair_brownian`
  - `pair_hybrid overlay`
- Generalized Langevin Equation
- DPD
  - `pair_dpd`
- Multi-Particle Collision Dynamics (SRD)
  - `fix_srd`
- Lattice-Boltzmann (coming soon)

Case Study: Langevin Eqn. + Interactions

- Brownian Dynamics Simulations
  - Markov assumption

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

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

  - $\mathbf{F}^B$ 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

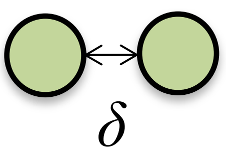
Simple Hydrodynamic Interactions

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

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

Isotropic Constant
(mean-field mobility)

$$\boxed{R = R_0 + R_\delta}$$

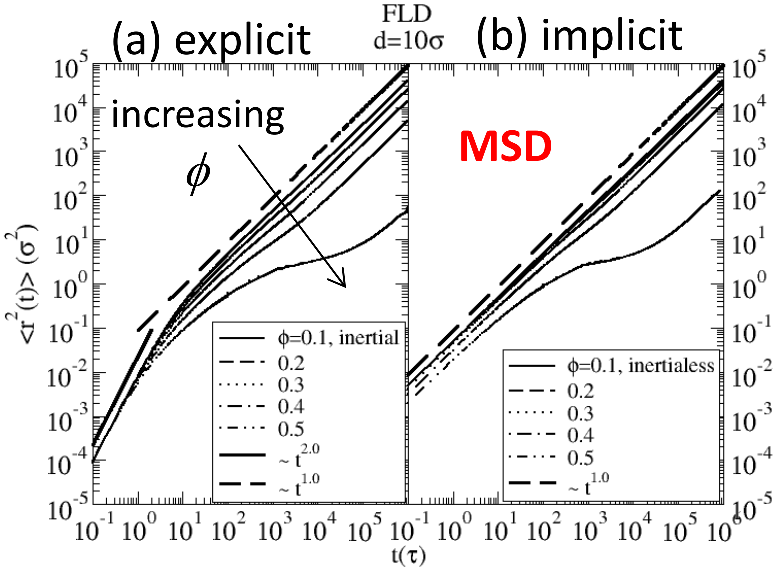


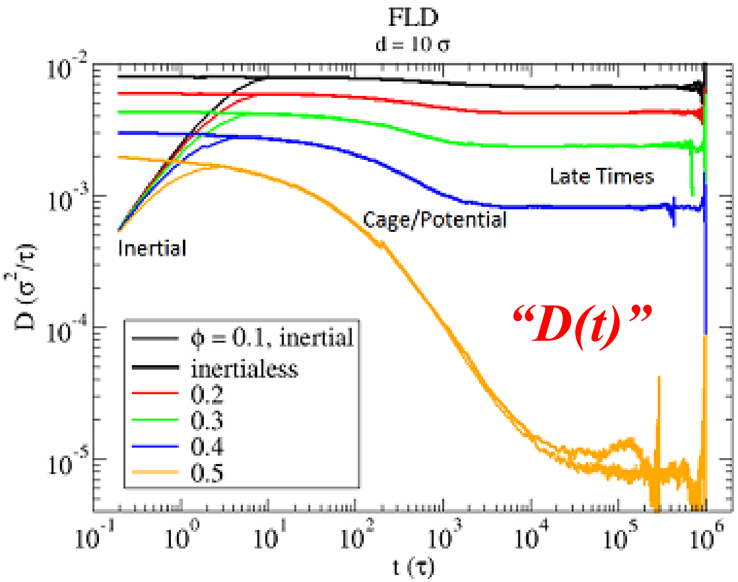
$$\mathbf{R}_0 = 3\pi\mu d(1+2.16\phi)\mathbf{I}$$

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

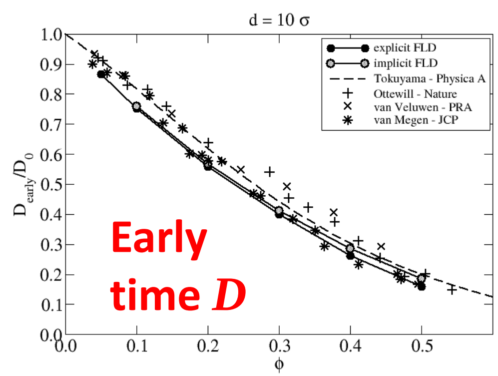
Kumar and Higdon, Phys Rev E, 82, 051401 (2010)
Ball and Melrose, Physica A, 247, 444-472 (1997)

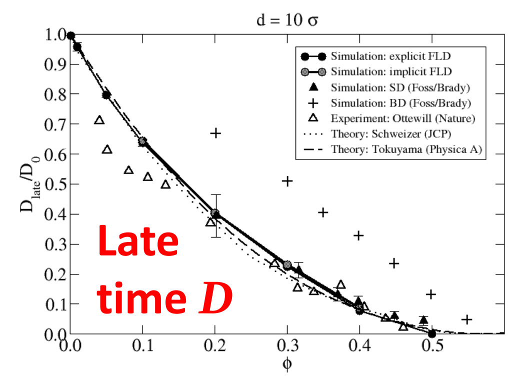
Simulation Results: MSD Validation





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





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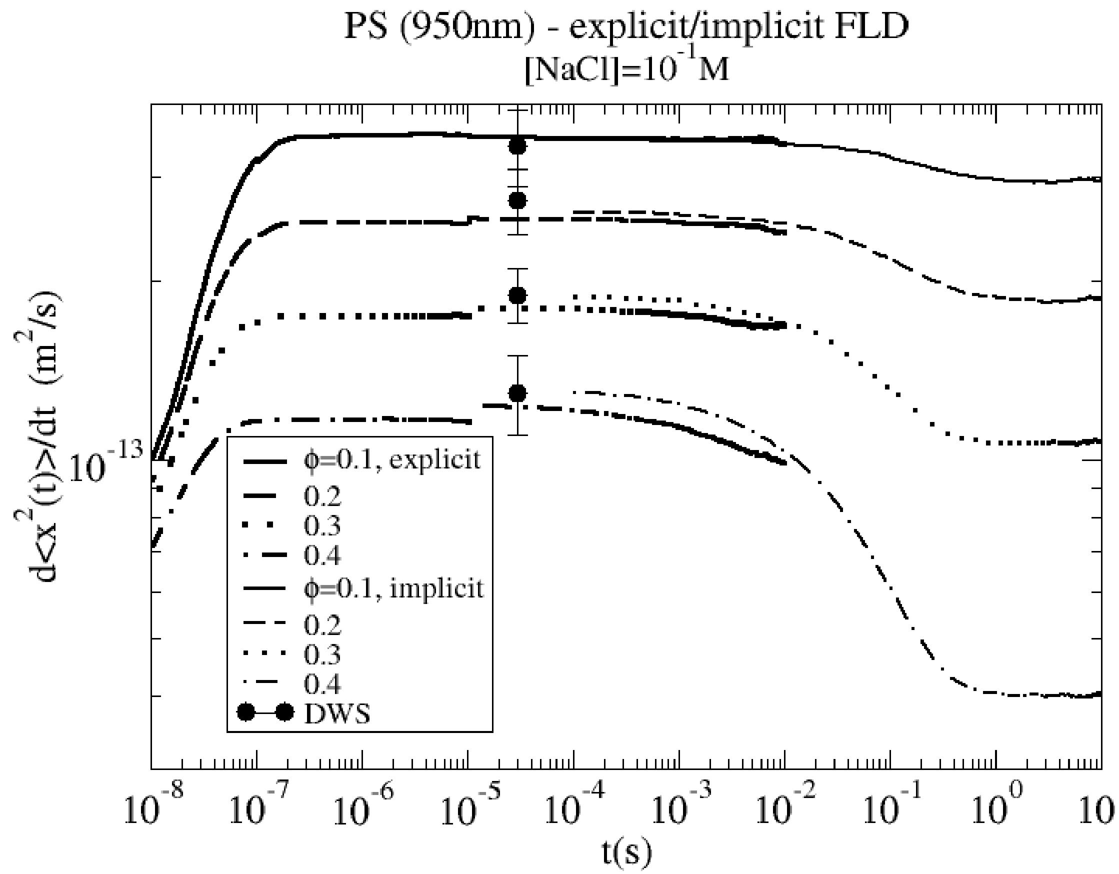
Combining Techniques

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



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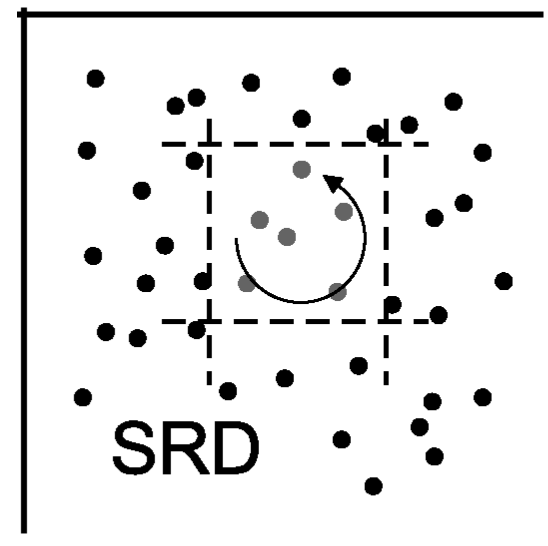
Stochastic Rotation Dynamics (SRD)

- 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



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

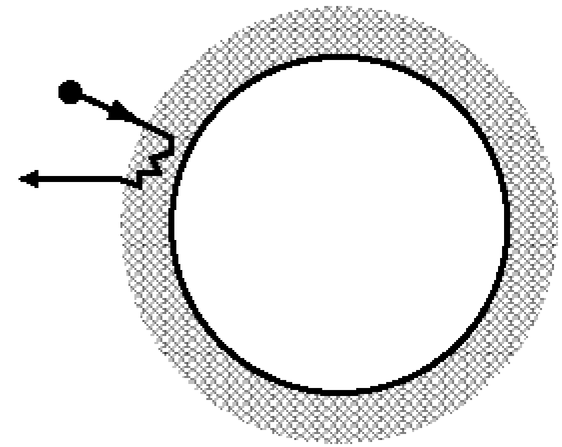
Padding and Louis (2006) http://arxiv.org/pdf/cond-mat/0603391v3.pdf
Gompper et al. (2008) http://arxiv.org/pdf/0808.2157.pdf

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, $U(r_{coll}-r_{SRD})$

Selecting Parameters for LJ System

- Dynamics of interest

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

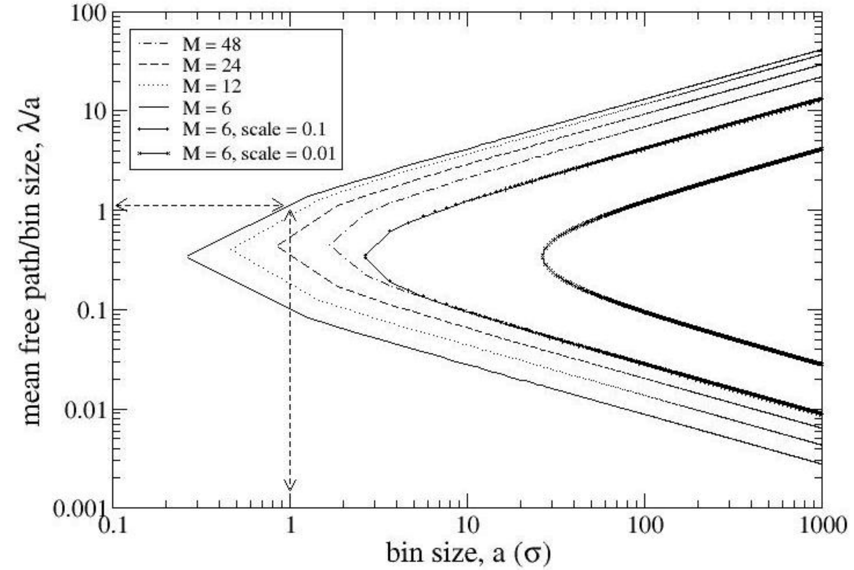
$$Pe = \frac{\tau_D}{t_s} = \frac{4R^2 / D_{coll}}{2R/u_s} = 12\pi u_s R^2 \left(\frac{\rho_f \nu_f}{k_B T}\right)$$

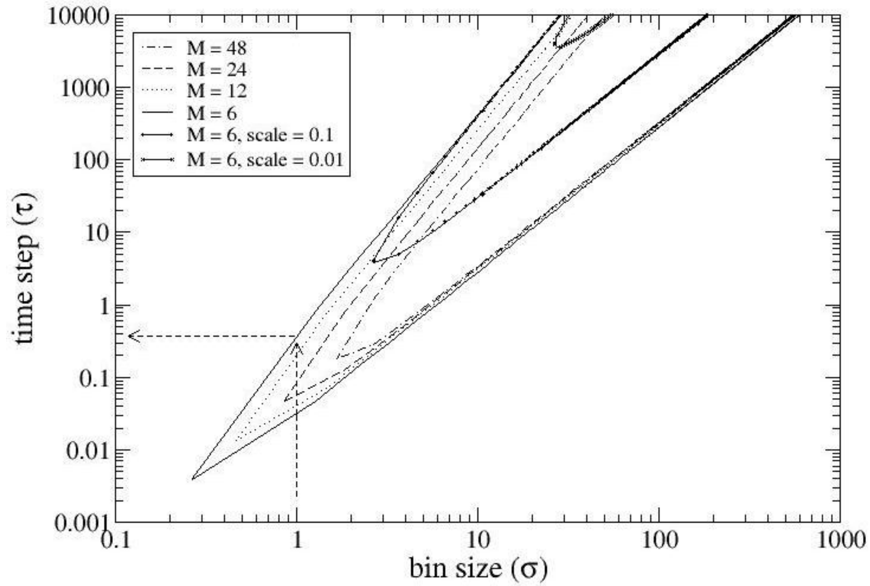
- Physical parameters: $\rho_f, \nu_f, k_B T, R, P$
- Computational parameters

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

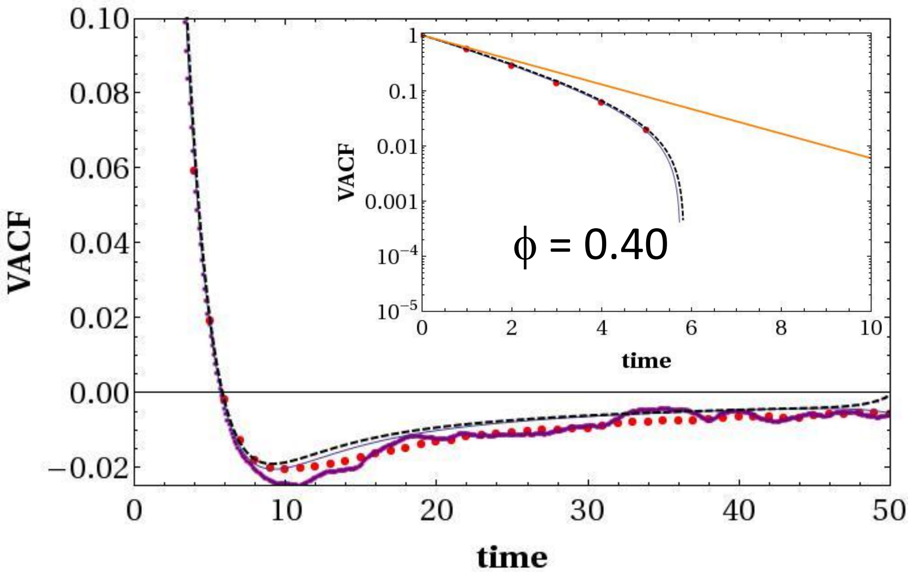
$$\lambda = \Delta t \sqrt{Mk_B T / \rho_f \Delta x^3}, \quad \lambda << R$$

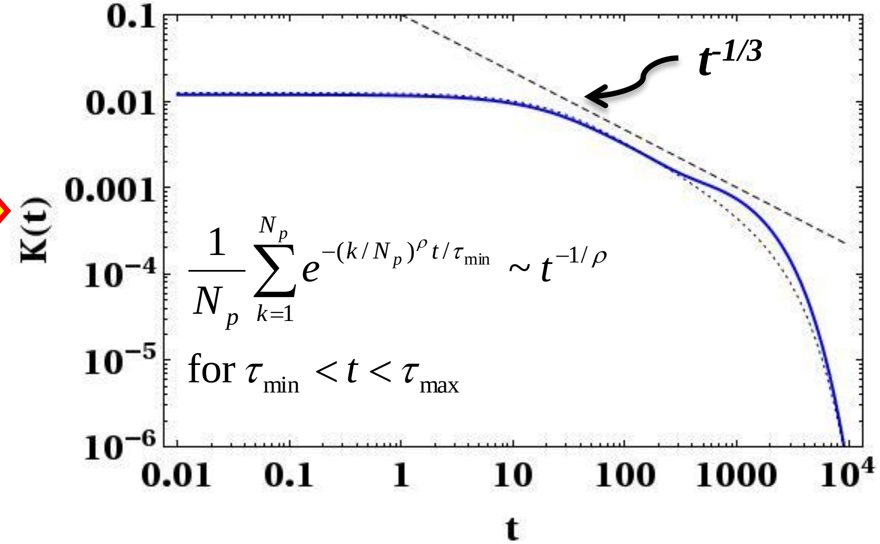
$$\rho_f = Mm_f / \Delta x^3, \quad \frac{P}{k_B T} = \frac{M}{\Delta x^3}, \quad \Delta x < R/2$$





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

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

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

  - Non-Markovian: Generalized Langevin

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

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

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

“Sticky” Particle Simulations: JKR Adhesion Theory for “Stiff” Spheres

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

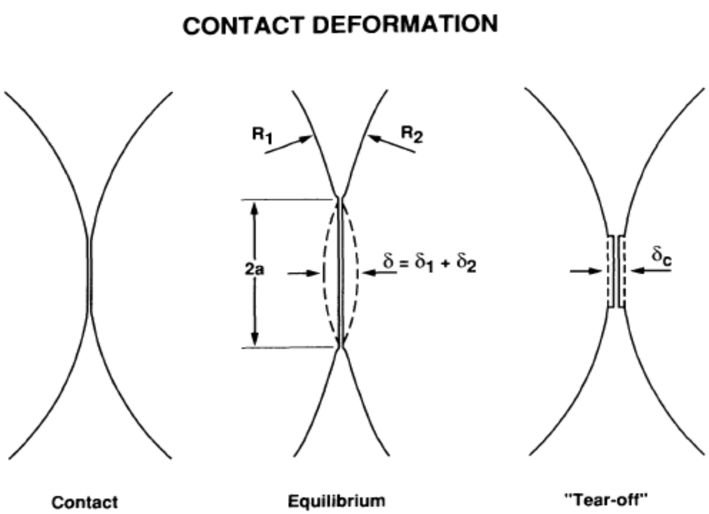
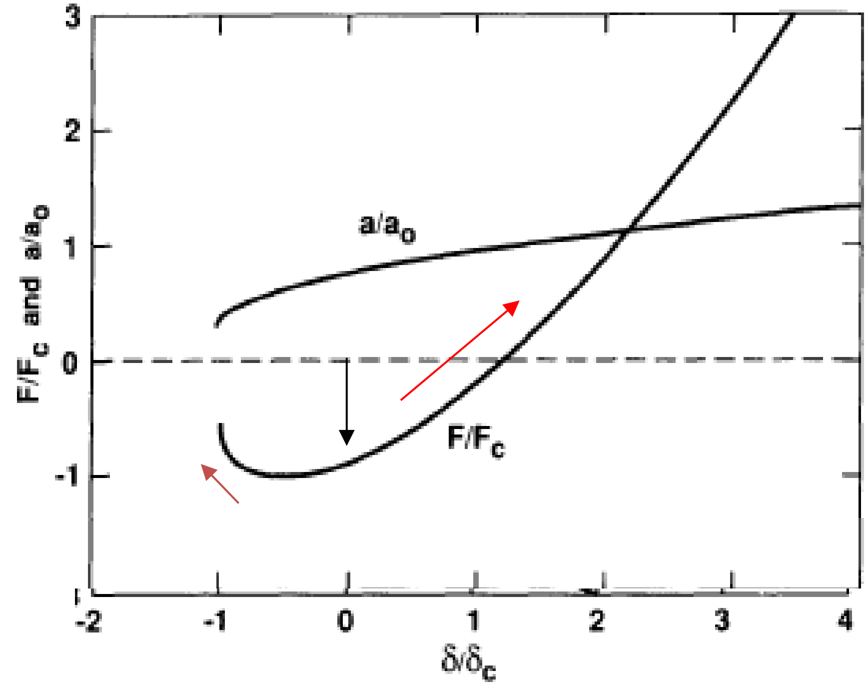


FIG. 2.—Schematic of the deformation during the collision process. At contact, a finite contact area is rapidly formed. This contact area grows in size during the compression and slowing down of the collision partners. Upon reversal of the collision process, the two grains will pull out a neck area, 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

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

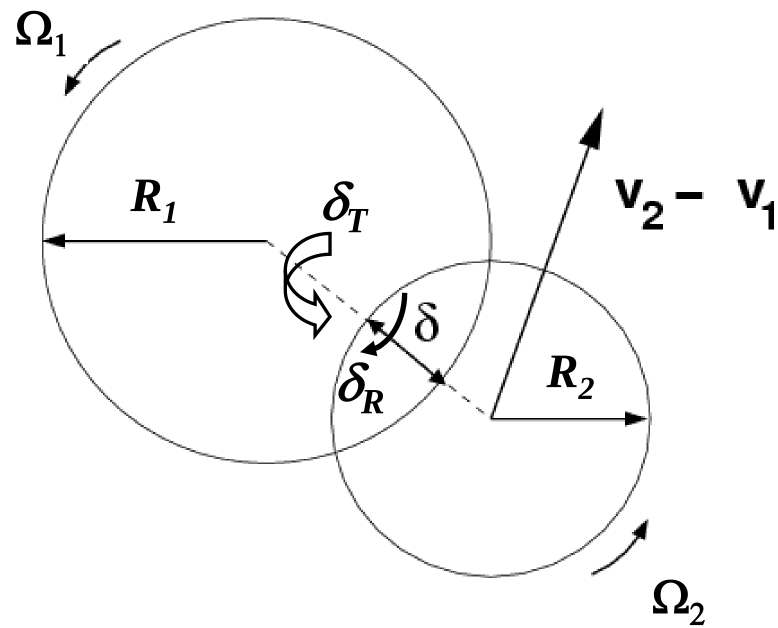
$$\mathbf{M}_i = \sum_j R_i F_t (\mathbf{n} \times \mathbf{t}_S) + M_R(\mathbf{t}_R \times \mathbf{n}) + M_T \mathbf{n}$$

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

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

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

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



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