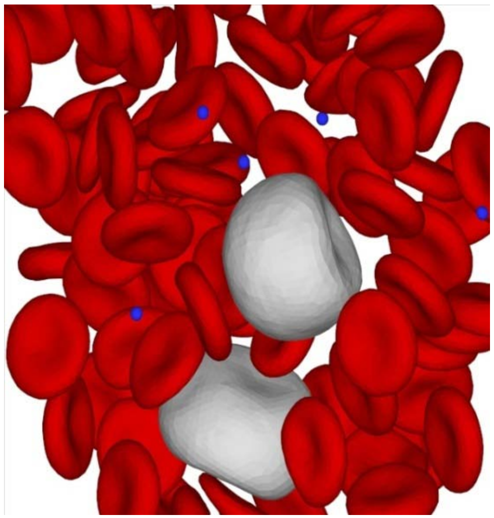
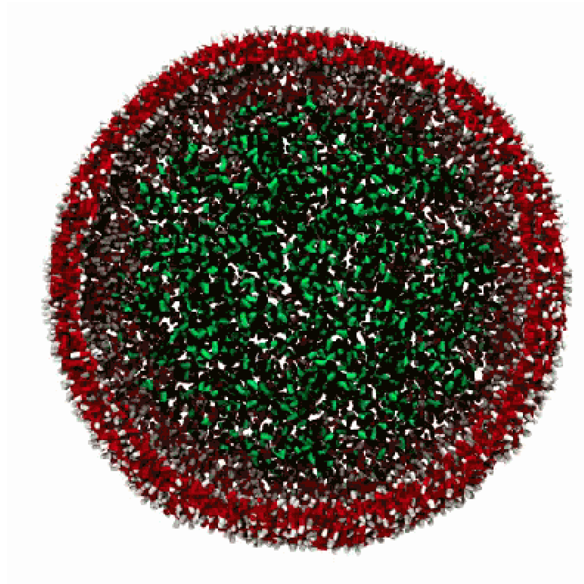
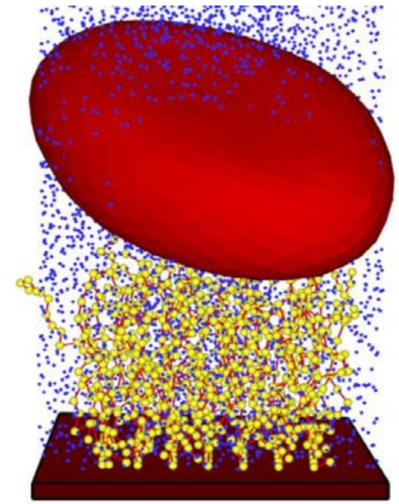
# Dissipative Particle Dynamics: Foundation, Evolution and Applications

## *Lecture 2:* Theoretical foundation and parameterization

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# Outline

1. Background
2. Fluctuation-dissipation theorem
3. Kinetic theory
4. DPD ----> Navier-Stokes
5. Navier-Stokes ----> (S)DPD
6. Microscopic ----> DPD
    - Mori-Zwanzig formalism

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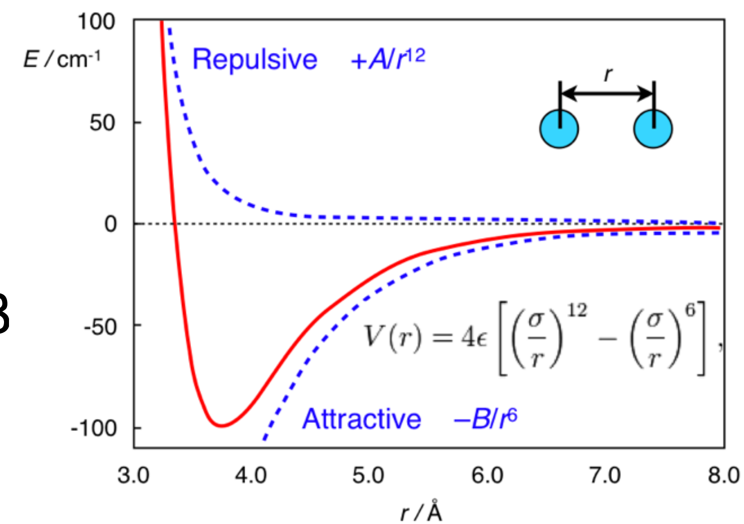
# 1. Background

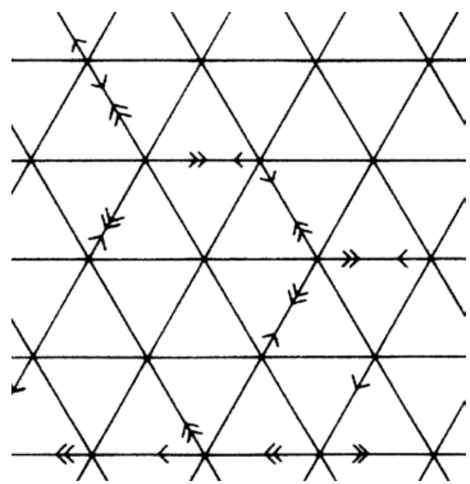
- Molecular dynamics (e.g. Lennard-Jones):
  - Lagrangian nature
  - Stiff force
  - Atomic time step

(Allen & Tildesley, Oxford Univ. Press, 198




- Coarse-grained (1980s): Lattice gas automata
  - Mesoscopic collision rules
  - Grid based particles

(Frisch et al, PRL, 1986)



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# Mesoscale + Langrangian?

- Physics intuition: Let particles represent clusters of molecules and interact via pair-wise forces

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

Conditions:

- Conservative force is softer than Lennard-Jones
- System is thermostated by two forces $\vec{\mathbf{F}}^{R}, \vec{\mathbf{F}}^{D}$
- Equation of motion is Lagrangian as:

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

This innovation is named as DPD method!

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Hoogerbrugge & Koelman, EPL, 1992

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# 2. Fluctuation-dissipation theorem

- Langevin equations (SDEs)

$$
\begin{cases}
\mathrm{d}\boldsymbol{r}_i = \dfrac{\boldsymbol{p}_i}{m_i}\,\mathrm{d}t \\[2ex]
\mathrm{d}\boldsymbol{p}_i = \left[\sum\limits_{j\neq i}\boldsymbol{F}^{\mathrm{C}}_{ij}(\boldsymbol{r}_{ij}) + \sum\limits_{j\neq i} -\gamma\omega_{\mathrm{D}}(r_{ij})(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij})\boldsymbol{e}_{ij}\right]\mathrm{d}t + \sum\limits_{j\neq i}\sigma\omega_{\mathrm{R}}(r_{ij})\boldsymbol{e}_{ij}\,\mathrm{d}W_{ij}
\end{cases}
$$

With $\mathrm{d}W_{ij} = \mathrm{d}W_{ji}$ the independent Wiener increment: $\mathrm{d}W_{ij}\,\mathrm{d}W_{i'j'} = (\delta_{ii'}\delta_{jj'} + \delta_{ij'}\delta_{ji'})\,\mathrm{d}t$

- Corresponding Fokker-Planck equation (FPE)

$$
\partial_t \rho(r,\,p;\,t) = L_{\mathrm{C}}\rho(r,\,p;\,t) + L_{\mathrm{D}}\rho(r,\,p;\,t)
$$

$$
\begin{cases}
L_{\mathrm{C}}\rho(r,\,p;\,t) \equiv -\left[\sum\limits_{i}\dfrac{\boldsymbol{p}_i}{m}\dfrac{\partial}{\partial\boldsymbol{r}_i} + \sum\limits_{i,\,j\neq i}\boldsymbol{F}^{\mathrm{C}}_{ij}\dfrac{\partial}{\partial\boldsymbol{p}_i}\right]\rho(r,\,p;\,t) \\[2ex]
L_{\mathrm{D}}\rho(r,\,p;\,t) \equiv \sum\limits_{i,\,j\neq i}\boldsymbol{e}_{ij}\dfrac{\partial}{\partial\boldsymbol{p}_i}\left[\gamma\omega_{\mathrm{D}}(r_{ij})(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij}) + \dfrac{\sigma^2}{2}\omega^2_{\mathrm{R}}(r_{ij})\boldsymbol{e}_{ij}\left(\dfrac{\partial}{\partial\boldsymbol{p}_i} - \dfrac{\partial}{\partial\boldsymbol{p}_j}\right)\right]\rho(r,\,p;\,t)
\end{cases}
$$

# 2. Fluctuation-dissipation theorem

- **Gibbs distribution:** steady state solution of FPE

$$\rho^{\mathrm{eq}}(r, p) = \frac{1}{Z}\exp[-H(r, p)/k_{\mathrm{B}}T] = \frac{1}{Z}\exp\left[-\left(\sum_i \frac{p_i^2}{2m_i} + V(r)\right)\Big/ k_{\mathrm{B}}T\right]$$

Conservative Potential $\mathbf{F}^C = -\nabla V(r)$ ⟶ $L_{\mathrm{C}}\rho^{\mathrm{eq}} = 0$

Require $L_{\mathrm{D}}\rho^{\mathrm{eq}} = 0$ Energy dissipation and generation balance

**DPD version of fluctuation-dissipation theorem**

$$\omega_{\mathrm{R}}(r) = \omega_{\mathrm{D}}^{1/2}(r) \qquad \sigma = (2k_{\mathrm{B}}T\gamma)^{1/2}$$

DPD can be viewed as canonical ensemble (NVT)

Espanol & Warren, EPL, 1995

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# 3. Kinetic theory

How to choose simulation parameters?

Strategy: match DPD thermodynamics to atomistic system

I. How to choose repulsion parameter? (See Lecture I)

Match the static thermo-properties, i.e.,

Isothermal compressibility (water)

Mixing free energy, Surface tension (polymer blends)

II. How to choose dissipation (or fluctuation) parameter?

Match the dynamic thermo-properties, i.e.,

Self-diffusion coefficient, kinematic viscosity

(however, can not match both easily)

Schmidt number $\mathrm{Sc} = \nu / D$ usually lower than atomic fluid

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# Friction parameters for simple fluids

Simple argument by Groot & Warren, JChemPhys., 1997

Consider an uniform linear flow $v_\alpha = e_{\alpha\beta} r_\beta$

Dissipative contribution to stress

$$\sigma_{\alpha\beta} = \frac{1}{V}\left\langle \sum_{i>j} r_{ij\alpha} \mathbf{F}^{\mathrm{D}}_{ij\beta} \right\rangle = \frac{\rho^2}{2}\int d^3\mathbf{r}\ \gamma w^{\mathrm{D}}(r) r_\alpha \hat{r}_\beta \hat{r}_\gamma r_\delta\, e_{\gamma\delta} = \frac{2\pi\gamma\rho^2}{15}\int_0^\infty dr\ r^4 w^{\mathrm{D}}(r)[e_{\alpha\beta} + e_{\beta\alpha} + \delta_{\alpha\beta} e_{\gamma\gamma}]$$

Dissipative viscosity $\eta^{\mathrm{D}} = \frac{2\pi\gamma\rho^2}{15}\int_0^\infty dr\ r^4 w^{\mathrm{D}}(r)$

---

Motion of single particle:

ignore conservative forces, average out other particle velocities

$$\frac{d\mathbf{v}_i}{dt} + \frac{\mathbf{v}_i}{\tau} = \mathbf{F}^{\mathrm{R}}$$

$$\frac{1}{\tau} = \sum_{j\neq i} \gamma w^{\mathrm{D}}(r_{ij}) \frac{\hat{\mathbf{r}}_{ij}\cdot\hat{\mathbf{r}}_{ij}}{3} = \frac{4\pi\gamma\rho}{3}\int_0^\infty dr\ r^2 w^{\mathrm{D}}(r)$$

$$\langle \mathbf{F}^{\mathrm{R}} \rangle = 0, \quad \langle \mathbf{F}^{\mathrm{R}}(t)\cdot\mathbf{F}^{\mathrm{R}}(t') \rangle = 4\pi\sigma^2\rho\int_0^\infty dr\ r^2[w^{\mathrm{R}}(r)]^2\,\delta(t-t')$$

Self-diffusion coefficient

$$D = \frac{1}{3}\int_0^\infty dt \langle \mathbf{v}_i(0)\cdot\mathbf{v}_i(t)\rangle = \tau k_{\mathrm{B}} T.$$

Viscosity $\nu \approx \nu^{\mathrm{K}} + \nu^{\mathrm{D}} = D/2 + \eta^{\mathrm{D}}/\rho$

# Kinetic theory: Fokker-Planck-Boltzmann Equation

Marsh et al, EPL & PRE, 1997

## Single-particle and pair distribution functions

$$f(x,t) = \langle \sum_i \delta(x - x_i(t)) \rangle \qquad f^{(2)}(x,x',t) = \langle \sum_{i \neq j} \delta(x - x_i(t)) \delta(x' - x_j(t)) \rangle$$

Assume molecular chaos $\quad f^{(2)}(x,x',t) \; = \; f(x,t) f(x',t)$

## Fokker-Planck-Boltzmann equation

$$\partial_t f(x) + v \cdot \nabla f(x) = I(f)$$

with collision term

$$I(f) = \partial \cdot \int \mathrm{d}x' \gamma(x,x') f(x') f(x) + \frac{1}{2} \partial\partial : \int \mathrm{d}x' \sigma(x,x') \sigma(x,x') f(x') f(x)$$

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# Kinetic theory: dynamic properties

Integration of FPB over v yields continuity equation

$$\partial_t n = -\boldsymbol{\nabla} \cdot n\boldsymbol{u}.$$

Multiplying FPB by v and integrate over v yields momentum equation

$$\partial_t \rho \boldsymbol{u} = -\boldsymbol{\nabla} \cdot \int \mathrm{d}\boldsymbol{v}\boldsymbol{v}\boldsymbol{v} f(x) - m \int \mathrm{d}\boldsymbol{v}\mathrm{d}x' \gamma(x,x') f(x') f(x) \equiv -\boldsymbol{\nabla} \cdot (\rho \boldsymbol{u}\boldsymbol{u} + \boldsymbol{\Pi}_\mathrm{K} + \boldsymbol{\Pi}_\mathrm{D})$$

kinetic part of the pressure tensor

$$\boldsymbol{\Pi}_\mathrm{K} = \int \mathrm{d}\boldsymbol{v} m \boldsymbol{v}\boldsymbol{v} f - \rho \boldsymbol{u}\boldsymbol{u} = \int \mathrm{d}\boldsymbol{v} m \boldsymbol{V}\boldsymbol{V} f, \text{ where } \boldsymbol{V} = \boldsymbol{v} - \boldsymbol{u}(\boldsymbol{r},t)$$

dissipative part of the pressure tensor

$$\boldsymbol{\nabla} \cdot \boldsymbol{\Pi}_\mathrm{D} = m\gamma \int \mathrm{d}\boldsymbol{R} w(R) \widehat{\boldsymbol{R}}\widehat{\boldsymbol{R}} \cdot (\boldsymbol{u}(\boldsymbol{r}) - \boldsymbol{u}(\boldsymbol{r}')) n(\boldsymbol{r}) n(\boldsymbol{r}')$$

transport properties in terms of density $n$, temperature $\theta_0$, friction $\gamma$ and range $R_0$.

Compare with NS equation

$$\eta_\mathrm{D} = mn\omega_0 \langle R^2 \rangle_w / 2(d+2), \qquad \zeta_\mathrm{D} = mn\omega_0 \langle R^2 \rangle_w / 2d$$

$$\eta_\mathrm{K} = n\theta_0 / 2\omega_0; \qquad \zeta_\mathrm{K} = n\theta_0 / d\omega_0$$

$$\theta_0 = m\sigma^2 / 2\gamma$$

$$\omega_0 \equiv 1/t_0 = (n\gamma/d)[w]$$

$$\langle R^2 \rangle_w = [R^2 w]/[w^2]$$

$$[w] = \int \mathrm{d}\boldsymbol{R} w(R)$$

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# 4. DPD ----> Navier-Stokes

**Strategy:**

Stochastic differential equations

↓ Mathematically equivalent

Fokker-Planck equation

↓ Mori projection for relevant variables

Hydrodynamic equations
(sound speed, viscosity)

Espanol, PRE, 1995

# Stochastic differential equations

- DPD equations of motion

$$d\mathbf{r}_i = \frac{\mathbf{p}_i}{m_i} dt,$$

$$d\mathbf{p}_i = \left[ \sum_{j \neq i} \mathbf{F}_{ij}^C(\mathbf{r}_{ij}) + \sum_{j \neq i} -\gamma \omega(r_{ij})(\mathbf{e}_{ij} \cdot \mathbf{v}_{ij})\mathbf{e}_{ij} \right] dt$$

$$+ \sum_{j \neq i} \sigma \omega^{1/2}(r_{ij}) \mathbf{e}_{ij} dW_{ij},$$

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# Fokker-Planck equation

- Evolution of probability density in phase space
  - ➢Conservative/Liouville operator
  - ➢Dissipative and random operators

$$\partial_t \rho(r, p;\ t) = L_{\mathrm{C}}\, \rho(r, p;\ t) + L_{\mathrm{D}}\, \rho(r, p;\ t)$$

$$\begin{cases} L_{\mathrm{C}}\, \rho(r, p;\ t) \equiv -\left[ \sum_i \frac{\boldsymbol{p}_i}{m} \frac{\partial}{\partial \boldsymbol{r}_i} + \sum_{i, j \neq i} \boldsymbol{F}_{ij}^{\mathrm{C}} \frac{\partial}{\partial \boldsymbol{p}_i} \right] \rho(r, p;\ t) \\ L_{\mathrm{D}}\, \rho(r, p;\ t) \equiv \sum_{i, j \neq i} \boldsymbol{e}_{ij} \frac{\partial}{\partial \boldsymbol{p}_i} \left[ \gamma \omega_{\mathrm{D}}(r_{ij})(\boldsymbol{e}_{ij} \cdot \boldsymbol{v}_{ij}) + \frac{\sigma^2}{2} \omega_{\mathrm{R}}^2(r_{ij}) \boldsymbol{e}_{ij} \left( \frac{\partial}{\partial \boldsymbol{p}_i} - \frac{\partial}{\partial \boldsymbol{p}_j} \right) \right] \rho(r, p;\ t) \end{cases}$$

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# Mori projection
## (linearized hydrodynamics)

- Relevant hydrodynamic variables to keep

$$\delta\rho_{\mathbf{r}} = \sum_i m\delta(\mathbf{r}-\mathbf{r}_i) - \rho_0,$$

$$\mathbf{g}_{\mathbf{r}} = \sum_i \mathbf{p}_i\delta(\mathbf{r}-\mathbf{r}_i),$$

$$\delta e_{\mathbf{r}} = \sum_i \left[\frac{p_i^2}{2m} + \frac{1}{2}\sum_{j\neq i}\phi_{ij}\right]\delta(\mathbf{r}-\mathbf{r}_i) - e_0,$$

- Equilibrium averages vanish

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# Mori projection

- Navier-Stokes

$$\partial_t \mathbf{g}(\mathbf{r},t) = -c_0^2 \nabla \delta\rho(\mathbf{r},t) + \eta \nabla^2 \mathbf{v}(\mathbf{r},t)$$

$$+ \left(\zeta - \frac{2\eta}{3}\right) \boldsymbol{\nabla}[\boldsymbol{\nabla} \cdot \mathbf{v}(\mathbf{r},t)]$$

- Sound speed

$$c_0^2 = \left.\frac{\partial p}{\partial \rho}\right|_T$$

Espanol, PRE, 1995

# Mori projection

- Stress tensor via Irving-Kirkwood formula:

$$\Sigma^C = \int d^3\mathbf{r}\sigma^C_{\mathbf{r}} = \sum_i \frac{\mathbf{p}_i}{m}\mathbf{p}_i + \sum_{ij}(\mathbf{r}_i - \mathbf{r}_j)\mathbf{F}^C_{ij},$$

$$\Sigma^D = \int d^3\mathbf{r}\sigma^D_{\mathbf{r}} = \sum_{ij}(\mathbf{r}_i - \mathbf{r}_j)\mathbf{F}^D_{ij}$$

$$= -\gamma \sum_{ij}(\mathbf{r}_i - \mathbf{r}_j)\omega_{ij}(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})\mathbf{e}_{ij}.$$

- Contributions:
  - Conservative force
  - Dissipative force

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# Mori projection

- Viscosities via with Green-Kubo formulas
  - Shear viscosity η and bulk viscosity ζ

$$\eta^C = \beta \int_0^\infty du \frac{1}{V} [\Sigma^C_{\mu\nu}(u), \mathcal{Q}\Sigma^C_{\mu\nu}],$$

$$\left(\zeta^C - \frac{2}{3}\eta^C\right) = \beta \int_0^\infty du \frac{1}{V} [\Sigma^C_{\mu\mu}(u), \mathcal{Q}\Sigma^C_{\nu\nu}],$$

$$\eta^D = \beta \int_0^\infty du \frac{1}{V} [\Sigma^D_{\mu\nu}(u), \mathcal{Q}\Sigma^D_{\mu\nu}],$$

$$\left(\zeta^D - \frac{2}{3}\eta^D\right) = \beta \int_0^\infty du \frac{1}{V} [\Sigma^D_{\mu\mu}(u), \mathcal{Q}\Sigma^D_{\nu\nu}],$$

Projection operator $\mathcal{P}\Psi_t$

Orthogonal Projection operator $\mathcal{Q}\Psi_t \equiv (1 - \mathcal{P})\Psi_t$

- Note the squared dependence of viscosity on γ

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# 5. Navier-Stokes ---> (S)DPD

Story begins with

smoothed particle hydrodynamics (SPH) method

- Originally invented for Astrophysics

(Lucy. 1977, Gingold & Monaghan, 1977)

- Popular since 1990s for physics on earth

(Monaghan, 2005)

# SPH 1st step: kernel approximation

A($\mathbf{r}$): function of spatial coordinates

- integral interpolant:

$$A_I(\mathbf{r}) = \int A(\mathbf{r}')W(\mathbf{r}-\mathbf{r}', h)d\mathbf{r}',$$

where weighting function/kernel $W$: *(Monaghan, RepProgPhys 2005)*

$$\lim_{h\to 0} W(\mathbf{r}-\mathbf{r}', h) = \delta(\mathbf{r}-\mathbf{r}'), \quad \int W(\mathbf{r}-\mathbf{r}', h)d\mathbf{r}' = 1$$

- Gaussian; B-Splines; Wendland functions.

*(Schoneberg, QApplMath 1946; Wendland, AdvComputMath, 1995)*

- $h > 0$: kernel error

$$A(\mathbf{r}) = A_I(\mathbf{r}) + E_1(h^2)$$

*(Quinlan et al., IntJNumerMethEng 2006)*

# SPH 2nd step: particle approximation

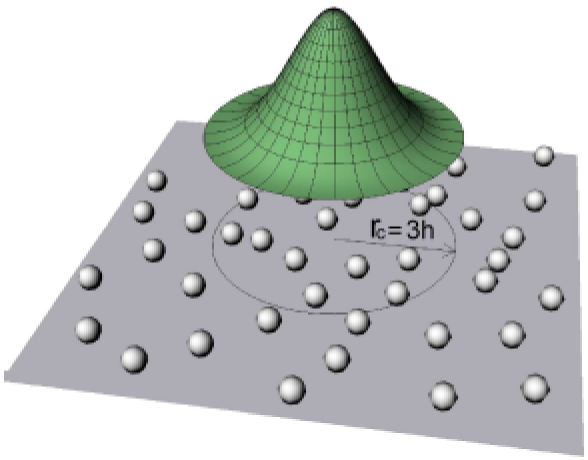
- summation form ($r_c = 3h$):

$$A_S(\mathbf{r}) = \sum_j \frac{A_j}{d_j} W(\mathbf{r} - \mathbf{r}_j, h)$$

$$\nabla A_S(\mathbf{r}) = \sum_j \frac{A_j}{d_j} \nabla W(\mathbf{r} - \mathbf{r}_j, h)$$

$$\ldots = \ldots$$

*(Español&Revenga, PRE 2003)*




compact support: neighbor list

- $\Delta x > 0$: summation error
  $A_I(\mathbf{r}) = A_S(\mathbf{r}) + E_2(\Delta x / h)$

- $A(\mathbf{r}) = A_S(\mathbf{r}) + E_1(h^2) + E_2(\Delta x / h)$
  *(Quinlan et al., IntJNumerMethEng 2006)*

- Error estimated for particles on grid
- Actual error depends on configuration of particles

(Price, JComputPhys. 2012)

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# SPH: isothermal Navier-Stokes

- Continuity equation

$$d_i = \frac{\rho_i}{m_i} = \sum_j W_{ij}, \quad \dot{\mathbf{r}}_i = \mathbf{v}_i$$

- Momentum equation

$$\begin{aligned} m_i \dot{\mathbf{v}}_i &= -\sum_{j \neq i} \left( \frac{\bar{p}_{ij}}{d_i^2} + \frac{\bar{p}_{ij}}{d_j^2} \right) \frac{\partial W}{\partial r_{ij}} \mathbf{e}_{ij} + \sum_{j \neq i} \eta \left( \frac{1}{\mathbf{d}_i^2} + \frac{1}{\mathbf{d}_j^2} \right) \frac{\partial \mathbf{W}}{\partial \mathbf{r}_{ij}} \frac{\mathbf{v}_{ij}}{\mathbf{r}_{ij}} + \mathbf{F}_i^{Ext} \\ &= \sum_{j \neq i} \left( \mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D \right) + \mathbf{F}_i^{Ext} \end{aligned}$$

- Input equation of state: pressure and density

Hu & Adams, JComputPhys. 2006

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# SPH: add Brownian motion

- Momentum with fluctuation (Espanol & Revenga, 2003)

$$m_i \dot{\mathbf{v}}_i = \sum_{j\neq i}\left(\mathbf{F}^C_{ij} + \mathbf{F}^D_{ij} + \mathbf{F}^R_{ij}/\sqrt{dt}\right) + \mathbf{F}^{Ext}_i$$

- Cast dissipative force in GENERIC → random force

$$\mathbf{F}^R_{ij} = \left[\frac{-4k_B T\eta}{r_{ij}}\left(\frac{1}{d_i^2}+\frac{1}{d_j^2}\right)\frac{\partial W}{\partial r_{ij}}\right]^{1/2} d\overline{\overline{\mathbf{W}}}_{ij}\cdot\mathbf{e}_{ij}$$

$$d\overline{\overline{\mathbf{W}}}_{ij} = \left(d\mathbf{W}_{ij} + d\mathbf{W}^T_{ij}\right)/2 - tr[d\mathbf{W}_{ij}]\mathbf{I}/D$$

- dW is an independent increment of Wiener process

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# SPH + fluctuations = SDPD

- Discretization of Landau-Lifshitz's fluctuating hydrodynamics (Landau & Lifshitz, 1959)

- Fluctuation-dissipation balance on discrete level

- Same numerical structure as original DPD formulation

$$m_i \dot{\mathbf{v}}_i = \sum_{j \neq i} \left( \mathbf{F}_{ij}^{C} + \mathbf{F}_{ij}^{D} + \mathbf{F}_{ij}^{R} / \sqrt{dt} \right) + \mathbf{F}_i^{Ext}$$

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# GENERIC framework (part 1)

(General equation for nonequilibrium reversible-irreversible coupling)

- Dynamic equations of a deterministic system:

$$\frac{dx}{dt} = L\frac{\delta E}{\delta x} + M\frac{\delta S}{\delta x}$$

State variables x: position, velocity, energy/entropy
E(x): energy; S(x): entropy
L and M are linear operators/matrices and represent reversible and irreversible dynamics

- First and second Laws of thermodynamics

$$L\frac{\delta S}{\delta x} = 0 \qquad M\frac{\delta E}{\delta x} = 0$$

- For any dynamic invariant variable I, e.g, linear momentum

if $\frac{\partial I}{\partial x}L\frac{\partial E}{\partial x} = 0,\ \frac{\partial I}{\partial x}M\frac{\partial S}{\partial x} = 0,$ then $\dot{I} = 0$

Grmela & Oettinger, PRE, 1997; Oettinger & Grmela, PRE, 1997

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# GENERIC framework (part 2)

(General equation for nonequilibrium reversible-irreversible coupling)

- Dynamic equations of a stochastic system:

$$dx = \left[ L \frac{\partial E}{\partial x} + M \frac{\partial S}{\partial x} + k_B \frac{\partial}{\partial x} M \right] dt + d\tilde{x}$$

Last term is thermal fluctuations

- Fluctuation-dissipation theorem: compact form

$$d\tilde{x}\, d\tilde{x}^T = 2 k_B M\, dt$$

✓No Fokker-Planck equation needs to be derived

✓Model construction becomes simple linear algebra

Grmela & Oettinger, PRE, 1997; Oettinger & Grmela, PRE, 1997

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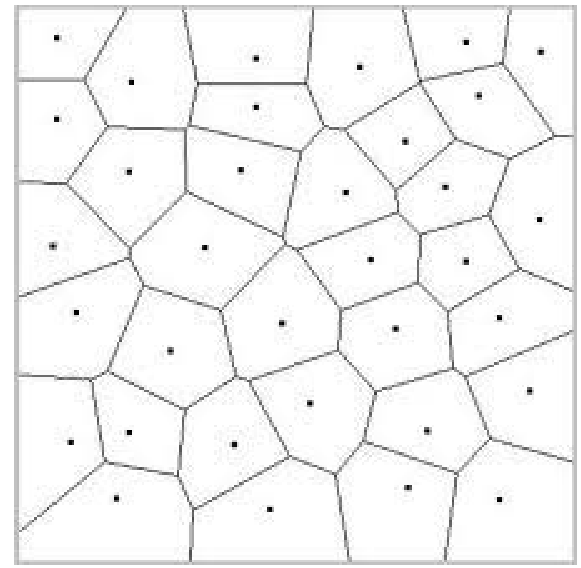
# Coarse-graining: Voronoi tessellation

- **Procedure:**

1. Partition of particles of molecular dynamics
2. Measuring fluxes at edges
3. Update center of mass
4. Repeat 1, 2 and 3

5. Ensemble average interacting forces between neighboring Voronoi cells:
   similarly as DPD pairwise interactions



$$\frac{dM_k}{dt} = \sum_l \dot{M}_{kl} \equiv \sum_i f_{kl}(\mathbf{x}_i) m (\mathbf{v}_i' \cdot \mathbf{r}_{kl} + \mathbf{x}_i' \cdot \mathbf{U}_{kl}),$$

$$\frac{d\mathbf{P}_k}{dt} = M_k \mathbf{g} + \sum_l \dot{M}_{kl} \frac{\mathbf{U}_k + \mathbf{U}_l}{2} + \sum_{li} f_{kl}(\mathbf{x}_i) \mathbf{\Pi}_i' \cdot \mathbf{r}_{kl},$$

$$\frac{dE_k}{dt} = \sum_l \frac{\dot{M}_{kl}}{2} \left( \frac{\mathbf{U}_{kl}}{2} \right)^2 + \sum_{li} f_{kl}(\mathbf{x}_i) \left( \mathbf{J}_i' - \Pi_i' \cdot \frac{\mathbf{U}_{kl}}{2} \right) \cdot \mathbf{r}_{kl},$$

Conceptually: useful to support DPD as a coarse-grained (CG) model

Practically: force fields are useless and can not reproduce MD system

Flekkoy & Coveney, PRL, 1999

# Mori-Zwanzig Projection

Consider a canonical ensemble $\Gamma$.

**Def:** $A$, $B$ are two variables in $\Gamma$, noted by $A(\Gamma)$, $B(\Gamma)$.

**Def:** Projection Operator $P$, $Q$

$$PB(\Gamma,t) = \frac{(B(\Gamma,t), A(\Gamma,t))}{(A(\Gamma,t), A(\Gamma,t))} A(\Gamma) \tag{1}$$

$$Q = 1 - P \tag{2}$$

Consider the time evolution operator $e^{iLt}$.

$$e^{iLt} = e^{iQLt} + \int_0^t d\tau e^{iQL(t-\tau)} iPL e^{iQL\tau} \tag{3}$$

The we have

$$\frac{dA(t)}{dt} = e^{iLt} iLA = e^{iLt} i(Q+P)LA \tag{4}$$

$$e^{iLt} iPLA = \frac{(iLA, A)}{(A, A)} e^{iLt} A = i\Omega A(t) \tag{5}$$

$$\begin{aligned} \frac{dA(t)}{dt} &= i\Omega A(t) + e^{iLt} iQLA \\ &= i\Omega A(t) + \int_0^t d\tau e^{iQL(t-\tau)} iPL e^{iQL\tau} iQLA + e^{iQLT} iQLA \end{aligned} \tag{6}$$

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# Mori-Zwanzig Projection

Given $A$ the coarse-grained velocity term, we identify $e^{iQLT}iQLA$ as the random force $\delta F(t)$. Since

$$(\delta F(t), A) = (e^{iQLt}iQLA, A) = (Q\delta F(t), A) = 0 \tag{7}$$

$$\begin{aligned} iPLe^{iQLt}iQLA &= iPL\delta F(t) = iPLQ\delta F(t) \\ &= \frac{(iLQ\delta F(t), A)}{(A, A)}A = -\frac{(\delta F(t), iQLA)}{(A, A)}A \\ &= -\frac{(\delta F(t), \delta F(0))}{(A, A)}A = -K(t)A \end{aligned} \tag{8}$$

$$\begin{aligned} \frac{dA(t)}{dt} &= i\Omega A(t) - \int_0^t d\tau e^{iQL(t-\tau)}K(\tau)A + \delta F(t) \\ &= i\Omega A(t) - \int_0^t d\tau K(\tau)A(t-\tau) + \delta F(t) \end{aligned} \tag{9}$$

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# Mori-Zwanzig Projection

Specifically, if $A(t)$ is the coarse-grained $V(t)$, then

$$\frac{dV(t)}{dt} = i\Omega V(t) - \int_0^t d\tau \frac{< \delta F(\tau)\delta F(0) >}{V(t)^2} V(t-\tau) + \delta F(t) \tag{10}$$

$$i\Omega V(t) = \frac{1}{\beta}\frac{\partial \ln \omega(\mathbf{R})}{\partial R} \tag{11}$$

$$\omega(\mathbf{R}) = \frac{\int d^N\hat{\mathbf{r}}\ \delta\left(\hat{\mathbf{R}} - \mathbf{R}\right) e^{-\beta U}}{\int d^N\hat{\mathbf{r}}\ e^{-\beta U}}, \tag{12}$$

Mori, ProgTheorPhys., 1965
Zwanzig, Oxford Uni. Press, 2001
Kinjo & Hyodo, PRE, 2007

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# MZ formalism as practical tool

Consider an atomistic system consisting of $N$ atoms which are grouped into $K$ clusters, and $N_C$ atoms in each cluster. The Hamiltonian of the system is:

$$H = \sum_{\mu=1}^{K} \sum_{i=1}^{N_C} \frac{\mathbf{p}_{\mu,i}^2}{2m_{\mu,i}} + \frac{1}{2} \sum_{\mu,\nu} \sum_{i,j\neq i} V_{\mu i,\nu j}$$

Theoretically, the dynamics of the atomistic system can be mapped to a coarse-grained or mesoscopic level by using Mori-Zwanzig projection operators.

The equation of motion for coarse-grained particles can be written as: (in the following page)

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# MZ formalism as practical tool

- Equation of motion for coarse-grained particles

$$\dot{\mathbf{P}}_\mu = k_B T \frac{\partial}{\partial \mathbf{R}_\mu} \ln \omega(\mathbf{R})$$

→ **Conservative force**

$$- \frac{1}{k_B T} \sum_{\nu=1}^{K} \int_0^t ds \left\langle \left[ \delta \mathbf{F}_\mu^\vartheta (t-s) \right] \times \left[ \delta \mathbf{F}_\nu^\vartheta (0)^T \right] \right\rangle \cdot \frac{\mathbf{P}_\nu(s)}{M_\nu}$$

→ **Friction force**

$$+ \delta \mathbf{F}_\mu^\vartheta (t)$$

→ **Stochastic force**

Kinjo & Hyodo, PRE, 2007

**1. Pairwise approximation:** $\mathbf{F}_\mu \approx \sum_{\mu \neq \nu} \mathbf{F}_{\mu\nu}$

**2. Markovian approximation:** $\left\langle \delta \mathbf{F}_\mu^\vartheta (t) \cdot \delta \mathbf{F}_\nu^\vartheta (0) \right\rangle = \Gamma_{\mu\nu} \cdot \delta(t)$

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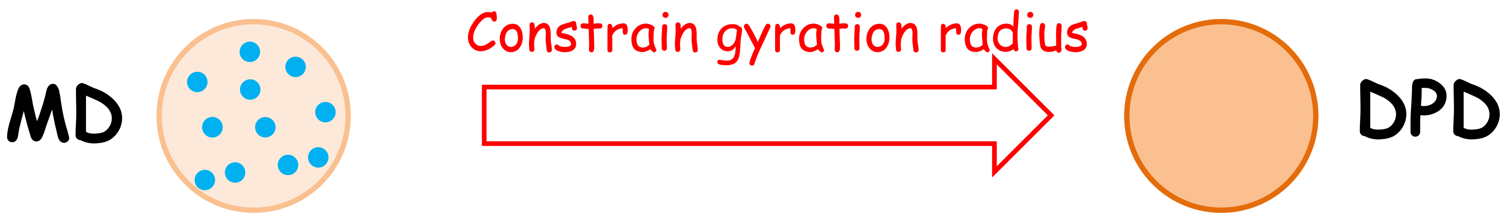
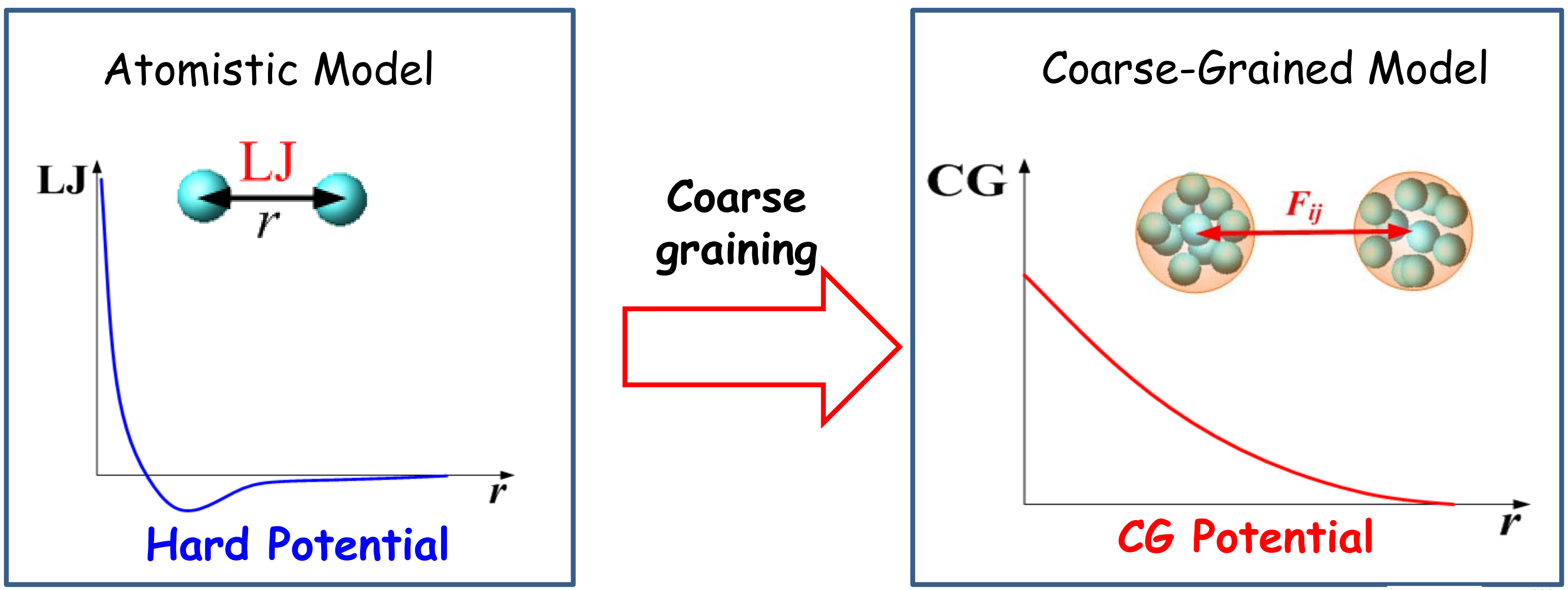
# Coarse-graining constrained fluids

- **Degree of coarse-graining : $N_c$ to 1**



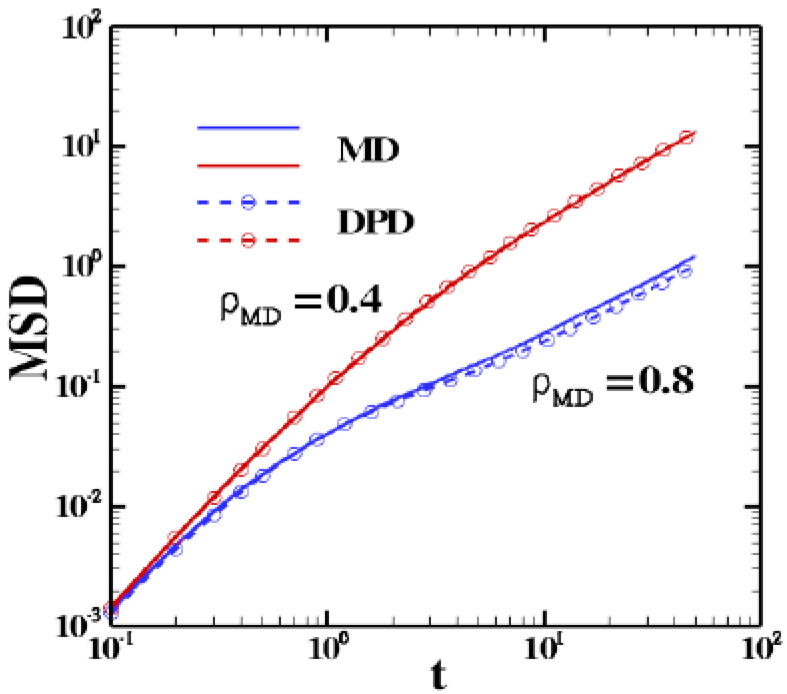

Lei, Caswell, & Karniadakis, PRE, 2010

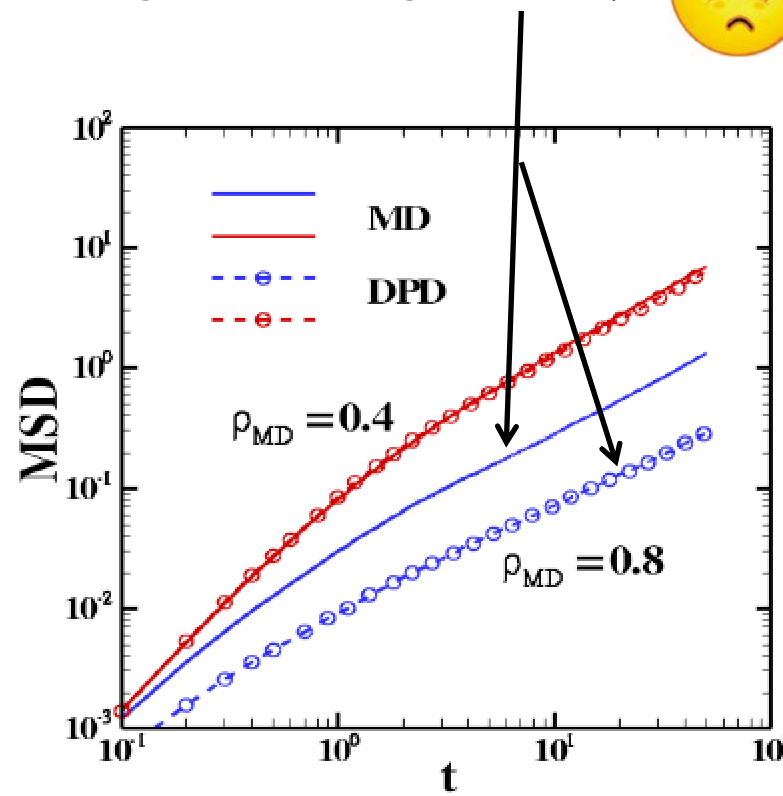
# Dynamical properties of constrained fluids

## Mean square displacement (long time scale)

Small $R_g$ always fine

Large $R_g$ and high density




MSD with $R_g$ = 0.95 (left) and $R_g$ = 1.4397(right)

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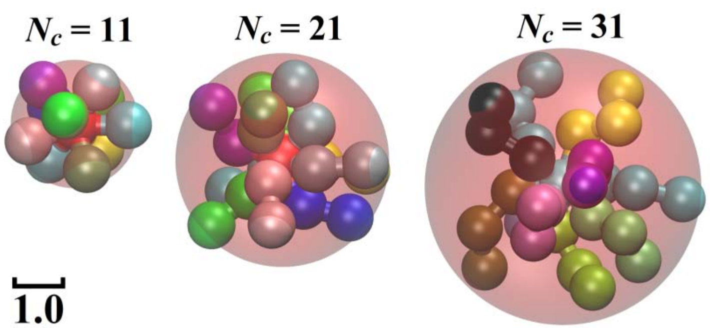
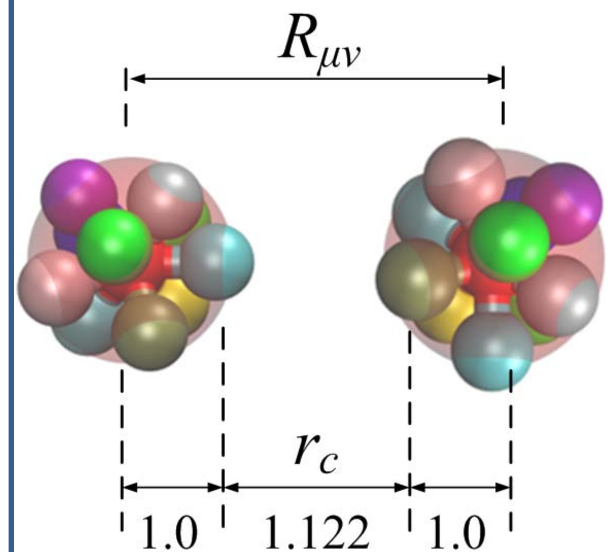
# Coarse-graining unconstrained polymer melts

- Natural bonds




$$M_\mu = \sum_{\mu,i} m_{\mu,i}$$

$$\mathbf{P}_\mu = \sum_{\mu,i} \mathbf{p}_{\mu,i}$$

$$\mathbf{R}_\mu = \frac{1}{M_\mu} \sum_{\mu,i} m_{\mu,i} \mathbf{r}_{\mu,i}$$

$$\mathbf{L} = \sum_{\mu,i} (\mathbf{r}_{\mu,i} - \mathbf{R}_\mu) \times (\mathbf{p}_{\mu,i} - \mathbf{P}_\mu)$$

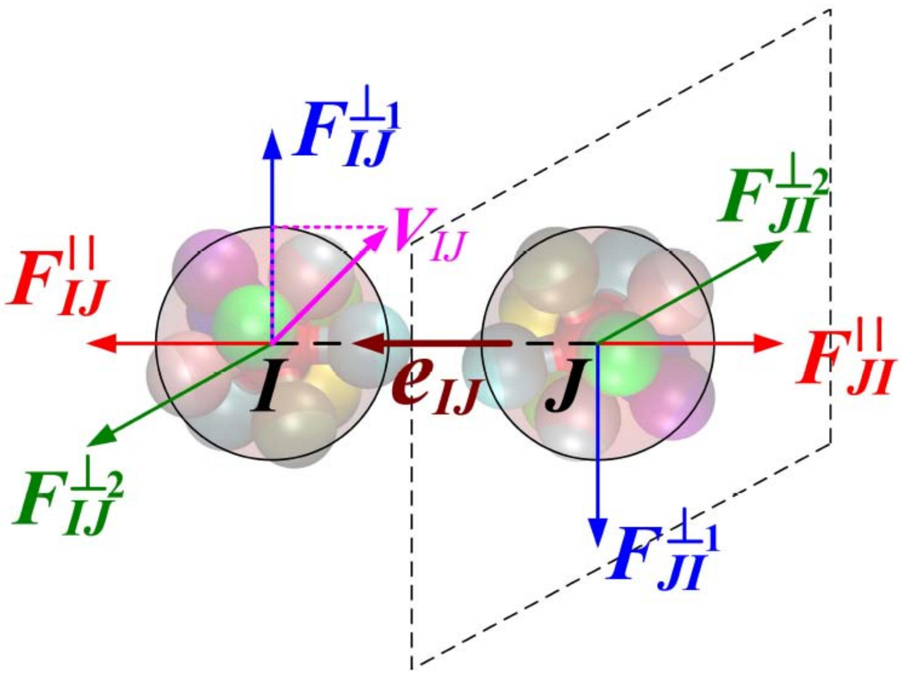
WCA Potential + FENE Potential

$$V_{WCA}(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right]; & r \leq 2^{1/6}\sigma \\ 0; & r > 2^{1/6}\sigma \end{cases}$$

$$V_B(r) = \begin{cases} -\frac{1}{2} k R_0^2 \ln\left[1 - (r/R_0)^2\right]; & r \leq R_0 \\ \infty; & r > R_0 \end{cases}$$

NVT ensemble with Nose-Hoover thermostat.

# Directions for pairwise interactions between neighboring clusters




1. Parallel direction:

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$$

$$\mathbf{e}_{ij} = \mathbf{r}_{ij} / |r_{ij}|$$

2. Perpendicular direction #1:

$$\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$$

$$\mathbf{v}_{ij}^{\perp} = \mathbf{v}_{ij} - \left(\mathbf{v}_{ij} \cdot \mathbf{e}_{ij}\right) \cdot \mathbf{e}_{ij}$$

$$\mathbf{e}_{ij}^{\perp 1} = \mathbf{v}_{ij}^{\perp} / |v_{ij}^{\perp}|$$

3. Perpendicular direction #2:

$$\mathbf{e}_{ij}^{\perp 2} = \mathbf{e}_{ij} \times \mathbf{e}_{ij}^{\perp 1}$$

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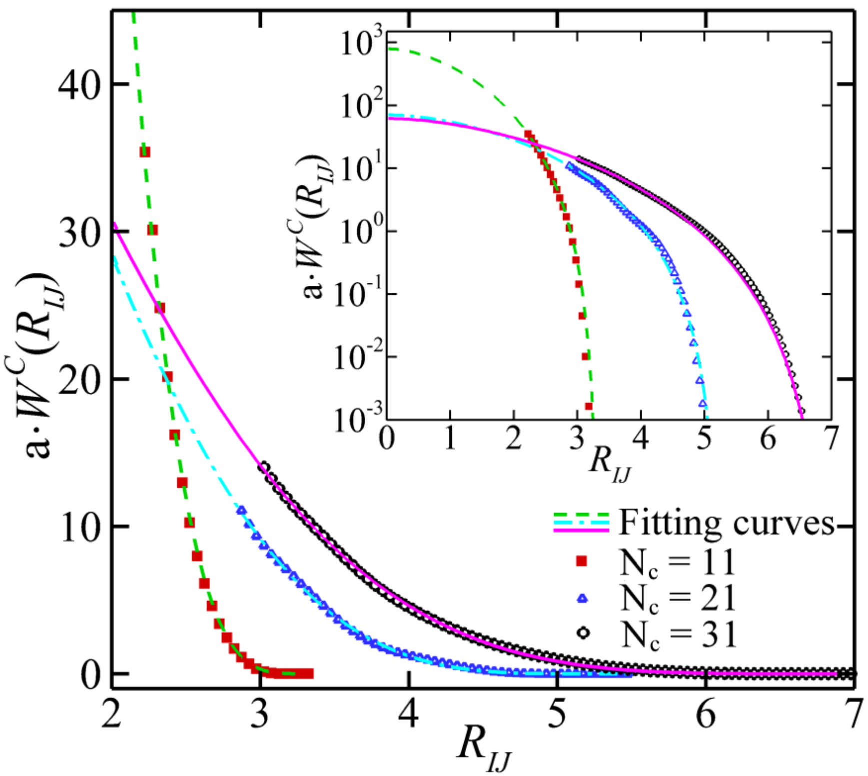
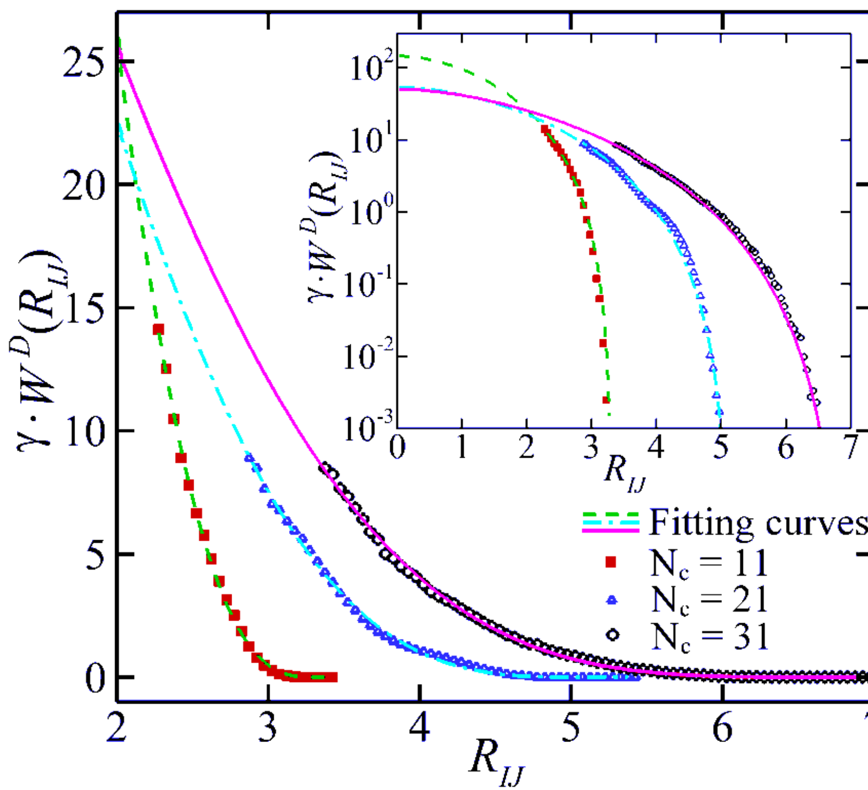
# DPD force fields from MD simulation

Conservative




Dissipative (parallel one)




Li, Bian, Caswell, & Karniadakis, 2014

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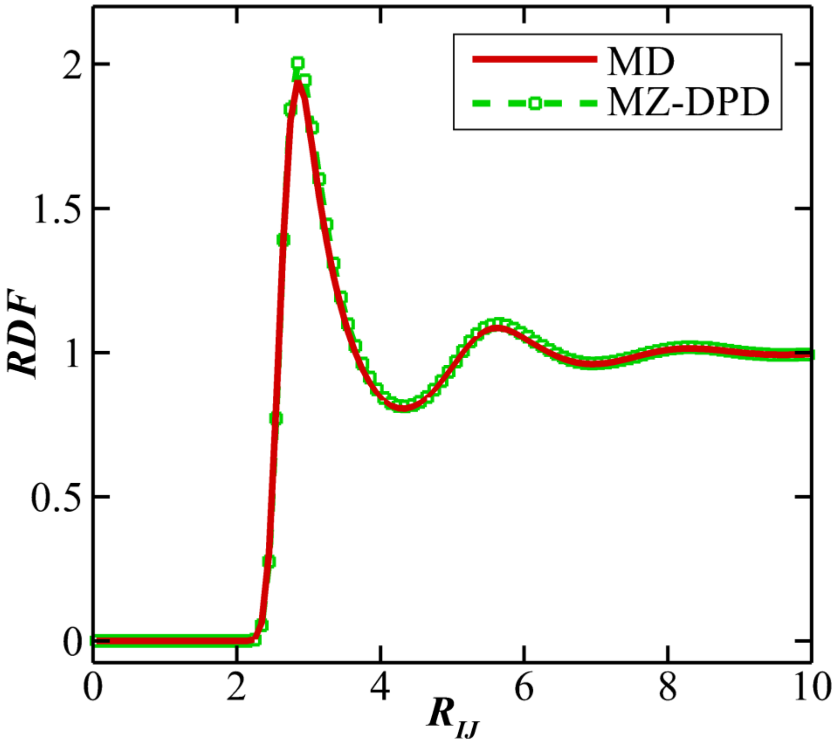
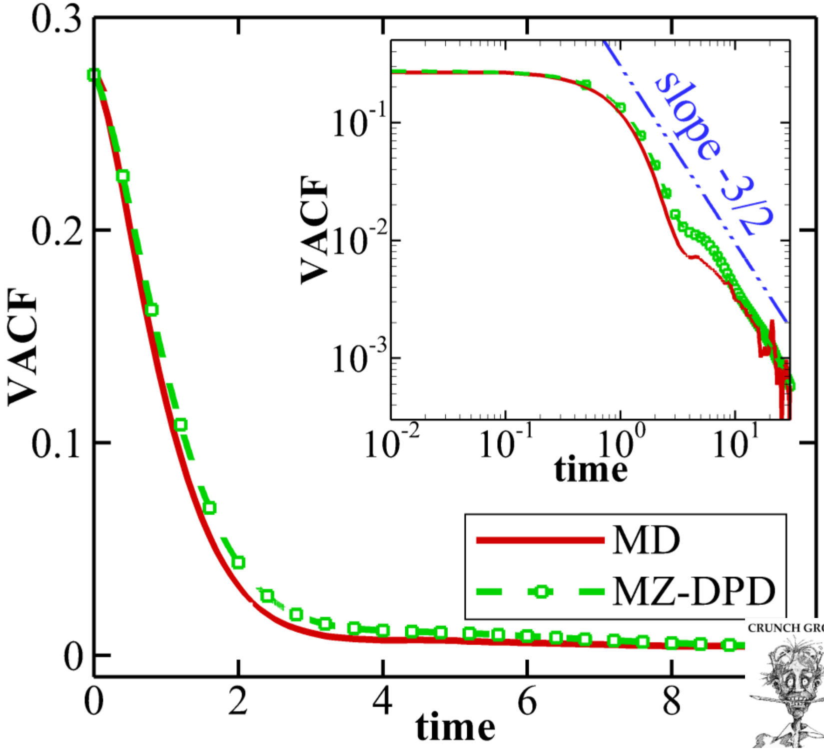
# Performance of the MZ-DPD model ($N_c$ = 11)

| Quantities | MD | MZ-DPD (error) |
|---|---|---|
| Pressure | **0.191** | **0.193 (+1.0%)** |
| Diffusivity (Integral of VACF) | **0.119** | **0.138 (+16.0%)** |
| Viscosity | **0.965** | **0.851 (-11.8%)** |
| Schmidt number | **8.109** | **6.167 (-23.9%)** |
| Stokes-Einstein radius | **1.155** | **1.129 (-2.2%)** |

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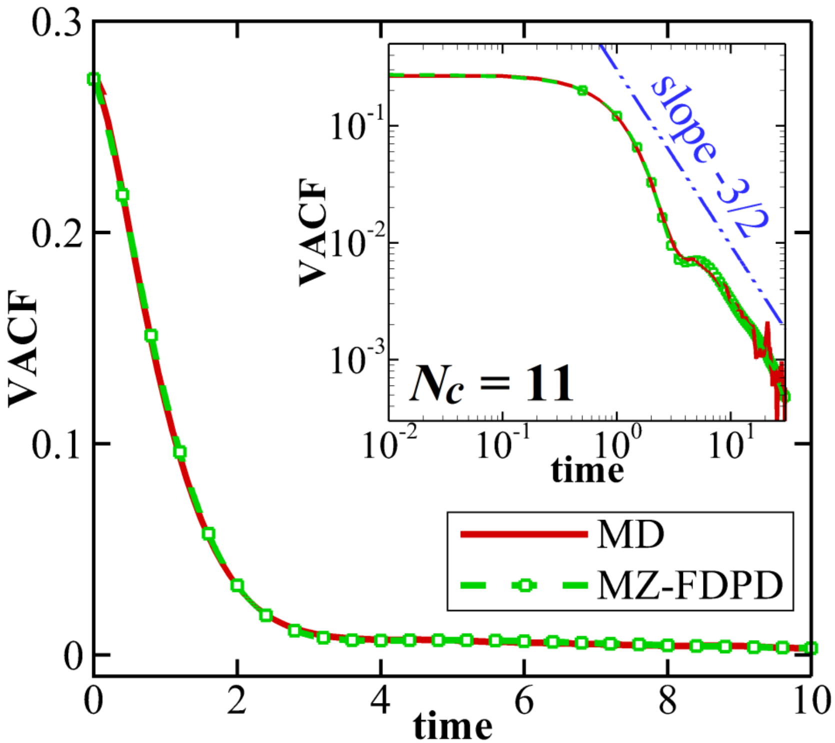
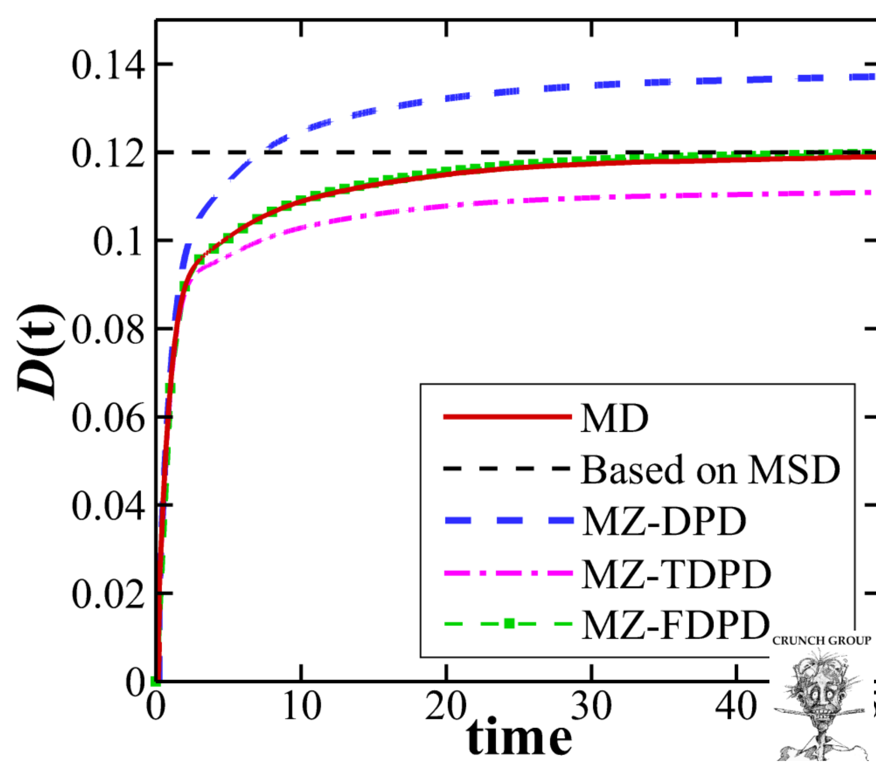
# Performance of the MZ-FDPD model ($N_c$ = 11)

| Quantities | MD | **MZ-FDPD (error)** |
|---|---|---|
| Pressure | **0.191** | **0.193 (+1.0%)** |
| Diffusivity (Integral of VACF) | **0.119** | **0.120 (+0.8%)** |
| Viscosity | **0.965** | **0.954 (-1.1%)** |
| Schmidt number | **8.109** | **7.950 (-2.0%)** |
| Stokes-Einstein radius | **1.155** | **1.158 (+0.3%)** |



# Conclusion & Outlook

- Invented by physics intuition
- Statistical physics on solid ground
  - Fluctuation-dissipation theorem
  - Canonical ensemble (NVT)
- DPD <------> Navier-Stokes equations
- Coarse-graining microscopic system
  - Mori-Zwanzig formalism

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