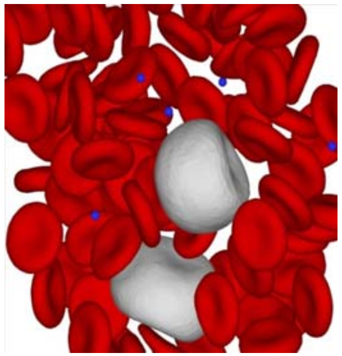
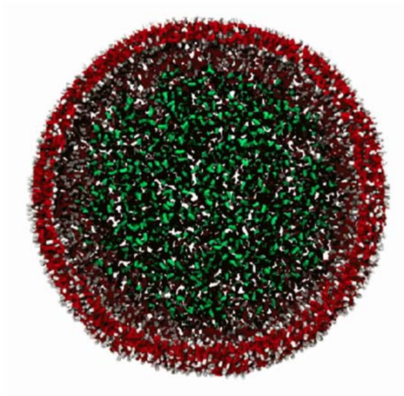
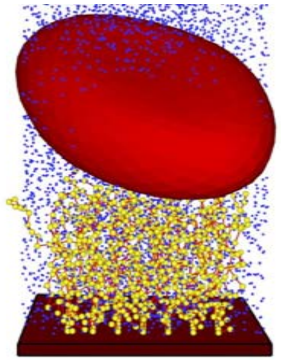
APMA 2811T
Dissipative Particle Dynamics

Instructor: Professor George Karniadakis
Location: 170 Hope Street, Room 118
Time: Thursday 12:00pm - 2:00pm

Today's topic:

Dissipative Particle Dynamics: Foundation, Evolution and Applications

Lecture 2: Theoretical foundation and parameterization

By **Zhen Li**
Division of Applied Mathematics, Brown University
Sep. 15, 2016

Outline

1. Background
2. Fluctuation-dissipation theorem
3. Parameterization
   - Static properties
   - Dynamic properties
4. DPD ----> Navier-Stokes
5. Navier-Stokes ----> (S)DPD
6. Microscopic ----> DPD
   - Mori-Zwanzig formalism

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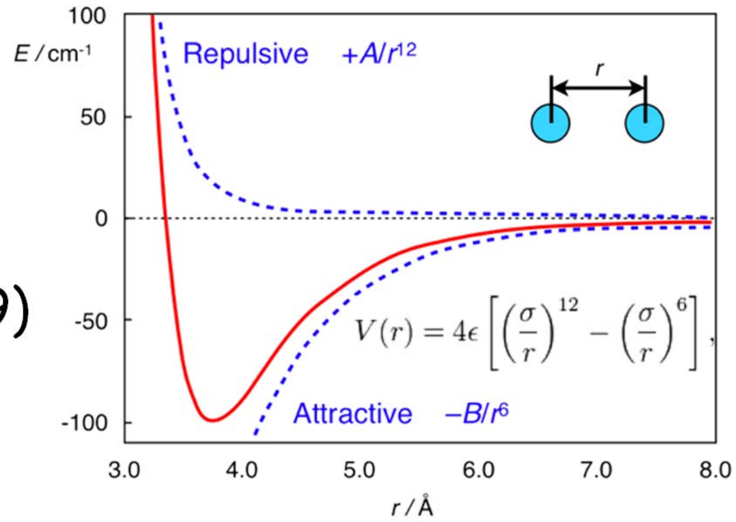
1. Background

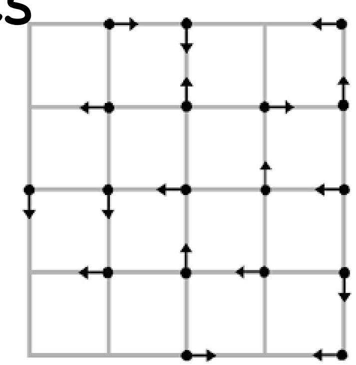
- Molecular dynamics (e.g. Lennard-Jones):
  - Lagrangian nature
  - Stiff force
  - Atomic time step

  (Allen & Tildesley, Oxford Uni. Press, 1989)

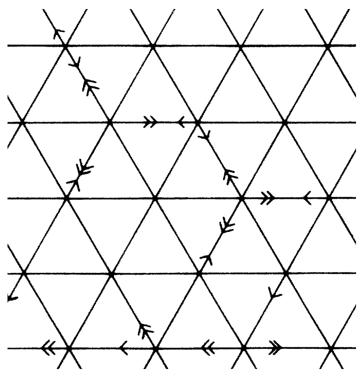


- Coarse-grained: Lattice gas automata
  - Mesoscopic collision rules
  - Grid based particles

  (Hardy et al, PRL, 1973) HPP
  (Frisch et al, PRL, 1986) FHP



Square lattice



Hexagonal grids

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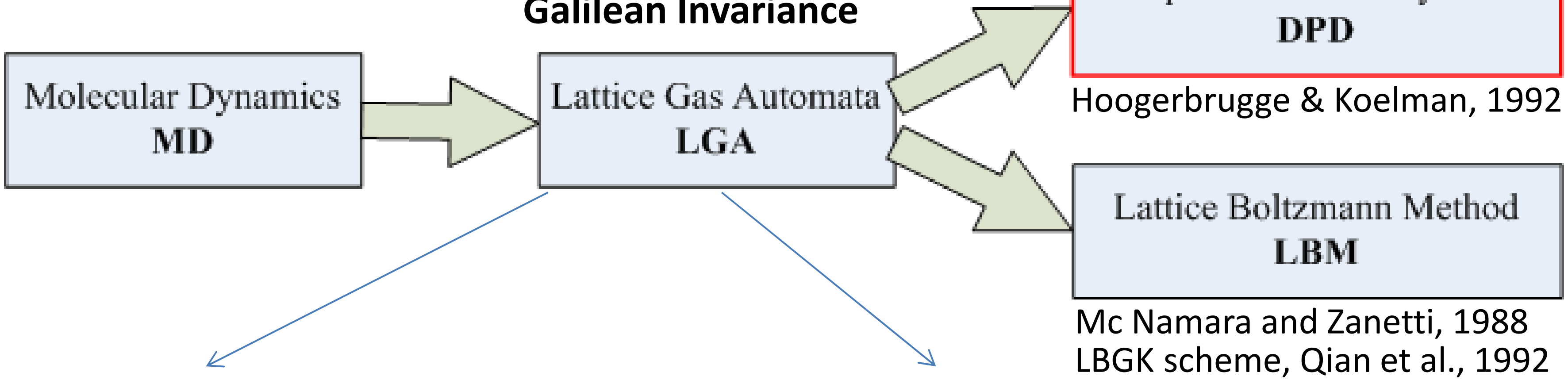
1. Background

❖ History of DPD

Violation of **Isotropy** and **Galilean Invariance**

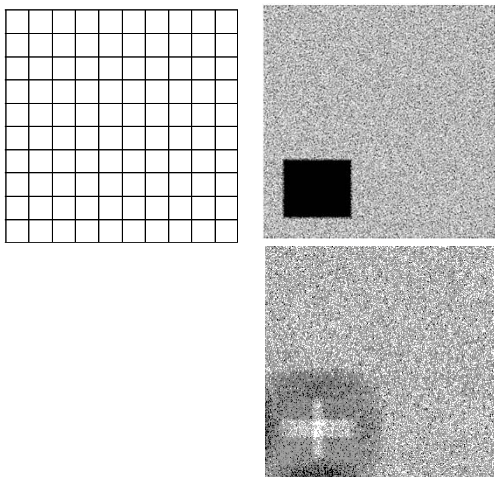


Hoogerbrugge & Koelman, 1992

Mc Namara and Zanetti, 1988
LBGK scheme, Qian et al., 1992

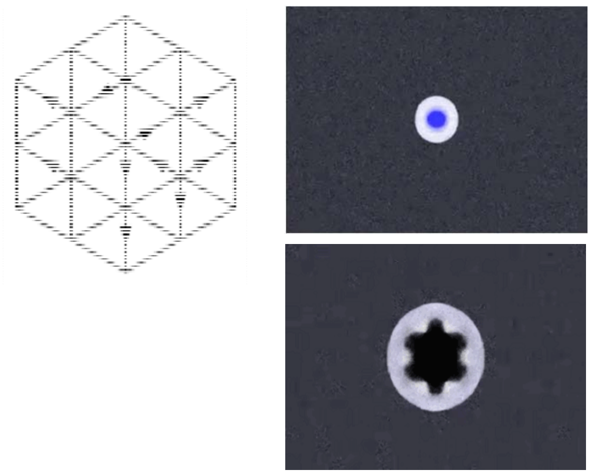
HPP LGA model was introduced by **H**ardy, **P**omeau and de **P**azzis in **1973**

Square lattice



FHP LGA model was introduced by U. **F**risch, B. **H**asslacher and Y. **P**omeau in **1986**

Hexagonal grids



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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 dissipative particle dynamics (DPD).

Hoogerbrugge & Koelman, EPL, 1992

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2. Fluctuation-dissipation theorem

- Langevin equations (SDEs)

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

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)

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

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

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2. Fluctuation-dissipation theorem

- Gibbs distribution: steady state solution of FPE

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

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

Require $L_D \rho^{eq} = 0$ Energy dissipation and generation balance

DPD version of fluctuation-dissipation theorem

$$\omega_R(r) = \omega_D^{1/2}(r) \qquad \sigma = (2k_B T\gamma)^{1/2}$$

DPD can be viewed as canonical ensemble (NVT)

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Espanol, EPL, 1995

2. Fluctuation-dissipation theorem

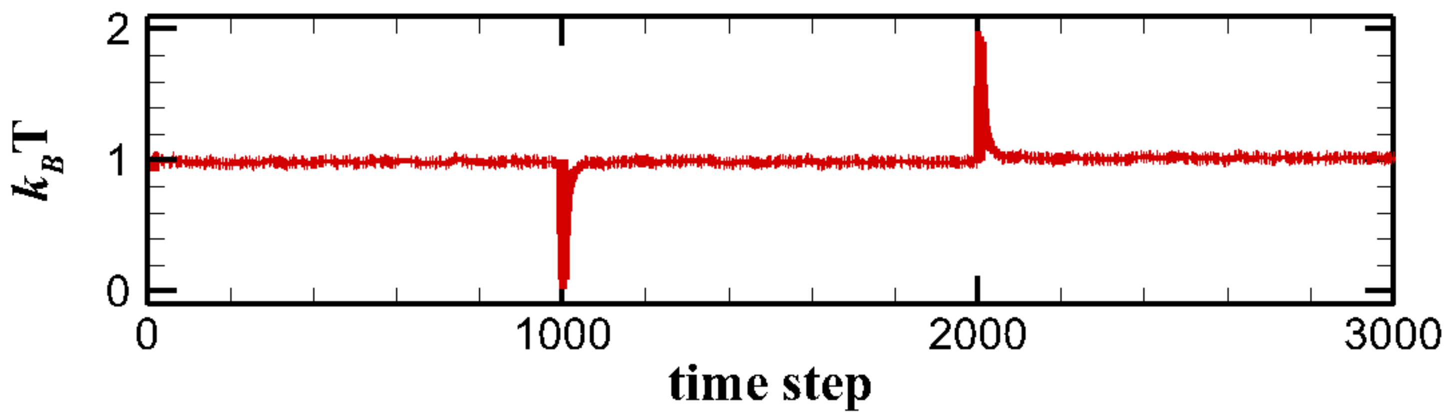
DPD thermostat

$$\boldsymbol{F}_i = \sum_{i \neq j} \left(\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R \right) \qquad \begin{aligned} \boldsymbol{F}_{ij}^D &= \gamma w_D(r_{ij}) (\boldsymbol{e}_{ij} \boldsymbol{v}_{ij}) \boldsymbol{e}_{ij} \\ \boldsymbol{F}_{ij}^R &= \sigma w_R(r_{ij}) dt^{-1/2} \xi_{ij} \boldsymbol{e}_{ij} \end{aligned}$$

To satisfy the fluctuation-dissipation theorem (FDT):

$$[w_R(r)]^2 = w_D(r) \text{ and } \sigma^2 = 2\gamma k_B T$$

Then, **the dissipative force $\boldsymbol{F}_{ij}^D$ and random force $\boldsymbol{F}_{ij}^R$** together act as a DPD thermostat.



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3. Parameterization

(How to choose DPD parameters?)

Strategy: match DPD thermodynamics to atomistic system

I. How to choose repulsion parameter?

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, cannot match both easily)

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

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3. Parameterization

(How to choose DPD parameters?)

Force field of classic DPD

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

$$\boldsymbol{F}_{ij}^C = a\left(1 - r_{ij}/r_c\right)\boldsymbol{e}_{ij}$$

$$\boldsymbol{F}_{ij}^D = \gamma\left(1 - r_{ij}/r_c\right)^2\left(\boldsymbol{e}_{ij}\boldsymbol{v}_{ij}\right)\boldsymbol{e}_{ij}$$

$$\boldsymbol{F}_{ij}^R = \sqrt{2\gamma k_B T}\left(1 - r_{ij}/r_c\right)dt^{-1/2}\xi_{ij}\boldsymbol{e}_{ij}$$

The conservative force $\boldsymbol{F}_{ij}^C$ is responsible for the static properties,

Pressure

Compressibility

Radial distribution function g(r)

The dissipative force $\boldsymbol{F}_{ij}^D$ **and random force** $\boldsymbol{F}_{ij}^R$ together act as a thermostat and determine the dynamics properties, i.e.,

Viscosity

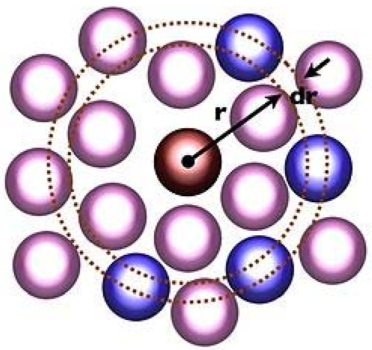
Diffusivity

Time correlation functions

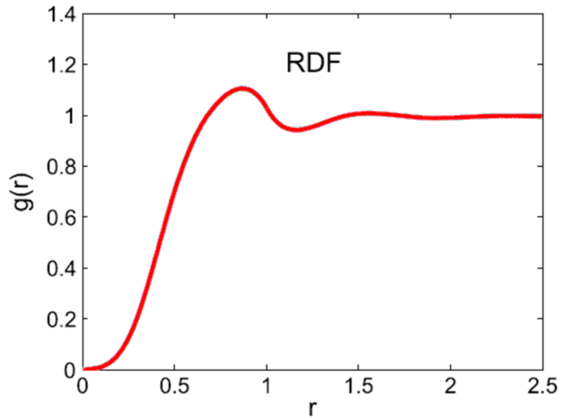
3. Parameterization

(How to choose DPD parameters?)

Radial distribution function



$$g(r) = \frac{n(r)}{4\pi\, r^2\, \Delta r}\frac{1}{\rho}$$



Pressure

$$\mathrm{P} = \rho \mathrm{k_B T} + \frac{1}{3V}\left\langle \sum_i \boldsymbol{r}_i \cdot \boldsymbol{F}_i \right\rangle$$

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

Compressibility

$$\kappa^{-1} = \frac{1}{k_B T}\left(\frac{\partial P}{\partial \rho}\right)_T$$

For linear conservative force

$$\boldsymbol{F}_{ij}^C = a\left(1 - r_{ij}/r_c\right)\boldsymbol{e}_{ij}$$

The equation of state is

$$P = \rho k_B T + 0.1 a \rho^2$$

Then

$$\kappa^{-1} = 1 + 0.2 a\rho / k_B T$$

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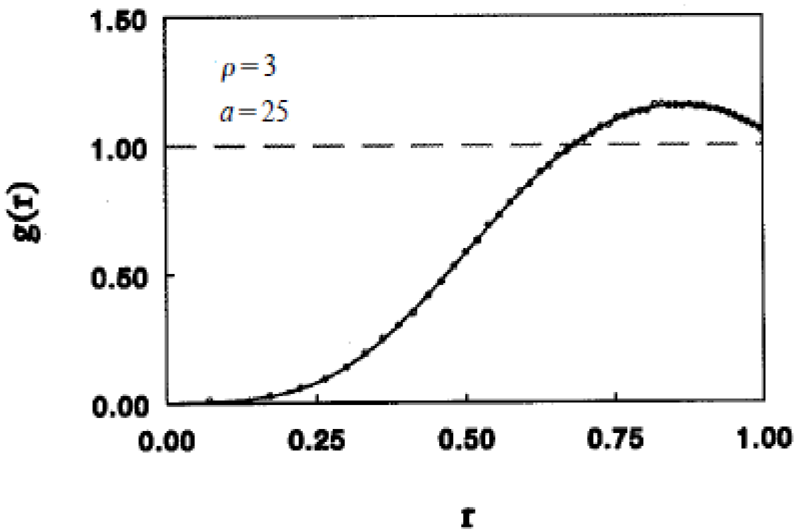
Repulsion parameter for water?

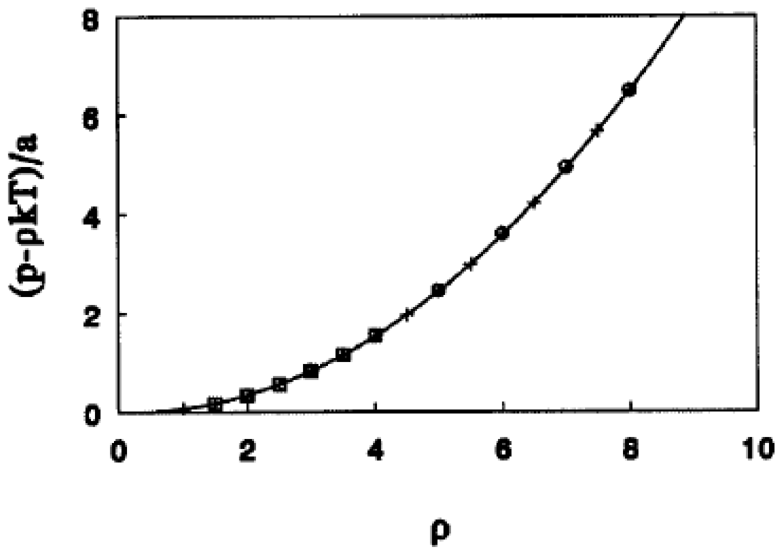
- Equation of state: self and pair contributions

$$p=\rho k_B T+\frac{1}{3V}\left\langle \sum_{j>i} (\mathbf{r}_i-\mathbf{r}_j)\cdot\mathbf{f}_i \right\rangle=\rho k_B T+\frac{1}{3V}\left\langle \sum_{j>i} (\mathbf{r}_i-\mathbf{r}_j)\cdot\mathbf{F}_{ij}^C \right\rangle=\rho k_B T+\frac{2\pi}{3}\rho^2\int_0^1 r f(r) g(r) r^2\,dr$$

- Match isothermal compressibility

$$\kappa^{-1}=\frac{1}{n k_B T \kappa_T}=\frac{1}{k_B T}\left(\frac{\partial p}{\partial n}\right)_T$$





$$p=\rho k_B T+\alpha a\rho^2 (\alpha=0.101\pm0.001)$$

$$\kappa^{-1}=1+2\alpha a\rho/k_B T\approx 1+0.2 a\rho/kT$$

$$\kappa_{water}^{-1}\approx 16 \qquad a\rho/k_B T\approx 75$$

Groot & Warren, JChemPhys, 1997

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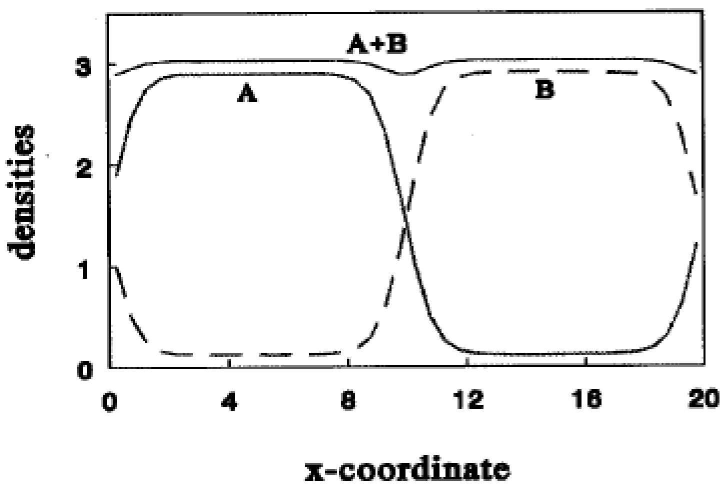
Repulsion parameter for polymers

- Lattice Flory-Huggins free energy $$\frac{F}{k_B T} = \frac{\phi_A}{N_A} \ln \phi_A + \frac{\phi_B}{N_B} \ln \phi_B + \chi \phi_A \phi_B$$

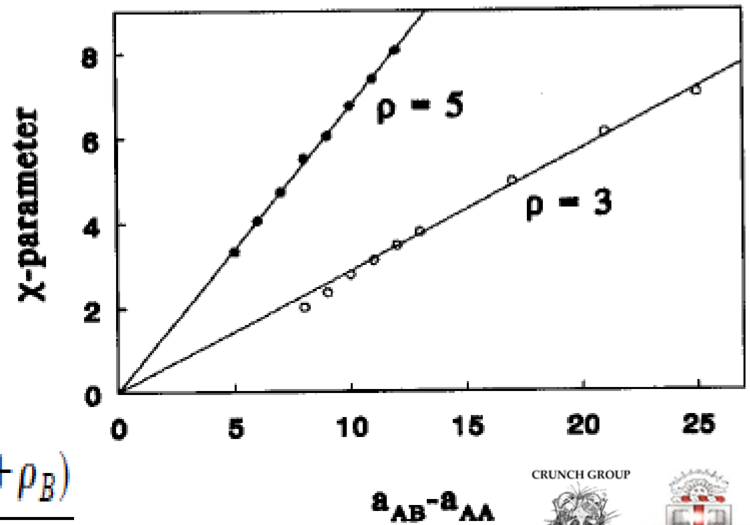
- DPD free energy corresponds to pressure

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

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



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



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Groot & Warren, JChemPhys, 1997

Friction parameter?

Diffusivity Consider the motion of single particle given by Langevin equation

$$m\frac{dv}{dt} = -\frac{v_i}{\tau} + F_i^R$$

$$\frac{1}{\tau} = \frac{4\pi\gamma\rho}{3}\int_0^\infty r^2 w_D(r) g(r) dr$$

Self-diffusion coefficient $D = \frac{1}{3}\int_0^\infty \langle \boldsymbol{v}(t)\boldsymbol{v}(0)\rangle dt = \tau k_B T$

Viscosity There are two contributions to the pressure tensor: the *kinetic* part ν_K and the *dissipative* part ν_D

$$\nu_K = \frac{D}{2}$$

$$\nu_D = \frac{2\pi\gamma\rho}{15}\int_0^\infty r^4 w_D(r) g(r) dr$$

If $w_D(r) = (1 - r/r_c)^2$, and using $g(r) = 1$, we have

$$\nu = \frac{45 k_B T}{4\pi\gamma\rho r_c^3} + \frac{2\pi\gamma\rho r_c^5}{1575}$$

Groot, R.D. and P.B. Warren, J. Chem. Phys., 1997.
Marsh, C.A., G. Backx, and M.H. Ernst, PRE, 1997.

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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

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

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

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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

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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

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

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

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

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

- Note that η^D and ζ^D contain a factor of γ^2

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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)

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SPH 1st step: kernel approximation

A(**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; cubic spline; quintic spline ... *(Morris et al, JComputPhys 1997)*
- $h > 0$: kernel error

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

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SPH 2nd step: particle approximation

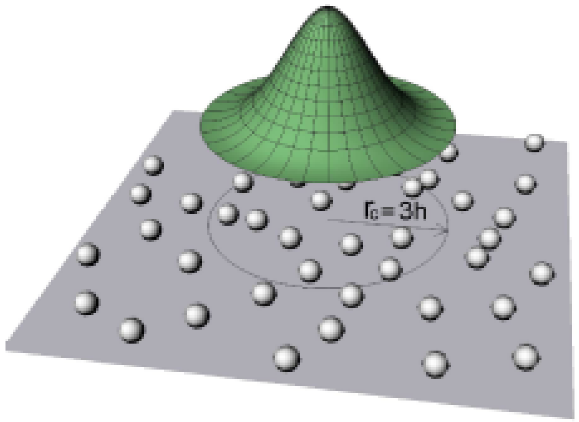
- summation form ($r_c = 3h$):

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

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

$$\ldots = \ldots$$

(Español&Revenga, PRE 2003)



compact support: cell list

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

- $A(\mathbf{r}) = A_S(\mathbf{r}) + E_1(h) + E_2(\Delta x/h)$
  (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

$$\underbrace{\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0}_{\text{Continuity Equation}} \qquad \underbrace{\rho \left(\frac{\partial \vec{u}}{\partial t} + \vec{u} \cdot \nabla \vec{u}\right)}_{\text{Acceleration}} = \underbrace{-\nabla p}_{\text{Pressure}} + \underbrace{\nu \triangle \vec{u}}_{\text{Viscosity}}$$

- Continuity equation

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

- Momentum equation

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

- 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)

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

- Cast dissipative force in GENERIC → random force

$$\begin{aligned} \mathbf{F}_{ij}^{R} &= \left[\frac{-4 k_B T \eta}{r_{ij}} \left(\frac{1}{d_i^2} + \frac{1}{d_j^2} \right) \frac{\partial W}{\partial r_{ij}} \right]^{1/2} d\overline{\overline{\mathbf{W}}}_{ij} \cdot \mathbf{e}_{ij} \\ d\overline{\overline{\mathbf{W}}}_{ij} &= \left(d\mathbf{W}_{ij} + d\mathbf{W}_{ij}^{T} \right) / 2 - tr[d\mathbf{W}_{ij}] \mathbf{I} / D \end{aligned}$$

- dW is an independent increment of Wiener process

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Espanol & Revenga, PRE, 2003

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

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

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GENERIC framework (part 1)

(General Equation for Non-Equilibrium 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

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

- 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

GENERIC framework (part 2)

(General Equation for Non-Equilibrium 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

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

Outline

1. Background
2. Fluctuation-dissipation theorem
3. Parameterization
    - Static properties
    - Dynamic properties
4. DPD ----> Navier-Stokes
5. Navier-Stokes ----> (S)DPD
6. Microscopic ----> DPD
    - Mori-Zwanzig formalism

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Coarse-Graining

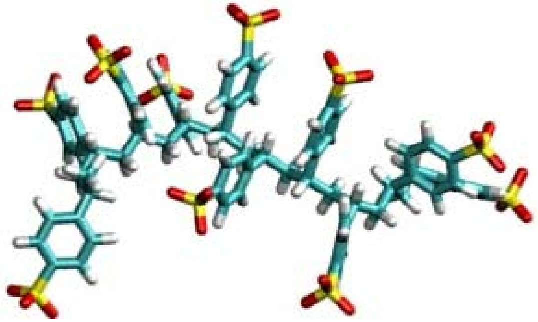
CG: remove irrelevant degrees of freedom from a system

Benefits:
Accelerations on
- Space
- Time

Microscopic system

All-atom model

MD



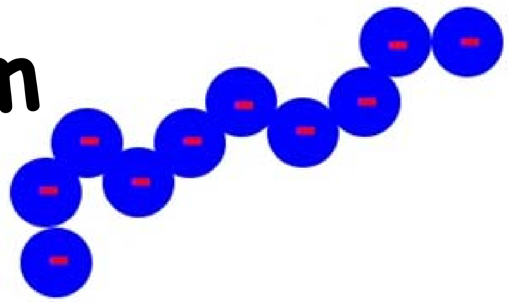
C
G

Irrelevant variables are eliminated

Mesoscopic system

Coarse-grained model

DPD



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Elimination of degrees of freedom from a system

Consider a linear differential system for two variables:

$$\frac{dx}{dt} = x + y, \qquad (1)$$

$$\frac{dy}{dt} = -y + x, \qquad (2)$$

Let $x_0 = x(t=0)$ and $y_0 = y(t=0)$ denote the corresponding initial values.
By solving the Eq. (2)

$$y = \int_0^t e^{-(t-s)} x(s) ds + y_0 e^{-t}$$

we can reduce the system into an equation for $x(t)$ alone:

$$\frac{dx}{dt} = x + \int_0^t e^{-(t-s)} x(s) ds + y_0 e^{-t}$$

The second term in above equation introduces memory.

Dimension Reduction leads to memory effect and noise term.

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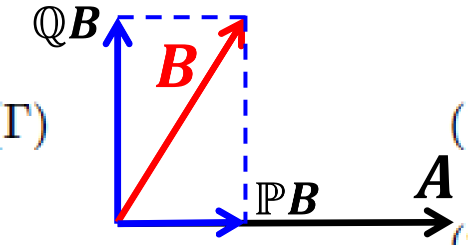
Mori-Zwanzig Projection

Consider a canonical ensemble Γ.

Def: A, B are two variables in Γ, 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

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

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

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

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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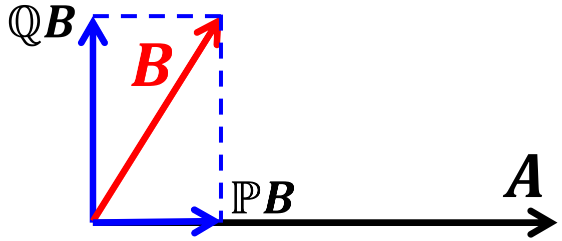
MZ formalism as practical tool

If the coordinates and momenta of the center of mass of the coarse-grained particles are defined as CG variable to be resolved

$$\boldsymbol{R}_I = \frac{1}{M_I}\sum_{\mathrm{I},i} m_{\mathrm{I},i}\mathbf{r}_{\mathrm{I},i} \qquad \boldsymbol{P}_I = \sum_{\mathrm{I},i} \mathbf{p}_{\mathrm{I},i} \qquad M_I = \sum_{\mathrm{I},i} m_{\mathrm{I},i}$$

Define $\mathbb{P}$ and $\mathbb{Q}$ as projection operators for a phase variable $\boldsymbol{A}$

$$\mathbb{P}(*) = \langle * \, \boldsymbol{A}^T\rangle\langle \boldsymbol{A}\boldsymbol{A}^T\rangle^{-1}$$
$$\mathbb{Q} = I - \mathbb{P}$$



Given $\boldsymbol{A}$ the coarse-grained momentum, we identify $e^{t\mathbb{Q}L}\mathbb{Q}L\boldsymbol{A}$ as the random force $\delta\boldsymbol{F}^Q(t)$. Finally, we have the equation of motion for coarse-grained particles

$$\frac{d}{dt}\boldsymbol{P}_I = \frac{1}{\beta}\frac{\partial}{\partial \boldsymbol{R}_I}\ln \boldsymbol{\omega}(\boldsymbol{R})$$
$$-\beta\sum_J \int_0^t ds\, \langle\left[\delta\boldsymbol{F}_I^Q(t-s)\right]\left[\delta\boldsymbol{F}_J^Q(0)\right]^T\rangle \frac{\boldsymbol{P}_J}{M_J} + \delta\boldsymbol{F}_I^Q(t)$$

Details see Kinjo, et. al., PRE 2007. Lei, et. al., PRE, 2010. Hijon, et. al., Farad. Discuss., 2010.

MZ formalism as practical tool

- Equation of motion for coarse-grained particles

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

→ Conservative force

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

→ Friction force

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

→ Stochastic force

Kinjo & Hyodo, PRE, 2007

1. Pairwise approximation: $\boldsymbol{F}_I \approx \sum_{I \neq J} \boldsymbol{F}_{IJ}$
2. No many-body correlation: $\langle [\delta \boldsymbol{F}_{IJ}^{Q}][\delta \boldsymbol{F}_{IK}^{Q}]^T \rangle_{J \neq K} \approx 0$

MZ formalism as practical tool

First term: Conservative Force:

$$\frac{1}{\beta}\frac{\partial}{\partial \mathbf{R}_I}\ln\omega(\mathbf{R}) = \langle \mathbf{F}_I \rangle \approx \sum_{J\neq I}\langle \mathbf{F}_{IJ}\rangle = \sum_{J\neq I} F^C_{IJ}(R_{IJ})\mathbf{e}_{IJ}$$

Second term: Dissipative Force:

$$-\beta\sum_{X=1}^{K}\int_0^t ds \left\langle [\delta\mathbf{F}^Q_I(t-s)][\delta\mathbf{F}^Q_X(0)]^T \right\rangle \frac{\mathbf{P}_X(s)}{M_X}$$

Based on the second approximation, $\langle [\delta \boldsymbol{F}^Q_{IJ}][\delta \boldsymbol{F}^Q_{IK}]^T \rangle_{J\neq K} = 0$
the correlation of fluctuating forces between different pairs is ignored.
Thus, we have

$$\begin{aligned}
&\beta\left\langle [\delta\mathbf{F}^Q_I(t-s)][\delta\mathbf{F}^Q_X(0)]^T \right\rangle \frac{\mathbf{P}_X(s)}{M_X}\\
&= \beta\sum_{J\neq I}\sum_{Y\neq X}\left\langle [\delta\mathbf{F}^Q_{IJ}(t-s)][\delta\mathbf{F}^Q_{XY}(0)]^T \right\rangle \mathbf{V}_X(s)\\
&= \beta\left\langle [\delta\mathbf{F}^Q_{IJ}(t-s)][\delta\mathbf{F}^Q_{IJ}(0)]^T \right\rangle \mathbf{V}_I(s)|_{X=I,Y=J} +\\
&\quad \beta\left\langle [\delta\mathbf{F}^Q_{IJ}(t-s)][\delta\mathbf{F}^Q_{JI}(0)]^T \right\rangle \mathbf{V}_J(s)|_{X=J,Y=I}\\
&= \beta\left\langle [\delta\mathbf{F}^Q_{IJ}(t-s)][\delta\mathbf{F}^Q_{IJ}(0)]^T \right\rangle \mathbf{V}_{IJ}(s)\\
&= K_{IJ}(t-s)\mathbf{V}_{IJ}(s)
\end{aligned}$$

MZ formalism as practical tool

The equation of motion (EOM) of coarse-grained particles resulting from the Mori-Zwanzig projection is given by:

$$\dot{\mathbf{P}}_I = \underbrace{k_B T \frac{\partial}{\partial \mathbf{R}_I} \ln \omega(\mathbf{R})}_{\text{Conservative force}} \underbrace{- \frac{1}{k_B T} \sum_{J=1}^{K} \int_0^t ds \left\langle \left[\delta \mathbf{F}_I^Q(t-s)\right] \left[\delta \mathbf{F}_J^Q(0)\right]^T \right\rangle \cdot \frac{\mathbf{P}_J(s)}{M_J}}_{\text{Dissipative force}} \underbrace{+ \delta \mathbf{F}_I^Q(t)}_{\text{Random force}}$$

Conservative force | Dissipative force | Random force

$$\boldsymbol{F}_I \approx \sum_{I \neq J} \boldsymbol{F}_{IJ} \qquad \langle [\delta \boldsymbol{F}_{IJ}^Q][\delta \boldsymbol{F}_{IK}^Q]^T \rangle_{J \neq K} \approx 0$$

The above EOM can be written into its pairwise form:

$$\dot{\mathbf{P}}_I = \sum_{J \neq I} \mathbf{F}_{IJ}(t) = \sum_{J \neq I} \left[\langle \mathbf{F}_{IJ} \rangle - \int_0^t \mathbf{K}_{IJ}(t-s) \mathbf{V}_{IJ}(s) ds + \delta \mathbf{F}_{IJ}^Q(t) \right]$$

where $\boldsymbol{F}_{IJ}$ is the instantaneous force whose ensemble average $\langle \boldsymbol{F}_{IJ} \rangle$ is taken as the conservative force, the memory kernel

$\boldsymbol{K}_{IJ}(t) = \beta \langle [\delta \boldsymbol{F}_{IJ}^Q(t)][\delta \boldsymbol{F}_{IJ}^Q(0)]^T \rangle$,

which satisfies the second fluctuation-dissipation theorem (FDT).

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MZ formalism as practical tool

Remark: The memory term can be further simplified with a Markovian assumption that the memory of fluctuating force in time is short enough to be approximated by a Dirac delta function

$$\beta\langle[\delta\mathbf{F}_{IJ}(t-s)][\delta\mathbf{F}_{IJ}(0)]^T\rangle = 2\gamma_{IJ}\delta(t-s) \ ,$$
$$\beta\int_0^t ds\,\langle[\delta\mathbf{F}_{IJ}(t-s)][\delta\mathbf{F}_{IJ}(0)]^T\rangle\,\mathbf{V}_{IJ}(s) = \gamma_{IJ}\cdot\mathbf{V}_{IJ}(t) \ ,$$

where γ_{IJ} is the friction tensor defined by $\gamma_{IJ} = \beta\int_0^\infty dt\,\langle[\delta\mathbf{F}_{IJ}(t)][\delta\mathbf{F}_{IJ}(0)]^T\rangle$. Then, the equation of motion of DPD particles based on the Markovian approximation can be expressed by

$$\frac{d\mathbf{P}_I}{dt} = \sum_{J\neq I}\{\,F_{IJ}^C(R_{IJ})\mathbf{e}_{IJ} - \gamma_{IJ}(R_{IJ})\,(\mathbf{e}_{IJ}\cdot\mathbf{V}_{IJ})\,\mathbf{e}_{IJ} + \delta\mathbf{F}_{IJ}(t)\,\}$$

DPD model

DPD model comes from coarse-graining of its underlying microscopic system.

- Irrelevant variables are eliminated using MZ projection.
- Only resolve the variables that we are interested in.
- Unresolved details are represented by the dissipative and random forces.

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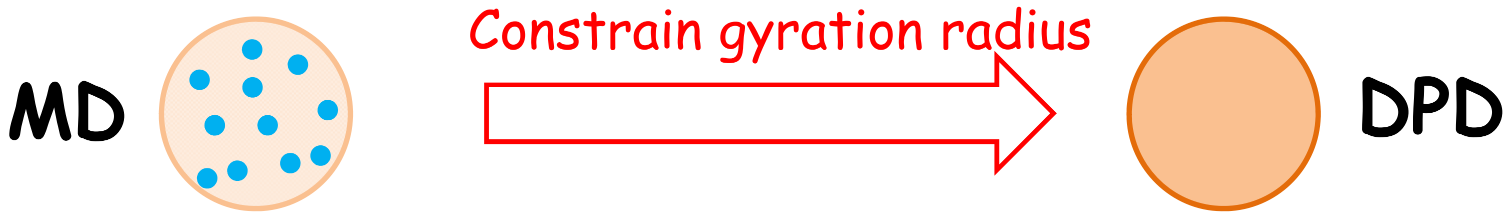
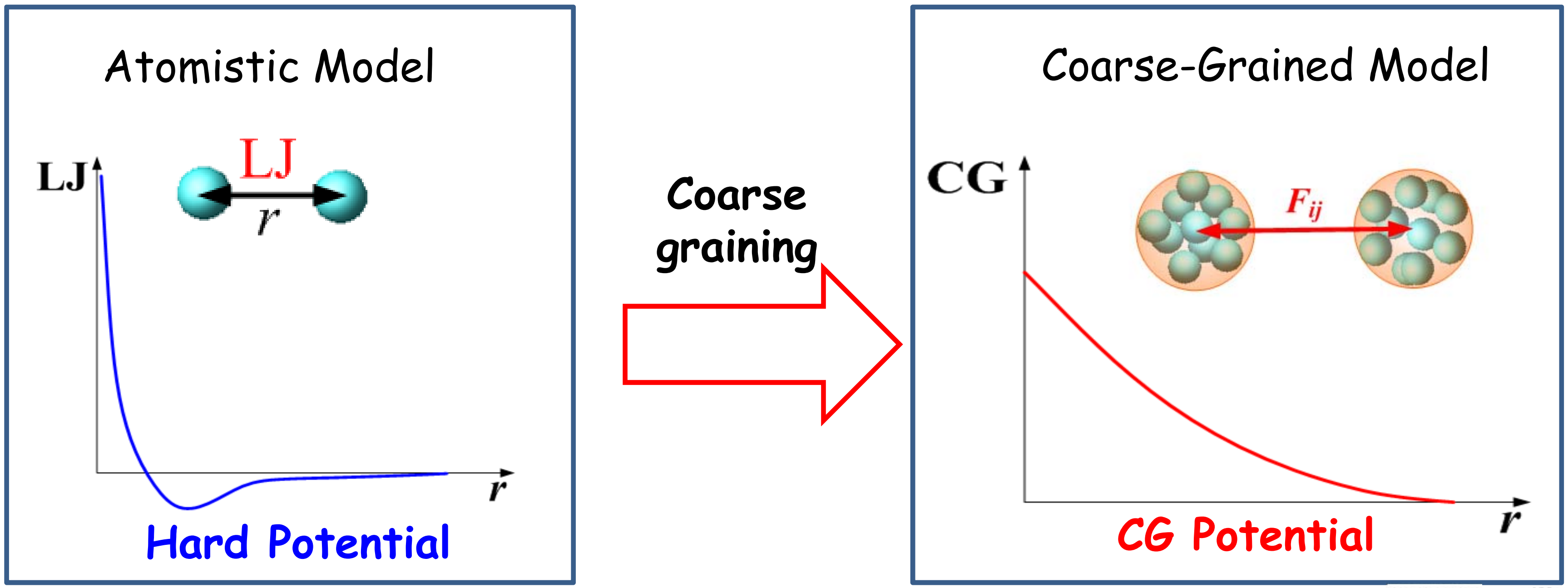
Coarse-graining constrained fluids

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





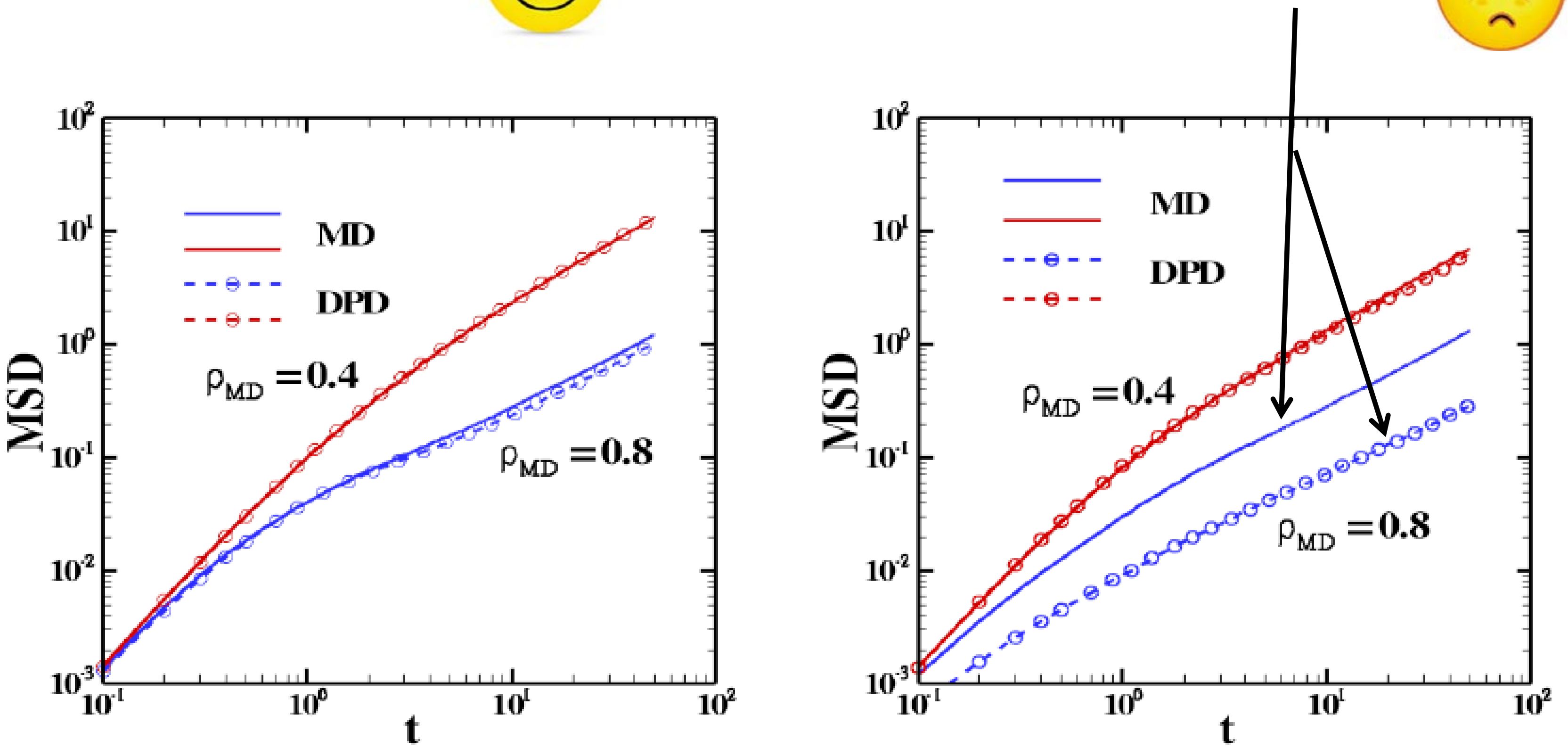
Lei, Caswell & Karniadakis, PRE, 2010

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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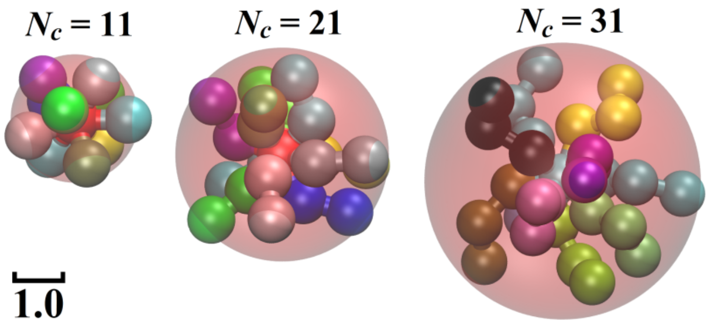
Coarse-graining unconstrained polymer melts

- Natural bonds

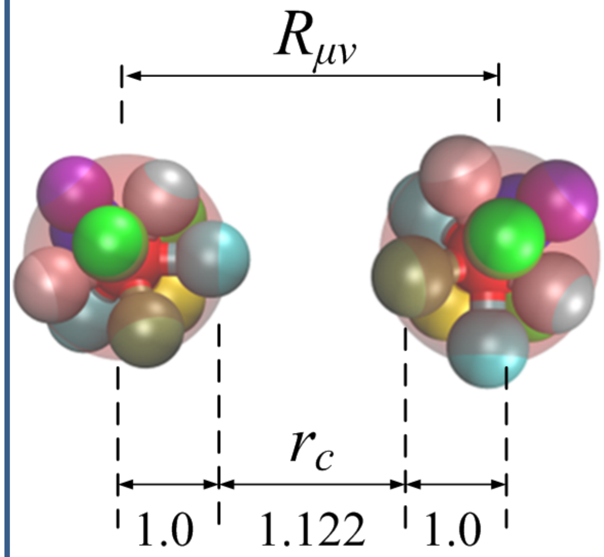


WCA Potential + FENE Potential

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

$$V_B(r) = \begin{cases} -\frac{1}{2}kR_0^2 \ln\left[1 - (r/R_0)^2\right]; & r \le R_0 \\ \infty; & r > R_0 \end{cases}$$

NVT ensemble with Nose-Hoover thermostat.



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

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

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

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

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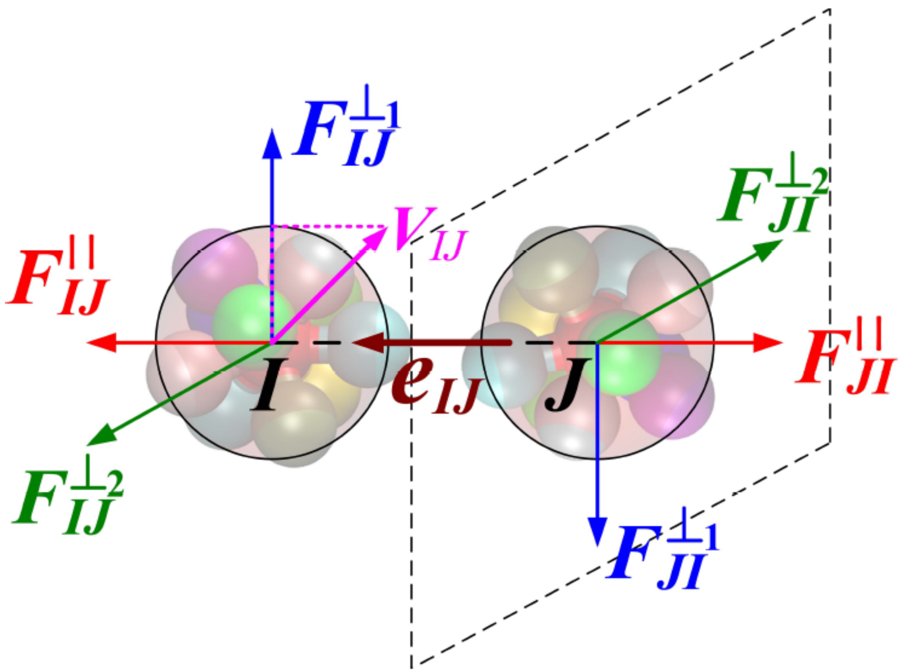
Directions for pairwise interactions between neighboring clusters



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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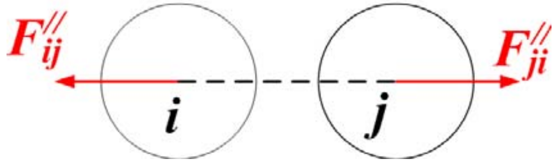
Three coarse-grained (DPD) models

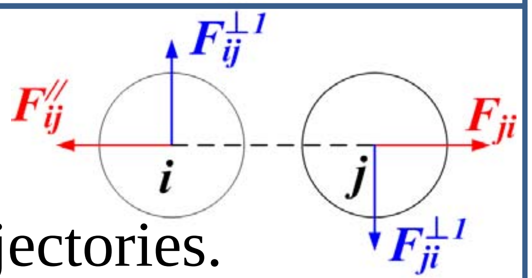
Translational momentum

$\mathbf{F}_{ij}^{//}$



1. **MZ-DPD model**:
   CG force field obtained from microscopic trajectories.

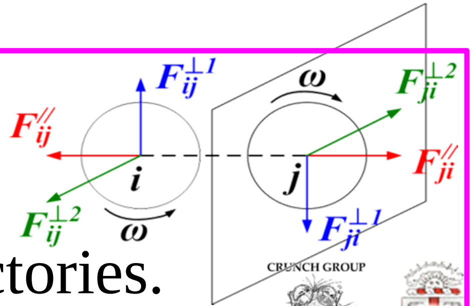
$\mathbf{F}_{ij}^{//} + \mathbf{F}_{ij}^{\perp 1}$



2. **MZ-TDPD model**:
   CG force field obtained from microscopic trajectories.

Translational + Angular momenta

$\mathbf{F}_{ij}^{//} + \mathbf{F}_{ij}^{\perp 1} + \mathbf{F}_{ij}^{\perp 2}$



3. MZ-FDPD model:
   CG force field obtained from microscopic trajectories.

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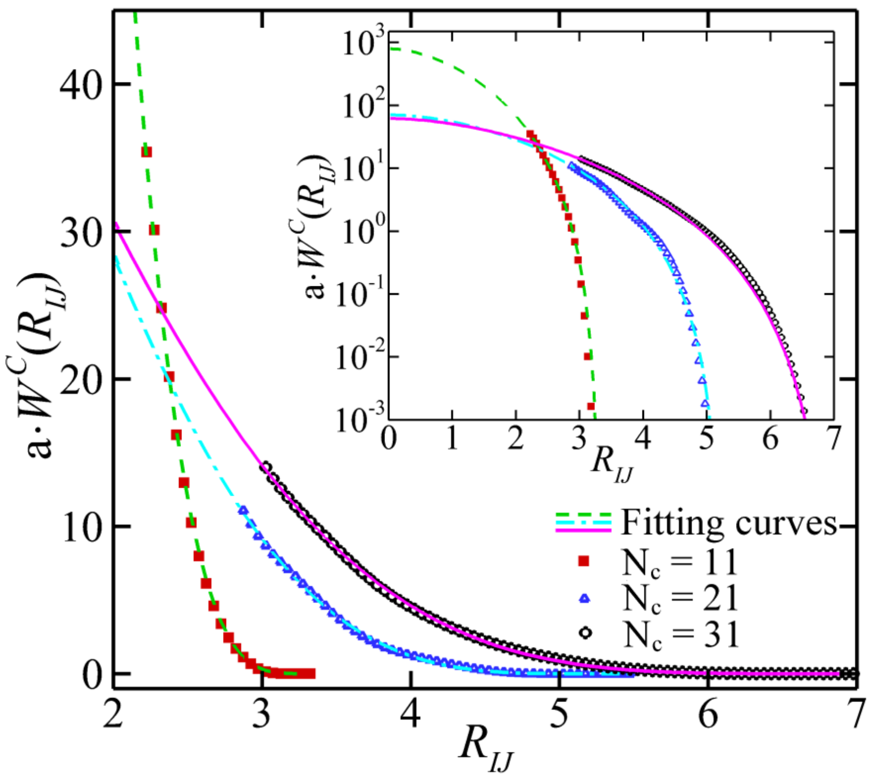
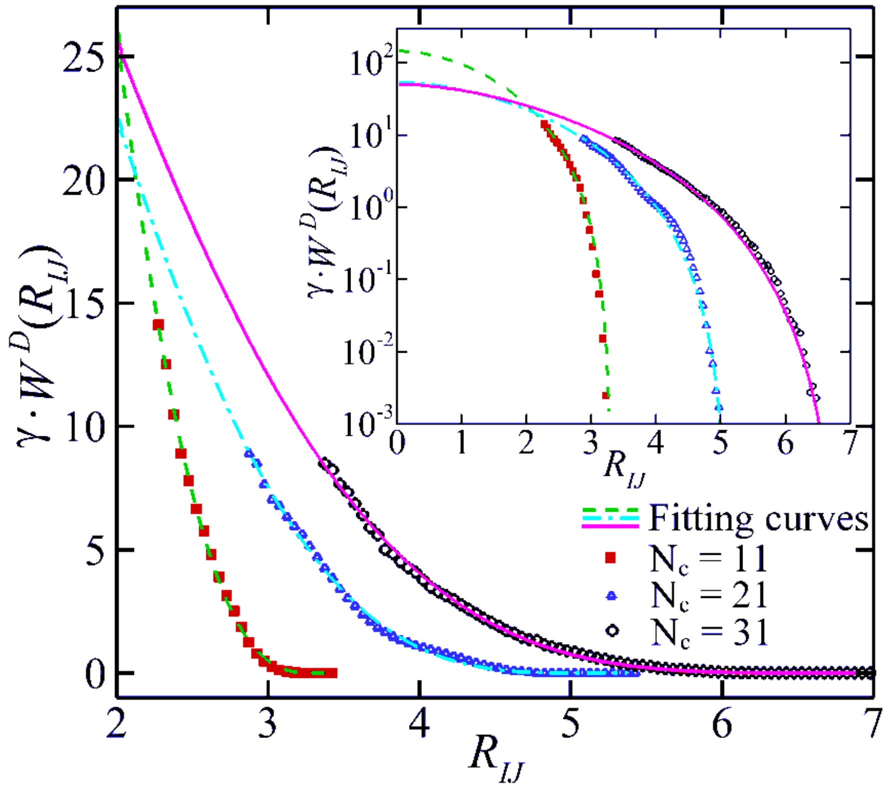
DPD force fields from MD simulation

Conservative

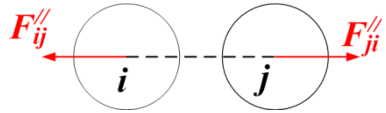


Dissipative (parallel one)

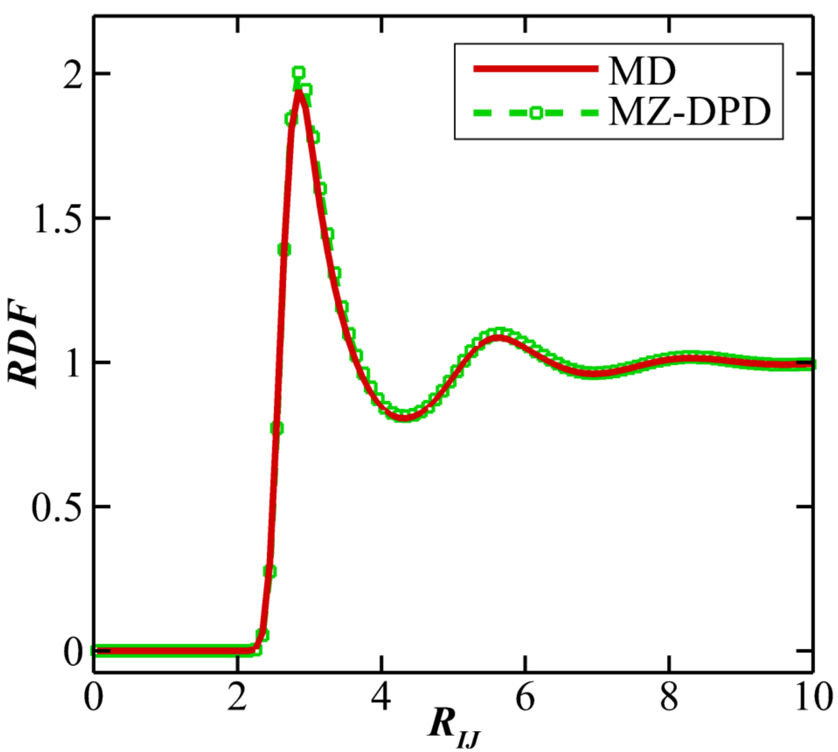


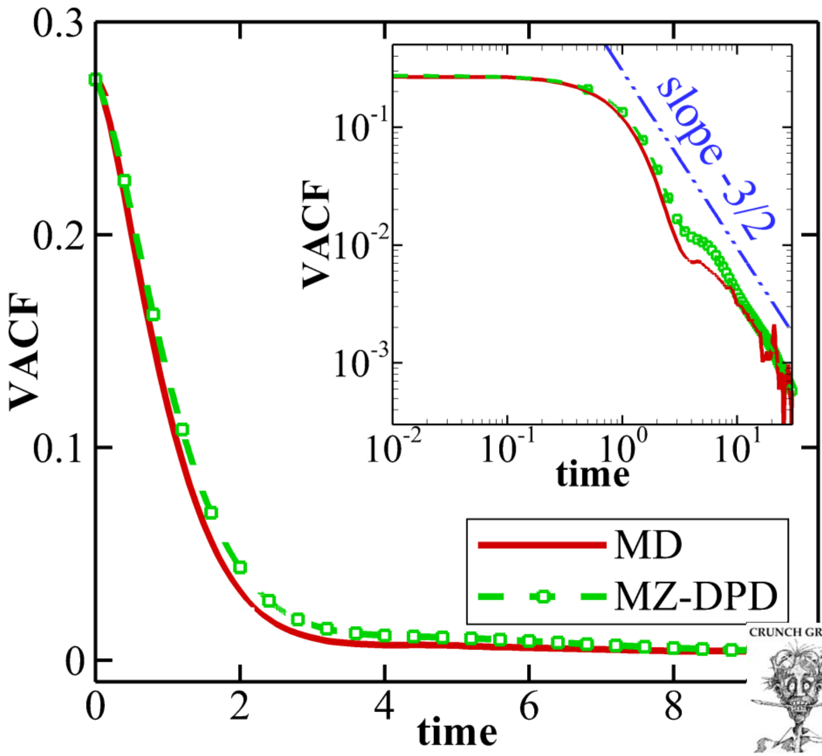
Li, Bian, Caswell & Karniadakis, 2014

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

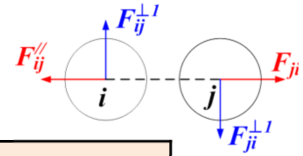


Quantities	MD	**MZ-DPD (error)**
Pressure	**0.191**	**0.193 (+1.0%)**
Diffusivity (Integral of VACF)	**0.119**	**0.138 (+16.0%)**
Viscosity	**0.965**	**0.851 (-11.8%)**
Schmidt number	**8.109**	**6.167 (-23.9%)**
Stokes-Einstein radius	**1.155**	**1.129 (-2.2%)**

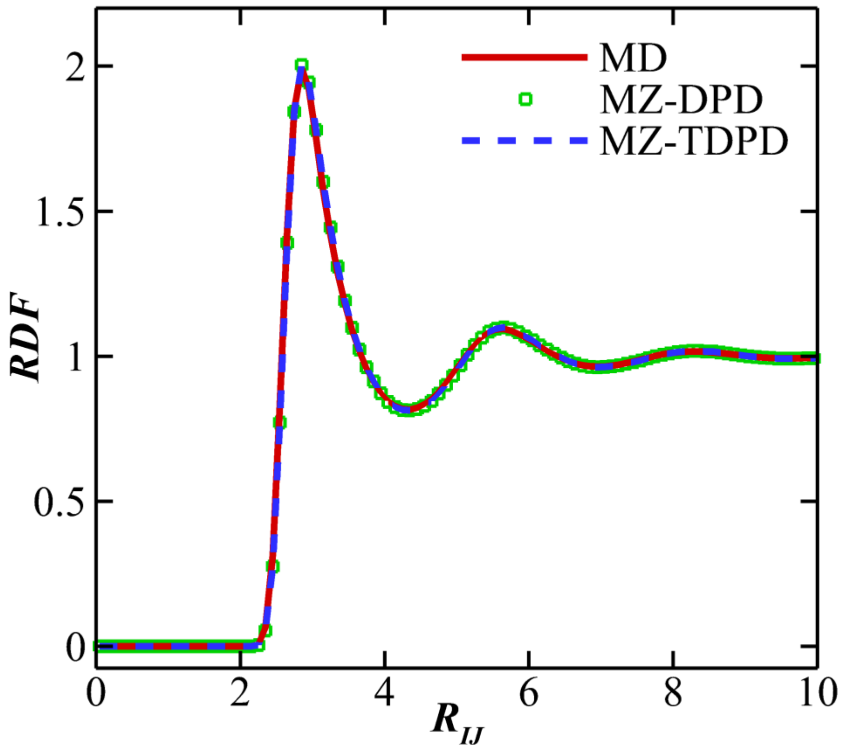


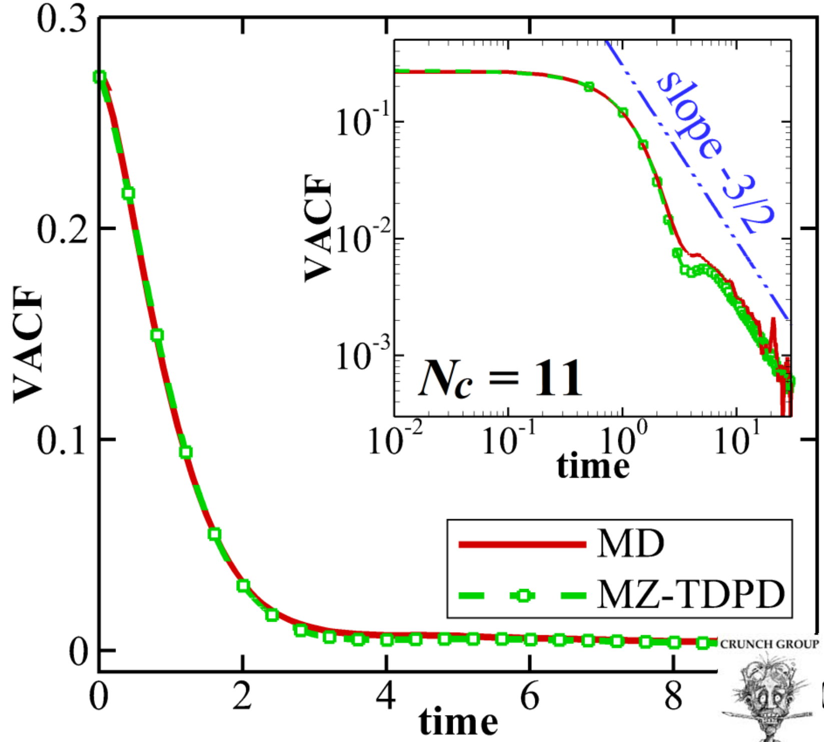


Performance of the MZ-TDPD model (Nc = 11)



Quantities	MD	MZ-TDPD (error)
Pressure	**0.191**	**0.193 (+1.0%)**
Diffusivity (Integral of VACF)	**0.119**	**0.111 (-6.7%)**
Viscosity	**0.965**	**1.075 (+11.4%)**
Schmidt number	**8.109**	**9.685 (+19.4%)**
Stokes-Einstein radius	**1.155**	**1.112 (-3.7%)**





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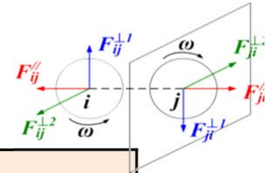
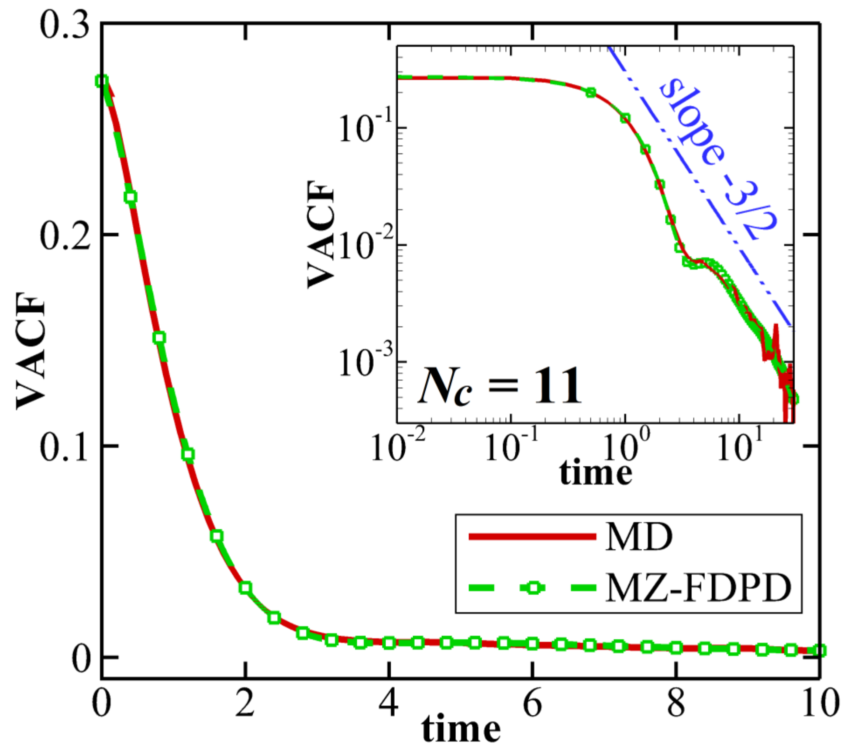
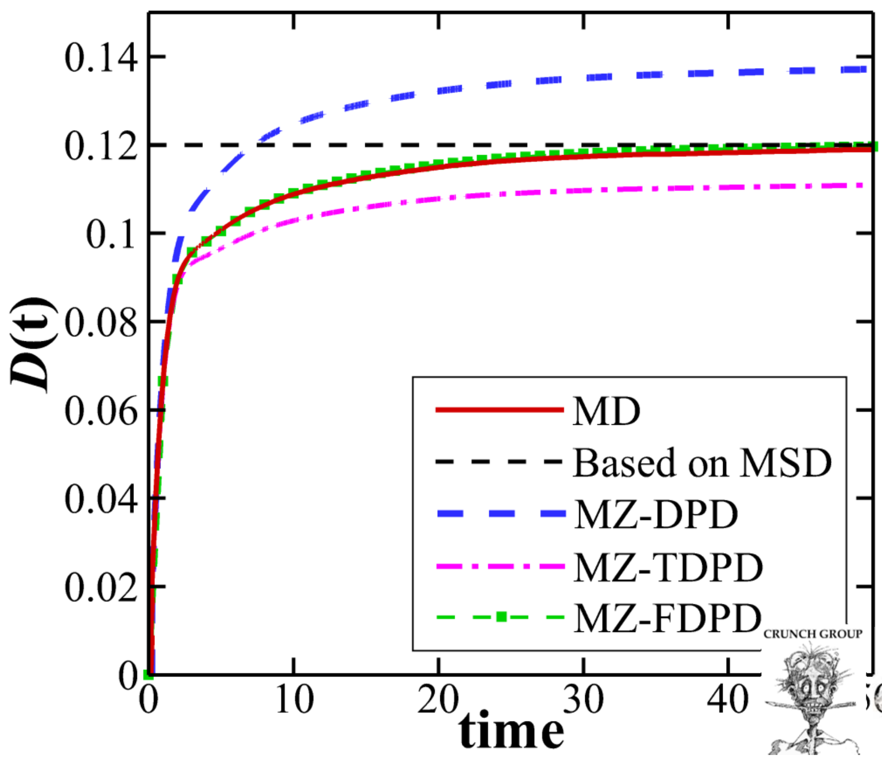
Performance of the MZ-FDPD model (N_c = 11)



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
  - Flucutation-dissipation theorem
  - Canonical ensemble (NVT)
- DPD <------> Navier-Stokes equations
- Coarse-graining microscopic system
  - Mori-Zwanzig formalism

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