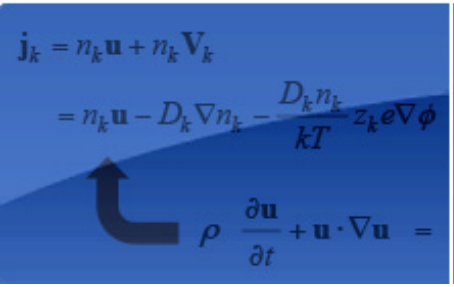
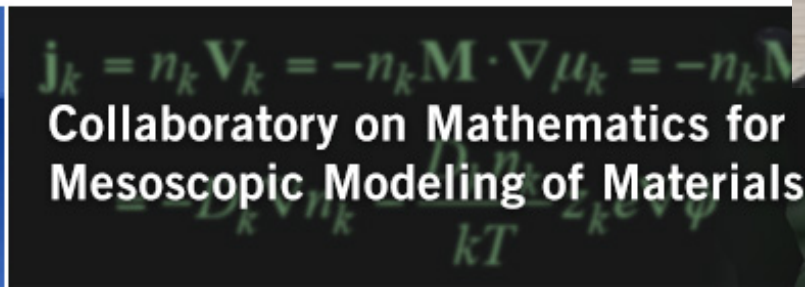
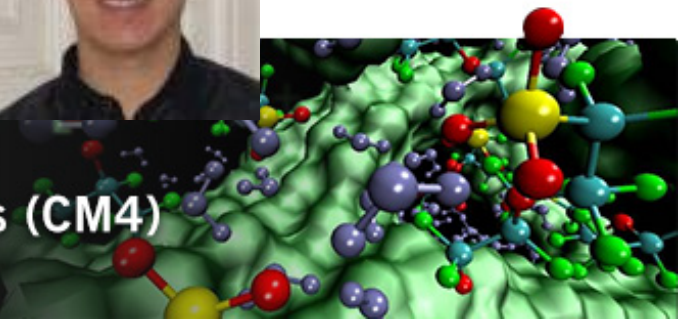
Coarse-Graining via the Mori-Zwanzig Formalism

George Em Karniadakis & Zhen Li







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Mori-Zwanzig can be used to:

1. Derive coarse-grained equations

2. Analyze systems with memory

3. Construct reduced-order models

4. Detect singularities - design meshes

5. Quantify uncertainty

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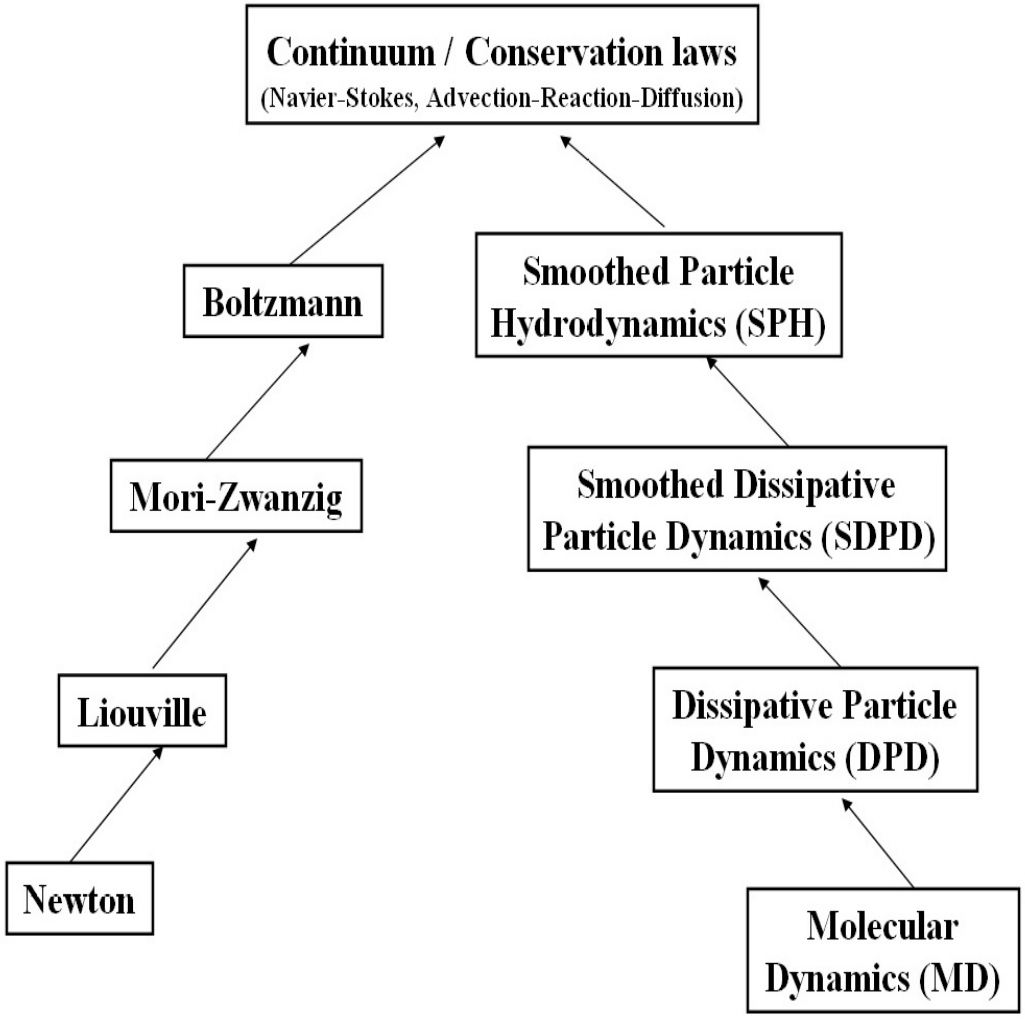
Hierarchy of Mathematical & Numerical Models



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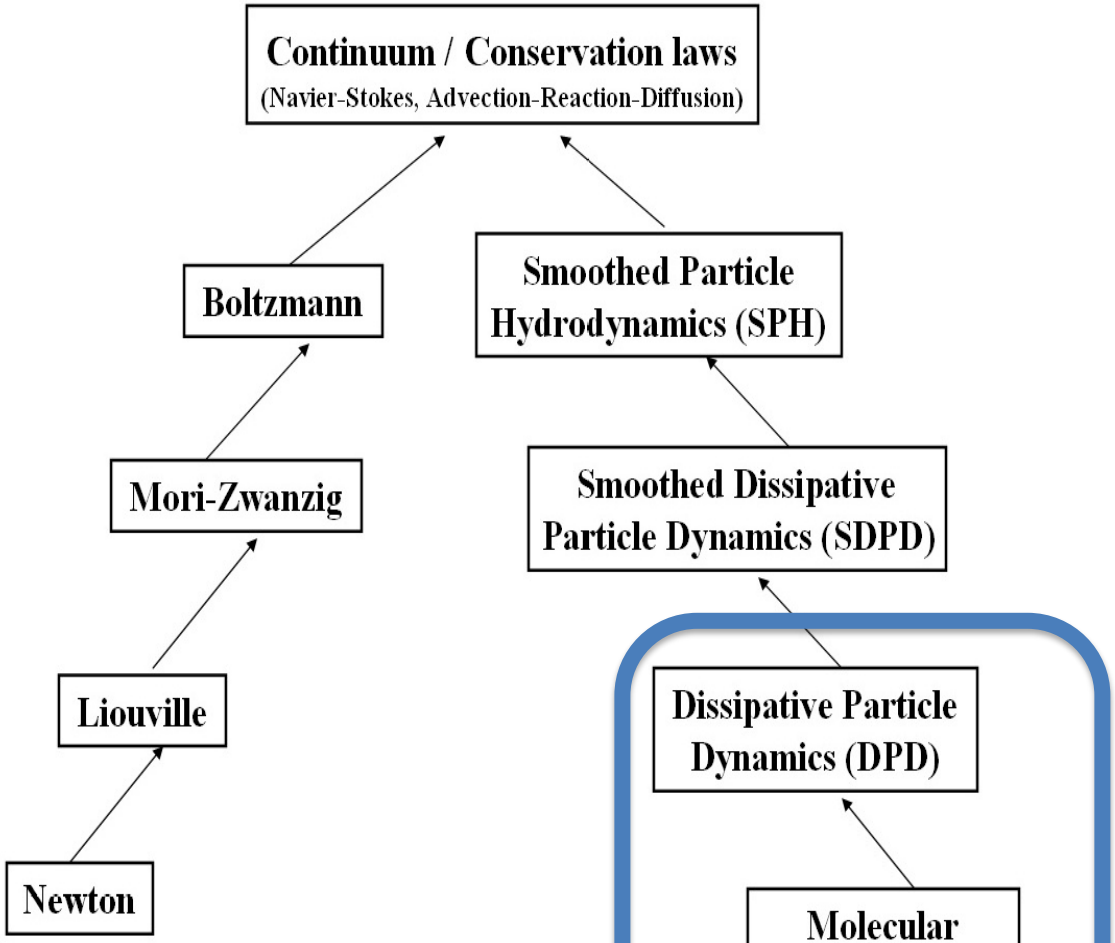
Hierarchy of Mathematical & Numerical Models



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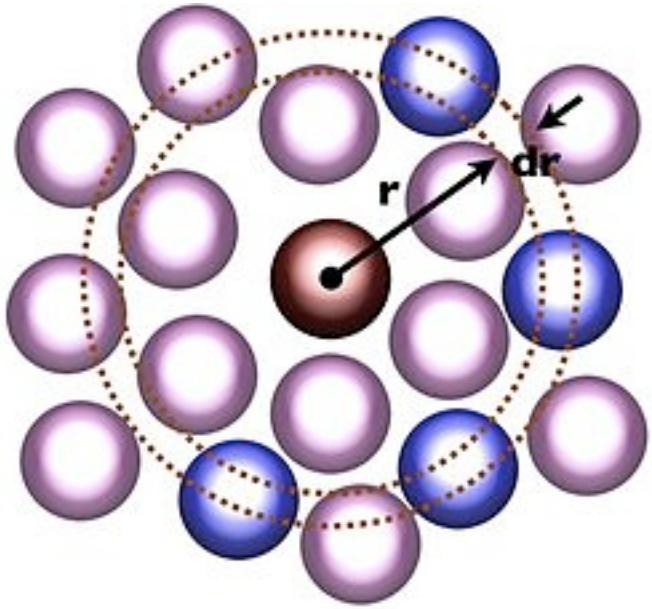
Radial Distribution Function (RDF)

The **radial distribution function** (or **pair correlation function**) $g(r)$ in a particle-based system describes how density varies as a function of distance from a reference particle.



$$g(r) = \frac{1}{\rho N} \sum_{i=1, j \neq i}^{N} \langle \delta(r - r_{ij}) \rangle$$

$\rho g(r)$ is the conditional probability to find another particle at a distance r away from the origin.

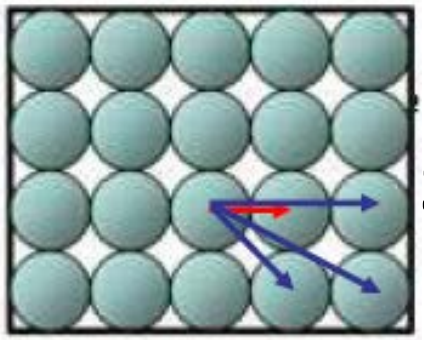
In discrete form: count the number of particles that lie in a spherical shell of radius r and thickness dr

$$g(r) = \frac{\rho(r)}{\rho} = \frac{1}{\rho} \frac{\langle N(r \pm \frac{dr}{2}) \rangle / 2}{4\pi r^2 dr}$$

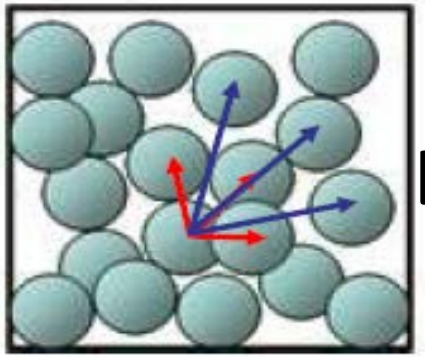
← Number of pairs

← Volume of the shell

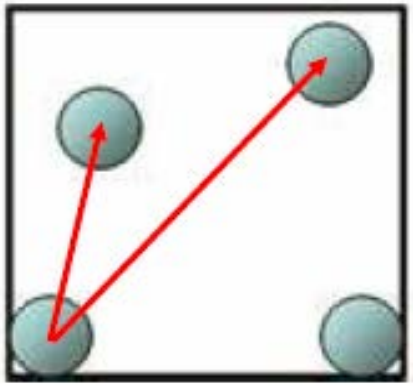
Radial Distribution Function (RDF)



Solid

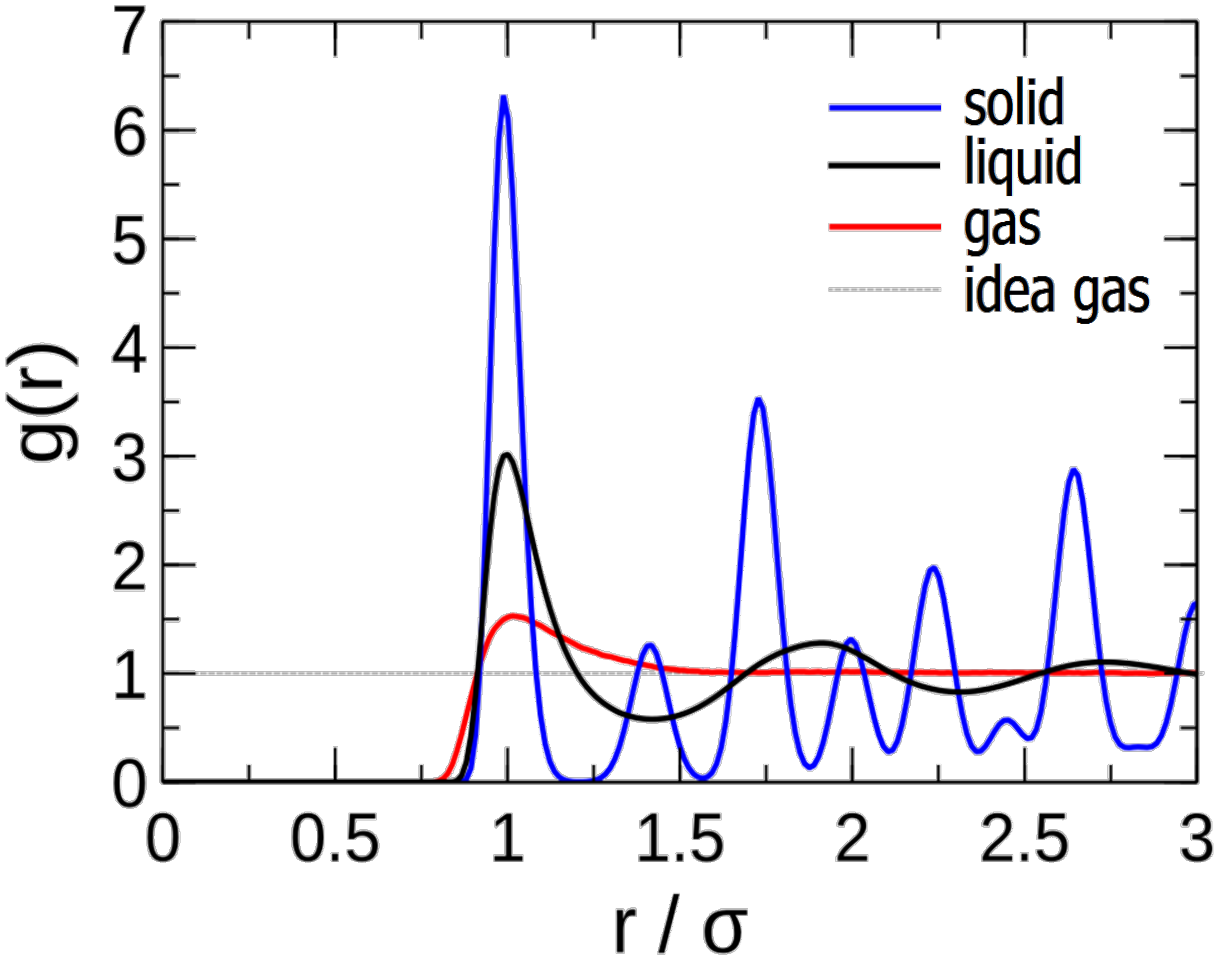


Liquid



Gas

Note: RDF can be measured experimentally using x-ray or neutron-scattering techniques.



Ideal gas: $g(r) = 1$

Radial Distribution Function (RDF)

Thermodynamic quantities from the computed g(r): **Internal Energy**

$$E = \frac{3}{2} N k_B T + \frac{N}{2} 4\pi\rho \int_0^\infty r^2 V(r) g(r) dr$$

Thermodynamic quantities from the computed g(r): **Pressure**

$$P = \rho k_B T - \frac{2}{3} \pi\rho^2 \int_0^\infty r^3 \frac{dV(r)}{dr} g(r) dr$$

Static structure factor: a mathematical description of how a material scatters incident radiation:

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

Velocity Autocorrelation Function (VACF)

Definition: $C(t) = \langle \boldsymbol{V}(t)\boldsymbol{V}(0) \rangle$

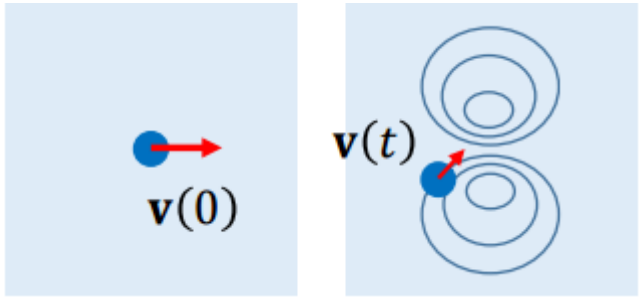
which reveals the underlying nature of the dynamical processes operating in a molecular system.

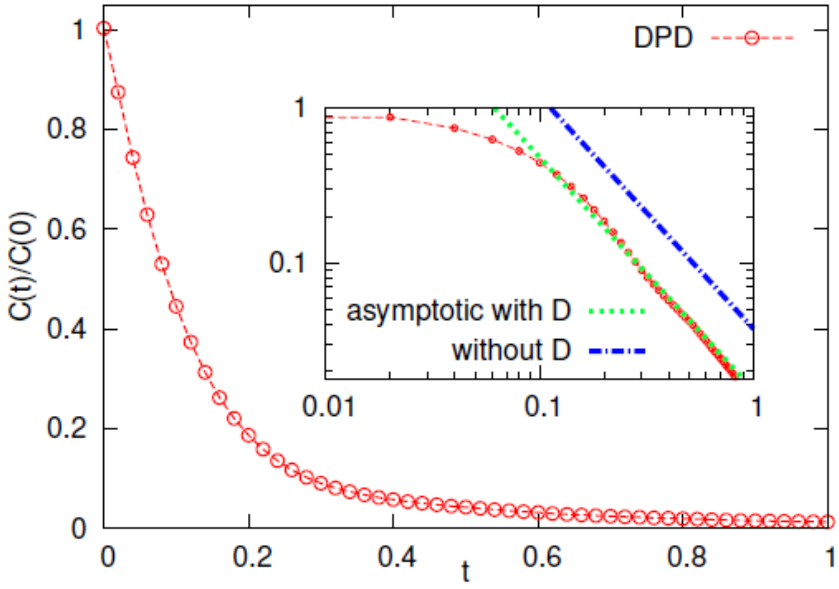
Short time: $C(t) \sim \exp(-\gamma t/M)$

Long time: $C(t) \sim t^{-3/2}$ (Bulk), $C(t) \sim t^{-5/2}$ or $t^{-7/2}$ (confinement)

$$C(t) = \frac{3k_BT}{M}\exp\left(-\frac{\gamma t}{M}\right) + \frac{2k_BT}{\rho M}[4\pi(D+\nu)t]^{-3/2}$$

Algebraic tail of the VACF:





Diffusion constant is the integral of VACF: $D = \frac{1}{3}\int_0^\infty d\tau \, \langle \boldsymbol{V}(\tau)\boldsymbol{V}(0) \rangle$

Fluctuation-Dissipation Theorem (FDT)

The FDT quantifies the relation between the fluctuations in a system at thermal equilibrium and the response of the system to applied perturbations.

Let $\boldsymbol{x}(t)$ be an observable of a dynamical system with Hamiltonian $H_0(\boldsymbol{x})$ subject to thermal fluctuations. $\boldsymbol{x}(t)$ fluctuates around its mean value $\langle x \rangle_0$ and the power spectrum of fluctuations is denoted by $S_x(\omega)$.

Consider a time-dependent field $f(t)$ that alters the Hamiltonian to $H(\boldsymbol{x}) = H_0(\boldsymbol{x}) + f(\mathrm{t})\mathbf{x}$. The response of $\boldsymbol{x}(t)$ to $f(t)$ is characterized by the linear response function $\chi(t)$ of the system

$$\langle \boldsymbol{x}(t) \rangle = \langle \boldsymbol{x} \rangle_0 + \int_{-\infty}^{t} f(\tau)\chi(t-\tau)d\tau$$

The fluctuation-dissipation theorem relates the power spectrum of $\boldsymbol{x}$ to the imaginary part of the Fourier transform $\hat{\chi}(\omega)$ of the susceptibility $\chi(t)$

$$S_x(\omega) = \frac{2k_B T}{\omega} \operatorname{Im} \hat{\chi}(\omega)$$

The left-hand side describes fluctuations in $\boldsymbol{x}$, the right-hand side relates to the energy dissipated by the system when pumped by an oscillatory field $f(t) = F\sin(\omega t + \phi)$.

For a particle-based stochastic system, a canonical ensemble is expected only if the FDT is satisfied. Otherwise, the system cannot reach a thermal equilibrium at the designed temperature.

R. Kubo, *The fluctuation-dissipation theorem*. 1966.

DPD : Pairwise Interactions

Forces exerted by particle J on particle I:

Fluctuation-dissipation relation:
$\sigma^2 = 2\,\gamma\,\kappa_B T \qquad \omega^D = [\,\omega^R]^2$

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

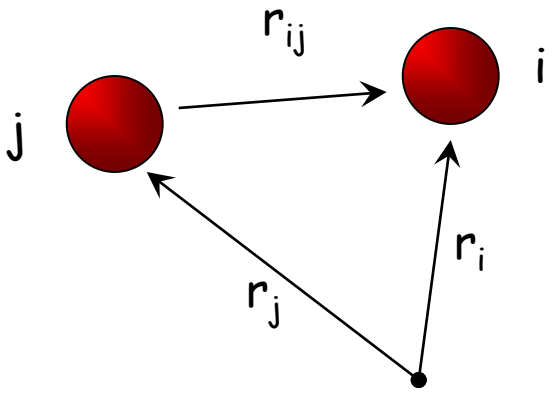
Conservative
fluid / system dependent

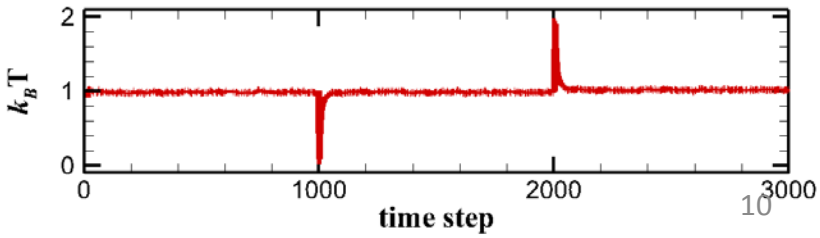
$$\vec{F}_{ij}^{D} = -\gamma\,\omega^{D}(r_{ij})(\vec{v}_{ij}\cdot\vec{e}_{ij})\vec{e}_{ij}$$

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

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

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





Outline

1. Introduction

— Bottom-up coarse-graining

2. Foundation: Coarse-Graining

— Introduction of the Mori-Zwanzig formalism.

— Markovian model

— Non-Markovian model

3. Construction of coarse-grained model directly from MD simulation

— Static properties

— Dynamics properties

4. Summary

Different coarse-graining strategies

Reverse-coarse-graining procedure

An initial guess of the CG force fields is posed at the beginning and many free parameters in a coarse-grained model are left undetermined.

Subsequently, an (iterative) inverse optimization is carried out to get the optimal free parameters so that target properties are obtained.

Target properties ⟵ **Optimization**

Note: No guarantee of correct properties beyond targets.

Forward-coarse-graining procedure (No prior targets assigned)

The CG force fields are constructed directly from MD trajectories via the Mori-Zwanzig projection.

This procedure may require additional assumptions for simplification of formulation; in principle, there are no free parameters to be specified.

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Coarse-Graining

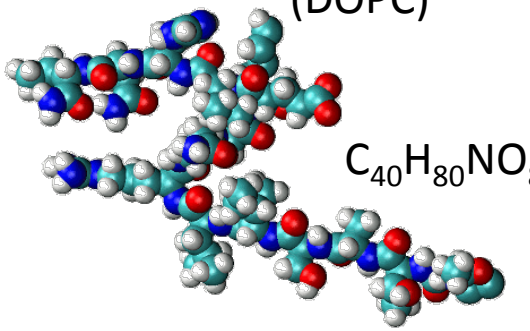
CG: remove irrelevant degrees of freedom from a system

Dipalmitoylphosphatidylcholine (DOPC)

Microscopic system

All-atom model

MD



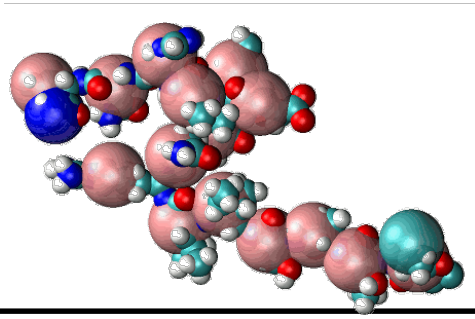
CG

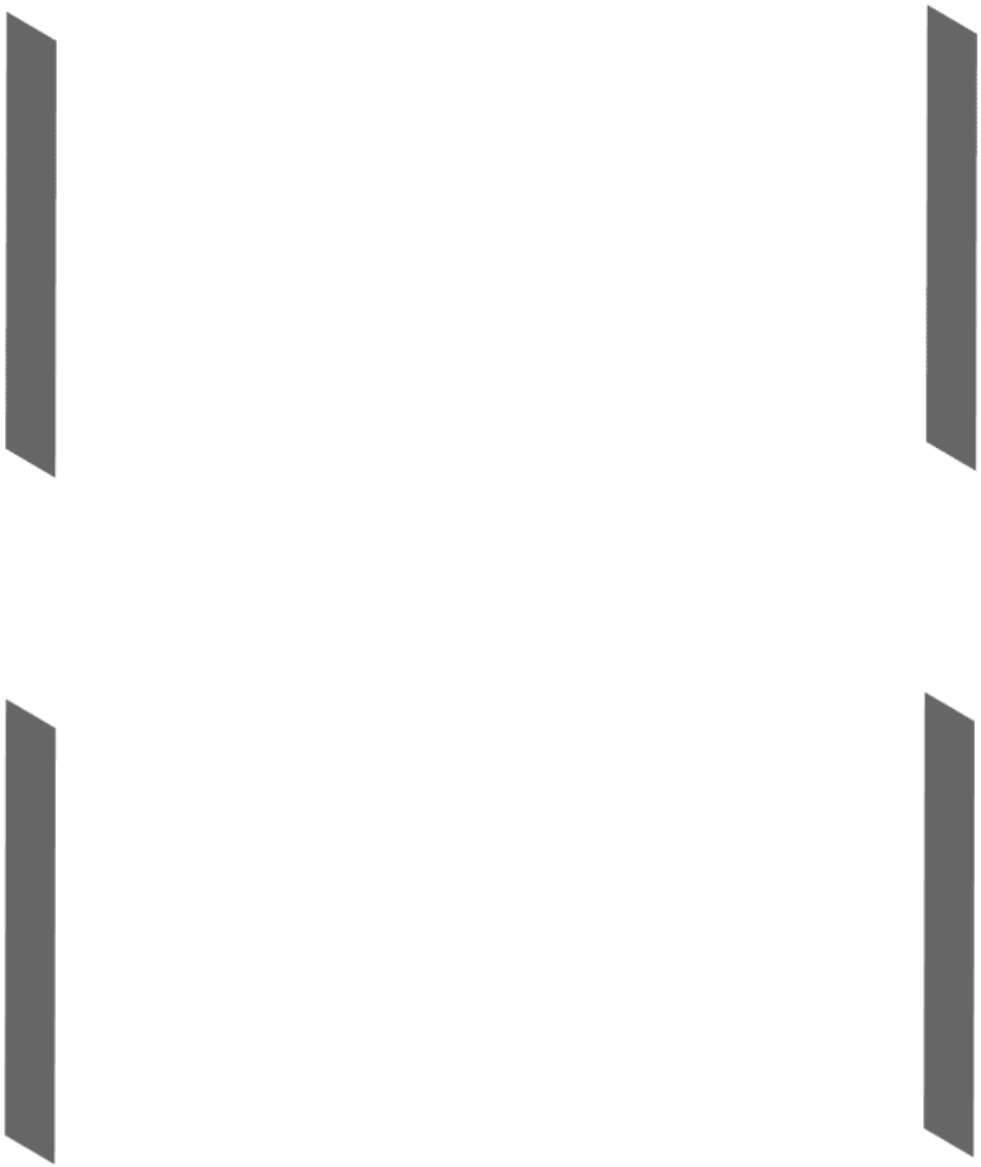
Irrelevant variables are eliminated

Mesoscopic system

Coarse-grained model

DPD





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:

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

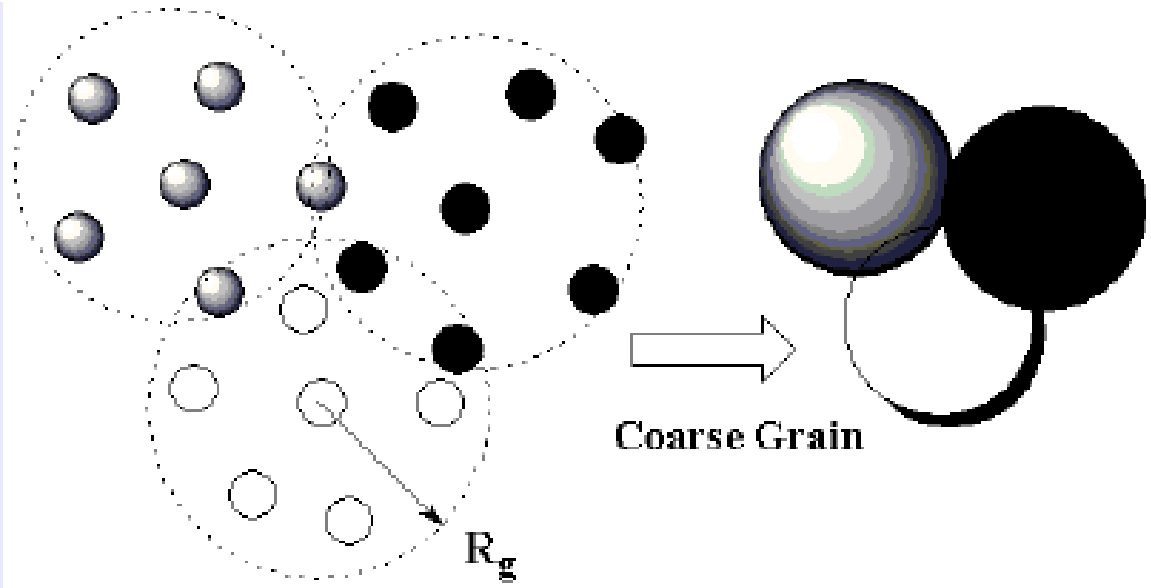
The second term in above equation introduces memory.

Dimension Reduction leads to memory effect and noise term.

Dissipative Particle Dynamics (DPD)

1. Mori-Zwanzig formulation

2. Direct construction of DPD from MD



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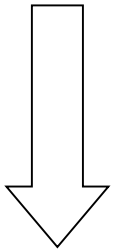
Equation of Coarse-Grained System

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i<j}^{N} v\left(|\mathbf{r}_i - \mathbf{r}_j|\right)$$

$$\mathbf{R}_\mu = \frac{1}{N_\mu} \sum_{i=0}^{N_\mu} \mathbf{r}_{\mu i}$$



$$\mathbf{P}_\mu = \sum_{i=0}^{N_\mu} \mathbf{p}_{\mu i}$$

$$H = \sum_{\mu=1}^{K} \frac{\mathbf{P}_\mu^{\,2}}{2M_\mu} + \sum_{\mu<\nu}^{K} V\left(|\mathbf{R}_\mu - \mathbf{R}_\nu|\right) + \sum_{\mu=1}^{K} \sum_{\mu_i=1}^{N_\mu} \frac{\mathbf{p'}_{\mu_i}^{\,2}}{2m_{\mu_i}} + \sum_{\mu=1}^{K} \sum_{\mu_i<\mu_j}^{N_\mu} v\left(\left|\mathbf{r'}_{\mu_i} - \mathbf{r'}_{\mu_j}\right|\right),$$

CG (slower) Variables

Atomistic (fast) variables

Mori-Zwanzig Formalism (Zwanzig, Nonequilibrium Statistical Mechanics, 2001)

Consider a *n*-dimensional system of ordinary differential equations

$$\frac{d\phi_i(x,t)}{dt} = R(\phi(x,t)),$$

$$\phi_i(x,0) = x_i, \quad 1 \le i \le n.$$

$$\phi = (\hat{\phi}, \tilde{\phi}), \quad \hat{\phi} = (\phi_1, \ldots, \phi_m), \quad \tilde{\phi} = (\phi_{m+1}, \ldots, \phi_n)$$

Form the Liouville equation $u_t = Lu$, the components $\hat{\phi}$ are

$$\hat{\phi}_j(x,t) = e^{tL} x_j$$

Let $\mathbb{P}$ be the conditional expectation projection $\mathbb{P}g(x) = E[g|\hat{x}]$.

Define $\mathbb{Q} = I - \mathbb{P}$ and keep in mind that $\mathbb{P}^2 = \mathbb{P}$, $\mathbb{Q}^2 = \mathbb{Q}$, and $\mathbb{P}\mathbb{Q} = 0$, as must be true for any projection.

Mori-Zwanzig Formalism (Zwanzig, Nonequilibrium Statistical Mechanics, 2001)

Consider $\mathbb{P} + \mathbb{Q} = I$, we have

$$\frac{\partial}{\partial t} e^{tL} x_j = e^{tL} L x_j = e^{tL}(\mathbb{P} + \mathbb{Q}) L x_j = e^{tL} \mathbb{P} L x_j + e^{Lt} \mathbb{Q} L x_j$$

Using Dyson's formula (Duhamel's principle)

$$e^{tL} = e^{t\mathbb{Q}L} + \int_0^t e^{(t-\tau)L}\, \mathbb{P} L e^{\tau \mathbb{Q} L} d\tau$$

We obtain the Mori-Zwanzig equation

$$\frac{\partial}{\partial t} e^{tL} x_j = e^{tL} \mathbb{P} L x_j + \int_0^t e^{(t-\tau)L}\, \mathbb{P} L e^{\tau \mathbb{Q} L} \mathbb{Q} L x_j d\tau + e^{t\mathbb{Q}L} \mathbb{Q} L x_j$$

This equation is exact and is an alternative way of writing the original system of ODEs.

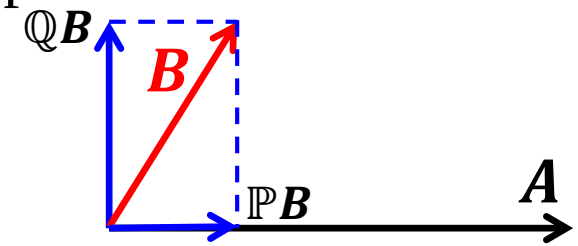
Mori-Zwanzig Formalism (Zwanzig, Nonequilibrium Statistical Mechanics, 2001)

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.

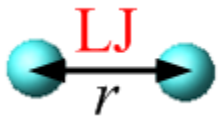
Mori-Zwanzig Formalism (Zwanzig, Nonequilibrium Statistical Mechanics, 2001)

Consider an atomistic system consisting of N atoms, which are grouped into K clusters, and N_C atoms in each cluster.

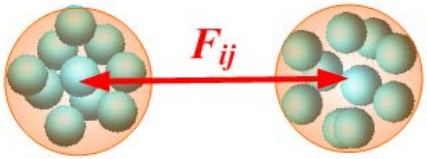
The Hamiltonian of the atomistic system is:

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

Atomistic Model



Our interest is on the molecular or CG level :



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

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

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

The equation of motion for CG particles can be written as:

$$\frac{d}{dt}\mathbf{P}_I = \frac{1}{\beta}\frac{\partial}{\partial \mathbf{R}_I}\ln\omega(\mathbf{R}) - \beta\sum_{X=1}^{K}\int_0^t ds\,\left\langle[\delta\mathbf{F}_I^{\mathcal{Q}}(t-s)][\delta\mathbf{F}_X^{\mathcal{Q}}(0)]^T\right\rangle\frac{\mathbf{P}_X(s)}{M_X} + \delta\mathbf{F}_I^{\mathcal{Q}}(t)$$

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

Bottom-up coarse-grained model:

The equation of motion (EOM) of the coarse-grained (CG) particles obtained from the Mori-Zwanzig projection is in a form of generalized Langevin equation, which is given by

$$\frac{d}{dt}\mathbf{P}_I = \frac{1}{\beta}\frac{\partial}{\partial \mathbf{R}_I}\ln\omega(\mathbf{R}) - \beta\sum_{X=1}^{K}\int_0^t ds\,\left\langle[\delta\mathbf{F}_I^{\mathcal{Q}}(t-s)][\delta\mathbf{F}_X^{\mathcal{Q}}(0)]^T\right\rangle\frac{\mathbf{P}_X(s)}{M_X} + \delta\mathbf{F}_I^{\mathcal{Q}}(t)$$

First approximation: Here, we assume that the non-bonded interactions between neighboring clusters in the microscopic system are explicitly **pairwise decomposable**, and hence the total force consists of pairwise forces, e.g.

$$\mathbf{F}_I \approx \sum_{J\neq I}\mathbf{F}_{IJ} \text{ and } \delta\mathbf{F}_I^{\mathcal{Q}} \approx \sum_{J\neq I}\delta\mathbf{F}_{IJ}^{\mathcal{Q}}$$

Second approximation: In practice, we **neglect the many-body correlations** between different pairs, and assume that the force $\mathbf{F}_{IJ}$ between two clusters I and J depends only on the relative COM positions $\mathbf{R}_I$ and $\mathbf{R}_J$ and is independent of the positions of the rest of clusters.

$$\langle[\delta\boldsymbol{F}_{IJ}^{\mathcal{Q}}][\delta\boldsymbol{F}_{IK}^{\mathcal{Q}}]^T\rangle_{J\neq K} = 0$$

Evaluation of coarse-grained interactions:

First term: Conservative Force:

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

Second term: Dissipative Force:

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

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

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

Coarse-Grained Modeling - Summary

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

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

Conservative force | Dissipative force | Random force

Approximations for computing the coarse-grained forces:

- Pairwise decomposable: total force consists of pairwise forces $\boldsymbol{F}_I \approx \sum_{I \neq J} \boldsymbol{F}_{IJ}$
- Negligible many-body correlations: $\langle [\delta \boldsymbol{F}_{IJ}^Q] [\delta \boldsymbol{F}_{IK}^Q]^T \rangle_{J \neq K} = 0$

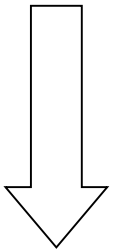
Then, the above EOM can be written into its pairwise form:

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

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).

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

$$\dot{\mathbf{r}}_i = \mathbf{p}_i \qquad \dot{\mathbf{p}}_i = \sum_{j\neq i} \mathbf{f}_{ij}$$



$$\dot{\mathbf{R}}_\mu = \mathbf{P}_\mu \quad (\star)$$

General Equation of Coarse-Grained particles

$$\dot{\mathbf{P}}_\mu = \frac{1}{\beta}\frac{\partial \ln\omega\left(\mathbf{R}\right)}{\partial \mathbf{R}_\mu} - \beta\sum_{\nu=1}^{K}\int_0^t ds \left\langle \left[\delta\mathbf{F}_\mu^{\mathcal{Q}}(t-s)\right]\left[\delta\mathbf{F}_\nu^{\mathcal{Q}}(0)\right]^T\right\rangle \mathbf{V}_\nu(s) + \delta\mathbf{F}_\mu^{\mathcal{Q}}(t)$$

Harmonic chain

Ensemble average

Dissipative force

Random force

(⋆) T. Kinjo and S. A. Hyodo, Physical Review E 75, 9 (2007).

Question

$$\dot{\mathbf{P}}_\mu = \frac{1}{\beta}\frac{\partial \ln\omega\left(\mathbf{R}\right)}{\partial \mathbf{R}_\mu} - \beta\sum_{\nu=1}^{K}\int_0^t ds\left\langle\left[\delta\mathbf{F}_\mu^{\mathcal{Q}}(t-s)\right]\left[\delta\mathbf{F}_\nu^{\mathcal{Q}}(0)\right]^T\right\rangle\mathbf{V}_\nu(s) + \delta\mathbf{F}_\mu^{\mathcal{Q}}\left(t\right)$$

Coupled term

General Coarse-grained Equation

?

Mesoscopic Dynamics

CRUNCH GROUP

Langevin Equation

$$\left\langle \delta \mathrm{F}^{\mathcal{Q}}_{\mu \mathrm{x}}(0) \cdot \delta \mathrm{F}^{\mathcal{Q}}_{\nu \mathrm{y}}(\mathrm{t}) \right\rangle = \sigma^2 \delta_{\mu\nu} \delta_{xy} \delta(t)$$

$$\beta \int_0^t ds \left\langle \left[\delta \mathbf{F}^{\mathcal{Q}}_{\mu}(t-s) \right] \otimes \left[\delta \mathbf{F}^{\mathcal{Q}}_{\nu}(0) \right]^T \right\rangle = \frac{1}{2} \beta \sigma^2 \delta_{\mu\nu} I$$

$$\dot{\mathbf{P}}_{\mu} = \frac{1}{\beta} \frac{\partial \ln \omega(\mathbf{R})}{\partial \mathbf{R}_{\mu}} - \beta \sum_{\nu=1}^{K} \int_0^t ds \left\langle \left[\delta \mathbf{F}^{\mathcal{Q}}_{\mu}(t-s) \right] \left[\delta \mathbf{F}^{\mathcal{Q}}_{\nu}(0) \right]^T \right\rangle \mathbf{V}_{\nu}(s) + \delta \mathbf{F}^{\mathcal{Q}}_{\mu}(t)$$

$\mathbf{V}_{\nu}(s) \rightarrow V_{\nu}(t)$

Markovian Approximation

$$\dot{\mathbf{P}}_{\mu} = \frac{1}{\beta} \frac{\partial}{\partial \mathbf{R}_{\mu}} \ln \omega(\mathbf{R}) - \gamma \mathbf{V}_{\mu} + \delta \mathbf{F}^{\mathcal{Q}}_{\mu},$$

$$\gamma = \tfrac{1}{2} \beta \sigma^2$$

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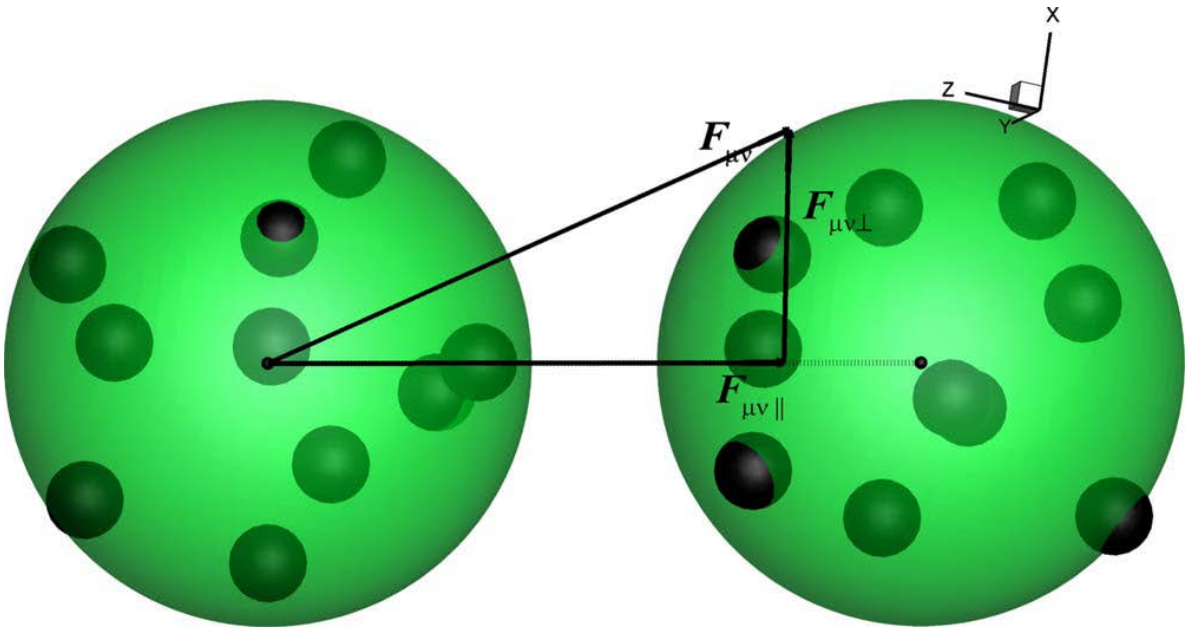
DPD from Coarse-Grained Equation



- The random force on each cluster is decomposed into pairwise style
- The instantaneous force between two clusters is not generally parallel to the radial vector.

$$\delta \mathbf{F}_{\mu}^{\mathcal{Q}} \approx \sum_{\nu \neq \mu} \delta \mathbf{f}_{\mu\nu}^{\mathcal{Q}}$$

$$\begin{aligned} \delta \mathbf{f}_{\mu\nu}^{\mathcal{Q}} &= \mathbf{e}_{\mu\nu}\mathbf{e}_{\mu\nu}^{T}\delta \mathbf{f}_{\mu\nu}^{\mathcal{Q}} + (\mathbf{I} - \mathbf{e}_{\mu\nu}\mathbf{e}_{\mu\nu}^{T})\delta \mathbf{f}_{\mu\nu}^{\mathcal{Q}} \\ &= \delta f_{\mu\nu,\parallel}^{\mathcal{Q}}\mathbf{e}_{\mu\nu} + \delta \mathbf{f}_{\mu\nu,\perp}^{\mathcal{Q}} \end{aligned}$$

(Cont'd)

$$\left\langle \delta f^{\mathcal{Q}}_{\mu\nu,\parallel}(0)\delta f^{\mathcal{Q}}_{\epsilon\eta,\parallel}(t)\right\rangle = \left[\sigma_\parallel w_\parallel(R)\right]^2\left(\delta_{\mu\epsilon}\delta_{\nu\eta}+\delta_{\mu\eta}\delta_{\nu\epsilon}\right)\delta(t)$$

$$\left\langle \delta \mathbf{f}^{\mathcal{Q}}_{\mu\nu,\perp}(0)\cdot\delta \mathbf{f}^{\mathcal{Q}}_{\epsilon\eta,\perp}(t)\right\rangle = 2\left[\sigma_\perp w_\perp(R)\right]^2\left(\delta_{\mu\epsilon}\delta_{\nu\eta}+\delta_{\mu\eta}\delta_{\nu\epsilon}\right)\delta(t)$$

$$\dot{\mathbf{P}}_\mu = \frac{1}{\beta}\frac{\partial \ln\omega(\mathbf{R})}{\partial \mathbf{R}_\mu} - \beta\sum_{\nu=1}^{K}\int_0^t ds\left\langle\left[\delta\mathbf{F}^{\mathcal{Q}}_\mu(t-s)\right]\left[\delta\mathbf{F}^{\mathcal{Q}}_\nu(0)\right]^T\right\rangle \mathbf{V}_\nu(s) + \delta\mathbf{F}^{\mathcal{Q}}_\mu(t)$$

Markovian approximation $V_\nu(t)$

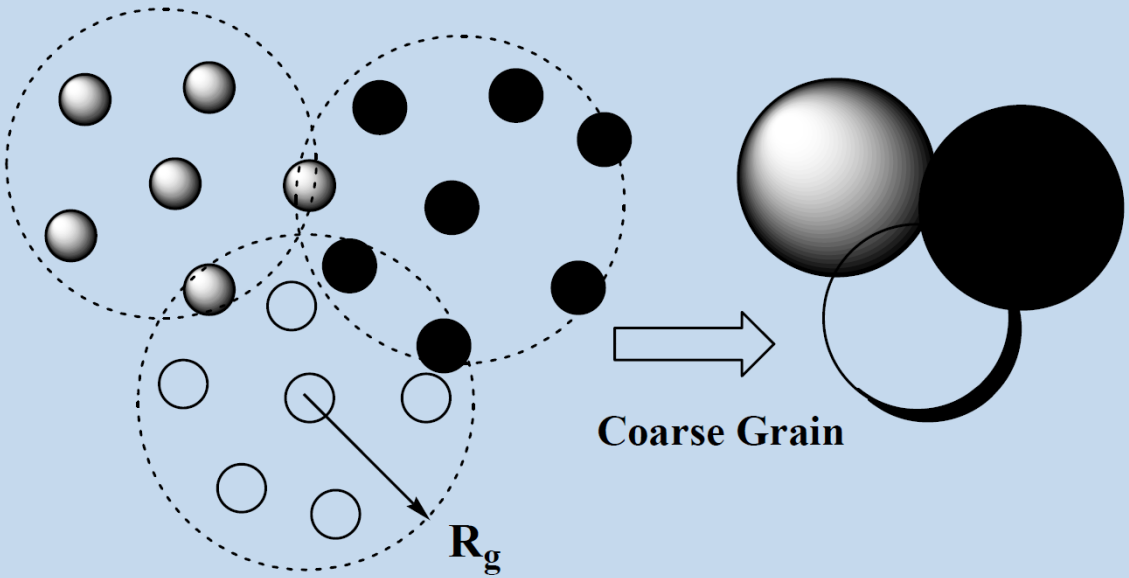
$$\dot{\mathbf{P}}_\mu = \frac{1}{\beta}\frac{\partial}{\partial \mathbf{R}_\mu}\ln\omega(\mathbf{R}) - \sum_{\nu\neq\mu}\gamma_\parallel(R_{\mu\nu})(\mathbf{e}_{\mu\nu}\cdot\mathbf{V}_{\mu\nu})\mathbf{e}_{\mu\nu} + \sum_\nu \delta f^{\mathcal{Q}}_{\mu\nu,\parallel}\mathbf{e}_{\mu\nu}$$

$$+\sum_{\nu\neq\mu}\gamma_\perp(R_{\mu\nu})(\mathbf{V}_{\mu\nu}-(\mathbf{e}_{\mu\nu}\cdot\mathbf{V}_{\mu\nu})\mathbf{e}_{\mu\nu}) + \sum_\nu \delta\mathbf{f}^{\mathcal{Q}}_{\mu\nu,\perp}$$

Standard DPD

Transverse term

Numerical Simulations*



$$\frac{1}{N_c}\sum_{i=1}^{N_c}(\mathbf{r}_i^{\mu}-\mathbf{R}_{\mu})^2 = R_g^2 \qquad \rho_c = \rho/N_c$$

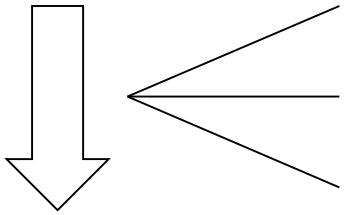
$$v_{ij}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] - U_{LJ}(2.5\sigma)$$

* H. Lei, B. Caswell, G. E. Karniadakis, Phys. Rev. E 81 (2) (2010) 026704.

MD to DPD

Microscopic system (Molecular Dynamics)

What is Preserved?
What is Lost?



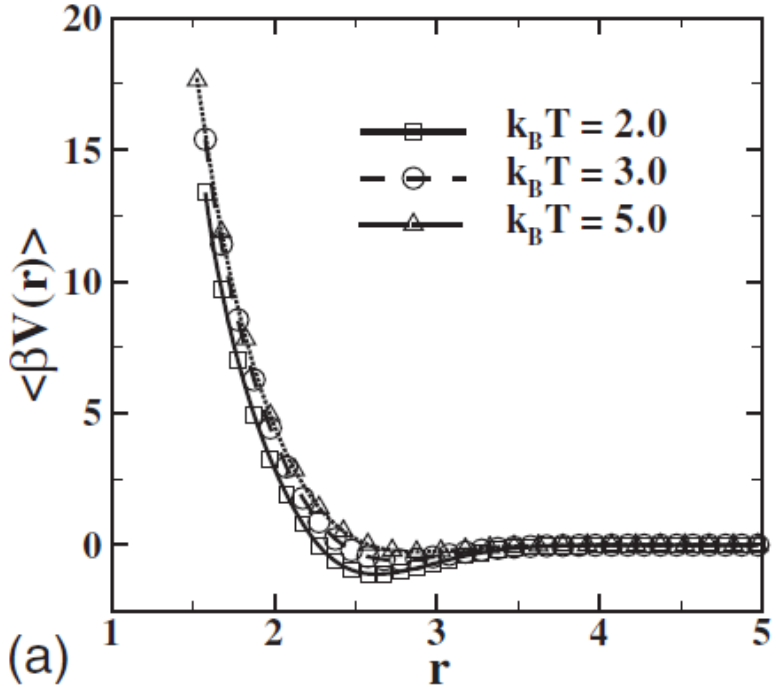
Conservative force

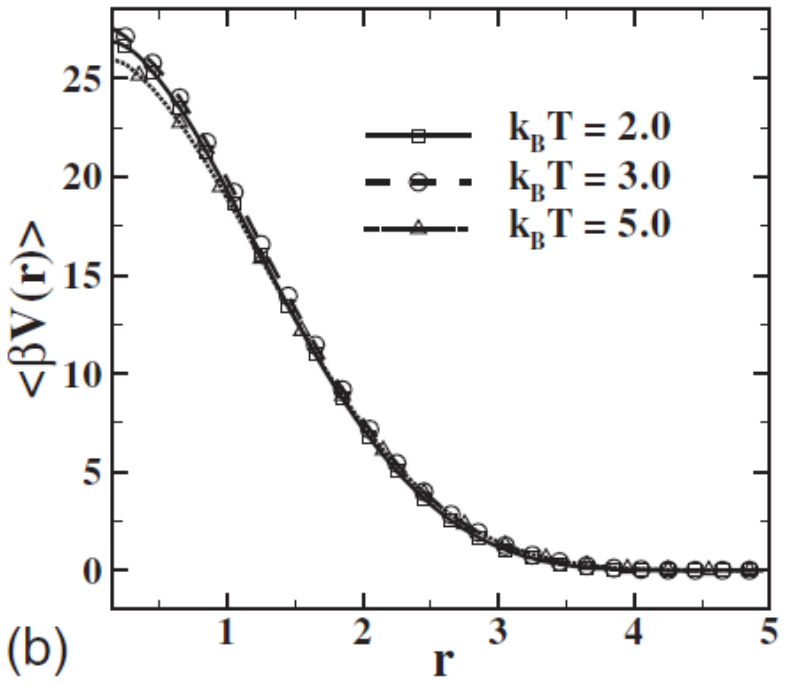
Dissipative force

Random force

Mesoscopic system (DPD)

Conservative potential (force) term



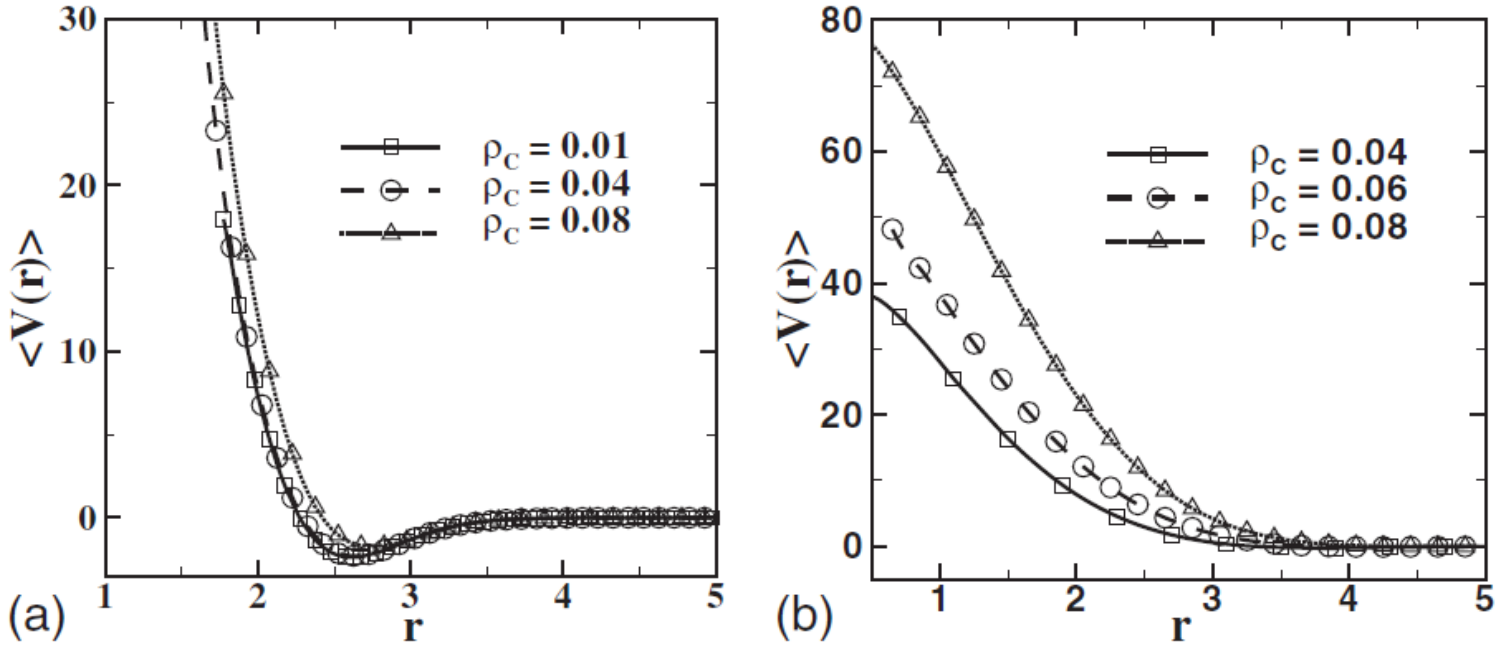


$R_g = 0.95, N_c = 10, \rho = 0.8$

$R_g = 1.4397, N_c = 10, \rho = 0.8$

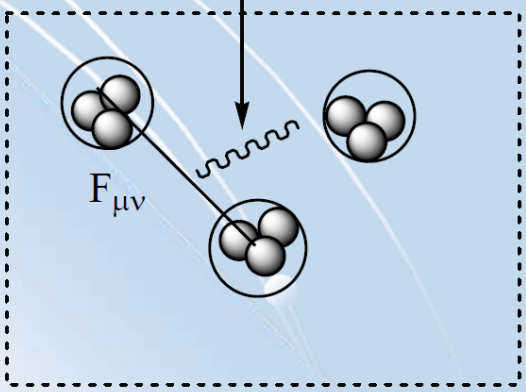
$$\frac{1}{\beta}\frac{\partial}{\partial \mathbf{R}_\mu}\ln\omega\left(\mathbf{R}\right) \approx \sum_{\nu\neq\mu}\left\langle f\left(R_{\mu\nu}\right)\right\rangle$$

$$\left\langle f(r)\right\rangle = \left\langle \mathbf{f}_{\mu\nu}\cdot\frac{\mathbf{R}_{\mu\nu}}{R_{\mu\nu}}\right\rangle_{r-dr/2<R_{\mu\nu}<r+dr/2}$$



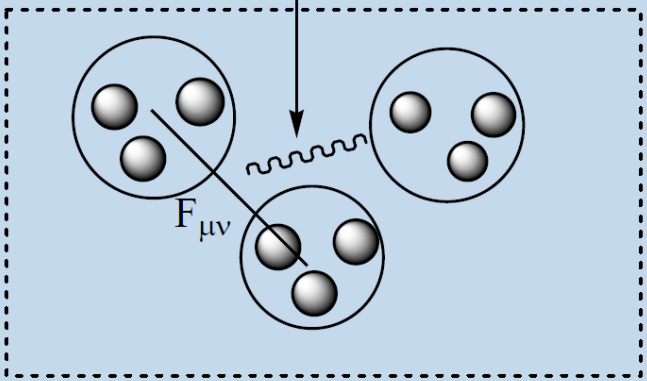
$R_g = 0.95, N_c = 10, k_BT = 3.0$

Weak dependence



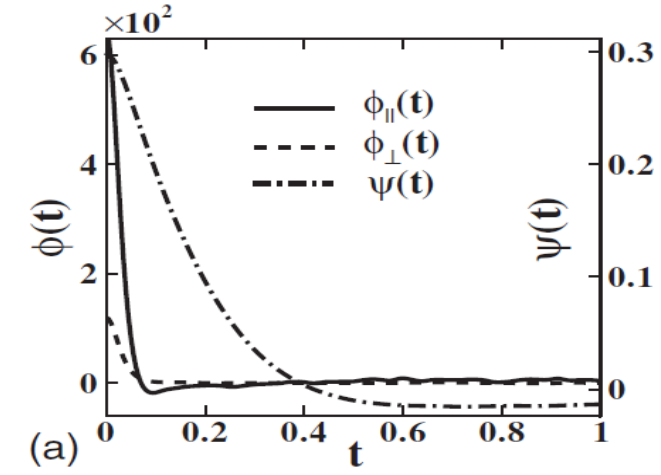
$R_g = 1.4397, N_c = 10, k_BT = 3.0$

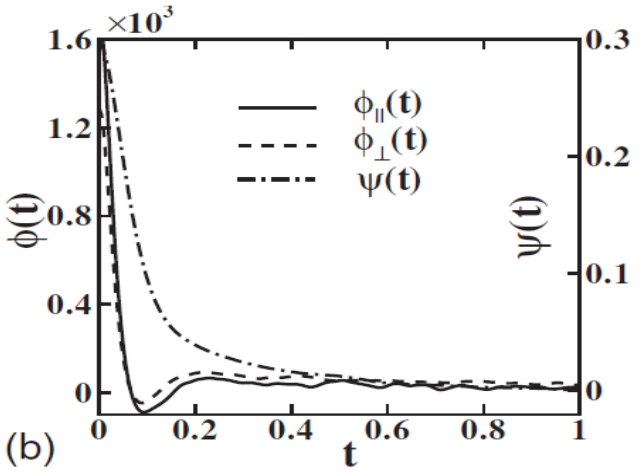
Strong dependence

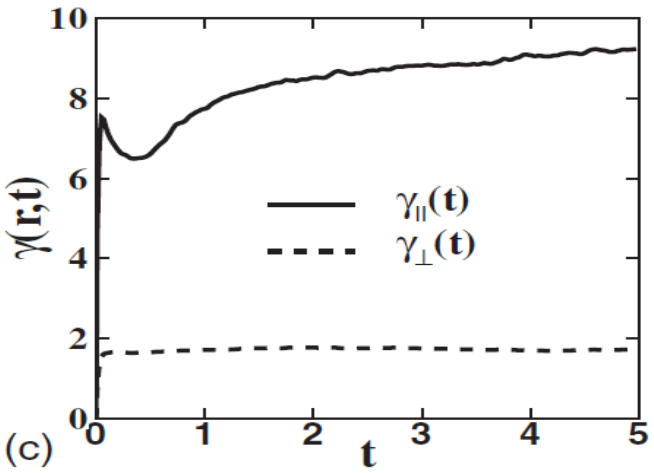


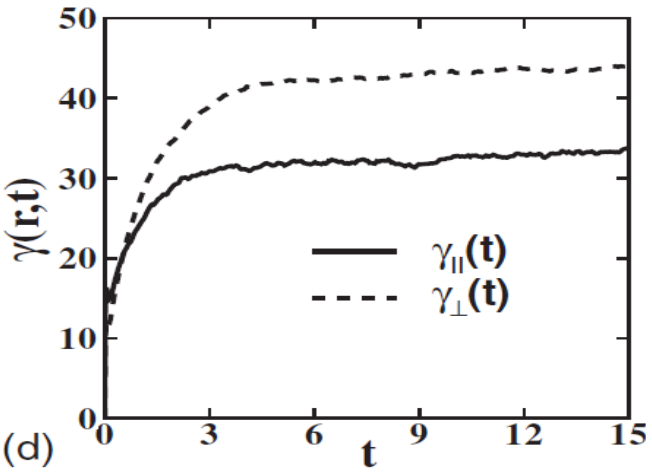
Dissipative force term

Rg = 0.95







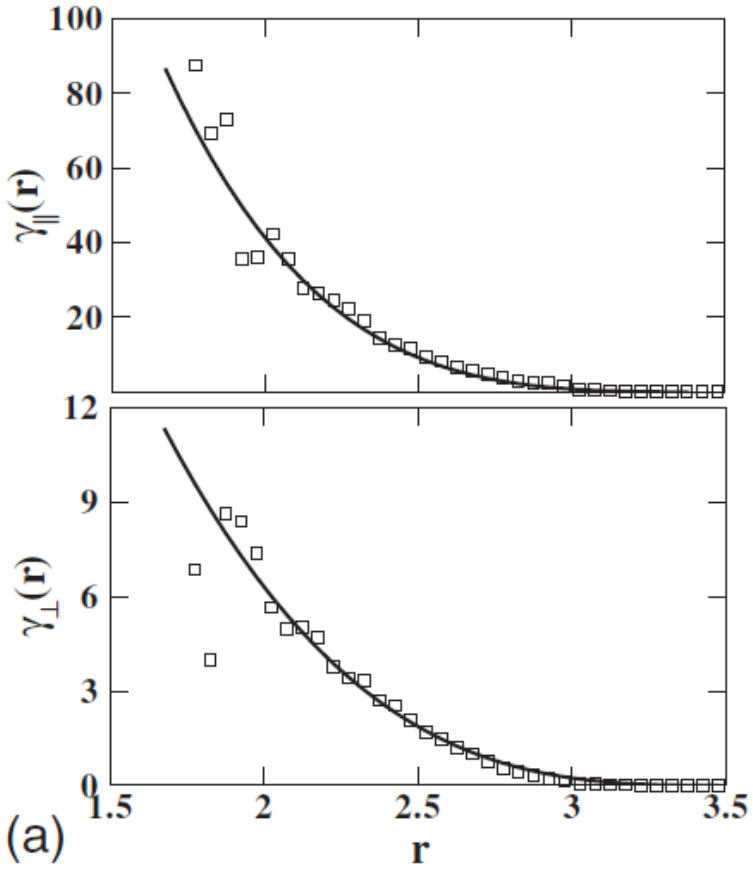


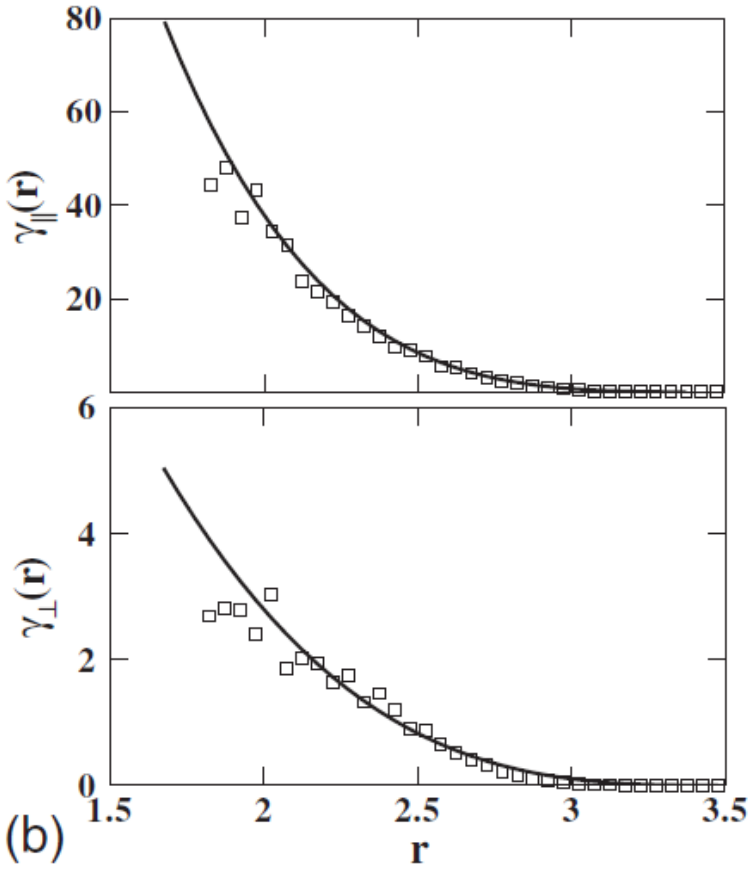
Rg = 1.4397

$$\phi_{\parallel}(t) = \left\langle \delta f^{\mathcal{Q}}_{\mu\nu,\parallel}(0)\delta f^{\mathcal{Q}}_{\mu\nu,\parallel}(t)\right\rangle \qquad \phi_{\perp}(t) = \frac{1}{2}\left\langle \delta \mathbf{f}^{\mathcal{Q}}_{\mu\nu,\perp}(0)\cdot\delta \mathbf{f}^{\mathcal{Q}}_{\mu\nu,\perp}(t)\right\rangle$$

$$\psi(t) = \langle v_{\mu x}(0)v_{\mu x}(t)\rangle \qquad \gamma_{\parallel,\perp} = \beta\int_0^t \phi_{\parallel,\perp}(t)\,dt$$

(Cont'd)



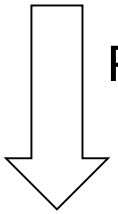


$R_g = 0.95, \rho = 0.8, N_c = 10$

$R_g = 0.95, \rho = 0.4, N_c = 10$

Question

Microscopic System



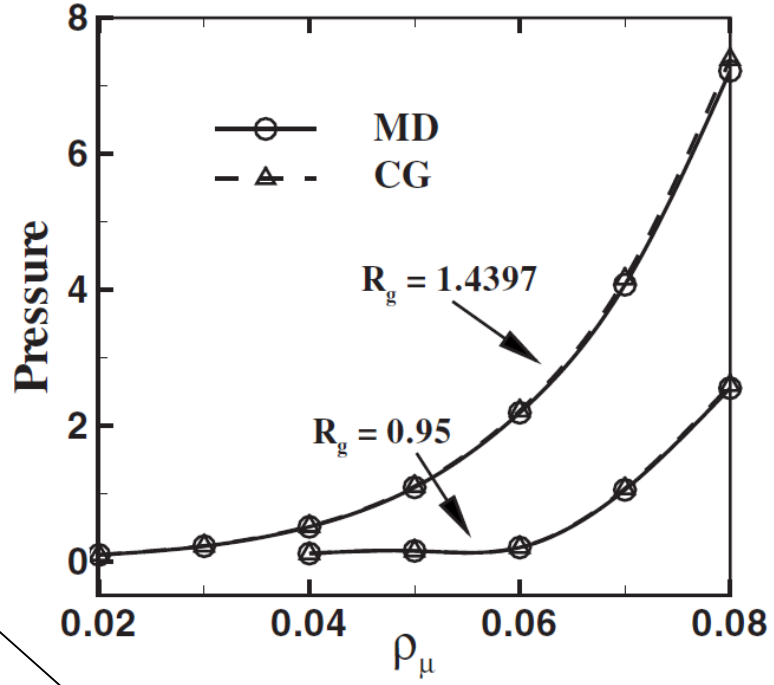
Fluid Structure?

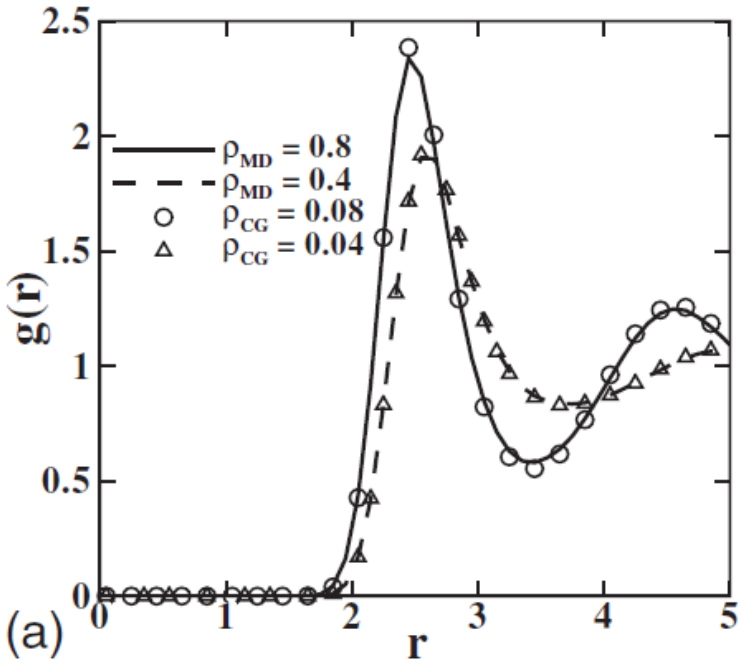
Mesoscopic System

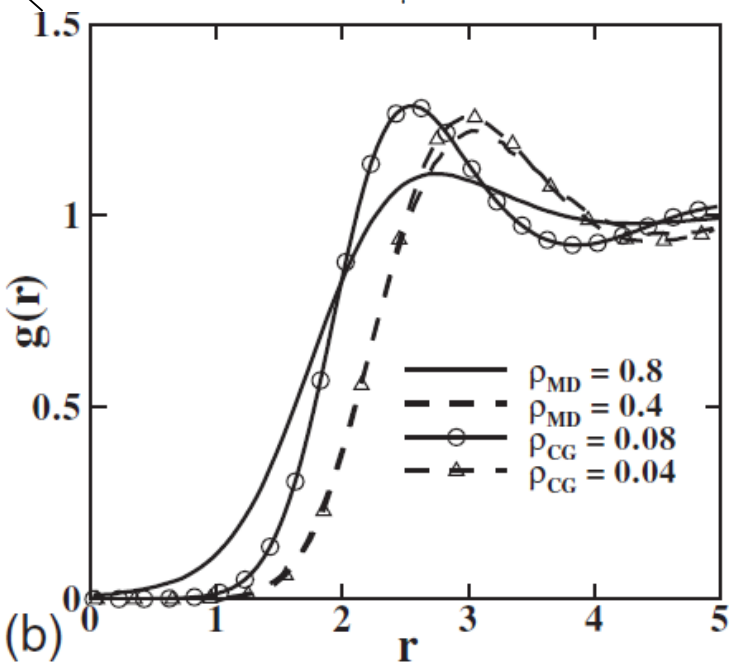
Static properties

$k_B T = 3.0, R_g = 1.4397$

$k_B T = 3.0, R_g = 0.95$

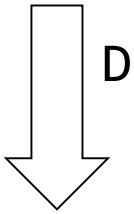






Question

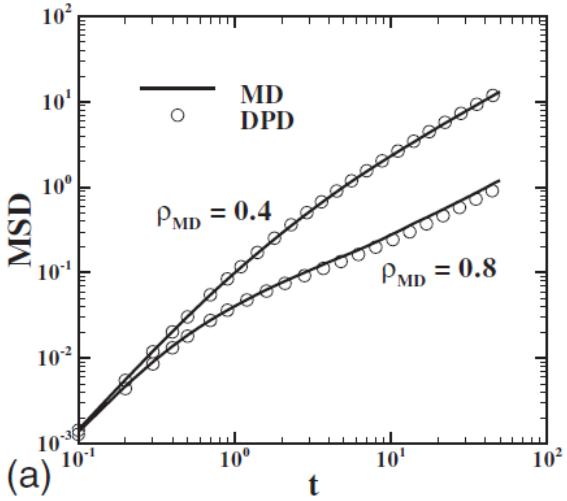
Microscopic System

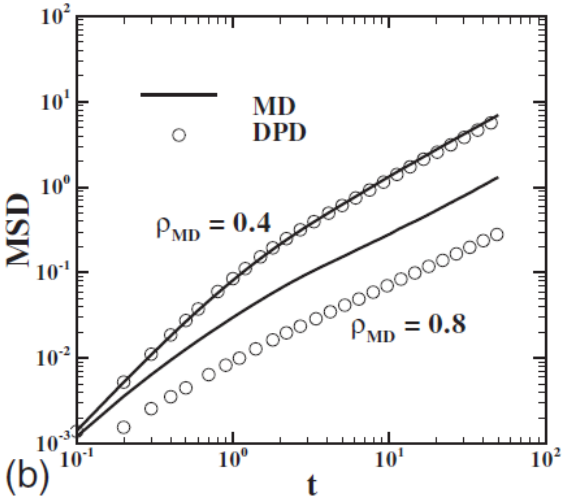


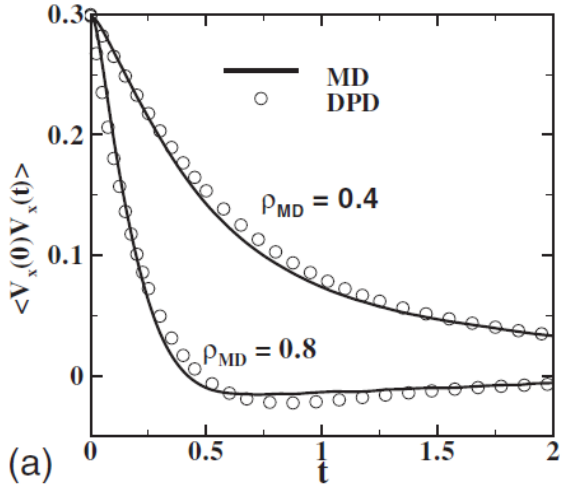
Dynamic Properties?

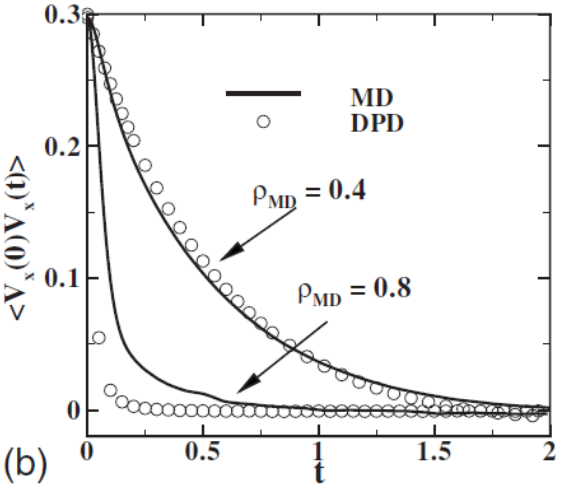
Mesoscopic System

Dynamic Properties









$R_g = 0.95$ $R_g = 1.4397$

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Computing CG interactions

Pairwise Potential

$$F_{IJ}^{C}(R) = \langle \mathbf{F}_{IJ}(t) \rangle \Big|_{R-\Delta/2<R_{IJ}<R+\Delta/2}$$

$$U_{\mathrm{MZ}}(R) = \int_{R}^{\infty} \langle F_{IJ}^{C}(r) \rangle dr$$

Memory Kernel K(t)

$$\frac{d}{dt}\mathbf{P}_I = \sum_{J \neq I} \mathbf{F}_{IJ}(t)$$

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

Let the difference of the instantaneous force from the mean force be the fluctuating force, e.g., $\delta \boldsymbol{F}_{IJ}(t) = \boldsymbol{F}_{IJ}(t) - \langle \boldsymbol{F}_{IJ} \rangle$. By multiplying $\boldsymbol{V}_{IJ}^{T}(0)$ on both sides of above equation

$$\langle \delta\mathbf{F}_{IJ}(t)\mathbf{V}_{IJ}^{T}(0) \rangle$$

$$= -\int_0^t \mathbf{K}_{IJ}(t-s)\langle \mathbf{V}_{IJ}(s)\mathbf{V}_{IJ}^{T}(0) \rangle ds$$

Markovian DPD model

If the typical time scales of random force and momentum are well separated, the **Markovian assumption** can be applied, where the time correlation of random force is approximated by the δ-function:

$$\boldsymbol{K}(t) \approx \gamma\delta(\mathrm{t}), \text{ where } \gamma = \int_0^\infty \boldsymbol{K}(t)dt$$

$$\int_0^t \mathbf{K}_{IJ}(t-s)\mathbf{V}_{IJ}(s)ds = \boldsymbol{\gamma}\cdot\mathbf{V}_{IJ}(t)$$

As a result, the EOM of DPD particles is given by:

$$\frac{d\mathbf{P}_I}{dt} = \sum_{J\neq I}\mathbf{F}_{IJ} = \sum_{J\neq I}\{F_{IJ}^C(R_{IJ})\mathbf{e}_{IJ}$$
$$-\gamma^{\parallel}(R_{IJ})\cdot\mathbf{V}_{IJ}^{\parallel} - \gamma^{\perp}(R_{IJ})\cdot\mathbf{V}_{IJ}^{\perp} - \gamma^{\perp}(R_{IJ})\left[\frac{\mathbf{R}_{IJ}}{2}\times(\boldsymbol{\Omega}_I+\boldsymbol{\Omega}_J)\right]$$
$$+\sigma^{\parallel}(R_{IJ})\Delta t^{-1/2}\xi_{IJ}\cdot\mathbf{e}_{IJ} + \sqrt{2}\sigma^{\perp}(R_{IJ})\Delta t^{-1/2}\cdot d\mathbf{W}_{IJ}^A\cdot\mathbf{e}_{IJ}\}$$

$$\frac{d\mathbf{L}_I}{dt} = \mathbf{T}_I = \sum_{J\neq I}\frac{\mathbf{R}_{IJ}}{2}\times\mathbf{F}_{IJ}$$

Non-Markovian DPD model

Without the Markovian approximation, we have to preserve the temporal memory of each pair in the NM-DPD model

$$\int_0^t \mathbf{K}_{IJ}(t-s)\mathbf{V}_{IJ}(s)ds$$

To avoid prohibitive computational cost, we assume that the **memory is finite**, e.g., history length $N\Delta t$. Then, the EOM of NM-DPD particles is given by:

$$\begin{aligned}
\frac{d\mathbf{P}_I}{dt} = \sum_{J\neq I}\mathbf{F}_{IJ} = \sum_{J\neq I}\Big\{ & F_{IJ}^{C}(R_{IJ})\mathbf{e}_{IJ} \\
& - \sum_{n=0}^{N}\Delta t\Gamma_{IJ,n}^{\parallel}\left(R_{IJ}(t-n\Delta t)\right)\cdot\mathbf{V}_{IJ}^{\parallel}(t-n\Delta t) \; - \sum_{n=0}^{N}\Delta t\Gamma_{IJ,n}^{\perp}\left(R_{IJ}(t-n\Delta t)\right)\cdot\mathbf{V}_{IJ}^{\perp}(t-n\Delta t) \\
& - \sum_{n=0}^{N}\Delta t\Gamma_{IJ,n}^{\perp}\left(R_{IJ}(t-n\Delta t)\right)\left[\frac{\mathbf{R}_{IJ}}{2}\times(\boldsymbol{\Omega}_I+\boldsymbol{\Omega}_J)\right] \\
& + \sum_{n=0}^{N}\alpha_{IJ,n}^{\parallel}\left(R_{IJ}(t-n\Delta t)\right)\xi_{IJ}(n\Delta t)\mathbf{e}_{IJ} \; + \sum_{n=0}^{N}\sqrt{2}\alpha_{IJ,n}^{\perp}\left(R_{IJ}(t-n\Delta t)\right)\,d\mathbf{W}_{IJ}^{A}(n\Delta t)\cdot\mathbf{e}_{IJ}\Big\}
\end{aligned}$$

$$\frac{d\mathbf{L}_I}{dt} = \mathbf{T}_I = \sum_{J\neq I}\frac{\mathbf{R}_{IJ}}{2}\times\mathbf{F}_{IJ}$$

Fluctuation-Dissipation Theorem

Markovian DPD Model

the time correlation of random force is approximated by the δ-function

$$\int_0^t \mathbf{K}_{IJ}(t-s)\mathbf{V}_{IJ}(s)ds = \boldsymbol{\gamma}_{IJ}\cdot\mathbf{V}_{IJ}(t)$$

Then, the random force is **white noise**, with variance given by

$$\langle[\delta\boldsymbol{F}_{IJ}^{Q}(t)][\delta\boldsymbol{F}_{IJ}^{R}(0)]^{T}\rangle = 2k_BT\gamma_{IJ}\delta(t)$$

Non-Markovian DPD Model

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

The FDT requires $\langle[\delta\boldsymbol{F}_{IJ}^{Q}(t)][\delta\boldsymbol{F}_{IJ}^{Q}(0)]^{T}\rangle = k_BTK_{IJ}(t)$,

Then, the random force is **colored noise.**

Colored noise generator 1 (Fourier transform):

Consider discrete time steps $t_n = n \cdot \delta t,\ n > 0$.

We define $R_n = R(t_n) \equiv \delta F(t_n), \quad \theta_n = \theta(t_n) \equiv K(t_n)$

In the discrete form, the second FDT is $\langle R_n R_m^T \rangle = k_B T \cdot \theta_{n-m}$

Let $0 \le n \le N$, we can use a periodic extension, which does not affect the values within the first N steps. We write θ_n as

$$\theta_n = \sum_{s=-N}^{N} \alpha_s \alpha_{s+n}$$

In this case, the Fourier transform is reduced to a discrete Fourier transform.

$$\hat{\theta}_n = \sum_{n=-N}^{N} \theta_n e^{-ikn2\pi/N}$$

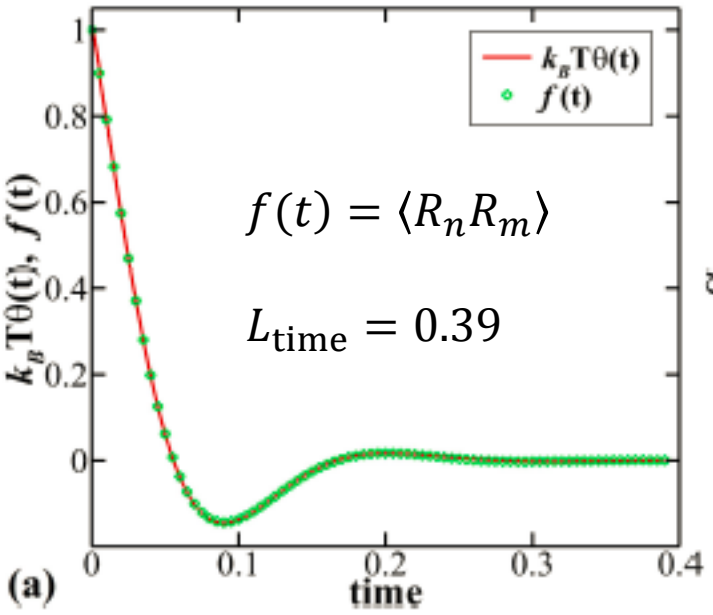
Define $\hat{\alpha}_k = \hat{\theta}_k^{0.5}$, the inverse Fourier transform is given by

$$\alpha_s = \frac{1}{2N+1} \sum_{n=-N}^{N} \hat{\alpha}_k e^{iks2\pi/N}$$

Let W_n be identically distributed random variables, we generate the colored noise by

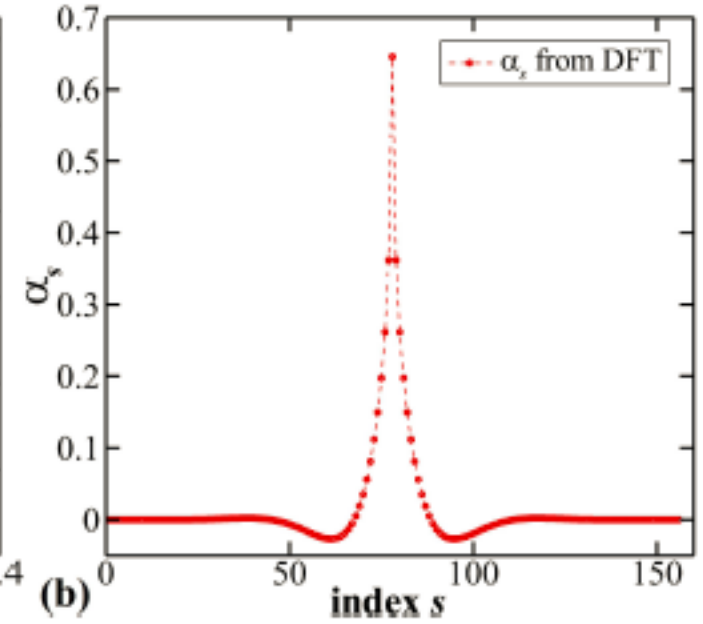
$$R_n = \sqrt{k_B T} \sum_{s=-N}^{N} \alpha_s W_{n+s}$$

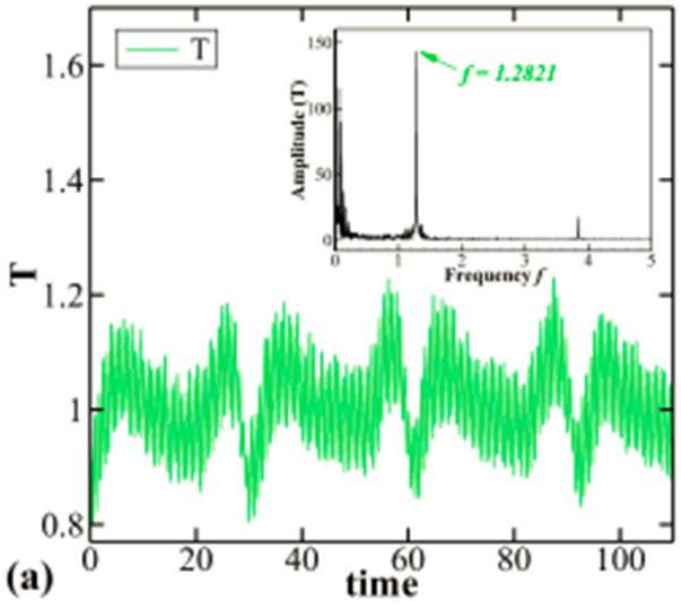
Colored noise generator 1 (Fourier transform): Test Case

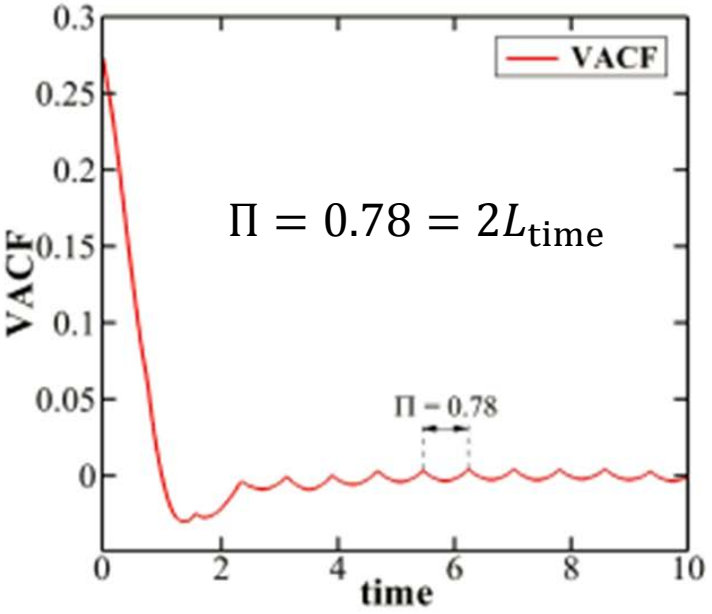


$$f(t) = \langle R_n R_m \rangle$$

$$L_{\text{time}} = 0.39$$







$$\Pi = 0.78 = 2L_{\text{time}}$$

Colored noise generator 2 (Optimization):

Let W_n be identically distributed random variables, the random force R_n is given by

$$R_n = \sqrt{k_B T} \sum_{s=-N}^{0} \alpha_s W_{n+s}$$

where α_n are undetermined coefficients. Then, the correlation of the random force can be computed by

$$\langle R_n R_m \rangle = k_B T \sum_{s=-N}^{0} \sum_{t=-N}^{0} \alpha_s \alpha_t \delta_{n+s-m-t}$$

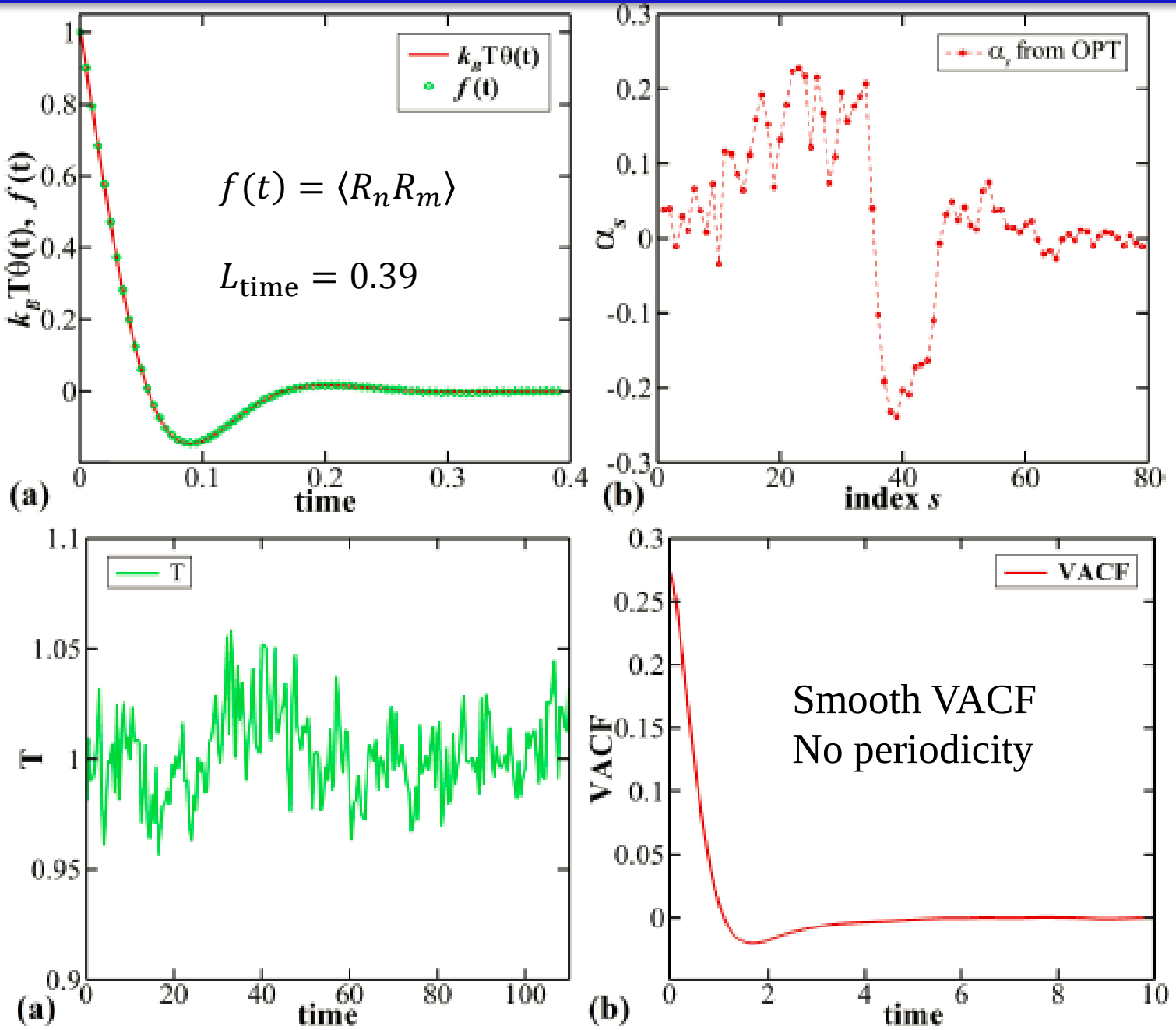
$$= k_B T \sum_{s=-N}^{0} \alpha_s \alpha_{n-m+s} = k_B T \cdot f_{n-m}$$

To satisfy the second FDT, we need

$$\langle R_n R_m \rangle = k_B T \theta_{n-m}$$

Numerical optimization techniques can be used to obtain a set of coefficients α_n by minimization of $L_2(f_{n-m} - \theta_{n-m})$.

Colored noise generator 2 (Optimization): Test Case



Outline

1. Introduction

— Bottom-up coarse-graining

2. Foundation: Coarse-Graining

— Introduction of the Mori-Zwanzig formalism.

— Markovian model

— Non-Markovian model

3. Construction of coarse-grained model directly from MD simulation

— Static properties

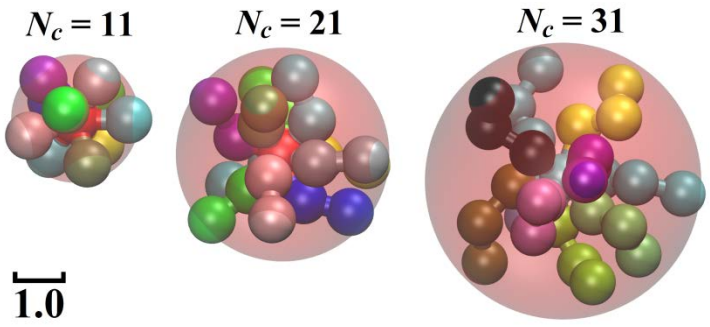
— Dynamics properties

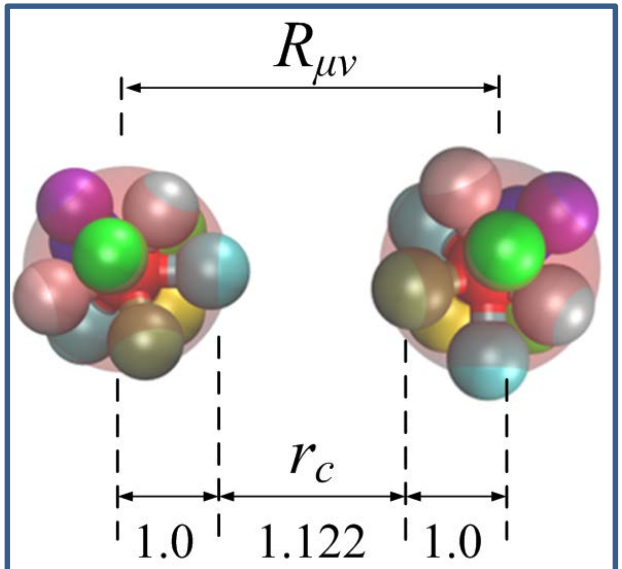
4. Summary

Microscopic system to be reproduced

Consider a well-defined atomistic system consisting of N atoms which are grouped into K clusters, and N_c atoms in each cluster.

Microscopic system:





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.

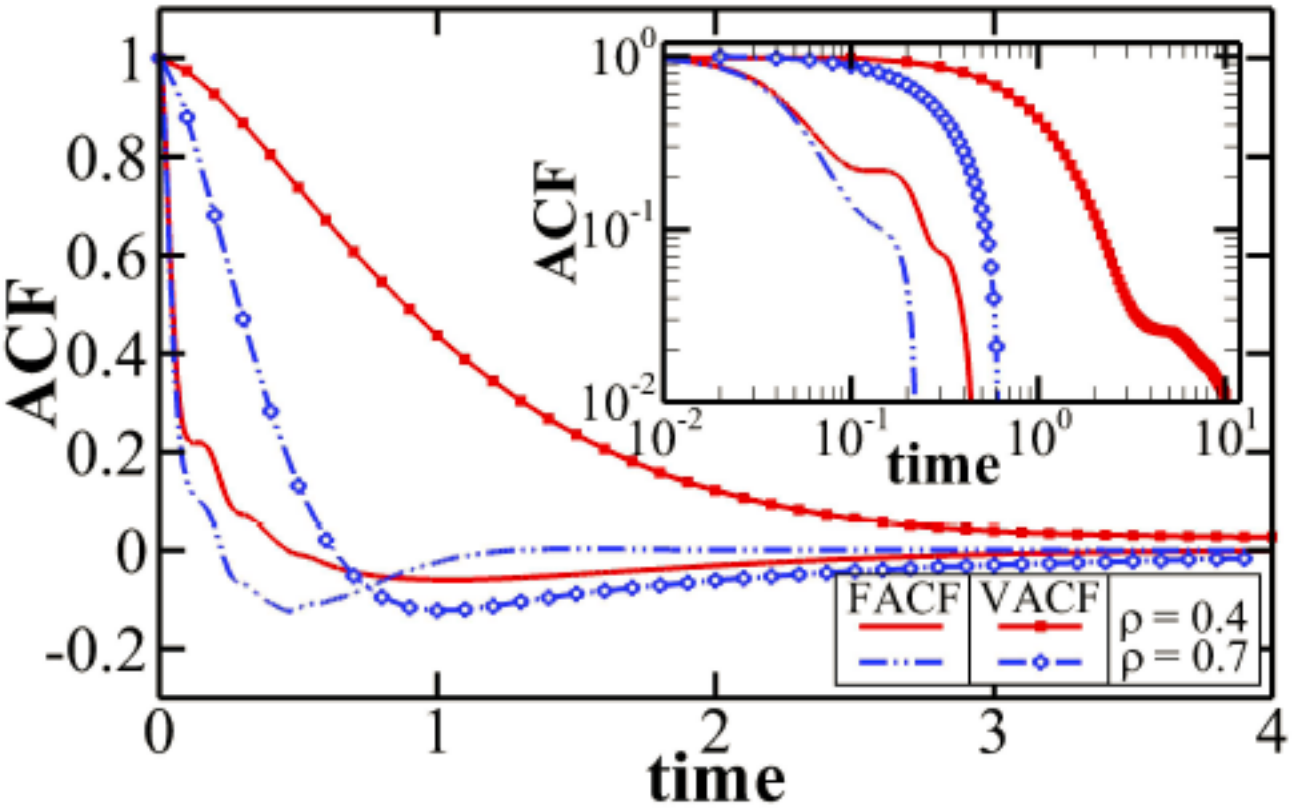
$$M_\mu = \sum_{\mu,i} m_{\mu,i}$$

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

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

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

Microscopic system to be reproduced



Two test systems: $\rho = 0.4,\ \tau_v = 10.30$ and $\tau_f = 0.44$

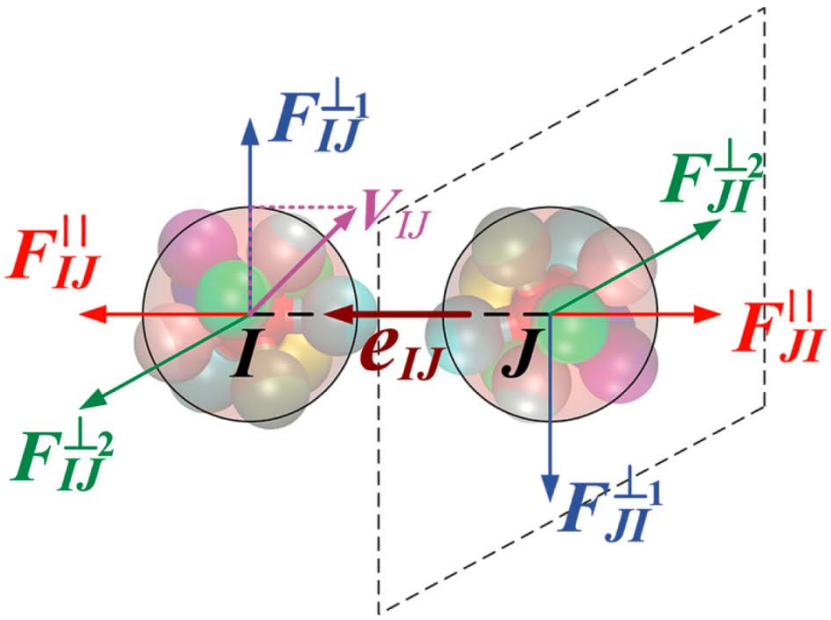
$$\kappa = \tau_v/\tau_f = 23.41$$

$\rho = 0.7,\ \tau_v = 0.61$ and $\tau_f = 0.22$

$$\kappa = \tau_v/\tau_f = 2.77$$

Coarse-Grained force field

Definition of the 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:

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

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

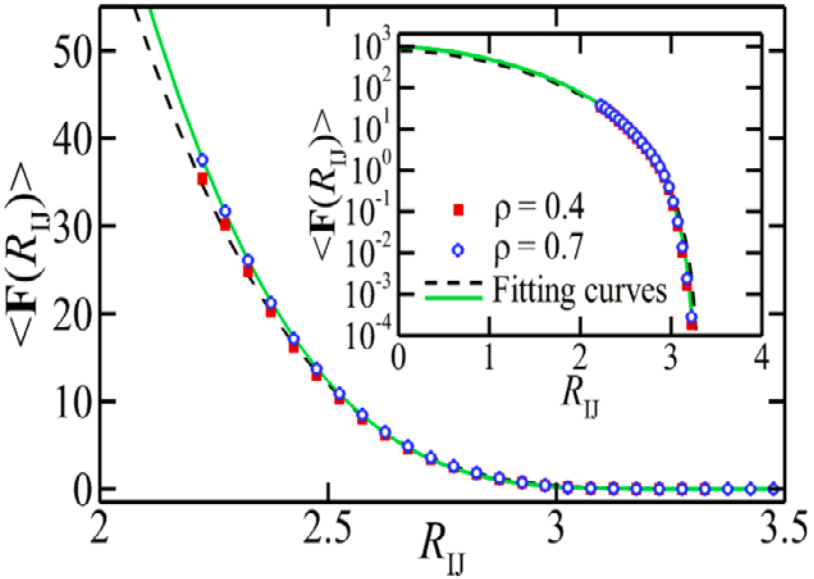
$$\mathbf{e}_{ij}^{\perp 1} = \mathbf{v}_{ij}^{\perp} / |v_{ij}^{\perp}|$$

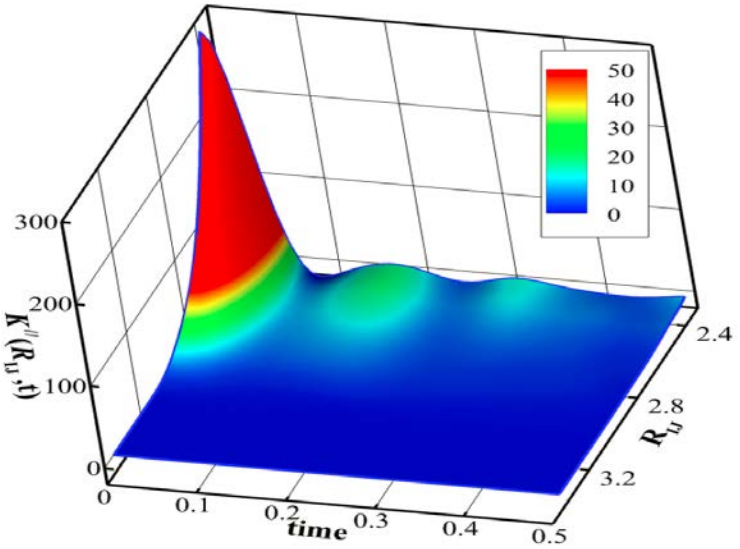
3. Perpendicular direction #2:

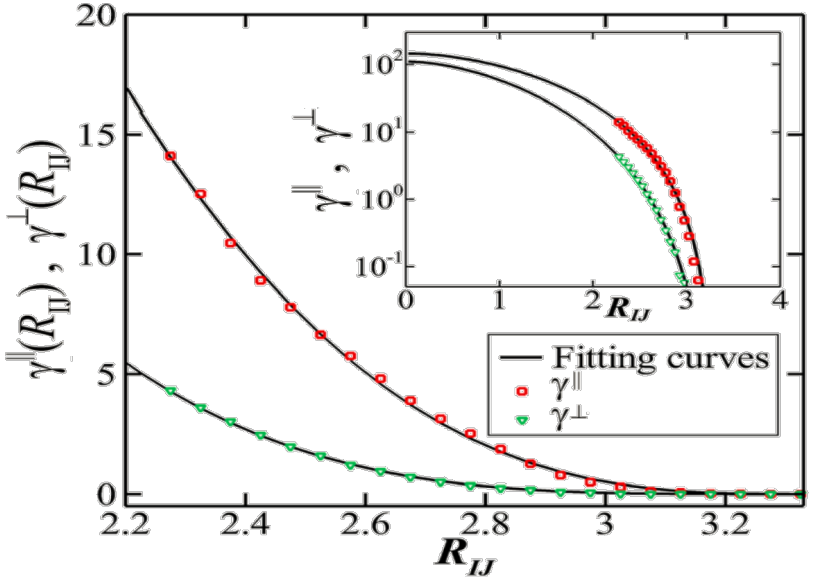
$$\mathbf{e}_{ij}^{\perp 2} = \mathbf{e}_{ij} \times \mathbf{e}_{ij}^{\perp 1}$$

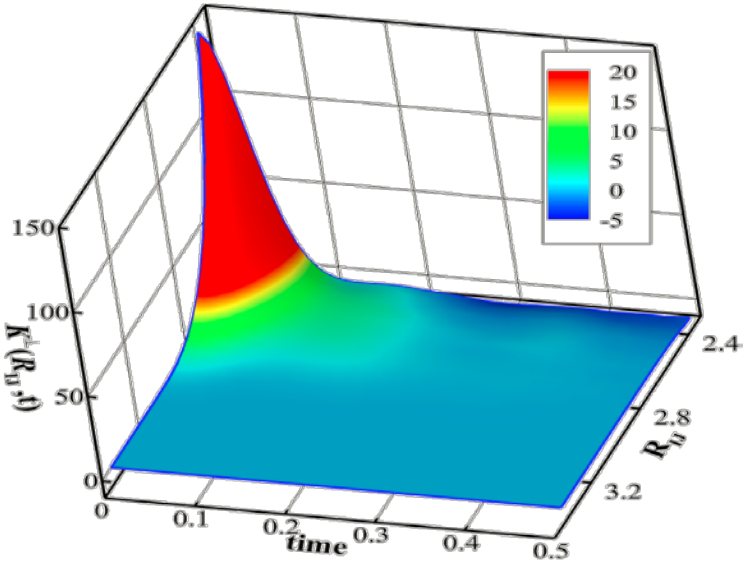
Coarse-Grained force field

- CG force field obtained directly from MD simulations
- **No freedom to adjust parameters**

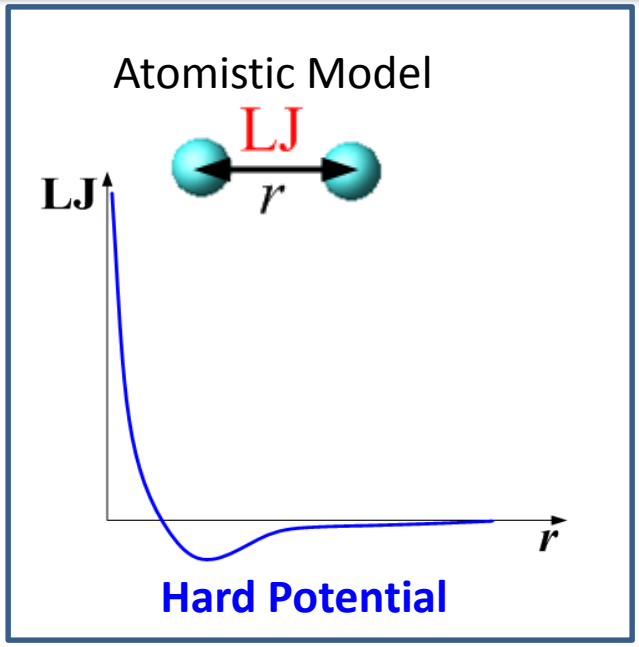




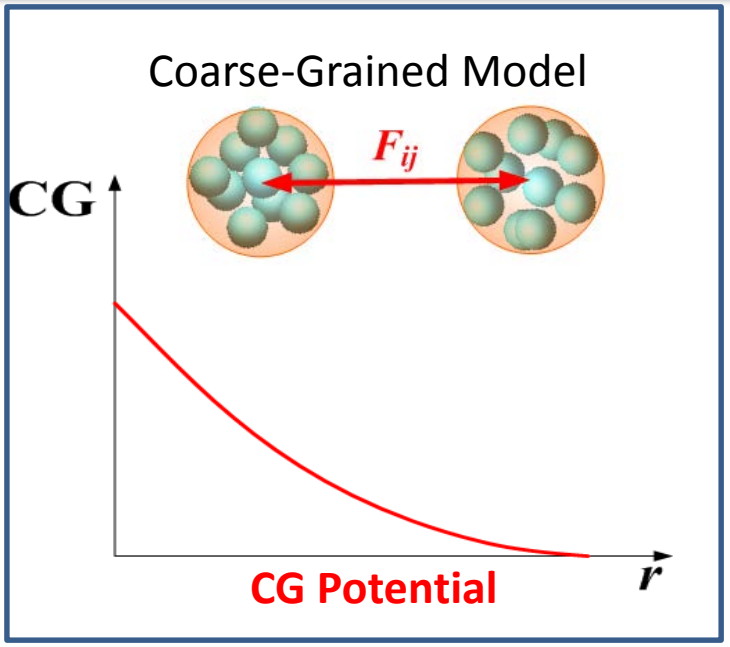


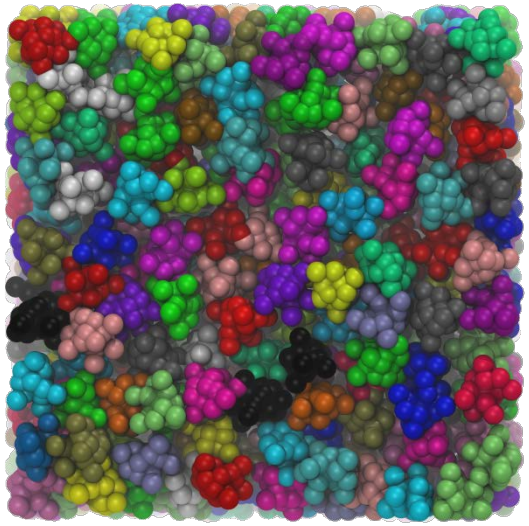


Comparison

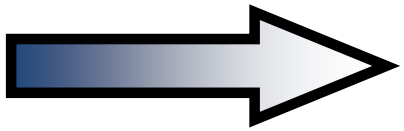


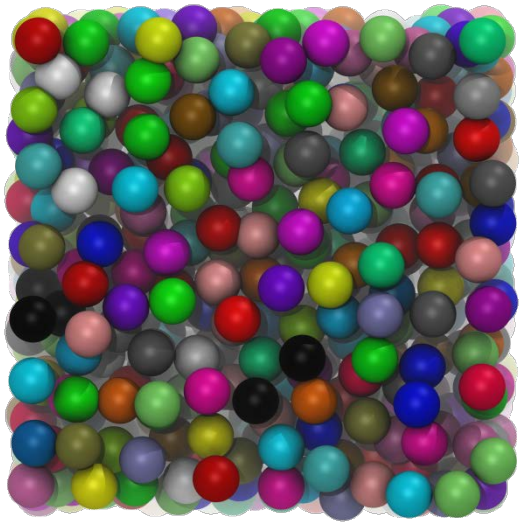
Coarse Graining





MD

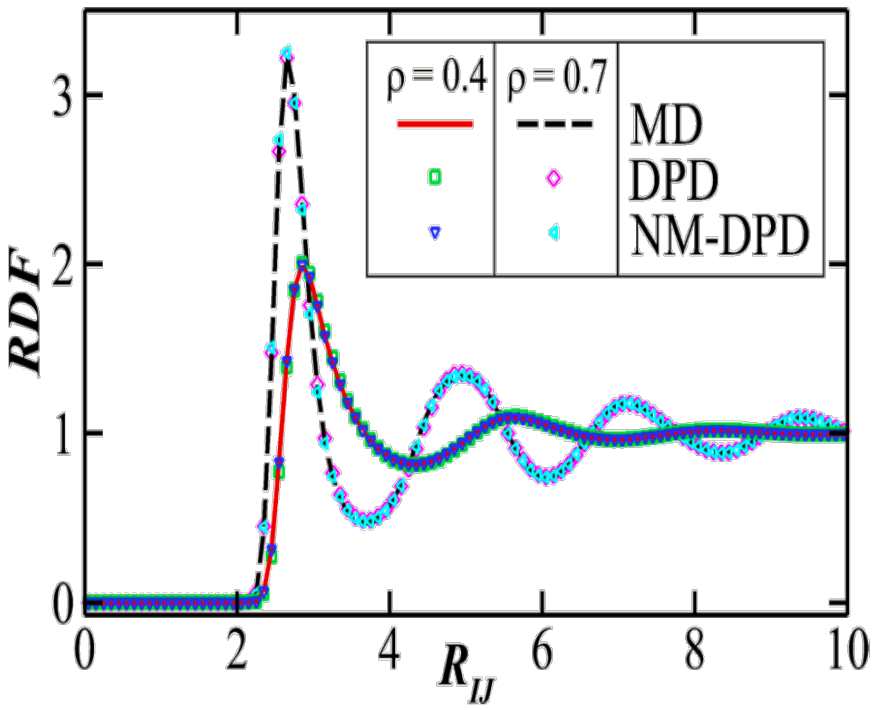


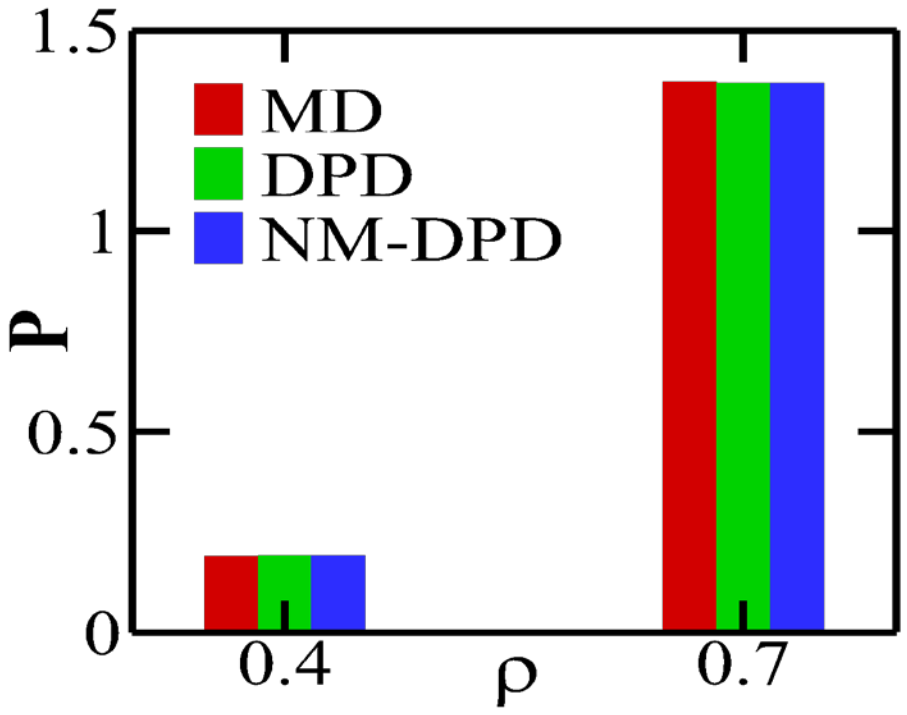


DPD

Comparison: Static Properties

Radial distribution function (RDF) and Pressure (P) of MD, DPD and NM-DPD systems:



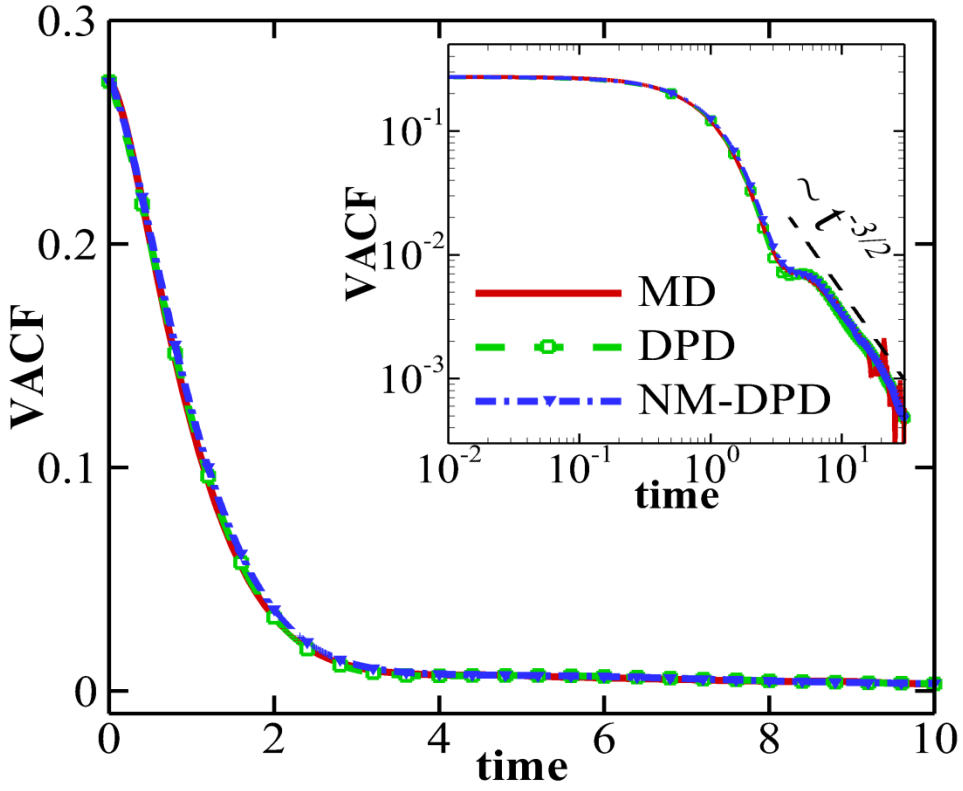


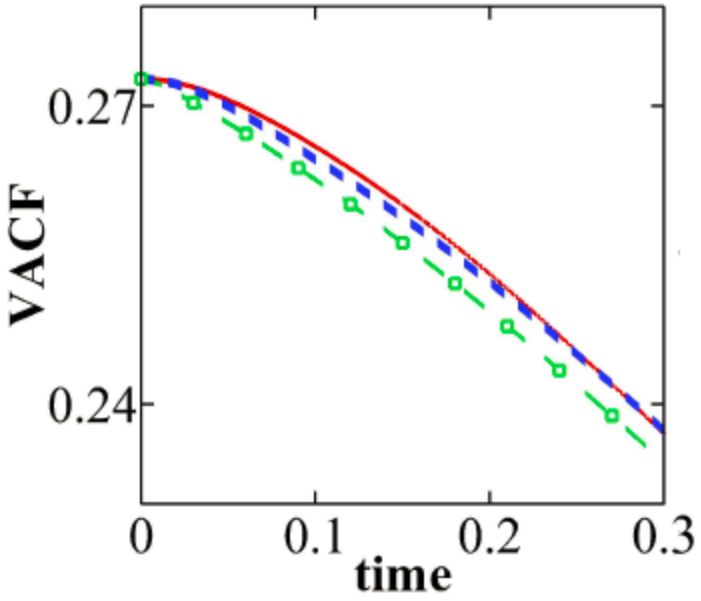
Observation: Including non-Markovian memory in the DPD system does not change its performance on reproducing RDF.

Reason: RDF of a DPD system is only determined by the conservative force, and the changes of non-conservative force do not affect RDF, even if the non-Markovian memory is introduced in the simulations.

Comparison: Dynamic Properties (ρ=0.4)

Performance of Markovian DPD model (DPD) and non-Markovian DPD model (NM-DPD) in reproducing the MD systems on the velocity autocorrelation function (VACF): $\kappa = \tau_v/\tau_f = 23.41$





MD: $D = 0.119, \nu = 0.965$

DPD: $D = 0.120, \nu = 0.954$

Both Markovian model and Non-Mavkovian model can reproduce the original MD system well.

Including memory does not change the results significantly, which indicates the Markovian assumption can be applied safely.

Comparison: Dynamic Properties (ρ=0.4)

The curve of Velocity Auto-Correlation Function (VACF) contains dynamic properties of the system

$$VACF(t) = \frac{3k_BT}{M}\exp\left(-\frac{\gamma t}{M}\right) + \frac{2k_BT}{\rho M}\frac{1}{\left[4\pi(D+\nu)t\right]^{3/2}}$$

M is the mass of a spherical particle.
γ is the Stokes viscous drag coefficient.

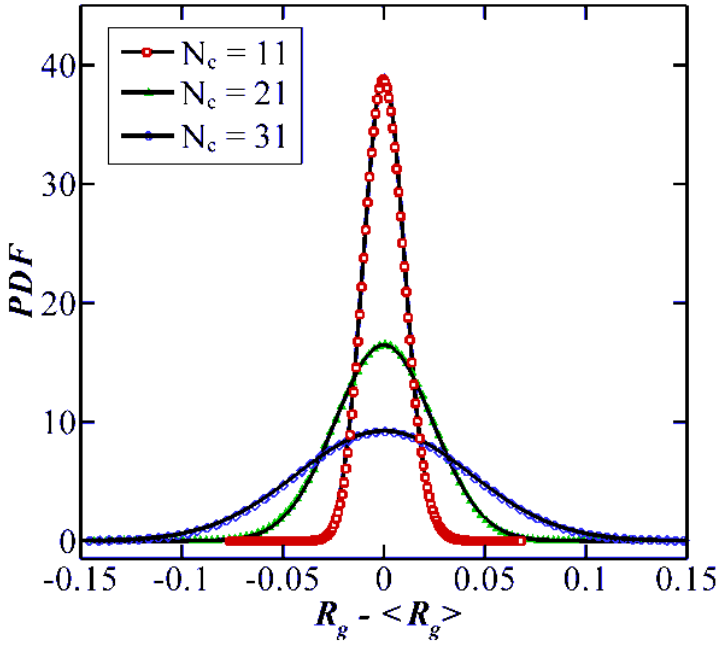
Short time: $VACF \sim \exp(-t/\tau_p)$

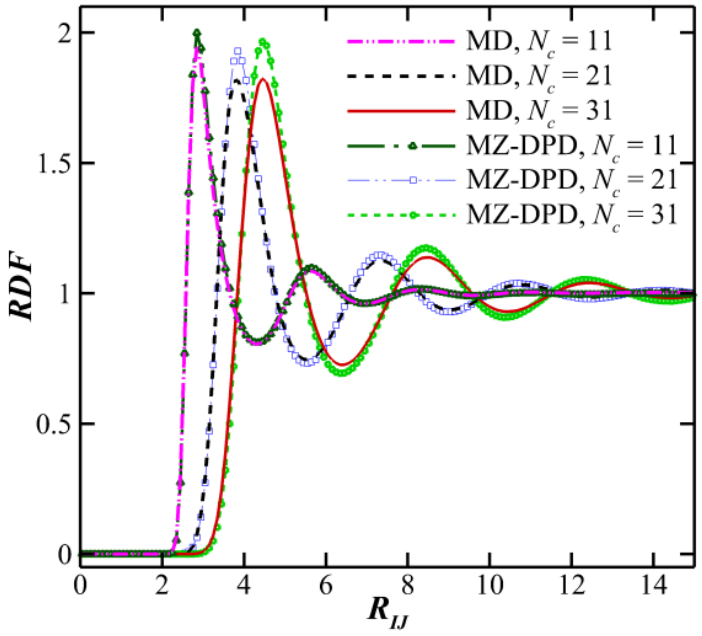
Long time: $VACF \sim t^{-3/2}$

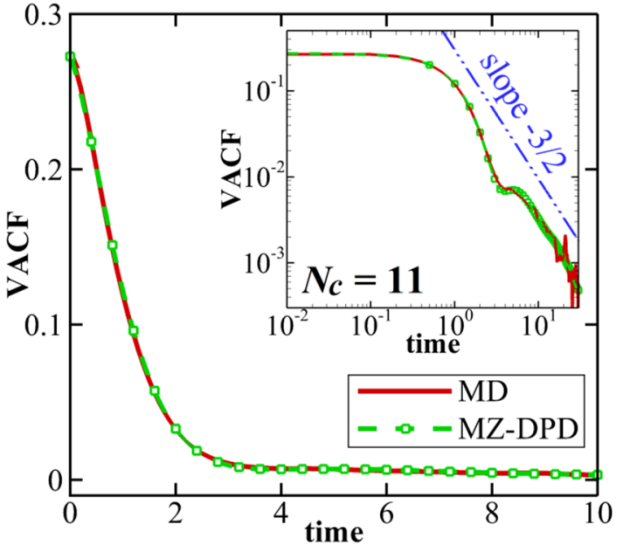
Timescales: $\tau_p = M/\gamma$

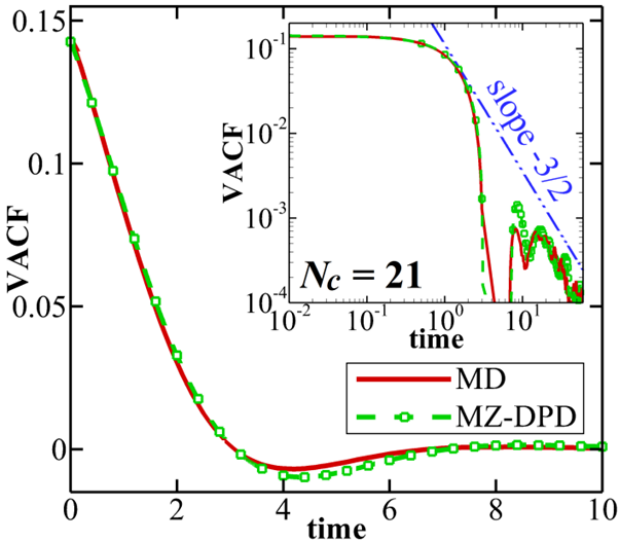
Quantities	MD	**DPD (error)**
Pressure	**0.191**	**0.193 (+1.0%)**
Diffusivity (Integral of VACF)	**0.119**	**0.120 (+0.8%)**
Viscosity	**0.965**	**0.954 (-1.1%)**
Schmidt number	**8.109**	**7.950 (-2.0%)**
Stokes-Einstein radius	**1.155**	**1.158 (+0.3%)**

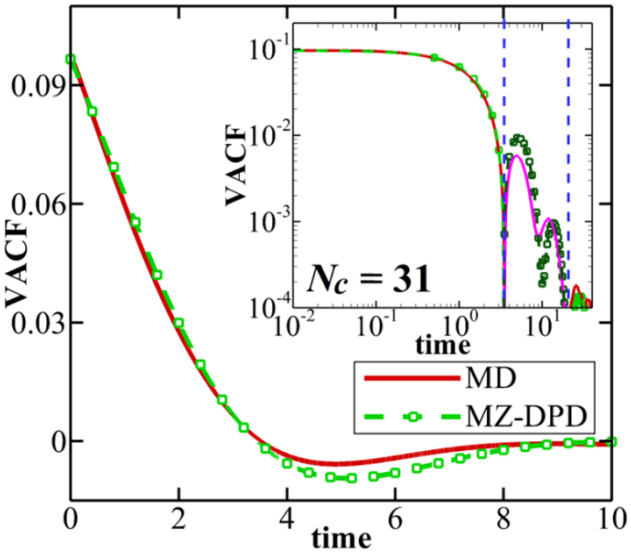
Discussion: Many-Body effect (ρ=0.4)











Discussion: Many-Body effect (ρ=0.4)

	Quantities	MD	DPD (error)
$N_c = 21$	Pressure	**0.198**	**0.194 (-2.0%)**
	Diffusivity (Integral of VACF)	**0.061**	**0.060 (-1.6%)**
	Viscosity	**1.413**	**1.457 (+3.1%)**
	Schmidt number	**23.16**	**24.28 (+4.8%)**
	Stokes-Einstein radius	**1.539**	**1.517 (-1.4%)**

	Quantities	MD	DPD (error)
$N_c = 31$	Pressure	**0.210**	**0.202(-3.8%)**
	Diffusivity (Integral of VACF)	**0.040**	**0.036 (-10.0%)**
	Viscosity	**1.878**	**2.087 (+11.1%)**
	Schmidt number	**46.95**	**57.97 (-23.5%)**
	Stokes-Einstein radius	**1.765**	**1.765 (0.0%)**

Forward CG strategy vs Reverse CG strategy

Suppose that the pairwise potential is given, the optimization process only considers the dynamics properties.

Set target properties (case $N_C = 21$ at $\rho = 0.4$)

$$[D, \nu]_{MD} = [0.061, 1.413]$$

The dissipative force is in the form of

$$\boldsymbol{F}_{IJ}^{D}(R) = \gamma(1 - R/R_{cut})^{s}\left(\boldsymbol{V}_{IJ}\boldsymbol{e}_{IJ}\right)\boldsymbol{e}_{IJ}$$

Reverse CG strategy optimizes a parameter set $[\gamma, s]$ to obtain targets.

Technically, we employ generalized polynomial chaos (gPC) to construct a surrogate model for DPD systems using a linear combination of a set of special basis functions defined in the parameter space.

$$[\gamma, s] = [\bar{\gamma}, \bar{s}] + \left[\delta_\gamma, \delta_s\right] \cdot diag(\xi_1, \xi_2)$$
$$[\bar{\gamma}, \bar{s}] = [100, 3.0]$$
$$\left[\delta_\gamma, \delta_s\right] = [50, 1.0]$$

ξ_1 and ξ_2 are *i.i.d.* uniform random variables distributed on [-1,1].

Forward CG strategy vs Reverse CG strategy

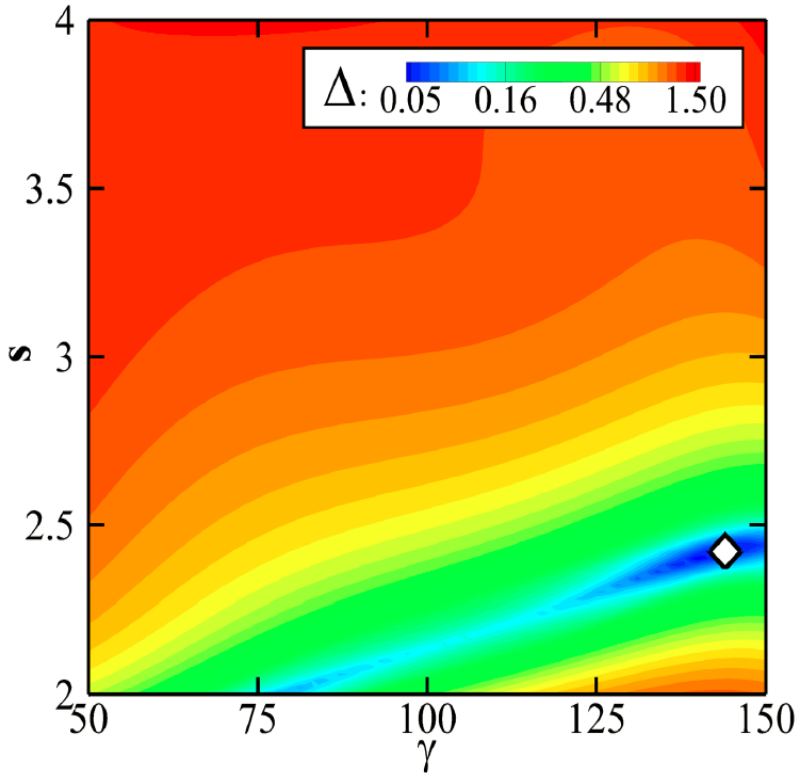
Define error function:

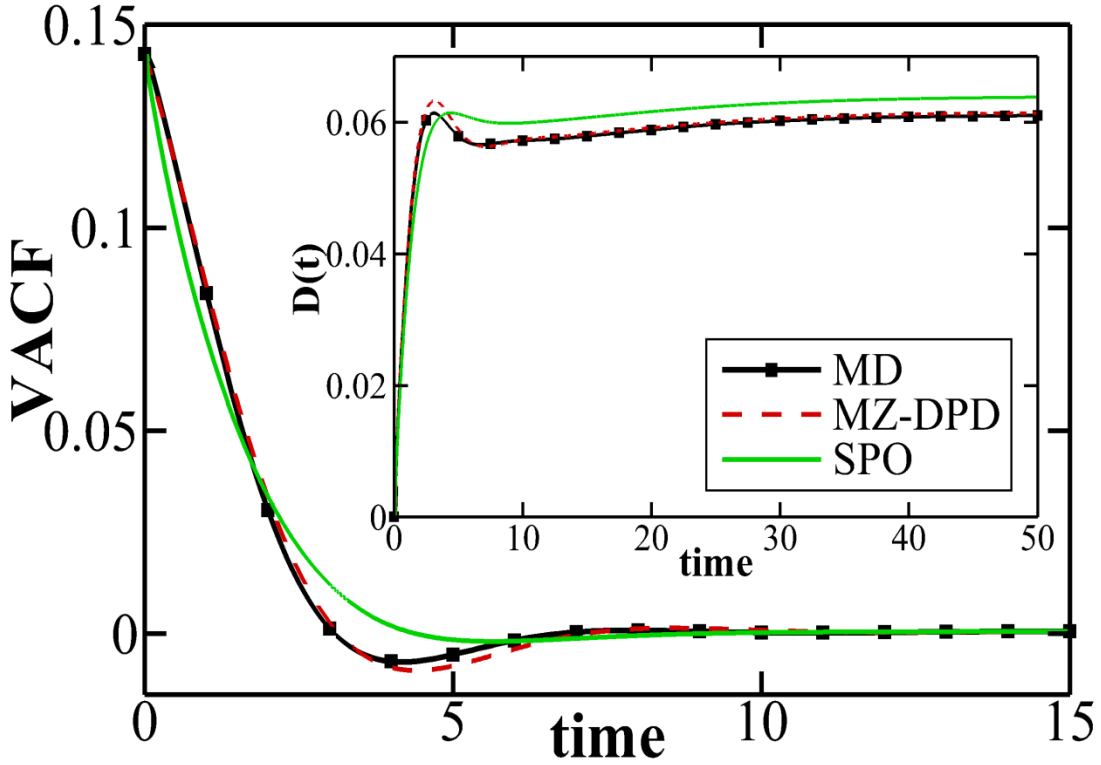
$$\Delta = \frac{|\nu - \nu_{\text{ref}}|}{\nu_{\text{ref}}} + \frac{|D - D_{\text{ref}}|}{D_{\text{ref}}}$$

Optimal choice: $\Delta_{\min} = 0.063$

$[\gamma, s] = [144.0, 2.42]$

yields $[D, \nu] = [0.064, 1.433]$



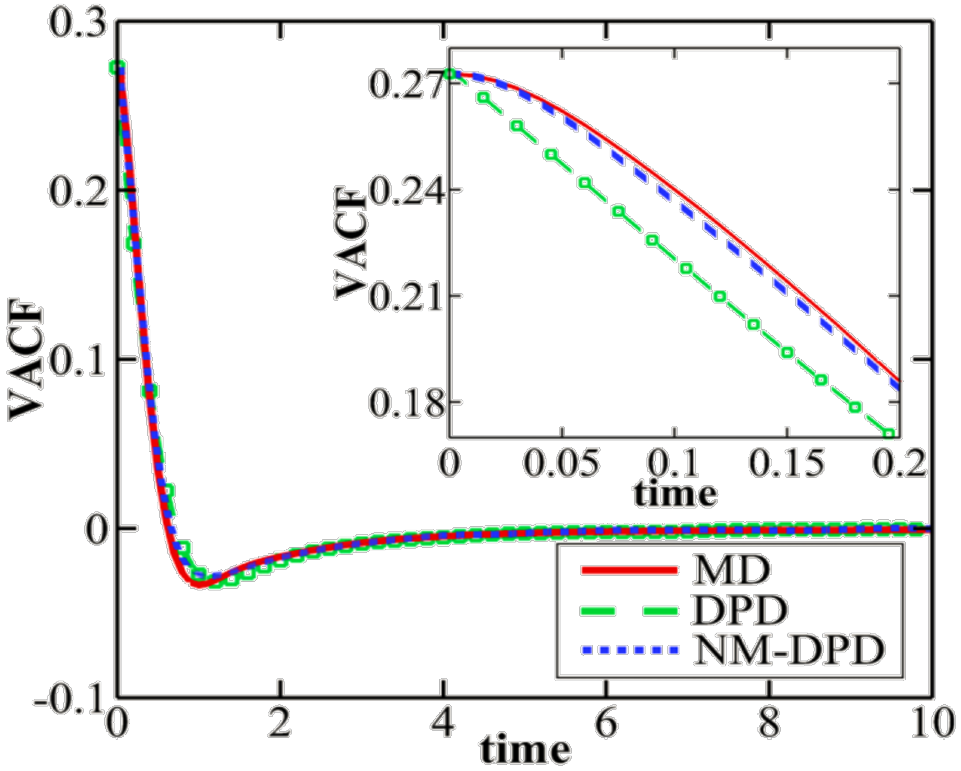


When reverse CG strategy is employed to construct CG models, even if the target properties are achieved, one should not expect that other behavior besides the targets can be correct automatically.

Z. Li, X. Bian, X. Yang and G.E. Karniadakis, J. Chem. Phys., 2016 (under review).

Comparison: Dynamic Properties (ρ=0.7)

Performance of Markovian DPD model (DPD) and non-Markovian DPD model (NM-DPD) in reproducing the MD systems on the velocity autocorrelation function (VACF): $\kappa = \tau_v / \tau_f = 2.77$



NM-DPD can reproduce correct short-time properties that are related to how the system responds to high-frequency disturbances, which cannot be captured by the Markovian-based DPD model.

However, computation of the time convolution is expensive.

Markovian system generating non-Markovian dynamics

Consider a Markovian system described by the stochastic differential equation

$$\begin{pmatrix} \dot{\mathbf{P}} \\ \dot{\mathbf{s}} \end{pmatrix} = - \begin{pmatrix} \mathbf{0} & \mathbf{A}_{ps} \\ \mathbf{A}_{sp} & \mathbf{A}_{ss} \end{pmatrix} \begin{pmatrix} \mathbf{P} \\ \mathbf{s} \end{pmatrix} + \begin{pmatrix} \mathbf{0} \\ \mathbf{B}_s \end{pmatrix} \begin{pmatrix} \mathbf{0} \\ \boldsymbol{\xi} \end{pmatrix}$$

where $\mathbf{A}_{sp} = -\mathbf{A}_{ps}^T$, $\boldsymbol{\xi}$ is a vector of uncorrelated Gaussian random numbers with

$$\langle \xi_i(t) \xi_j(0) \rangle = \delta_{ij} \delta(t)$$

Let $\mathbf{x} = (\mathbf{P}, \mathbf{s})^T$, the dynamics of $\mathbf{x}$ is the Ornstein-Uhlenbeck (OU) process

$$\dot{\mathbf{x}} = \mathbf{A}\mathbf{x} + \mathbf{B}_s \boldsymbol{\xi}$$

By solving the equation of $\mathbf{s}$ we arrive at

$$\mathbf{s}(t) = \int_{-\infty}^{t} e^{-(t-t')\mathbf{A}_{ss}} \left[-\mathbf{A}_{sp} \mathbf{P}(t') + \mathbf{B}_s \boldsymbol{\xi}(t') \right] dt'$$

Ceriotti et al., J. Chem. Theory Comput. (2010).

Markovian system generating non-Markovian dynamics

we can eliminate the auxiliary variables $\mathbf{s}$ from the dynamics of momentum $\mathbf{P}$ and have

$$\dot{\mathbf{P}}(t) = -\int_{-\infty}^{t} \mathbf{K}(t-t')\mathbf{P}(t')dt' + \boldsymbol{\zeta}(t)$$

$$\mathbf{K}(t) = -\mathbf{A}_{ps}e^{-t\mathbf{A}_{ss}}\mathbf{A}_{sp} \quad (t \geq 0)$$

$$\boldsymbol{\zeta}(t) = -\int_{-\infty}^{t} \mathbf{A}_{ps}e^{-(t-t')\mathbf{A}_{ss}}\mathbf{B}_s\boldsymbol{\xi}(t')dt'$$

which corresponds to a non-Markovian dynamics.

If the memory kernel can be approximated by an arbitrary combination of complex exponentials in the form of

$$\mathbf{K}(t) = -\mathbf{A}_{ps}\exp(-t\mathbf{A_{ss}})\mathbf{A}_{sp}$$

then, the non-Markovian dynamics can be approximated by the Markovian system whose momentum is coupled to auxiliary variables

$$\begin{pmatrix} \dot{\mathbf{P}} \\ \dot{\mathbf{s}} \end{pmatrix} = -\begin{pmatrix} \mathbf{0} & \mathbf{A}_{ps} \\ \mathbf{A}_{sp} & \mathbf{A}_{ss} \end{pmatrix}\begin{pmatrix} \mathbf{P} \\ \mathbf{s} \end{pmatrix} + \begin{pmatrix} \mathbf{0} \\ \mathbf{B}_s \end{pmatrix}\begin{pmatrix} \mathbf{0} \\ \boldsymbol{\xi} \end{pmatrix}$$

Ceriotti et al., J. Chem. Theory Comput. (2010).

Markovian system generating non-Markovian dynamics

Relation between the memory kernel $K(t)$ and the matrix A

Suppose we have the matrix $\boldsymbol{A} = \begin{bmatrix} \boldsymbol{A}_{pp} & \boldsymbol{A}_{ps} \\ \boldsymbol{A}_{sp} & \boldsymbol{A}_{ss} \end{bmatrix} = \begin{bmatrix} 0 & c_1 & c_2 \\ -c_1 & a & b \\ -c_2 & -b & 0 \end{bmatrix}$, where $\boldsymbol{A}_{ss} = \begin{bmatrix} a & b \\ -b & 0 \end{bmatrix}$

we can do the eigen-decomposition of $\boldsymbol{A}_{ss}$

$$\boldsymbol{A}_{ss} = QSQ^{-1}$$

$$= \begin{bmatrix} -\frac{a-\sqrt{a^2-4b^2}}{2b} & -\frac{a+\sqrt{a^2-4b^2}}{2b} \\ 1 & 1 \end{bmatrix} \begin{bmatrix} \frac{a-\sqrt{a^2-4b^2}}{2} & 0 \\ 0 & \frac{a+\sqrt{a^2-4b^2}}{2} \end{bmatrix} \begin{bmatrix} \frac{b}{\sqrt{a^2-4b^2}} & \frac{1}{2}+\frac{a}{2\sqrt{a^2-4b^2}} \\ \frac{-b}{\sqrt{a^2-4b^2}} & \frac{1}{2}-\frac{a}{2\sqrt{a^2-4b^2}} \end{bmatrix}$$

where $\frac{1}{2}a \pm \frac{1}{2}\sqrt{a^2-4b^2}$ are the eigenvalues of the matrix $\boldsymbol{A}_{ss}$.

Then the kernel function $K(t)$ can be computed by

$$K(t) = -\boldsymbol{A}_{ps} \exp(-t\boldsymbol{A}_{ss})\, \boldsymbol{A}_{sp}$$
$$= -A_{ps} Q exp(-tS) Q^{-1} A_{sp}$$
$$= \ldots$$
$$= \exp\left(-\tfrac{a}{2}t\right)\left[(c_1^2 + c_2^2)\cos\left(\frac{\sqrt{4b^2-a^2}}{2}t\right) + \frac{\left(c_2^2-c_1^2\right)a}{\sqrt{4b^2-a^2}}\sin\left(\frac{\sqrt{4b^2-a^2}}{2}t\right)\right]$$

Given a memory kernel $K(t)$, which is fitted by $K(t) = p\exp(-qt)\cos(rt+s)$

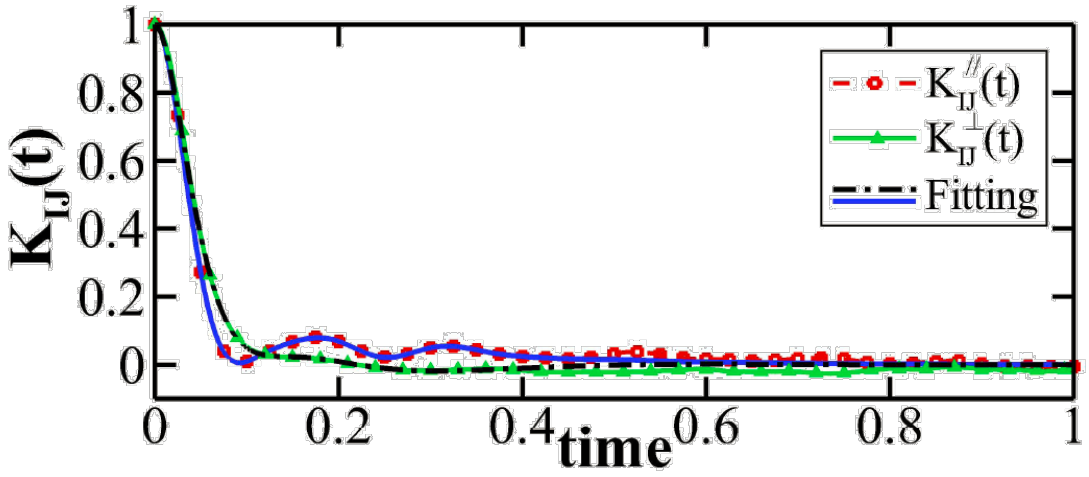
Then, we have

$$a = 2q,\ b = \sqrt{r^2+q^2},\ c_1 = \sqrt{\frac{q}{2}\cos(s) - \frac{rp}{2q}\sin(s)},\ c_2 = \sqrt{\frac{q}{2}\cos(s) + \frac{rp}{2q}\sin(s)}$$

Markovian system generating non-Markovian dynamics

The computed memory kernel can be fitted by a linear combination of many exponentially damped oscillations

$$f(t) = \sum_{i=1}^{n} \Lambda_i \exp(-t/\tau_i) \cos(\omega_i t + \varphi_i)$$



Parallel component is fitted by 4 terms

Perpendicular component is fitted by 2 terms

Based on the fitting function, the coupling matrices can be constructed:

$$\mathbf{A}_{ps}^{\parallel} = (\ 0,\ 0.280\lambda,\ 0,\ 0.611\lambda,\ 0,\ 0.658\lambda,\ 0,\ 0.339\lambda\ ),$$

$$\mathbf{A}_{sp}^{\parallel} = -[\mathbf{A}_{ps}^{\parallel}]^T,$$

$$\mathbf{A}_{ss}^{\parallel} = \begin{pmatrix} 19.66 & 60.55 & 0 & 0 & 0 & 0 & 0 & 0 \\ -60.55 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 26.30 & 23.87 & 0 & 0 & 0 & 0 \\ 0 & 0 & -23.87 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 23.55 & 39.44 & 0 & 0 \\ 0 & 0 & 0 & 0 & -39.44 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 14.29 & 7.15 \\ 0 & 0 & 0 & 0 & 0 & 0 & -7.15 & 0 \end{pmatrix}$$

$$\mathbf{A}_{ps}^{\perp} = (\ 0,\ 0.907\mu,\ 0,\ 0.421\mu\ ),$$

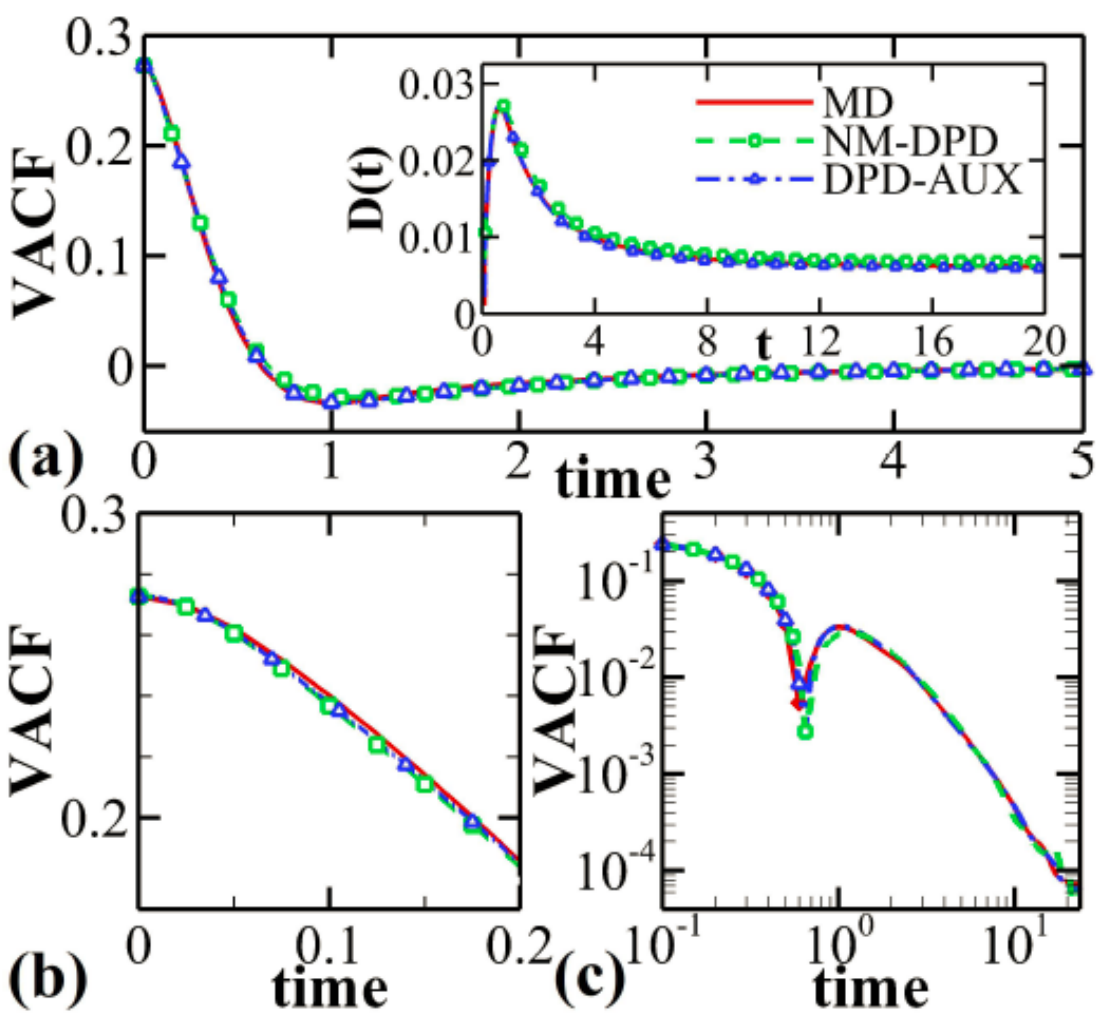
$$\mathbf{A}_{sp}^{\perp} = -[\mathbf{A}_{ps}^{\perp}]^T,$$

$$\mathbf{A}_{ss}^{\perp} = \begin{pmatrix} 51.69 & 38.78 & 0 & 0 \\ -38.78 & 0 & 0 & 0 \\ 0 & 0 & 15.00 & 12.72 \\ 0 & 0 & -12.72 & 0 \end{pmatrix}$$

To satisfy the fluctuation-dissipation theorem, the matrix $\boldsymbol{B}$ is determined by

$$\boldsymbol{B}\boldsymbol{B}^T = k_B T(\boldsymbol{A}_{ss} + \boldsymbol{A}_{ss}^T)$$

Markovian system generating non-Markovian dynamics



$$\frac{[Computational\ cost]_{NM-DPD}}{[Computational\ cost]_{DPD-AUX}} = \frac{8.3s}{0.42s} = 19.8$$

Z. Li, H.S. Lee, E. Darve and G.E. Karniadakis, 2016 (to be submitted).

Mori-Zwanzig formalism as a practical computational tool

Carmen Hijón[(1)], Pep Español[(1,2)], Eric Vanden-Eijnden[(3)], Rafael Delgado-Buscalioni[(4)]

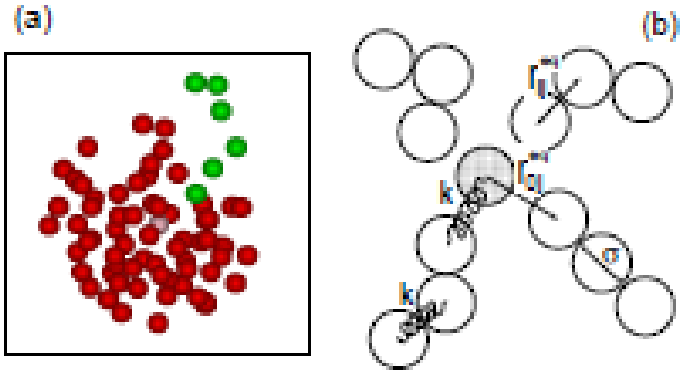
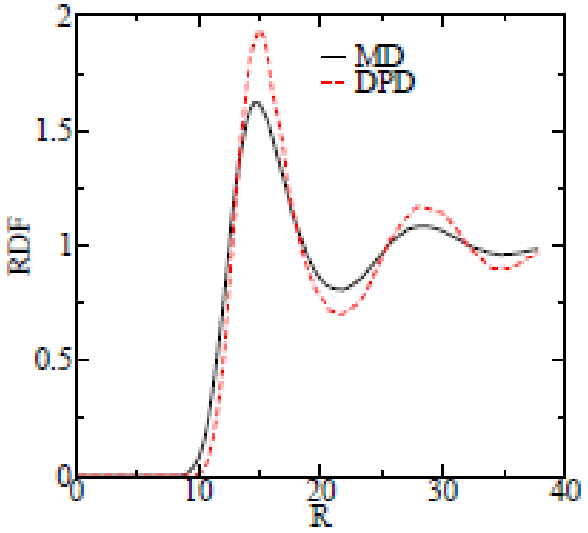
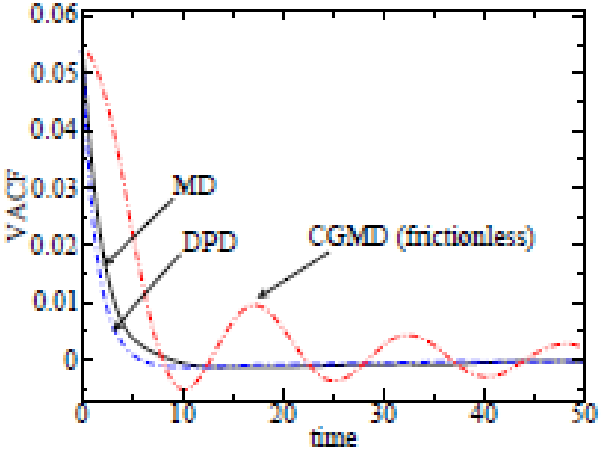


FIG. 1: (a) One of the star polymers in the polymer melt in a typical configuration. Seven monomers are lighter indicating one arm and the central monomer. It has $f = 12$ arms of $m = 6$ monomers each. (b) A sketch of the star polymer model: all monomers interact with the purely repulsive Lennard-Jones potential (truncated at $r_c = 2^{1/6}\sigma$ and shifted to zero potential energy, $\phi(r_c) = 0$) with units such that $\epsilon = 1$, $m = 1$ and $\sigma = 2.415$. Neighbour monomers are attached by springs of stiffness $k = 20\epsilon/\sigma^2$ and move around the equilibrium distance r_{ij}^{eq}, with $r_{ij}^{eq} = 1.147\sigma$ if i and j are non-center monomers and $r_{0j}^{eq} = 1.615\sigma$, if $i\,(=0)$ is the center monomer.





Outline

1. Introduction
   — Bottom-up coarse-graining
2. Foundation: Coarse-Graining
   — Introduction of the Mori-Zwanzig formalism.
   — Markovian model
   — Non-Markovian model
3. Construction of coarse-grained model directly from MD simulation
   — Static properties
   — Dynamics properties
4. Summary

Summary

- We demonstrated that coarse-grained models can be constructed directly from microscopic dynamics based on the Mori-Zwanzig (MZ) formalism.
- Given correct CG force field, CG system can reproduce its underlying MD system for both static and dynamic properties.
- The Markovian assumption works well for the system with clear timescale separation; the NM-DPD model has little improvement on the VACF compared with Markovian DPD model.
- When the timescales of a system are not fully separated, the NM-DPD can reproduce correct short-time properties that are related to how the system responds to high-frequency disturbances, which cannot be captured by the Markovian-based DPD model.
- A Markovian system with auxiliary variables coupled to momentum can be employed to generate accurate non-Markvoian dynamics with much less computational cost.

Z. Li, et al, *Soft Matter*, **10**, 8659, 2014. Z. Li, et al. *J. Chem. Phys*., 2015, **143**: 014101.

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