Coarse grained and accelerated dynamics tested on star polymers

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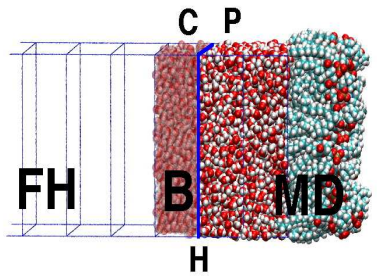
Dublin, May 2010

Multiscale/Hybrid aproaches for complex liquids

Domain decomposition

type A

Molecular detail,
interfases, surfaces,
macromolecule -fluid interaction



shear flows ✓
sound, heat
large molecules
multispecies ✗
electrostatics

Eulerian-Lagrangian Solute-solvent hydrodynamic coupling

Suspensions
of colloids or polymers,
small particles in flow

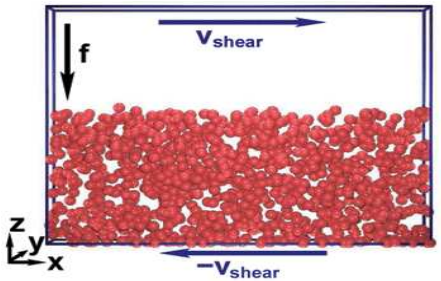


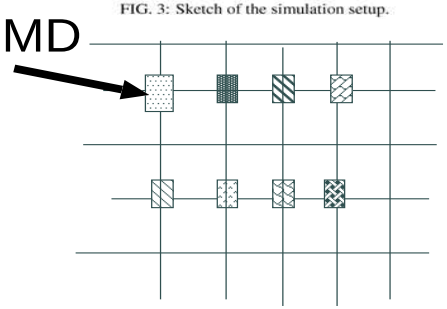
FIG. 3: Sketch of the simulation setup.

Point particle aproximation:
Stokes drag (point particle),
Faxen terms (finite size effects)
Basset memory effects...
Force Coupling
particles of finite size
Direct simulation
Immersed boundaries

Patch dynamics HMM Velocity-Stress coupling

type B

Non-Newtonian fluids
Unknown constitute relation
polymer mels...



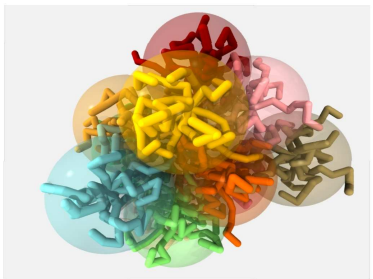
MD nodes used to evaluate the **local stress** for the Continuum solver.

Continuum solver provides the local **velocity gradient** imposed at each MD node.

how to "lift MD" ✗

Coarse-grained dynamics

How to reduce the degrees of freedom and keep the underlying dynamics

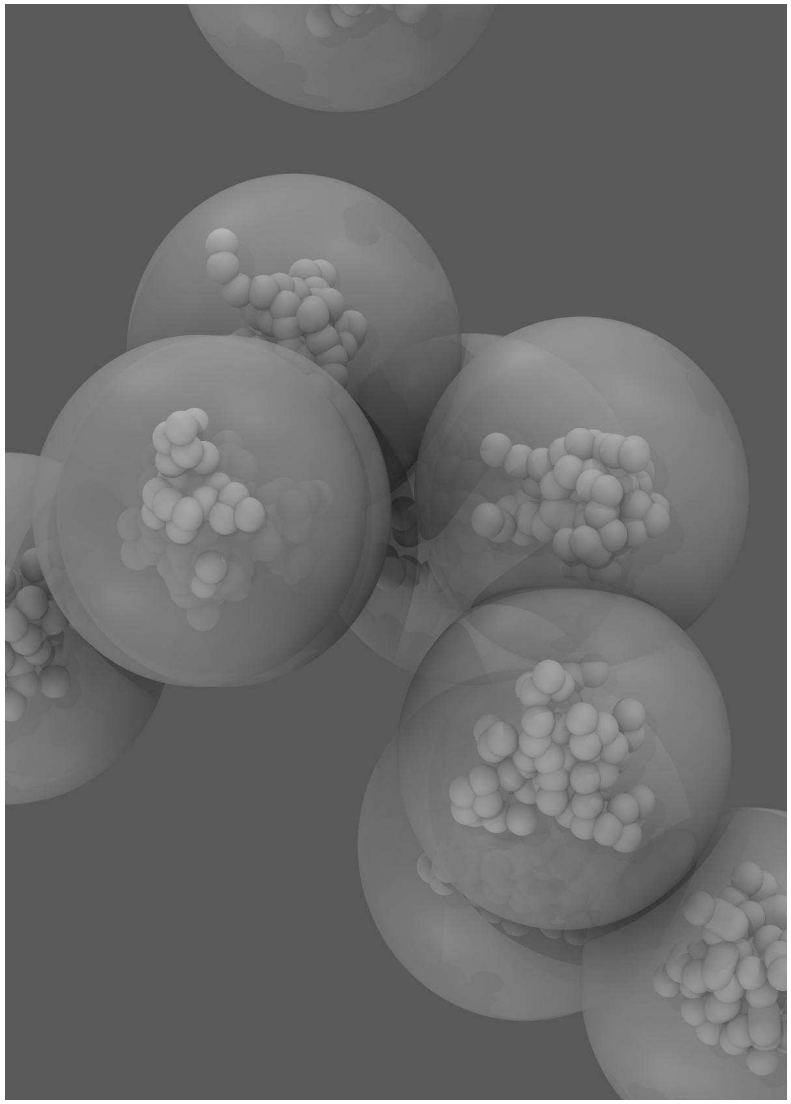


diffusion ✓
viscosity
anisotropy ✗
(nematics...)

Coworkers

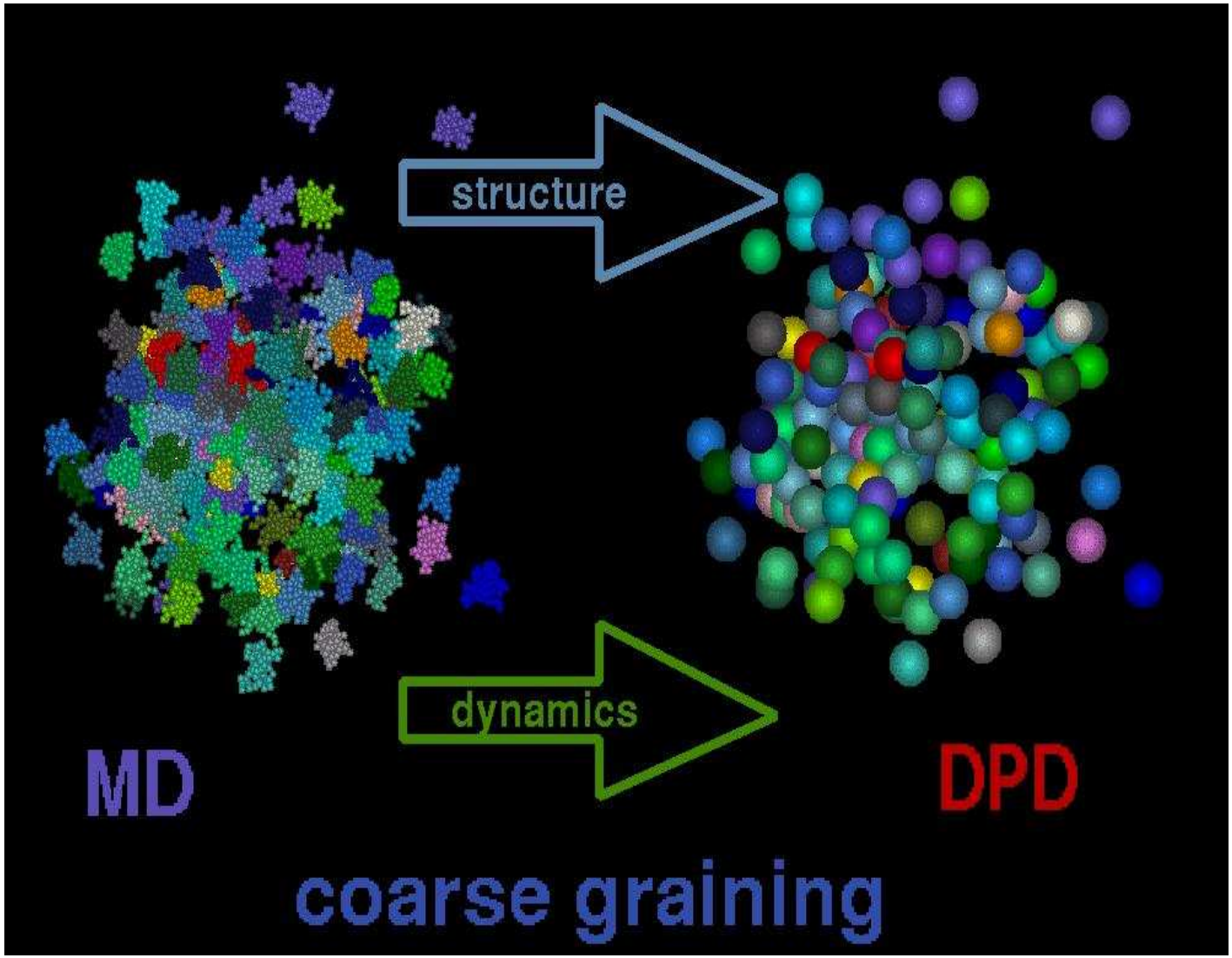
- Coarse grained dynamics
  - Carmen Hijón (ETH, Zurich)
  - Pep Español (UNED, Madrid)
  - Eric vanden-Eijnden (Courant Institute, NY)
- Accelerated molecular dynamics
  - Pep Español
  - Eric vanden-Eijnden

Coarse grained molecules



Melt of star polymers

Coarse graining dynamics



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- The hope is that this effective potential allows for realistic simulations.
- For static equilibrium properties the method works, but dynamic properties like diffusion are badly represented.
- The eliminated degrees of freedom should appear as dissipation and noise.

Faraday Discuss., **144**, *301, (2010)*

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- A well-defined method for coarse-graining exists: Zwanzig projection
- Deemed as a "formal" procedure (and therefore useless...).
- How to make Zwanzig Projection Operator a practical useful tool.
- Demonstrate the procedure for the case of star polymer melts.

Outline of Zwanzig theory

The microscopic state is $z = (\cdots, \mathbf{q}_i, \mathbf{p}_i, \cdots)$. Its dynamics is

$$\partial_t z_t = L z_t \qquad\qquad z_t = \exp\{tL\} z_0$$

where z_t is the microscopic state at time t and L is the Liouville operator.

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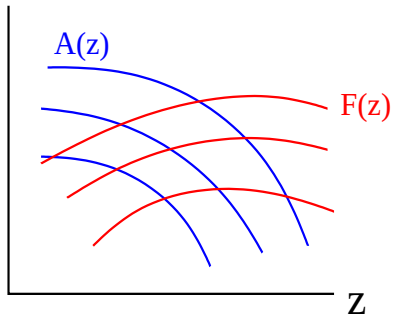
$$\partial_t A(z_t) \quad = \quad L A(z_t) = \exp\{tL\} L A(z_0) \qquad \text{Not closed!}$$

The projector

The essence of Zwanzig theory is the projection operator P

$$PF(z) = \langle F \rangle^{A(z)}$$



where

$$\langle \cdots \rangle^{\alpha} = \frac{1}{\Omega(\alpha)} \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) \cdots$$

$$\Omega(\alpha) = \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha)$$

and $\rho^{\mathrm{eq}}(z)$ is the equilibrium ensemble.

The tricks

From

$$\partial_t A(z_t) \quad = \quad LA(z_t) = \exp\{tL\}LA(z_0)$$

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and use Duhamel-Dyson identity

$$\exp\{tL\} \quad = \quad \exp\{tQL\} + \int_0^t ds \exp\{(t-s)L\}PL\exp\{sQL\}$$

The macro dynamics

By using the form of the projector we obtain the exact equation

$$\partial_t A(z_t) = \langle LA \rangle^{A(z_t)} + \int_0^t ds M(A(z_{t-s}), s) \frac{\partial S}{\partial \alpha}(A(z_{t-s})) + \tilde{R}_t(z)$$

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where

$$S(\alpha) = k_B \ln \Omega(\alpha) = k_B \ln \int \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) dz$$

$$M(\alpha, t') = \frac{1}{k_B} \langle \tilde{R}_0 \tilde{R}_{t'} \rangle^{\alpha}$$

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Markovian approximation

$$M(\alpha, t') = \frac{1}{k_B}\langle \tilde{R}_0 \tilde{R}_{t'} \rangle^{\alpha} \approx M(\alpha)\delta(t')$$

$$M(\alpha) = \frac{1}{k_B}\int_0^{\infty} \langle \tilde{R}_0 \tilde{R}_s \rangle^{\alpha} ds \qquad \text{Green-Kubo}$$

Then

$$\partial_t \alpha_t = \langle LA \rangle^{\alpha_t} + M(\alpha_t)\frac{\partial S}{\partial \alpha}(\alpha_t) + \tilde{R}_t(z)$$

Closed equation! (R_t is a known white noise).

How to compute the objects from MD?

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Zwanzig theory is formal...

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$$\tilde{R}_t \quad \approx \quad LA(z_t) - \langle LA \rangle^{A(z_t)}$$

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This is not very systematic. Worst: the friction matrix vanish!! (Plateau problem).

A more systematic approach

From the exact equation

$$\partial_t A(z_t) \quad = \quad \langle LA \rangle^{A(z_t)} + \int_0^t dt' M(A(z_{t-t'}), t') \frac{\partial S}{\partial \alpha}(A(z_{t-t'})) + \tilde{R}_t(z)$$

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Perform the change of variables $t' = \epsilon^2 \tau$,

$$\partial_t \alpha_t = \langle LA \rangle^{\alpha_t} + \int_0^{t/\epsilon^2} d\tau \epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2 \tau) \frac{\partial S}{\partial \alpha}(\alpha_{t-\epsilon^2\tau}) + \tilde{R}_t(z)$$

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When the limit exists?

$$\epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2\tau) = \frac{1}{k_B}\langle(\epsilon QLA)\exp\{\tau\epsilon^2 QLQ\}(\epsilon QLA)\rangle^{\alpha_{t-\epsilon^2\tau}}$$

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Then the limit exists

$$\epsilon^2 M(\alpha_{t-\epsilon^2\tau}, \epsilon^2\tau) = \frac{1}{k_B}\langle L_1 A\exp\{\tau L_2\}L_1 A\rangle^{\alpha} + \mathcal{O}(\epsilon)$$

A more systematic approach

Therefore, if $L = L_0 + \frac{1}{\epsilon}L_1 + \frac{1}{\epsilon^2}L_2$, with $L_2 A = 0$ and $PL_1 A = 0$ then for $\epsilon \longrightarrow 0$, we have a Markovian SDE

$$\partial_t \alpha_t \quad = \quad \langle L_0 A \rangle^{\alpha_t} + \overline{M}(\alpha_t)\frac{\partial S}{\partial \alpha}(\alpha_t) + \tilde{R}_t(z)$$

where the Green-Kubo friction matrix is given by

$$\overline{M}(\alpha_t) \quad = \quad \frac{1}{k_B}\int_0^\infty \langle L_1 A \exp\{\tau L_2\} L_1 A \rangle^{\alpha} d\tau$$

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It is always possible to decompose the Liouville operator as

$$L = L_0 + L_1 + L_2$$

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By construction, $L_2 A = 0$ and $PL_1 A = 0$.

A more systematic approach

Now, instead of $L = L_0 + L_1 + L_2$, *model* the system with L^ϵ

$$L^\epsilon \equiv L_0 + \frac{1}{\epsilon} L_1 + \frac{1}{\epsilon^2} L_2$$

This is not the real dynamics except when $\epsilon = 1$. Hopefully, it is very similar, even in the $\epsilon \to 0$ limit.

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Instead of perpetrating unsystematic approximation errors, we prefer to perpetrate systematic modelling errors.

A more systematic approach

In terms of the new operator $\mathcal{R}$

$$\begin{aligned} \langle L_0 A \rangle^\alpha &= \langle LA \rangle^\alpha \\ \overline{M}(\alpha) &= \frac{1}{k_B} \int_0^\infty \langle (LA - \langle LA \rangle^\alpha) \exp\{\tau \mathcal{R}\} (LA - \langle LA \rangle^\alpha) \rangle^\alpha d\tau \end{aligned}$$

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The basic difference with the "usual" aproximation (plateau-problematic) is that instead of

$$\exp\{QLt\} \approx \exp\{Lt\}$$

we now approximate

$$\exp\{QLt\} \approx \exp\{\mathcal{R}t\}$$

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Note that because $\mathcal{R}A = 0, \mathcal{R}H = 0$, the dynamics $\exp\{\tau\mathcal{R}\}$ samples $\rho^{\rm eq}(z)\delta(A(z) - \alpha)$.
By ergodicity, we have now a *practical* method for computing constrained averages and correlations with time averages

$$\langle F\rangle^\alpha = \lim_{T\to\infty}\frac{1}{T}\int_0^T d\tau\,\exp\{\tau\mathcal{R}\}F(z)$$

$$\begin{aligned}\langle \delta J\exp\{\tau\mathcal{R}\}\delta J\rangle^\alpha &= \lim_{T\to\infty}\frac{1}{T}\int_0^T d\tau_0\,\exp\{\tau_0\mathcal{R}\}\delta J(z)\\ &\times \exp\{(\tau_0+\tau)\mathcal{R}\}\delta J(z)\end{aligned}$$

where the initial condition z satisfies $A(z) = \alpha$.

A more systematic approach

Yet, we need to define $\mathcal{R}$.

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- In case $A(z)$ is linear, $\mathcal{R}$ can be easily defined. We will see a trivial example soon.
- Not fully solved for non-linear $A(z)$.

Summary

The equivalent Fokker-Planck equation

$$\partial_t \rho(\alpha, t) = \frac{\partial}{\partial \alpha} \mathbf{v}(\alpha) \rho(\alpha, t) + k_B \frac{\partial}{\partial \alpha} \Omega(\alpha) \mathbf{M}(\alpha) \cdot \frac{\partial}{\partial \alpha} \frac{\rho(\alpha, t)}{\Omega(\alpha)}$$

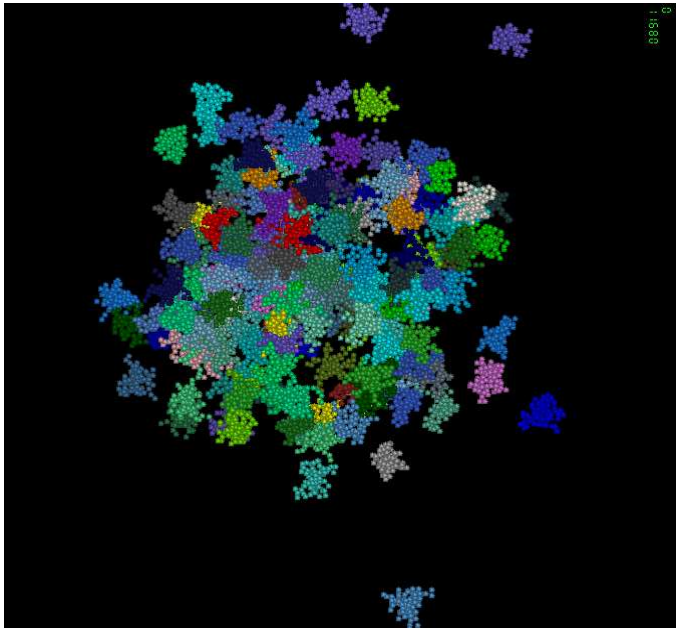
where

$$\begin{aligned} \Omega(\alpha) &= \int dz \rho^{\mathrm{eq}}(z) \delta(A(z) - \alpha) \\ \mathbf{v}(\alpha) &= \langle LA \rangle^{\alpha} \\ \mathbf{M}(\alpha) &= \frac{1}{k_B} \int_0^{\infty} \langle (LA - \langle LA \rangle^{\alpha}) \exp\{\tau \mathcal{R}\} (LA - \langle LA \rangle^{\alpha}) \rangle^{\alpha} d\tau \end{aligned}$$

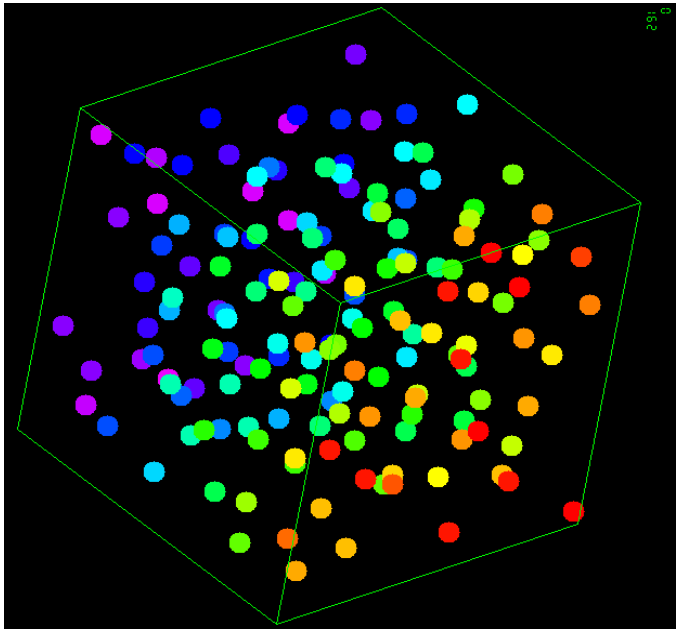
All these objects may be computed from simulating the constrained dynamics

Coarsening star polymers

MD



CoM



160 star molecules: 12 arms, 6 monomers each. L-J non-bonded interaction, FENE bonded interaction

Coarsening star polymers

Level	Variables	Dynamics
Micro	$z = \{\mathbf{r}_{i_\mu}, \mathbf{p}_{i_\mu}\}$	$\dot{z} = Lz$
Macro	$A(z) = \begin{cases} \mathbf{R}_\mu(z) = \frac{1}{m_\mu}\sum_{i_\mu} m_{i_\mu}\mathbf{r}_{i_\mu} \\ \mathbf{P}_\mu(z) = \sum_{i_\mu} \mathbf{p}_{i_\mu} \end{cases}$	SDE

Coarsening star polymers

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So we need to find out $\Omega(\alpha)$, $v(\alpha)$ and $M(\alpha)$ of the SDE.

Coarsening star polymers

The equilibrium distribution $\Omega(\alpha)$ is

$$\Omega(R,P) = \int dz \rho^{\mathrm{eq}}(z)\delta(R-\hat{R}(z))\delta(P-\hat{P}(z))$$

Integrating out momenta

$$\Omega(R,P) = \Omega(R)\frac{1}{\sqrt{2\pi T\prod_\mu M_\mu}}\exp\left\{-\beta\sum_\mu \frac{P_\mu^2}{2M_\mu}\right\}$$

The effective potential is defined through

$$\Omega(R) = \frac{1}{Q}\exp\left\{-\frac{V^{\mathrm{eff}}(R)}{k_B T}\right\}$$

Coarsening star polymers

The drift term $v(\alpha) = \langle LA \rangle^{\alpha}$ is now

$$\left\langle L\hat{\mathbf{R}}_\mu \right\rangle^{RP} = \frac{\mathbf{P}_\mu}{M_\mu} \rightarrow L\mathbf{R} - \left\langle L\hat{\mathbf{R}}_\mu \right\rangle^{RP} = 0$$

$$\left\langle L\hat{\mathbf{P}}_\mu \right\rangle^{RP} = \langle \mathbf{F}_\mu \rangle^{RP} \rightarrow \langle \mathbf{F}_\mu \rangle^{R} = -\frac{\partial V^{\text{eff}}}{\partial \mathbf{R}_\mu}$$

Coarsening star polymers

The friction matrix $M(\alpha)\frac{1}{k_B}\int_0^\infty \langle \delta L A \exp\{\tau \mathcal{R}\}\delta L A\rangle^\alpha d\tau$ is now

$$\mathbf{M}_{\mu\nu}(R,P) = \begin{pmatrix} \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\gamma}_{\mu\nu}(R,P) \end{pmatrix}$$

The mutual friction coefficients between molecules μ, ν are

$$\boldsymbol{\gamma}_{\mu\nu}(R,P) = \int_0^\infty dt \langle \delta\mathbf{F}_\nu \exp\{\mathcal{R}t\}\delta\mathbf{F}_\mu\rangle^{RP}$$

$$\delta\mathbf{F}_\mu = \hat{\mathbf{F}}_\mu - \left\langle \hat{\mathbf{F}}_\mu \right\rangle^{RP}$$

Coarsening star polymers

The SDE for the CoM provided by Zwanzig theory are

$$\begin{aligned} \partial_t \mathbf{R}_\mu &= \mathbf{V}_\mu \\ \partial_t \mathbf{P}_\mu &= \langle \mathbf{F}_\mu \rangle^R - \sum_\nu \gamma_{\mu\nu}(R)\mathbf{V}_{\mu\nu} + \tilde{\mathbf{F}}_\mu \end{aligned}$$

where $\mathbf{V}_{\mu\nu} = \mathbf{V}_\mu - \mathbf{V}_\nu$
The fluctuation-dissipation balance requires,

$$\begin{aligned} \tilde{\mathbf{F}}_\mu dt &= \sum_\nu B_{\mu\nu} dW_\nu \text{ Sum of indep. Wiener processes} \\ B_{\mu\lambda}B_{\nu\lambda} &= 2k_BT\gamma_{\mu\nu} \;\; 3M \times 3M \text{ matrix equation} \end{aligned}$$

These equations *resemble* the standard Dissipative Particle Dynamics.

Coarsening star polymers

The constrained dynamics $\mathcal{R}$ are now simply

$$\begin{aligned} \dot{\mathbf{r}}_{i_\mu} &= \mathbf{v}_{i_\mu} - \mathbf{V}_\mu \\ \dot{\mathbf{p}}_{i_\mu} &= \mathbf{F}_{i_\mu} - \frac{m_{i_\mu}}{M_\mu}\mathbf{F}_\mu \end{aligned}$$

That, obviously, satisfy $\dot{\mathbf{R}}_\mu = 0$ and $\dot{\mathbf{P}}_\mu = 0$.

By running this dynamic equations and performing time averages we may compute

$$\begin{aligned} \langle \mathbf{F}_\mu \rangle^{\{\mathbf{R}\}} & \\ \gamma_{\mu\nu}(\{\mathbf{R}\}) &= \frac{1}{k_B T}\int_0^\infty dt \langle \delta\mathbf{F}_\mu \exp\{t\mathcal{R}\}\delta\mathbf{F}_\nu \rangle^{\{\mathbf{R}\}} \end{aligned}$$

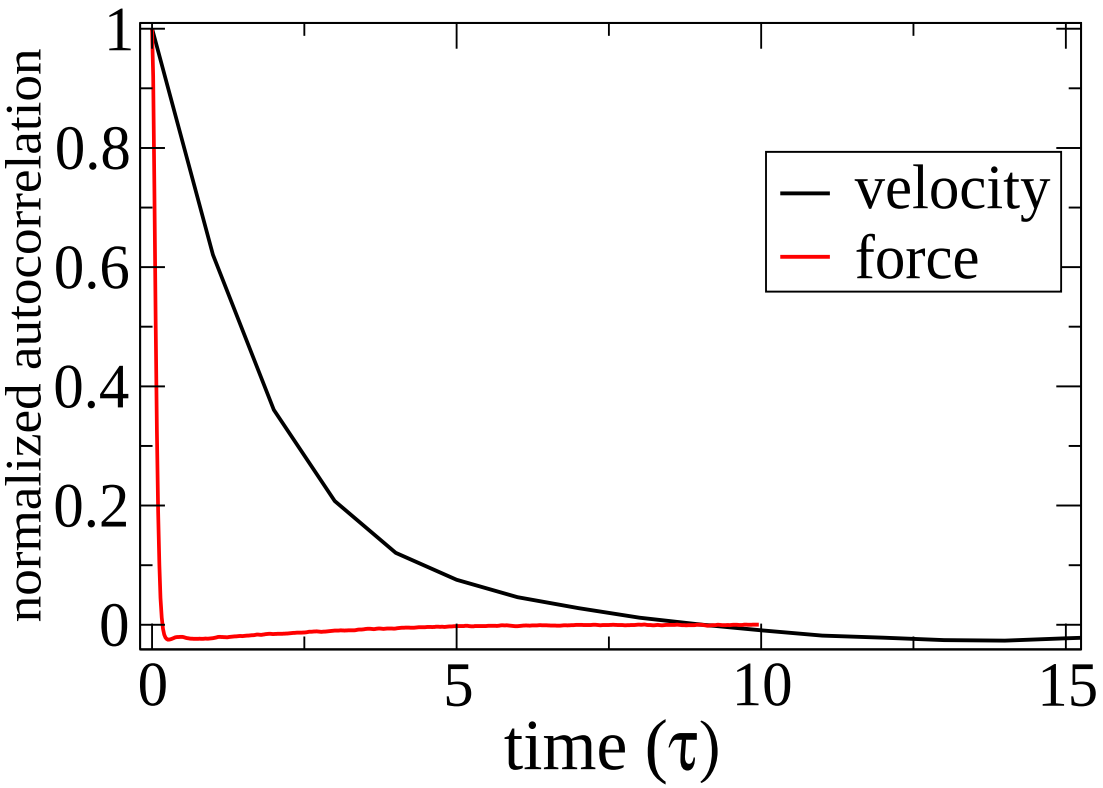
Coarsening star polymers

Approximations:

- Markovian approximation: $\tau_f << \tau_v$.
  Forces between molecules decorrelate much faster than molecule's velocities.
- Pair-wise additivity

Coarsening star polymers

Markovian behaviour expected.



Coarsening star polymers

1^{st} Pair-wise hypothesis:
On the effective force

$$\langle \mathbf{F}_\mu \rangle^{\{\mathbf{R}\}} = \langle F_\mu \rangle^{R_{\mu\nu}}$$

Two options:

- *Pure* pair-wise:

$$\langle \mathbf{F}_\mu \rangle^{R_{\mu\nu}} = \sum_\nu \langle \mathbf{F}_{\mu\nu} \rangle^{R_{\mu\nu}} \cdot \mathbf{e}_{\mu\nu}$$

Coarsening star polymers

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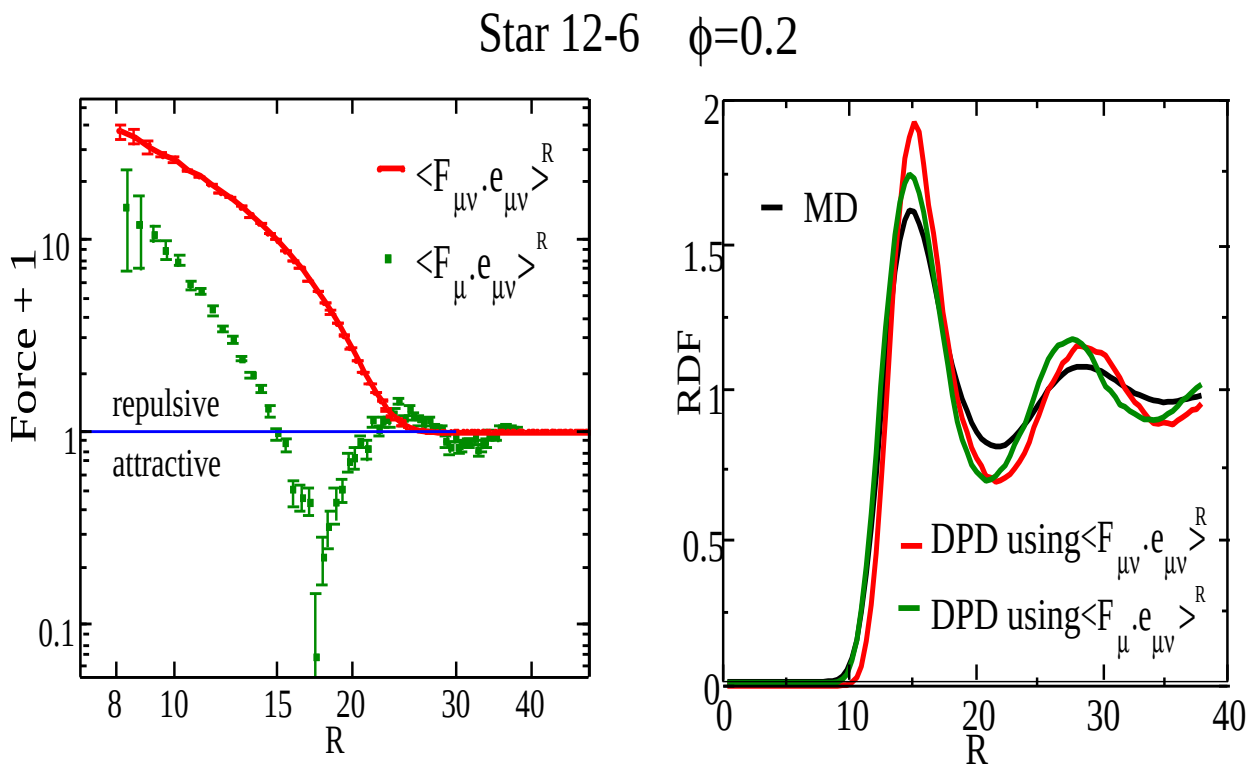
- Including (some) depletion effects:

$$\langle \mathbf{F}_\mu \rangle^{R_{\mu\nu}} = \sum_\nu \langle \mathbf{F}_\mu \cdot \mathbf{e}_{\mu\nu} \rangle^{R_{\mu\nu}} \cdot \mathbf{e}_{\mu\nu}$$

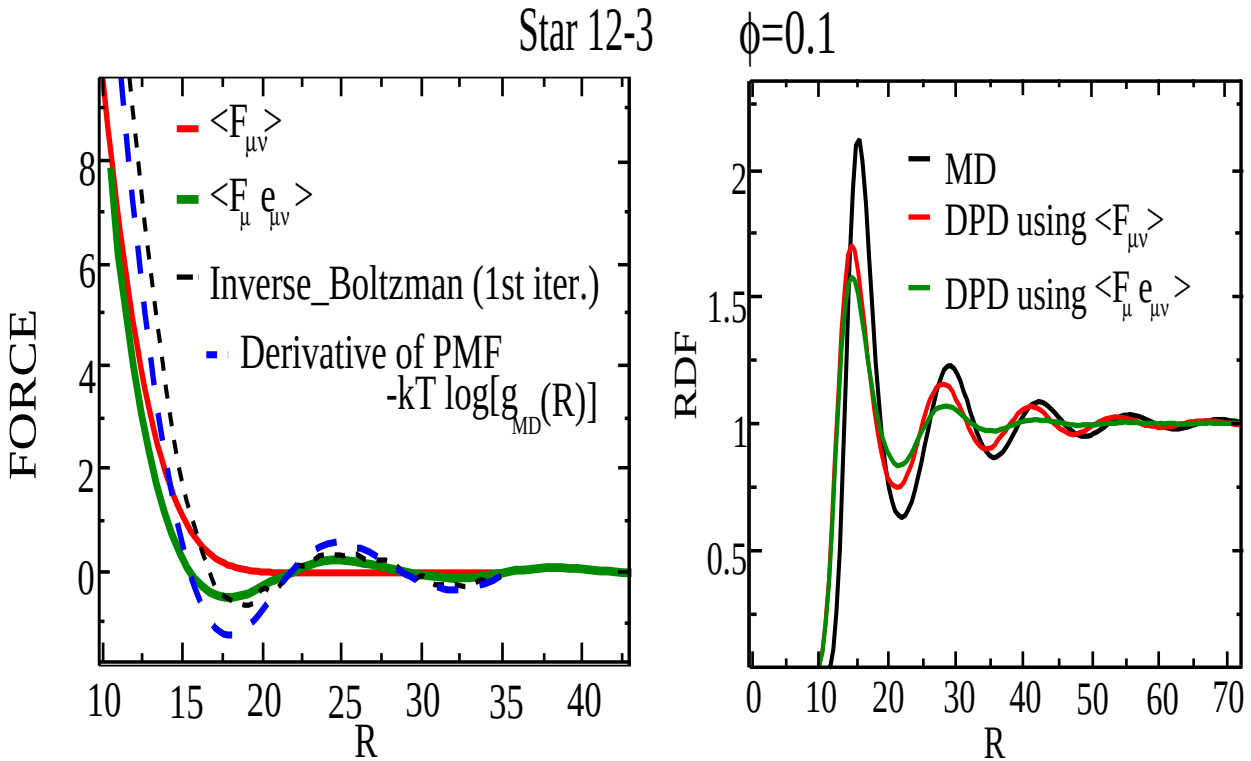
Coarsening star polymers: Effective forces

STAR 12-6: Star polymer melt. 12 arms, 6 monomers per arm. Volume concentration $\phi = 0.2$.



Coarsening star polymers: Effective forces

STAR 12-3: Star polymer melt. 12 arms, 3 monomers per arm. Volume concentration $\phi = 0.1$.



Coarsening star polymers: Friction

2^{nd} pair-wise approximation.

On friction matrix.

$$\gamma_{\mu\nu}(\{\mathbf{R}\}) = \frac{1}{k_B T} \int_0^\infty dt \langle \delta\mathbf{F}_\mu \exp\{t\mathcal{R}\} \delta\mathbf{F}_\nu \rangle^{\{\mathbf{R}\}}$$

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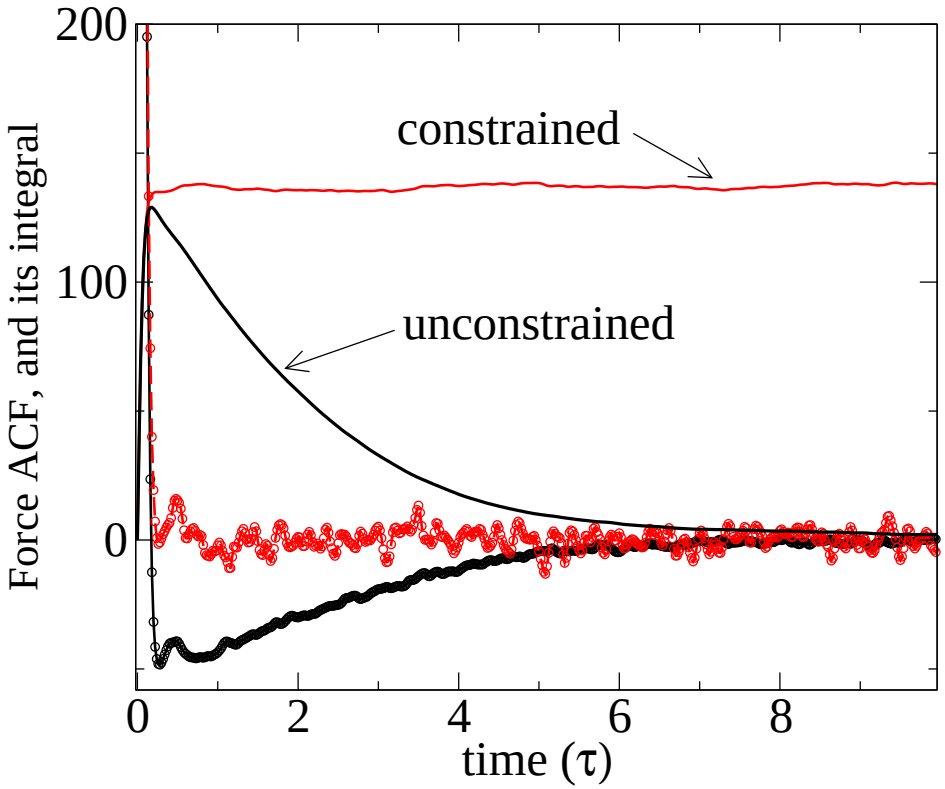
$$\begin{aligned}\gamma_{\mu\nu}(\{\mathbf{R}\}) \simeq \gamma_{\mu\nu}(R_{\mu\nu}) &= \frac{1}{k_B T}\int_0^\infty dt \langle \delta\mathbf{F}_\mu \exp\{t\mathcal{R}\}\delta\mathbf{F}_\nu\rangle^{R_{\mu\nu}} \\ \text{spherical sym. } \gamma_{\mu\nu}(R_{\mu\nu}) &= -\gamma^{||}(R_{\mu\nu})\mathbf{e}_{\mu\nu}\mathbf{e}_{\mu\nu} - \gamma^{\perp}(R_{\mu\nu})\left(\mathbf{1} - \mathbf{e}_{\mu\nu}\mathbf{e}_{\mu\nu}\right)\end{aligned}$$

Coarsening star polymers: Friction

Constrained dynamics avoid the **plateau problem**.

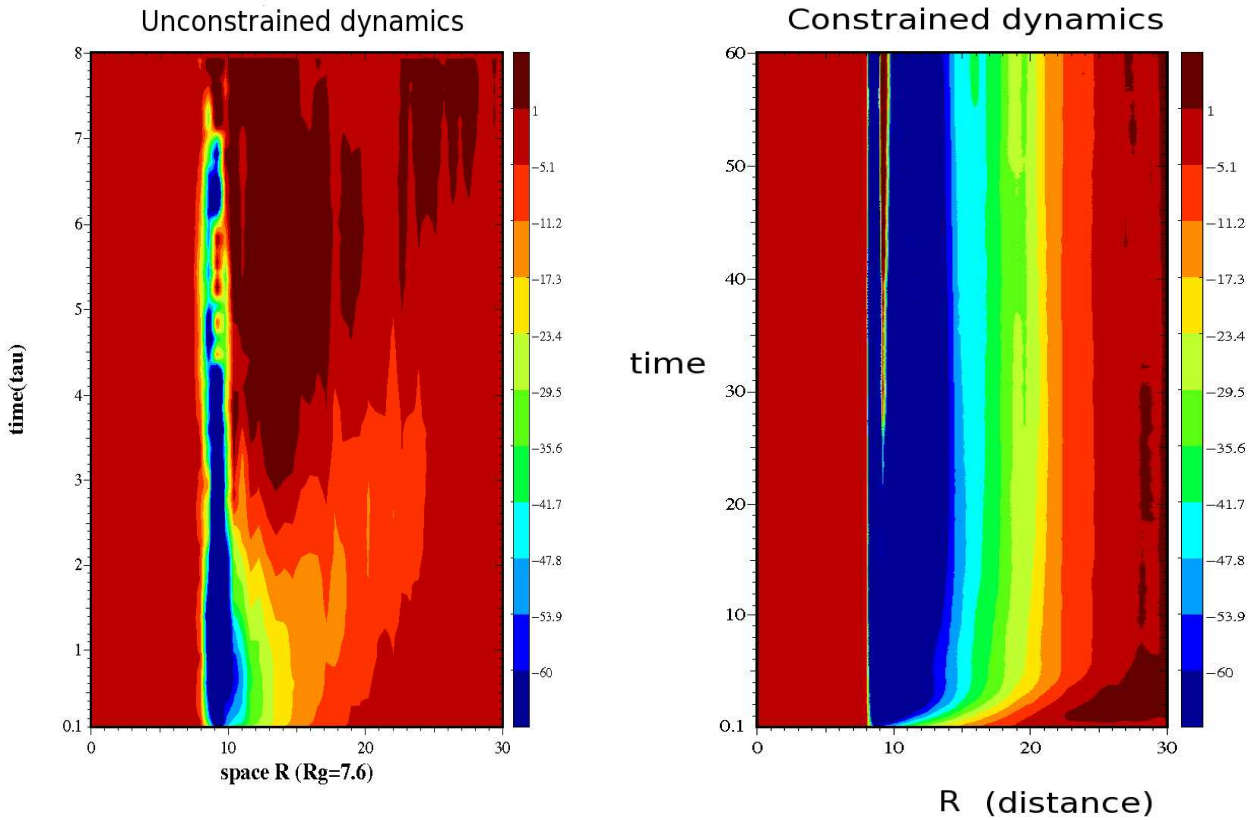
Single molecule friction coefficient: $\gamma = \frac{1}{kT}\int_0^\infty \langle \mathbf{F}(t)\cdot\mathbf{F}(0)\rangle$.



Coarsening star polymers: Friction

Constrained dynamics are **crucial** to evaluate mutual friction.

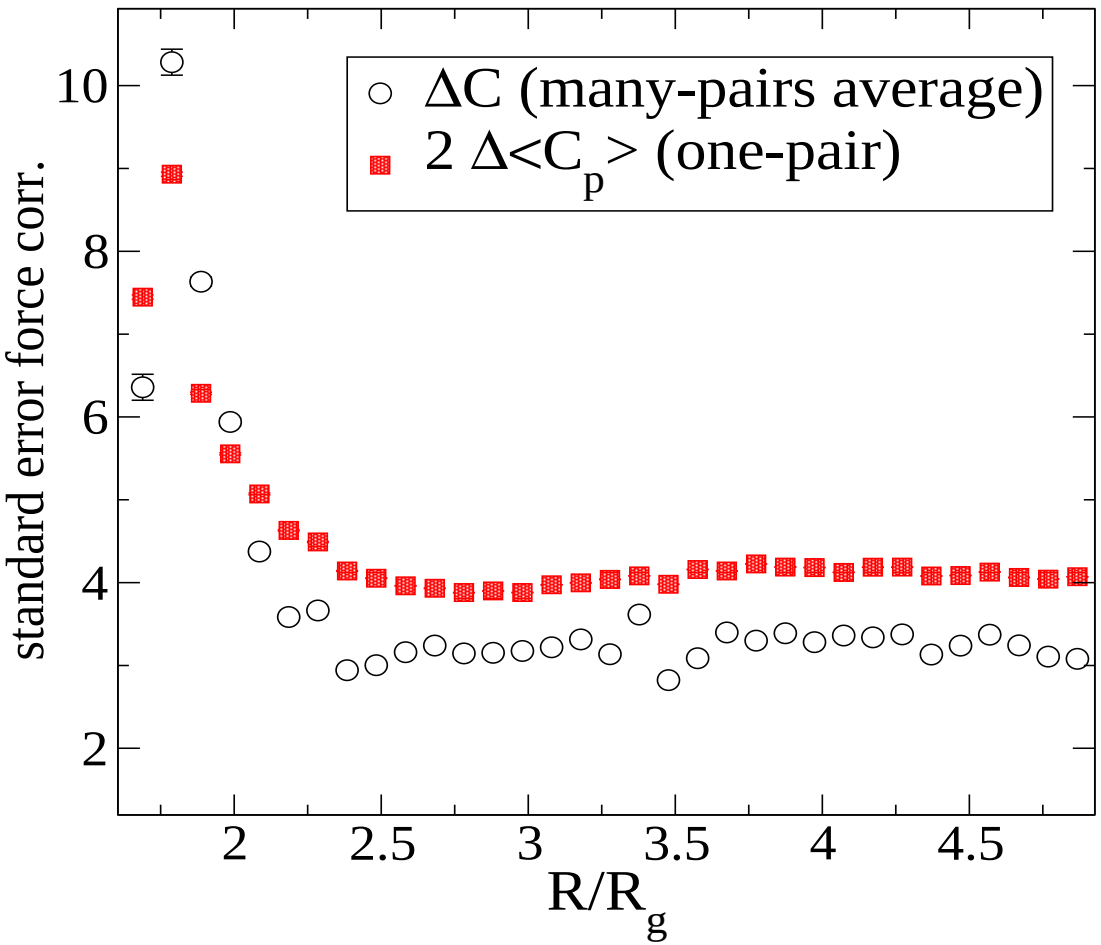
Mutual friction matrix: $\gamma_{\mu\nu}(R_{\mu\nu}) = \frac{1}{kT}\int_0^\infty \langle \mathbf{F}_\mu(t)\mathbf{F}_\nu(0)\rangle^{R_{\mu\nu}}$.



Coarsening star polymers

How good is the pair-wise assumption on friction ?

STAR 12-3



Coarsening star polymers

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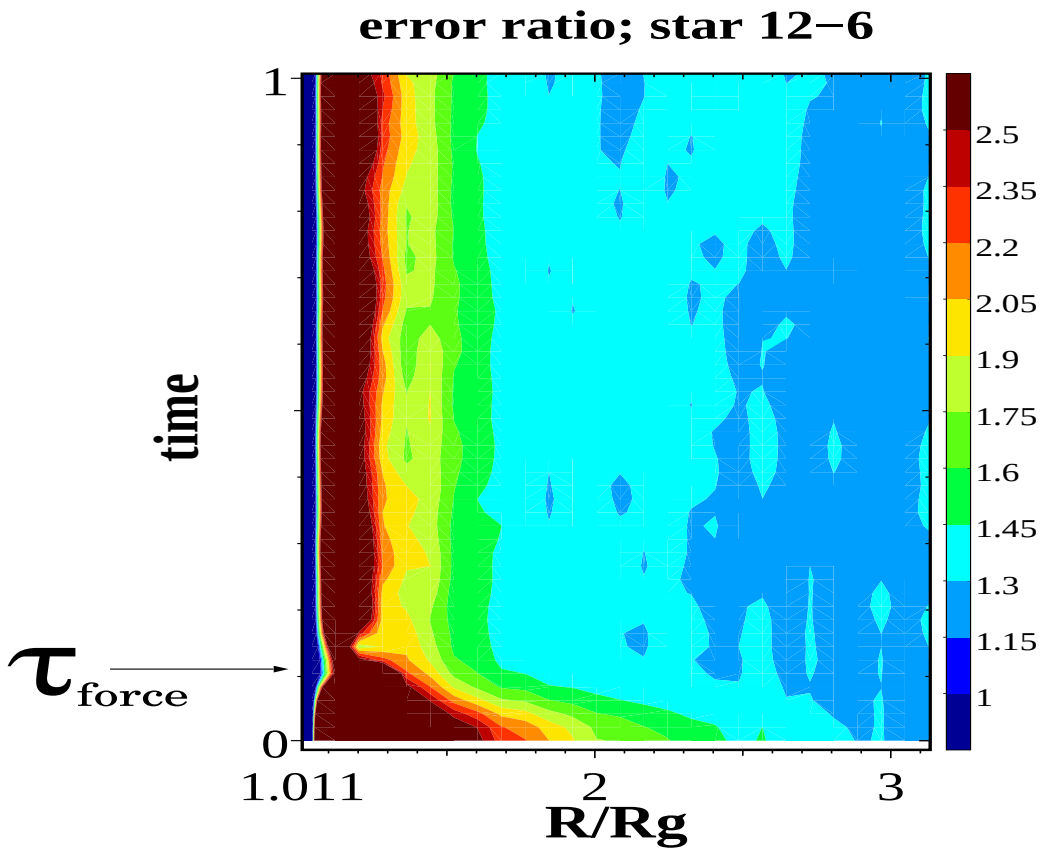
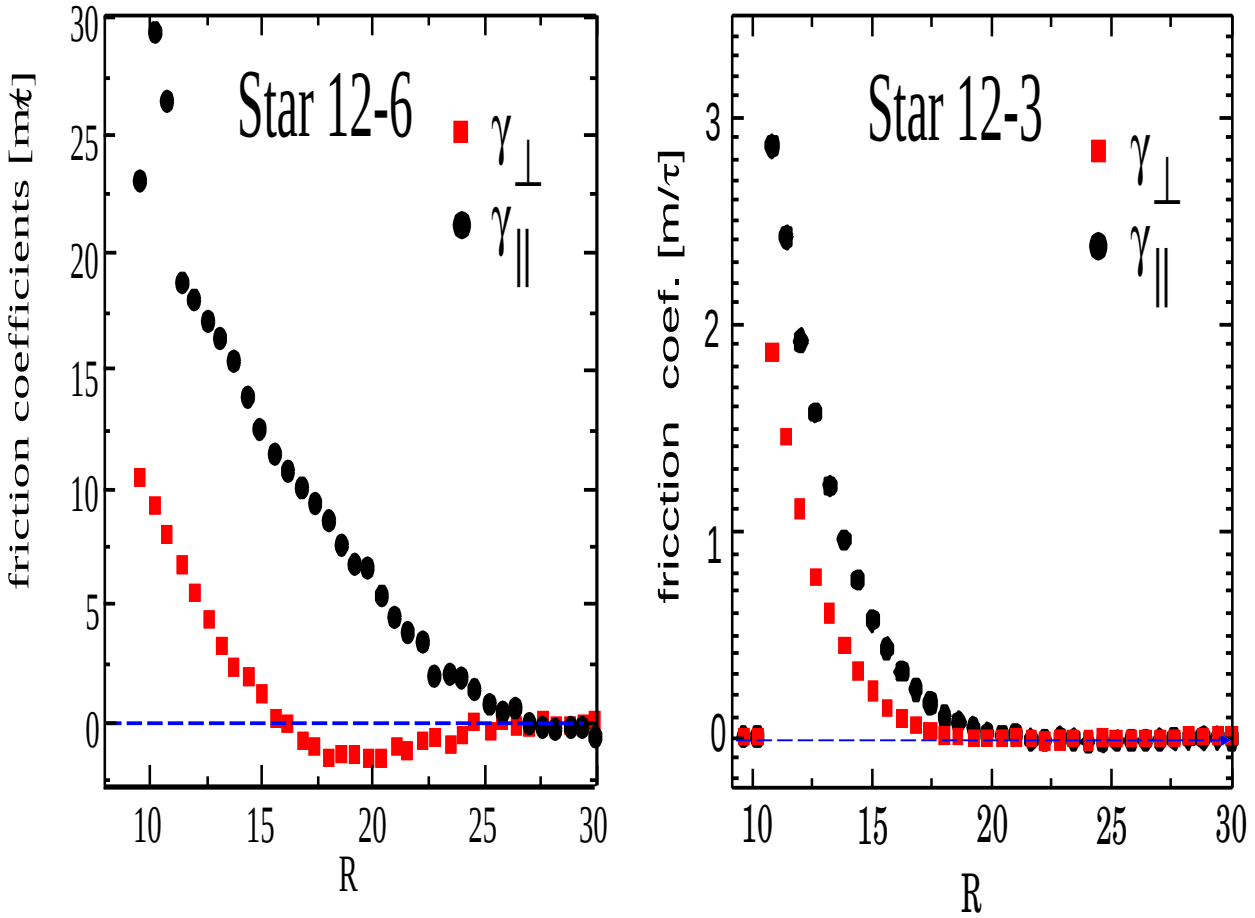


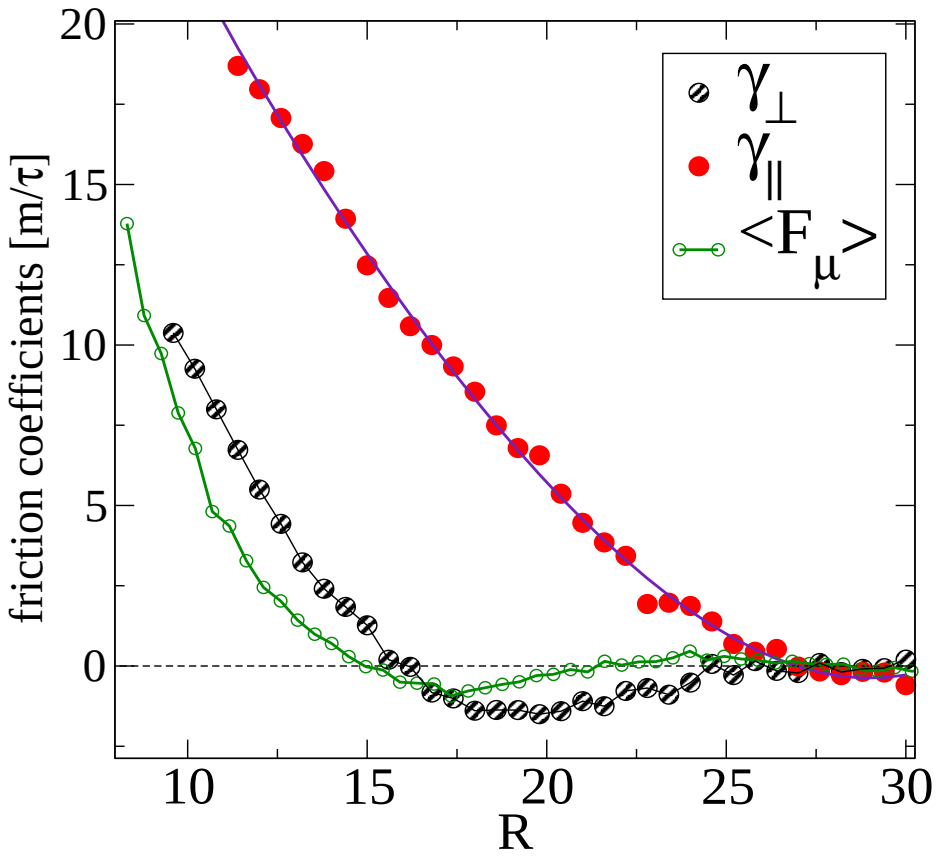
Coarsening star polymers

Friction coefficients in normal $\gamma^{||}$ and tangential $\gamma^{\perp}$ directions



Coarsening star polymers

Depletion effects are probably responsible for negative mutual tangential friction.



Coarsening star polymers

3^{rd} pair-wise approximation

On noise.

In general, the fluctuation-dissipation balance requires:

$$\tilde{\mathbf{F}}_\mu dt = \sum_\nu B_{\mu\nu} dW_\nu \text{ Sum of indep. Wiener processes}$$

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Coarsening star polymers

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We simplify the noise structure (by pairs):

$$\tilde{\mathbf{F}}_\mu dt = \sum_\nu \tilde{\mathbf{F}}_{\mu\nu}$$

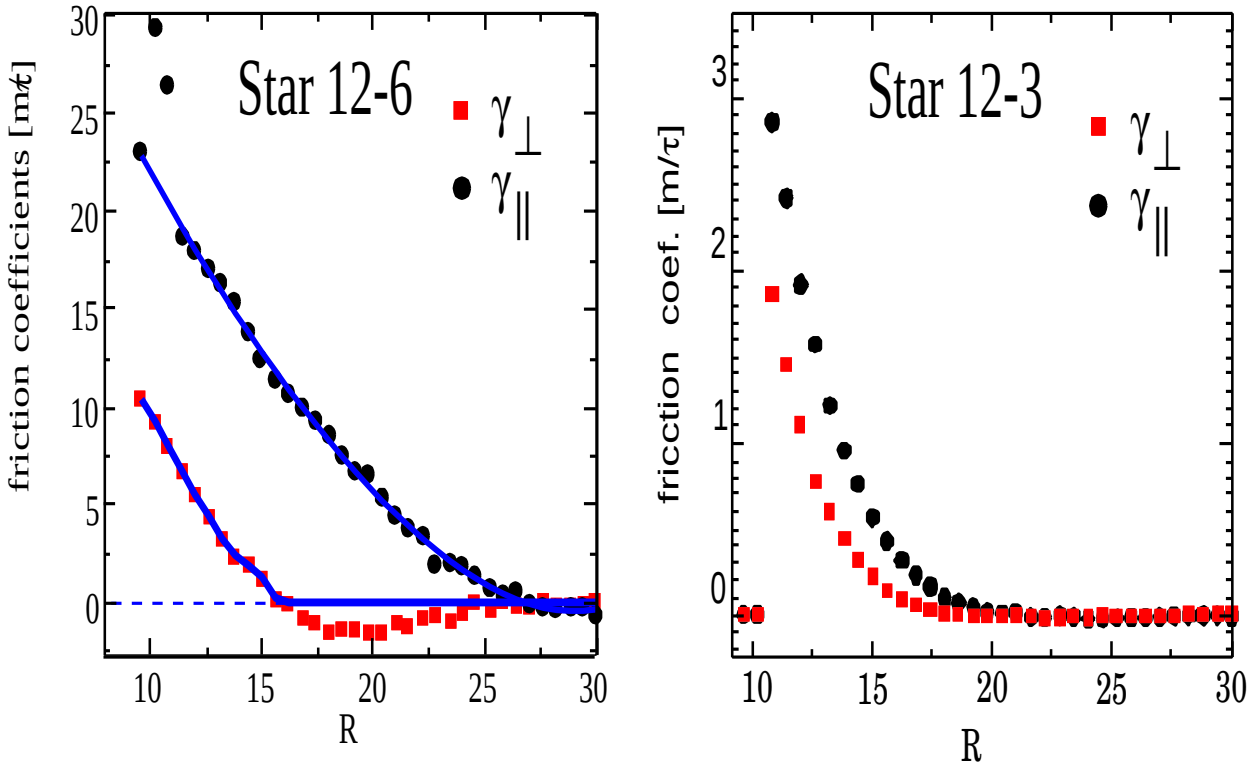
$$\tilde{\mathbf{F}}_{\mu\nu} dt = (2kT)^{1/2} \left(a(R_{\mu\nu}) d\bar{W}^S_{\mu\nu} + b(R_{\mu\nu}) \frac{Tr[dW^S_{\mu\nu}]}{3} \right)$$

$$a(R) = \left(2\gamma^{\perp}(R) \right)^{1/2} \quad \text{oops!}$$

$$b(R) = \left(3\gamma^{||}(R) - 4\gamma^{\perp}(R) \right)^{1/2}$$

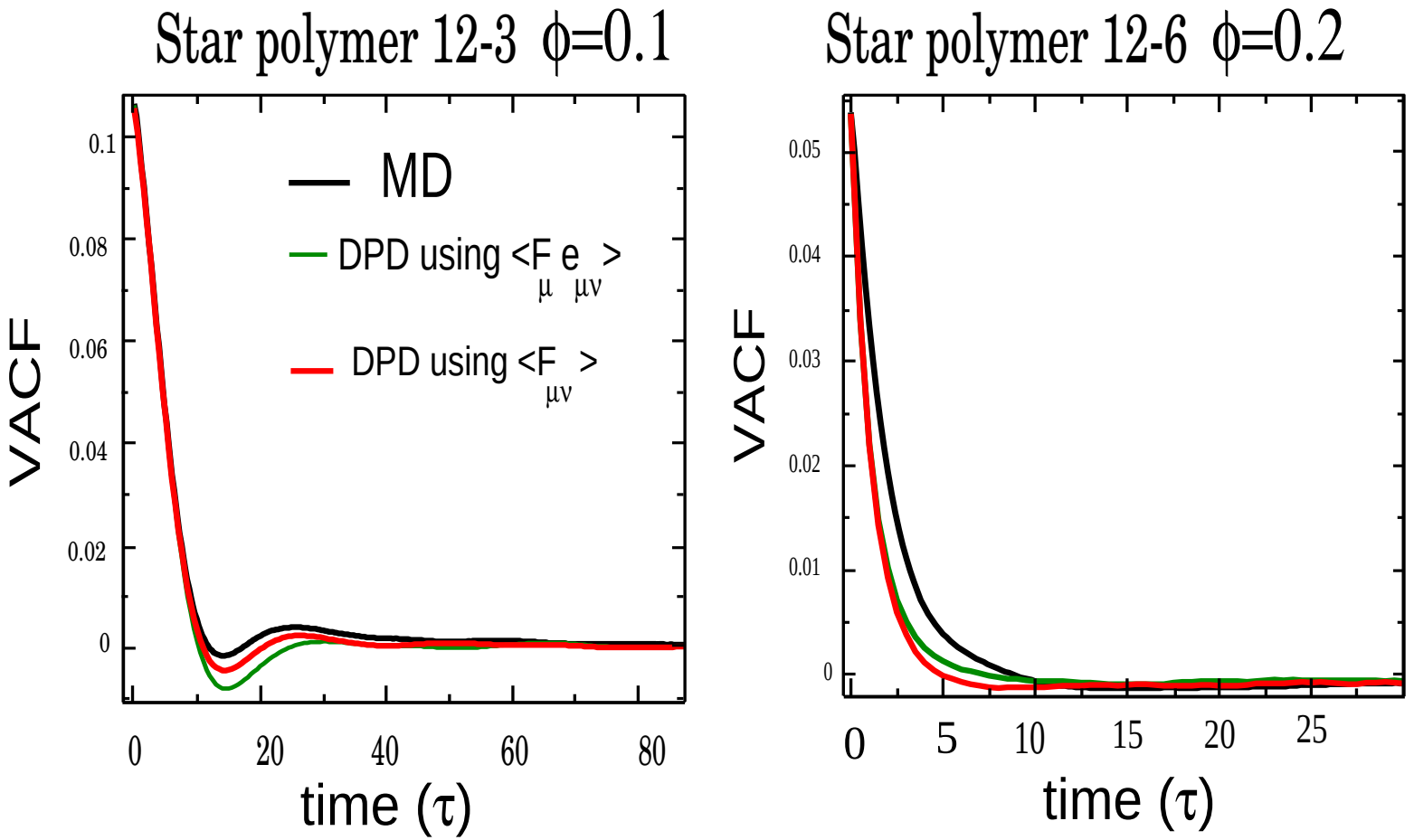
Coarsening star polymers

Normal $\gamma^{||}$ and tangential $\gamma^{\perp}$ friction coeff. used in DPD.
Negative values of $\gamma^{||}$ are neglected.



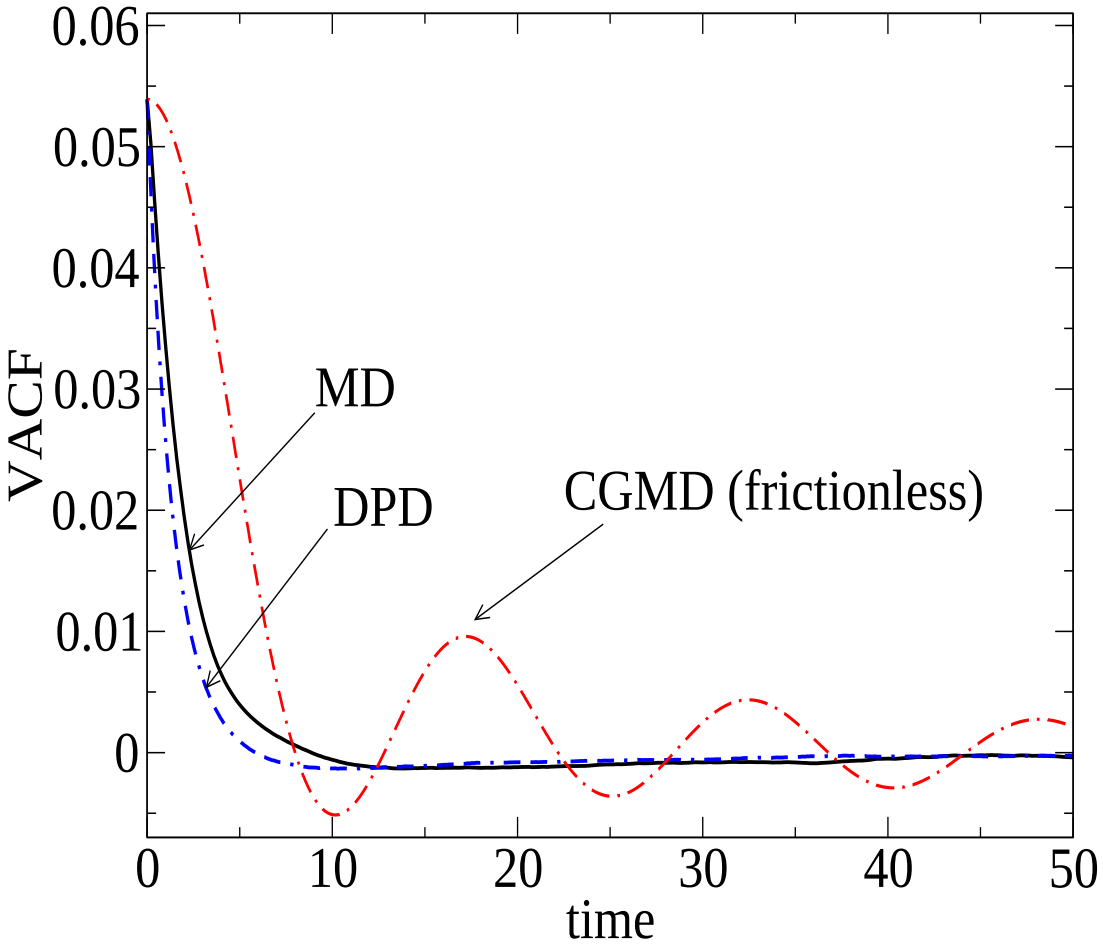
Coarsening star polymers

Results: CoM velocity autocorrelation



Coarsening star polymers

Indeed, friction is crucial



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  - Viscosity?
  - Molecule structure (non-spherical)?

Possible connexions with Heterogeneous Multiscale Modelling

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- Alternative methods (accelerated MD: tune $\epsilon > 1$ to accelerate slow variables) may also enhance the lift operation (work in progress).