Coarse grained and accelerated dynamics tested on star polymers

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Multiscale/Hybrid approaches for complex liquids

**Domain decomposition**
- type A
  - Molecular detail, interfaces, surfaces, macromolecule-fluid interaction

**Eulerian-Lagrangian**
- Suspensions
  - of colloids or polymers, small particles in flow

**Patch dynamics**
- Non-Newtonian fluids
  - Unknown constitutive relation
  - polymer melts...

**Coarse-grained dynamics**
- How to reduce the degrees of freedom and keep the underlying dynamics

**shear flows**
- sound, heat
- large molecules
- multispecies
- electrostatics

**Eulerian-Lagrangian**
- Point particle approximation:
  - Stokes drag (point particle), Faxen terms (finite size effects)
  - Basset memory effects...

**Force Coupling**
- particles of finite size
- Direct simulation
- Immersed boundaries

**Patch dynamics**
- MD nodes used to evaluate the local stress for the Continuum solver.
- Continuum solver provides the local velocity gradient imposed at each MD node.

**Coarse-grained dynamics**
- diffusion
- viscosity
- anisotropy (nematics...)

**Conclusions**
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
The current idea is to obtain effective potentials from the distribution probability of distances between CoM.
The state of the art

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- The current idea is to obtain effective potentials from the distribution probability of distances between CoM.
- 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.
A well-defined method for coarse-graining exists: Zwanzig projection.
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How to make Zwanzig Projection Operator a practical useful tool.

Demonstrate the procedure for the case of star polymer melts.
The microscopic state is $z = (\cdots, q_i, p_i, \cdots)$. Its dynamics is

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

where $z_t$ is the microscopic state at time $t$ and $L$ is the Liouville operator.
Outline of Zwanzig theory

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The macroscopic state of the system is represented by a set of functions $A(z)$. Its dynamics is

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

The essence of Zwanzig theory is the projection operator $P$

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

where

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

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

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

From

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

Insert \( 1 = P + Q \)

\[ \partial_t A(z_t) = \exp\{tL\}PLA(z_0) + \exp\{tL\}QLA(z_0) \]
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insert 1 = \( P + Q \)

\[ \partial_t A(z_t) = \exp\{tL\}PLA(z_0) + \exp\{tL\}QLA(z_0) \]

and use Duhamel-Dyson identity

\[ \exp\{tL\} = \exp\{tQL\} + \int_0^t ds \exp\{(t - s)L\}PL \exp\{sQL\} \]
The macro dynamics

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

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

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

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

where

\[
S(\alpha) = k_B \ln \Omega(\alpha) = k_B \ln \int \rho_{eq}(z) \delta(A(z) - \alpha) \, dz
\]

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

\[
\tilde{R}_t(z) = \exp\{tQL\} QLA(z)
\]
**The macro dynamics**

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

$$\tilde{R}_t(z) = \exp\{t Q L\} Q L A(z) \quad \text{Not closed!}$$
Markovian approximation

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

\[ M(\alpha) = \frac{1}{k_B} \int_{0}^{\infty} \langle \tilde{R}_0 \tilde{R}_s \rangle^\alpha ds \quad \text{Green-Kubo} \]

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?

The three basic objects to compute in Zwanzig’s theory are $\langle LA\rangle^\alpha$, $S(\alpha)$, and $M(\alpha)$. 
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Zwanzig theory is formal...
How to compute the objects from MD?

From the exact equation

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

At “short times”, we may approximate the projected current by

$$\tilde{R}_t \approx LA(z_t) - \langle LA \rangle^A(z_t)$$
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This is not very systematic. Worst: the friction matrix vanish!! (Plateau problem).
A more systematic approach

From the exact equation

\[ \partial_t A(z_t) = \langle LA \rangle^A(z_t) + \int_0^t dt' M(A(z_{t-t'}), t') \frac{\partial S}{\partial \alpha}(A(z_{t-t'})) + \tilde{R}_t(z) \]
**A more systematic approach**

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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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Assume

$$\lim_{\epsilon \to 0} \epsilon^2 M(\alpha_{t-\epsilon^2 \tau}, \epsilon^2 \tau) \equiv m(\alpha_t, \tau)$$
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Then

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A more systematic approach

When the limit exists?

\[ \epsilon^2 M(\alpha_{t-\epsilon^2 \tau}, \epsilon^2 \tau) = \frac{1}{k_B} \langle (\epsilon QLA) \exp{\tau \epsilon^2 QLQ} (\epsilon QLA) \rangle^{\alpha_{t-\epsilon^2 \tau}} \]
A more systematic approach

When the limit exists?

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

Assume

\[ L = L_0 + \frac{1}{\epsilon} L_1 + \frac{1}{\epsilon^2} L_2 \]
A more systematic approach

When the limit exists?

\[
\epsilon^2 M(\alpha_{t-\epsilon^2 \tau}, \epsilon^2 \tau) = \frac{1}{k_B} \langle (\epsilon Q L A) \exp\{\tau \epsilon^2 Q L Q\} (\epsilon Q L A) \rangle^{\alpha_{t-\epsilon^2 \tau}}
\]

Assume

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with

\[
L_2 A = 0 \\
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with

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Then the limit exists

\[ \epsilon^2 M(\alpha_{t-\epsilon^2 \tau}, \epsilon^2 \tau) = \frac{1}{k_B} \langle L_1 A \exp\{\tau L_2\}L_1 A \rangle^{\alpha} + O(\epsilon) \]
**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 \( P L_1 A = 0 \) then for \( \epsilon \to 0 \), we have a Markovian SDE

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

where the Green-Kubo friction matrix is given by

\[
\overline{M(\alpha_t)} = \frac{1}{k_B} \int_0^\infty \langle L_1 A \exp\{\tau L_2\} L_1 A \rangle^{\alpha} d\tau
\]
A more systematic approach

However, $L \neq L_0 + \frac{1}{\epsilon} L_1 + \frac{1}{\epsilon^2} L_2$ in general...
A more systematic approach

However, \( L \neq L_0 + \frac{1}{\epsilon} L_1 + \frac{1}{\epsilon^2} L_2 \) in general...

Introduce an evolution operator \( \mathcal{R} \) “similar” to \( L \) and such that

\[
\begin{align*}
\mathcal{R}A(z) &= 0 \\
\mathcal{R}H(z) &= 0
\end{align*}
\]
**A more systematic approach**

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It is always possible to decompose the Liouville operator as

$$L = L_0 + L_1 + L_2$$

$$L_0 = P(L - \mathcal{R})$$
$$L_1 = Q(L - \mathcal{R})$$
$$L_2 = \mathcal{R}$$
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$$L_2 = \mathcal{R}$$

By construction, $L_2 A = 0$ and $P L_1 A = 0$. 
A more systematic approach

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

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

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 $\mathcal{R}$

\[
\langle L_0 A \rangle^\alpha = \langle L A \rangle^\alpha
\]

\[
\bar{M}(\alpha) = \frac{1}{k_B} \int_0^\infty \langle (L A - \langle L A \rangle^\alpha) \exp\{\tau \mathcal{R}\}(L A - \langle L A \rangle^\alpha) \rangle^\alpha d\tau
\]
A more systematic approach

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

$$\langle L_0 A \rangle^\alpha = \langle LA \rangle^\alpha$$

$$M(\alpha) = \frac{1}{k_B} \int_0^\infty \langle (LA - \langle LA \rangle^\alpha) \exp\{\tau \mathcal{R}\}(LA - \langle LA \rangle^\alpha) \rangle^\alpha d\tau$$

The basic difference with the “usual” approximation (plateau-problematic) is that instead of

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

we now approximate

$$\exp\{QLt\} \approx \exp\{\mathcal{R}t\}$$
A more systematic approach

Note that because $\mathcal{R}A = 0$, $\mathcal{R}H = 0$, the dynamics $\exp\{\tau \mathcal{R}\}$ samples $\rho^{eq}(z)\delta(A(z) - \alpha)$. 
A more systematic approach

Note that because $\mathcal{R}A = 0, \mathcal{R}H = 0$, the dynamics $\exp\{\tau \mathcal{R}\}$ samples $\rho_{eq}(z)\delta(A(z) - \alpha)$.

By ergodicity, we have now a \textit{practical} method for computing constrained averages and correlations with \textit{time averages}

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

\[
\langle \delta J \exp\{\tau \mathcal{R}\} \delta J \rangle^\alpha = \lim_{T \to \infty} \frac{1}{T} \int_0^T d\tau_0 \exp\{\tau_0 \mathcal{R}\} \delta J(z) \times \exp\{(\tau_0 + \tau) \mathcal{R}\} \delta J(z)
\]

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

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

- 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

\[
\Omega(\alpha) = \int dz \rho^\text{eq}(z) \delta(A(z) - \alpha)
\]

\[
\mathbf{v}(\alpha) = \langle LA \rangle^\alpha
\]

\[
\mathbf{M}(\alpha) = \frac{1}{k_B} \int_0^\infty \langle (LA - \langle LA \rangle^\alpha) \exp\{\tau \mathcal{R}\} (LA - \langle LA \rangle^\alpha) \rangle^\alpha d\tau
\]

All these objects may be computed from simulating the constrained dynamics
Coarsening star polymers

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

<table>
<thead>
<tr>
<th>Level</th>
<th>Variables</th>
<th>Dynamics</th>
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<tbody>
<tr>
<td>Micro</td>
<td>$z = {r_{i\mu}, p_{i\mu}}$</td>
<td>$\dot{z} = Lz$</td>
</tr>
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<td>Macro</td>
<td>$A(z) = \left{ \begin{array}{l} R_{\mu}(z) = \frac{1}{m_{\mu}} \sum_{i\mu} m_{i\mu} r_{i\mu} \ P_{\mu}(z) = \sum_{i\mu} p_{i\mu} \end{array} \right.$</td>
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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

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

Integrating out momenta

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

The effective potential is defined through

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

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

\[
\langle L \hat{R}_\mu \rangle^{RP} = \frac{P_\mu}{M_\mu} \quad \rightarrow \quad LR - \langle L \hat{R}_\mu \rangle^{RP} = 0
\]

\[
\langle L \hat{P}_\mu \rangle^{RP} = \langle F_\mu \rangle^{RP} \quad \rightarrow \quad \langle F_\mu \rangle^R = -\frac{\partial V^{\text{eff}}}{\partial R_\mu}
\]
Coarsening star polymers

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

$$M_{\mu\nu}(R, P) = \begin{pmatrix} 0 & 0 \\ 0 & \gamma_{\mu\nu}(R, P) \end{pmatrix}$$

The mutual friction coefficients between molecules $\mu, \nu$ are

$$\gamma_{\mu\nu}(R, P) = \int_0^\infty dt \langle \delta F_\nu \exp\{Rt\} \delta F_\mu \rangle^{RP}$$

$$\delta F_\mu = \hat{F}_\mu - \langle \hat{F}_\mu \rangle^{RP}$$
The SDE for the CoM provided by Zwanzig theory are

\[
\begin{align*}
\partial_t R_\mu &= V_\mu \\
\partial_t P_\mu &= \langle F_\mu \rangle^R - \sum_\nu \gamma_{\mu\nu}(R)V_{\mu\nu} + \tilde{F}_\mu
\end{align*}
\]

where \( V_{\mu\nu} = V_\mu - V_\nu \)

The fluctuation-dissipation balance requires,

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

\[
B_{\mu\lambda} B_{\nu\lambda} = 2k_B T \gamma_{\mu\nu} \quad 3M \times 3M \text{ matrix equation}
\]

These equations resemble the standard Dissipative Particle Dynamics.
Coarsening star polymers

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

\[
\begin{align*}
\dot{r}_{i\mu} &= \mathbf{v}_{i\mu} - \mathbf{V}_\mu \\
\dot{p}_{i\mu} &= \mathbf{F}_{i\mu} - \frac{m_{i\mu}}{M_\mu} \mathbf{F}_\mu
\end{align*}
\]

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

\[
\begin{align*}
\langle \mathbf{F}_\mu \rangle^{\{\mathbf{R}\}}
\end{align*}
\]

\[
\gamma_{\mu\nu}(\{\mathbf{R}\}) = \frac{1}{k_B T} \int_0^\infty dt \langle \delta \mathbf{F}_\mu \exp \{t\mathbf{R}\} \delta \mathbf{F}_\nu \rangle^{\{\mathbf{R}\}}
\]
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\textsuperscript{st} Pair-wise hypothesis:

\begin{equation*}
\langle F_{\mu}\rangle^{\{R\}} = \langle F_{\mu}\rangle^{R_{\mu\nu}}
\end{equation*}

Two options:

- **Pure** pair-wise:

\begin{equation*}
\langle F_{\mu}\rangle^{R_{\mu\nu}} = \sum_{\nu} \langle F_{\mu\nu}\rangle^{R_{\mu\nu}} \cdot e_{\mu\nu}
\end{equation*}
Coarsening star polymers

$1^{st}$ Pair-wise hypothesis:

On the effective force

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

Two options:

- Pure pair-wise:

$$\langle F_\mu \rangle^{R_{\mu\nu}} = \sum_\nu \langle F_{\mu\nu} \rangle^{R_{\mu\nu}} \cdot e_{\mu\nu}$$

- Including (some) depletion effects:

$$\langle F_\mu \rangle^{R_{\mu\nu}} = \sum_\nu \langle F_\mu \cdot e_{\mu\nu} \rangle^{R_{\mu\nu}} \cdot e_{\mu\nu}$$
**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 $\phi = 0.1$. 

![Graph showing force and RDF for STAR 12-3 at $\phi = 0.1$.]
Coarsening star polymers: Friction

2nd pair-wise approximation.

On friction matrix.

\[ \gamma_{\mu\nu}([R]) = \frac{1}{k_B T} \int_0^\infty dt \langle \delta F_\mu \exp \{ t R \} \delta F_\nu \rangle^{[R]} \]
Coarsening star polymers: Friction

2nd pair-wise approximation.

On friction matrix.

\[
\gamma_{\mu\nu}(\{R\}) = \frac{1}{k_B T} \int_0^\infty dt \langle \delta F_\mu \exp \{tR\} \delta F_\nu \rangle^{\{R\}}
\]

spherical sym. \( \gamma_{\mu\nu}(R_{\mu\nu}) = -\gamma^\parallel (R_{\mu\nu}) e_\mu e_\nu - \gamma^\perp (R_{\mu\nu}) (1 - e_\mu e_\nu) \)
**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: \( \gamma_{\mu\nu}(R_{\mu\nu}) = \frac{1}{kT} \int_{0}^{\infty} \langle F_{\mu}(t)F_{\nu}(0) \rangle R_{\mu\nu} \).
Coarsening star polymers

How good is the pair-wise assumption on friction?

STAR 12-3

\[ \Delta C \text{ (many-pairs average)} \]
\[ 2 \Delta \langle C_p \rangle \text{ (one-pair)} \]
Coarsening star polymers

How good is the pair-wise assumption on friction?

STAR 12-6

![Error ratio for STAR 12-6](image)
Coarsening star polymers

Friction coefficients in normal $\gamma^\parallel$ and tangential $\gamma^\perp$ directions

![Graph showing friction coefficients for Star 12-6 and Star 12-3](image-url)
Depletion effects are probably responsible for negative mutual tangential friction.
Coarsening star polymers
3rd pair-wise approximation
On noise.

In general, the fluctuation-dissipation balance requires:

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

$$B_{\mu \lambda}B_{\nu \lambda} = 2k_B T \gamma_{\mu \nu} 3M \times 3M \text{ matrix equation}$$
**Coarsening star polymers**

3rd pair-wise approximation

**On noise.**

In general, the fluctuation-dissipation balance requires:

\[ \tilde{F}_\mu dt = \sum \tilde{F}_{\mu \nu} dW_\nu \] Sum of indep. Wiener processes

\[ B_{\mu \lambda} B_{\nu \lambda} = 2k_B T \gamma_{\mu \nu} \] 3M \times 3M matrix equation

We simplify the noise structure (by pairs):

\[ \tilde{F}_\mu dt = \sum \tilde{F}_{\mu \nu} \]

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

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

\[ b(R) = \left( 3\gamma^\parallel(R) - 4\gamma^\perp(R) \right)^{1/2} \]
Normal $\gamma^\parallel$ and tangential $\gamma^\perp$ friction coeff. used in DPD. Negative values of $\gamma^\parallel$ are neglected.
**Results: CoM velocity autocorrelation**

Coarsening star polymers

**Star polymer 12-3 \( \phi=0.1 \)**

- MD
- DPD using \( \langle F_{\mu e}^{\mu \nu} \rangle \)
- DPD using \( \langle F_{\mu \nu}^{\mu} \rangle \)

**Star polymer 12-6 \( \phi=0.2 \)**

- MD
- DPD using \( \langle F_{\mu e}^{\mu \nu} \rangle \)
- DPD using \( \langle F_{\mu \nu}^{\mu} \rangle \)
Indeed, friction is crucial

![Graph showing VACF over time for different simulations: MD, DPD, and CGMD (frictionless).](image)
Conclusions

- Coarse graining with proper dynamics
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  - A well-defined method for coarse-graining exists: Zwanzig projection
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- Viscosity?
- Molecule structure (non-spherical)?
Possible connexions with Heterogeneous Multiscale Modelling

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- **Open MD** can be used to reconstruct a macroscopic state given based on the fluxes across boundaries ("lift" operation for dense liquids).
- It could be easily adapted to impose Dirichlet boundary conditions (state coupling).
- Alternative methods (accelerated MD: tune $\epsilon > 1$ to accelerate slow variables) may also enhance the lift operation (work in progress).