Thermodynamically-guided nonequilibrium Monte Carlo methodology for generating realistic shear flows

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Motivation

Limitations of the conventional atomistic MD and NEMD simulations

• Only applicable to short-chain systems with a small relaxation time (e.g., $\leq C_{150}$)
• Even more difficult for branched polymers
• Problem in statistical accuracy at low strain rates
• Slow achievement of the steady-state, especially at low strain rates

Prediction of the shear viscosity

• Brown-Clarke, 1983; Clarke-Brown, 1986; Edberg et al., 1986; Morriss et al., 1991; Daivis et al., 1992; Xu et al., 1995; 1996; Mondello et al., 1997

State-of-the art

• $C_{16}$, $C_{22}$ [de Pablo et al., 1994]
• $C_{100}$ but for shear rates $\geq 109$ s$^{-1}$ [Cummings et al., 2000]
• $C_{100}$ (linear and its non-linear isomers) for shear rates $\geq 108.5$ s$^{-1}$ [Jabbarzadeh et al., 2003]
• $C_{128}$ [Baig, Keffe, Edwards, 2006]
Powerful Monte Carlo Algorithms based on a set of Simple and Complex moves

- **End-Mer Rotation**
  - End-Mer Rotation
  - Internal Flip [Mavrantzas & Theodorou, 1999]
  - Reptation [Vacatello et al., 1980]
  - Generalized Reptation

- **Configurational Bias (CB)** [Smit et al., 1992; Siepmann & Frenkel, 1992]

- **Concerted Rotation** [Dodd et al., 1993]

- **Volume Fluctuation**
End Bridging (EB)
[Pant & Theodorou, 1995; Mavrantzas et al., 1999]

**Features**
- changes chain connectivity
- induces and requires polydispersity
- reduced performance with decreasing
  a) polydispersity index and/or
  b) number of chain ends
- performance increases as chain length increases!
Self End-Bridging (SEB)

(a) BEFORE IEB

(b) AFTER IEB
Double Bridging (DB)

[Karayiannis et al., 2002; 2003]
Intramolecular Double Rebridging (IDR)

[Karayiannis et al., 2002]
MC SIMULATION OF LONG LINEAR PE MELTS

[24-chain C_{1000} PE melt, I=1.04, T=450K, P=1atm]

**Atomistic Model**

- **United atom model:** Each methylene and methyl considered as a single interacting site
- **Constant bond lengths** \((l=1.54\text{Å})\)
- **Flexible bond angles** [Martin and Siepmann, 1998]
- **Torsional potential** [Toxvaerd, 1997]
- A **6-12 Lennard-Jones** potential (inter-molecular interactions) [TraPPe]
Molecular Model in detail

- **United atom description** *(United atom model - UA)*

- **Groups CH₃, CH₂, CH are considered as spherical interacting sites**

- **Potential force-fields:**
  - Fixed bond lengths *(1.54Å)*
  
  ![Fixed bond lengths](image)

  - Bond bending potential
    *(TraPPE)* *[Martin & Siepmann, 1998]*
    
    \[ V_{bend}(\theta) = \frac{1}{2} k_\theta (\theta - \theta_o)^2 \]

  ![Bond bending potential](image)

  - Torsion angle potential
    *(Toxvaerda)* *[Toxvaerda, 1997]*
    
    \[ V_{tor} = \sum_{i=0}^{8} c_i \cos(\phi)^i \]

  ![Torsion angle potential](image)

  - Nonbonded potential *(Lennard-Jones)*
    *(TraPPE)*
    
    \[ V_{L-J} = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right) \]
Static structure factor of a Linear Monodisperse PE melt
\[ C_{1000}, T = 450K, P = 1\text{atm} \]
Density of Linear Monodisperse PE melts

[T = 450K, P = 1 atm]
Monte Carlo algorithm has also been extended to H-shaped PE melts.

DB move applying between:
(a)–(b) main backbones and
(c) branches
of two different H-shaped chains

IDR move applies between different branches of the same chain

Double Conrot for the displacement of the branch point and its 8 neighboring atoms

intramolecular EB for displacing the branch points
Extension to Branched Polymers: Atomistic snapshots

Typical atomistic snapshots of an H\(_{400\_70}\) system

(A) Before equilibration

(B) After equilibration with the new algorithm (\(T = 450K, P = 1\text{atm}\))

[With blue and green are shown the atoms of the main backbone and of the branches, respectively, of an arbitrarily selected H-molecule]
**Key Question**

Would it be possible to employ Monte Carlo also in order to:

- simulate systems beyond equilibrium?
- generate realistic shear or elongational flows?

**First attempt to apply MC to a nonequilibrium system** [Mavrantzas-Theodorou, 1998]  
- demonstrated how to excite chain molecules in a 1-d elongational flow by introducing field terms in the Metropolis criterion  
- the field was chosen arbitrarily  
- did not compare against direct NEMD simulations quantitatively

**In a later study** [Mavrantzas-Öttinger, 2002]  
- need to be guided by principles of non-equilibrium thermodynamics  
- General Equation for the NonEquilibrium Reversible-Irreversible Coupling \[ \Rightarrow \] GENERIC MC

**More recently** [Beris et al., 2006]  
- used such a method in the context of a lattice model to simulate high extensional flows  
- showed how one can use the new method in order to formulate also more accurate viscoelastic models
Fundamentals of the GENERIC MC Methodology
[Grmela-Öttinger, 1997; Öttinger-Grmela, 1997]

• Evolution equation

\[ \frac{dx}{dt} = L(x) \cdot \frac{\delta E(x)}{\delta x} + M(x) \cdot \frac{\delta S(x)}{\delta x} \]

- \(E\sim\) Energy functional
- \(S\sim\) Entropy functional
- \(L\sim\) Reversible matrix
- \(M\sim\) Dissipative matrix

• Degeneracy conditions

\[ \begin{align*}
L(x) \cdot \frac{\delta S(x)}{\delta x} &= 0 \\
M(x) \cdot \frac{\delta E(x)}{\delta x} &= 0
\end{align*} \]

• Energy and Entropy functional

\[ E(x) = \int \left[ \frac{u(r)^2}{2\rho(r)} + \varepsilon(r) \right] dr \]
\[ S(x) = \int s(\rho(r), \varepsilon(r), X(r)) dr \]

• Thermodynamic state variables, \(x\)

\[ x = \{\rho(r), u(r), \varepsilon(r), X(r)\} \]

- \(\rho\sim\) mass density
- \(u\sim\) momentum density
- \(\varepsilon\sim\) internal energy density
- \(X\sim\) structural variables
<table>
<thead>
<tr>
<th>Energy</th>
<th>field strength $\times$ extensive variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal</td>
<td>$U$ $T$</td>
</tr>
<tr>
<td>Mechanical</td>
<td>$U$ $P$</td>
</tr>
<tr>
<td>Material</td>
<td>$U$ $\mu$</td>
</tr>
<tr>
<td>Deformation</td>
<td>$U$ $k_B T \alpha$</td>
</tr>
</tbody>
</table>

- Coarse-grained thermodynamic structural variable [Beris-Edwards, 1994]

$$\widetilde{c} = \frac{3 \langle RR \rangle}{\langle R^2 \rangle_{eq}} \quad \sim \text{Conformation tensor}$$

- Fundamental thermodynamic function of nonequilibrium system

$$U(S,V,N,\tilde{N}\tilde{c}) = TS - PV + \mu N + k_B T \alpha : N \tilde{c}$$
FROM THE POINT OF VIEW OF STATISTICAL MECHANICS

1. Formal definition of the input parameters - the corresponding thermodynamic fields:

\[
P = p^2 \left[ \frac{\partial}{\partial \rho} \frac{\Delta A}{N_{ch}} (\rho, T, C) \right] \frac{N_A}{M}, \quad \alpha = \frac{1}{k_B T} \left[ \frac{\partial}{\partial C} \frac{\Delta A}{N_{ch}} (\rho, T, C) \right] \rho, T
\]

where \( N_A \) is Avogadro’s number and \( M \) the mean number MW

2. The relevant probability density function in the phase space is given through

\[
Q(N_{ch}, n, P, T, \alpha) = \text{const.} \int d^3n \, dV \, \exp \left[ -\frac{1}{k_B T} \left( U(r) + PV - k_B T \sum_{\gamma \delta} \alpha_{\gamma \delta} \sum_{i=1}^{N_{ch}} c_{i, \gamma \delta} \right) \right]
\]

3. The corresponding generalized statistical ensemble is \([N_{ch} n PT \mu^* \alpha] \):

- \( N_{ch} \), total number of chains
- \( n \), total number of atoms
- \( P \), pressure
- \( T \), temperature
- \( \mu^* \), reduced chemical potentials (to control the MW distribution)
- \( \alpha \), tensorial field
How to choose the field $\alpha$ for a given shear flow rate $\nabla \mathbf{u}$

$$
\rho \sim \exp \left[ -\frac{1}{k_B T} \left( -k_B T \alpha : (N\mathbf{c}) + U(r_1, r_2, \cdots, r_n) \right) \right]
$$

**UCM:**

$$
\lambda_H \dot{\tau}^{(1)} + \tau = \eta \dot{\gamma}
$$

$$
\dot{\tau}^{(1)} = \frac{\partial \tau}{\partial t} + \mathbf{u} \cdot \nabla \tau - (\nabla \mathbf{u})^T \cdot \tau - \tau \cdot (\nabla \mathbf{u})
$$

**Giesekus:**

$$
\lambda_H \dot{\tau}^{(1)} + \tau + \frac{\beta}{G} \tau^2 = \eta \dot{\gamma}
$$

$$
\dot{\tau}^{(1)} = \frac{\partial \tau}{\partial t} + \mathbf{u} \cdot \nabla \tau - (\nabla \mathbf{u})^T \cdot \tau - \tau \cdot (\nabla \mathbf{u})
$$

**PTT:**

$$
\lambda_H \dot{\tau}^{[1]} + Y(tr\tau)\tau = \eta \dot{\gamma}
$$

$$
\dot{\tau}^{[1]} = \frac{\partial \tau}{\partial t} + \mathbf{u} \cdot \nabla \tau - (\nabla \mathbf{u})^T \cdot \tau - \tau \cdot (\nabla \mathbf{u}) + \frac{\xi}{2} (\tau \cdot \dot{\gamma} + \dot{\gamma} \cdot \tau)
$$

$$
Y(tr\tau) = \exp \left( \frac{\epsilon}{G} tr\tau \right) \approx I + \frac{\epsilon}{G} tr\tau
$$
Remark 1: All these single conformation tensor models have the form

\[
\tau = 2(1 - \xi)C \cdot \frac{\partial A}{\partial C}
\]

\[
\frac{\partial C}{\partial t} + u \cdot \nabla C - (\nabla u)^T \cdot C - C \cdot (\nabla u) + \frac{\xi}{2}(C \cdot \dot{\gamma} + \dot{\gamma} \cdot C) = -R \cdot \frac{\partial A}{\partial C}
\]

Remark 2: One can solve for the field \( \alpha \) by inverting the above equation.

Application: steady simple shear flow

\[
\nabla \upsilon = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}
\]

\[
\tilde{\upsilon} = \begin{bmatrix} \tilde{c}_{xx} & \tilde{c}_{xy} & 0 \\ \tilde{c}_{xy} & \tilde{c}_{yy} & 0 \\ 0 & 0 & \tilde{c}_{zz} \end{bmatrix}
\]

\[
\alpha = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ \alpha_{xy} & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{bmatrix}
\]
Examples of $\alpha$ from known viscoelastic models

**UCM**

$$\alpha = \frac{1}{2} \lambda_H \left( \nabla \mathbf{v} + \tilde{\mathbf{c}}^{-1} \cdot \nabla \mathbf{v} \cdot \tilde{\mathbf{c}}^{-1} \right)$$

$$\alpha = \begin{bmatrix}
\frac{1}{2} \frac{\lambda_H \dot{\gamma}^2}{1 + \lambda_H \frac{\dot{\gamma}^2}{\gamma^2}} & \frac{1}{2} \frac{\lambda_H \dot{\gamma}}{1 + \lambda_H \frac{\dot{\gamma}^2}{\gamma^2}} & 0 \\
\frac{1}{2} \frac{\lambda_H \dot{\gamma}}{1 + \lambda_H \frac{\dot{\gamma}^2}{\gamma^2}} & -\frac{1}{2} \frac{\lambda_H \frac{\dot{\gamma}^2}{\gamma^2}}{1 + \lambda_H \frac{\dot{\gamma}^2}{\gamma^2}} & 0 \\
0 & 0 & 0
\end{bmatrix}$$

**Giesekus Model**

$$\alpha = \frac{1}{2} \lambda_H \left[ \delta + \beta (\tilde{c} - \delta) \right]^{-1} \cdot \left( \nabla \mathbf{v} + \tilde{\mathbf{c}}^{-1} \cdot \nabla \mathbf{v}^T \cdot \tilde{\mathbf{c}} \right)$$

$$\begin{aligned}
(1 - 2\beta)\tilde{c}_{yy} + \beta (\tilde{c}_{xy}^2 + \tilde{c}_{yy}^2) &= 1 - \beta \\
(1 - 2\beta)\tilde{c}_{xy} - \lambda \dot{\gamma} \tilde{c}_{yy} + \beta (\tilde{c}_{xx} \tilde{c}_{xy} + \tilde{c}_{xy} \tilde{c}_{yy}) &= 0 \\
(1 - 2\beta)\tilde{c}_{xx} - 2\lambda \dot{\gamma} \tilde{c}_{xy} + \beta (\tilde{c}_{xx}^2 + \tilde{c}_{xy}^2) &= 1 - \beta \\
\tilde{c}_{zz} &= 1
\end{aligned}$$

**Remark**: The field $\alpha$ is model-dependent

**Idea**: Define $\alpha$ by mapping the resulting structure onto NEMD results (iteratively)
Overall procedure of the GENERIC MC methodology

- **Step 1:** Choose the thermodynamic state variables and determine **forms** of the corresponding conjugate variables for given flows \( x = \{ \rho(r), u(r), \varepsilon(r), \tilde{c}(r) \} \)

- **Step 2:** Select a viscoelastic model to **estimate** the conjugate field variable as a function of shear rate

- **Step 3:** Execute the GENERIC MC simulations and **analyze** the resulting structure

- **Step 4:** Check if the structure converges to the **true one** as obtained from NEMD simulations

- **Step 5:** **Iterate** until convergence

- **Step 6:** **Improve** the viscoelastic models based on the obtained results (it would require additional simulations for different chain lengths)
GENERIC MC and NEMD simulations

• Test System
  - A 120-chain C$_{50}$ PE oligomer melt in (93×45×45) Å$^3$
  - $T = 450$ K, $\rho = 0.7438$ g/cm$^3$ ; Rouse time, $\tau_R \approx 0.5$ ns
  - Five different states in a broad range: $0.43 \leq De \leq 106$

• Potential model
  - TraPPE (with flexible or fixed bond lengths)

• NEMD simulations
  - SLLOD equations of motion [Evans-Morriss, 1990]
  - Time duration: 4.7 ns for the highest shear rate, 47 ns for the lowest one

• GENERIC MC simulations
  - Total 500 million cycles for all the shear rate
  - Initial values of $\alpha$ using the Giesekus model
  - 6 to 8 iterations were sufficient for reproducing the non-equilibrium state
  - one iteration took approximately 4~5 days using 2.2 GHz Opteron CPUs
Thermodynamic field $\alpha$ vs. Deborah number $\text{De}$

\[ \alpha = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ \alpha_{xy} & \alpha_{yy} & 0 \\ 0 & 0 & 0 \end{bmatrix} \]
Comparison of $\tilde{\textbf{c}}$ between GENERIC MC and NEMD

(a) $\tilde{c}_{xx}$ vs $\tau_R\dot{\gamma}$

(b) $\tilde{c}_{xy}$ vs $\tau_R\dot{\gamma}$

(c) $\tilde{c}_{yy}$ vs $\tau_R\dot{\gamma}$

(d) $\tilde{c}_{zz}$ vs $\tau_R\dot{\gamma}$
A symmetry relation

- Elastic stress

\[ \tau_{\alpha\beta} = -2 \tilde{c}_{\alpha\gamma} \frac{\delta A(\tilde{c})}{\delta \tilde{c}_{\gamma\varepsilon}} = -2nk_B T \tilde{c}_{\alpha\gamma} \alpha_{\beta\gamma} \]

and

\[ \nabla v = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \]

\[ \tau_{xy} = \tau_{yx} ; \tilde{c}_{xy} = \tilde{c}_{yx} ; \alpha_{xy} = \alpha_{yx} \]

\[ \frac{\alpha_{xx} - \alpha_{yy}}{\alpha_{xy}} = \frac{\tilde{c}_{xx} - \tilde{c}_{yy}}{\tilde{c}_{xy}} \]

does it hold?
\[ \frac{(\alpha_{xx} - \alpha_{yy})}{\alpha_{xy}} = \frac{(\tilde{c}_{xx} - \tilde{c}_{yy})}{\tilde{c}_{xy}} \]
GENERIC MC SIMULATION OF LONG PE MELTS (80 chains, C_{78}, I=1.04, T=450K)

Steady-state 1d elongational flow

\[ \alpha = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & -\frac{\alpha_{xx}}{2} & 0 \\ 0 & 0 & -\frac{\alpha_{xx}}{2} \end{pmatrix} \]
Conclusions

• Developed a non-dynamic methodology (GENERIC MC) for simulating the steady state properties of an unentangled PE melt under a shear flow

• Advantages over NEMD simulations: reaches faster the steady-state
  reliable results even at low strain rate

• New method provides a means for calculating the free energy of the non-equilibrium system; thus it can serve as a guide for improving existing viscoelastic models

Current - Future plans

• Investigate the relation between $\alpha$ and $D_e$ as a function of chain length so that $\alpha$ can be defined without the need of any NEMD simulations

• For entangled polymer melts, we may have to excite additional modes along the chain or even the entire primitive path [Everaers, Kremer, et al., Science, 2005]

• Map results onto a new viscoelastic model (to provide good guesses for $\alpha$ for a given flow)

• In the long term: Apply the GENERIC MC to branched polymers (e.g., H-shaped melts)
Modified FENE-Cohen+Giesekus Model

\[ \Lambda_{\alpha\beta\gamma\varepsilon} = \frac{1}{2nk_s \lambda_H} \left( \frac{k_s}{k_BT} \right) \left[ (1 - \beta) \left( \dot{\varepsilon}_{\alpha\gamma} \delta_{\beta\varepsilon} + \ddot{\varepsilon}_{\alpha\varepsilon} \delta_{\beta\gamma} + \ddot{\varepsilon}_{\beta\varepsilon} \delta_{\alpha\gamma} + \ddot{\varepsilon}_{\beta\gamma} \delta_{\alpha\varepsilon} \right) \right. \]
\[ \left. + 2\beta \left( \frac{b - \frac{1}{3} \text{tr} \tilde{c}}{b - \text{tr} \tilde{c}} \right) \left( \dot{\varepsilon}_{\alpha\gamma} \ddot{\varepsilon}_{\beta\varepsilon} + \ddot{\varepsilon}_{\alpha\varepsilon} \ddot{\varepsilon}_{\beta\gamma} \right) \right] \]

\[ A(\tilde{c}) = \int d^3x \frac{1}{2nk_BT} \left[ \frac{1}{3} \text{tr} \tilde{c} - \frac{2}{3} b \ln \left( 1 - \frac{\text{tr} \tilde{c}}{b} \right) - \ln \text{det}(\tilde{c}) \right] \]

\[ \tilde{c}_{\alpha\beta} = -\Lambda_{\alpha\beta\varepsilon\varepsilon} \frac{\delta A(\tilde{c})}{\delta \tilde{c}_{\gamma\varepsilon}} \; ; \; \tau_{\alpha\beta} = \tau^{(el)}_{\alpha\beta} = -2c_{\alpha\gamma} \frac{\delta A(\tilde{c})}{\delta \tilde{c}_{\gamma\varepsilon}} \]

\[ \tilde{c}_{\alpha\beta} = -\frac{1}{\lambda_H} \left[ (1 - \beta) \dot{\varepsilon}_{\alpha\gamma} + \beta \left( \frac{b - \frac{1}{3} \text{tr} \tilde{c}}{b - \text{tr} \tilde{c}} \right) \ddot{\varepsilon}_{\alpha\gamma} \right] \left[ \left( \frac{b - \frac{1}{3} \text{tr} \tilde{c}}{b - \text{tr} \tilde{c}} \right) \ddot{\varepsilon}_{\gamma\beta} - \delta_{\gamma\beta} \right] \]

\[ \tau_{\alpha\beta} = -nk_BT \left[ \left( \frac{b - \frac{1}{3} \text{tr} \tilde{c}}{b - \text{tr} \tilde{c}} \right) \dddot{\varepsilon}_{\alpha\beta} - \delta_{\alpha\beta} \right] \]
Thermodynamic admissibility of the Modified FENE-Cohen+Giesekus Model

\[ \Lambda_{\alpha\beta\gamma\varepsilon} = \frac{1}{2nk_s \lambda H} \left( \frac{k_s}{k_B T} \right) \left[ (1 - \beta) \left( \bar{c}_{\alpha\gamma} \delta_{\beta\varepsilon} + \bar{c}_{\alpha\varepsilon} \delta_{\beta\gamma} + \bar{c}_{\beta\gamma} \delta_{\alpha\varepsilon} + \bar{c}_{\beta\varepsilon} \delta_{\alpha\gamma} \right) \right] + \frac{2\beta}{3} \frac{b - \text{tr} \bar{c}}{b - \text{tr} \bar{c}} \left( \bar{c}_{\alpha\gamma} \bar{c}_{\beta\varepsilon} + \bar{c}_{\alpha\varepsilon} \bar{c}_{\beta\gamma} \right) \]

\[ A(\bar{c}) = \int d^3 x \frac{1}{2nk_B T} \left[ \frac{1}{3} \text{tr} \bar{c} - \frac{2}{3} b \ln \left( 1 - \frac{\text{tr} \bar{c}}{b} \right) - \ln \det(\bar{c}) \right] \]

\[ \frac{\delta A(\bar{c})}{\delta \bar{c}_{\alpha\beta}} \Lambda_{\alpha\beta\gamma\varepsilon} \frac{\delta A(\bar{c})}{\delta \bar{c}_{\gamma\varepsilon}} \propto \sum_{i=1}^3 \frac{1}{\lambda_i} (\xi \lambda_i - 1)^2 [\beta \xi \lambda_i + (1 - \beta)] \geq 0 \]

where \( \xi = \frac{b - \frac{1}{3} \text{tr} \bar{c}}{b - \text{tr} \bar{c}} \geq 1 \)

\[ \text{The range for thermodynamic admissibility is} \quad 0 \leq \beta \leq 1 \]
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