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

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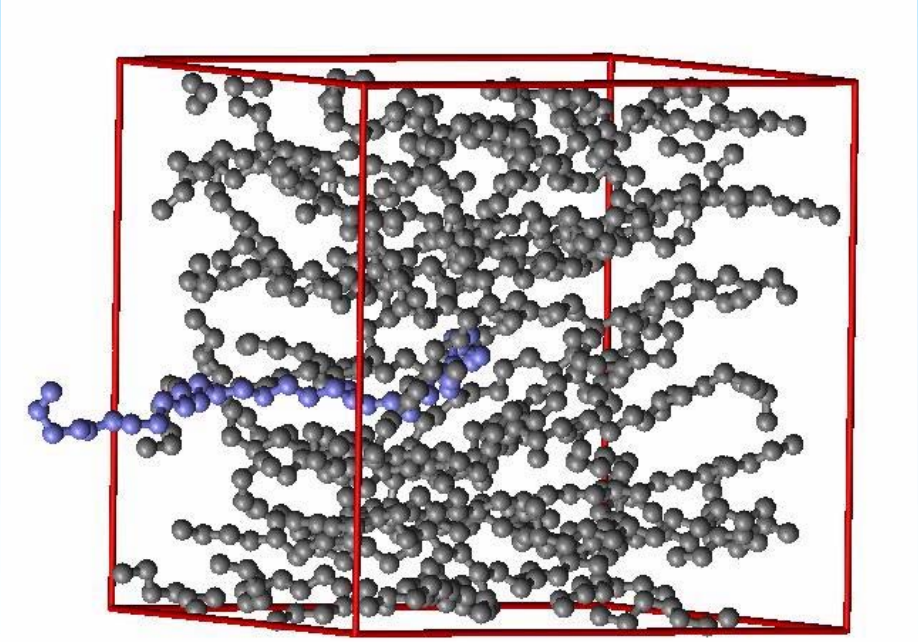


Motivation

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

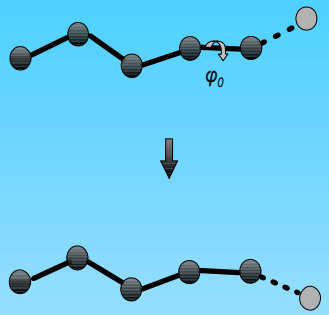
- Brown-Clarke, 1983; Clarke-Brown, 1986; Edberg et al., 1986; Morriss et al., 1991; Daivis et al., 1992; Xu et al., 1995; 1996; Mondello et al., 1997

State-of-the art

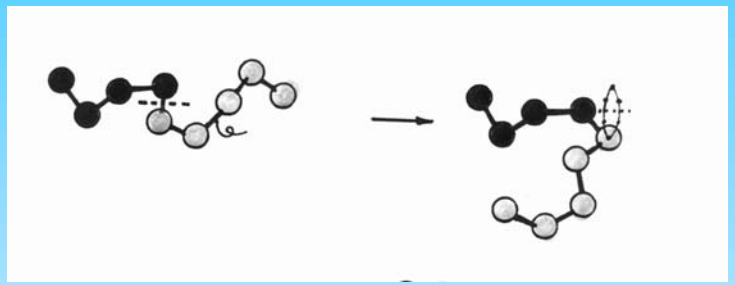
- C_{16}, C_{22} [de Pablo et al., 1994]
- C_{100} but for shear rates $\geq$ 109 s-1 [Cummings et al., 2000]
- C_{100} (linear and its non-linear isomers) for shear rates $\geq$ 108.5 s-1 [Jabbarzadeh et al., 2003]
- C_{128} [Baig, Keffe, Edwards, 2006]

Powerful Monte Carlo Algorithms based on a set of Simple and Complex moves

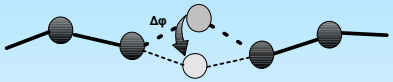
- **End-Mer Rotation**



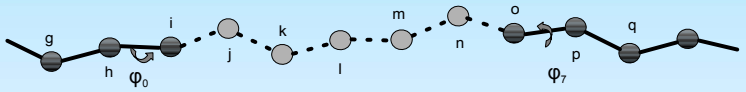
- **Configurational Bias (CB)** [Smit et al., 1992; Siepmann & Frenkel, 1992]

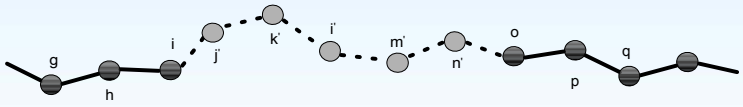


- **Internal Flip** [Mavrantzas & Theodorou, 1999]

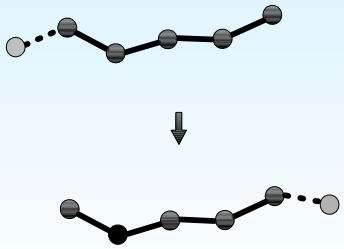


- **Concerted Rotation** [Dodd et al., 1993]





- **Reptation** [Vacatello et al., 1980]

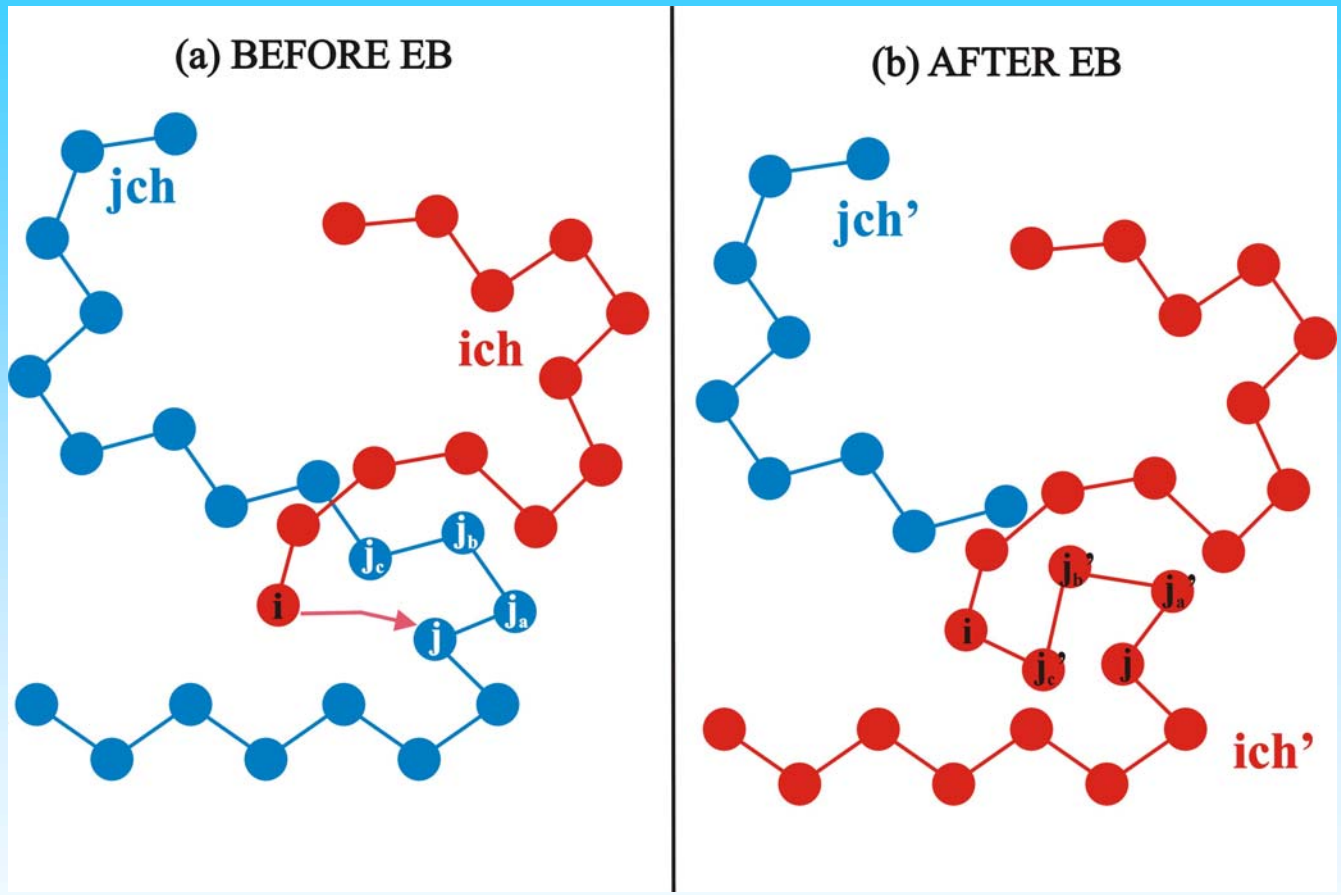


- **Generalized Reptation**

- **Volume Fluctuation**

End Bridging (EB)

[Pant & Theodorou, 1995; Mavrantzas et al., 1999]

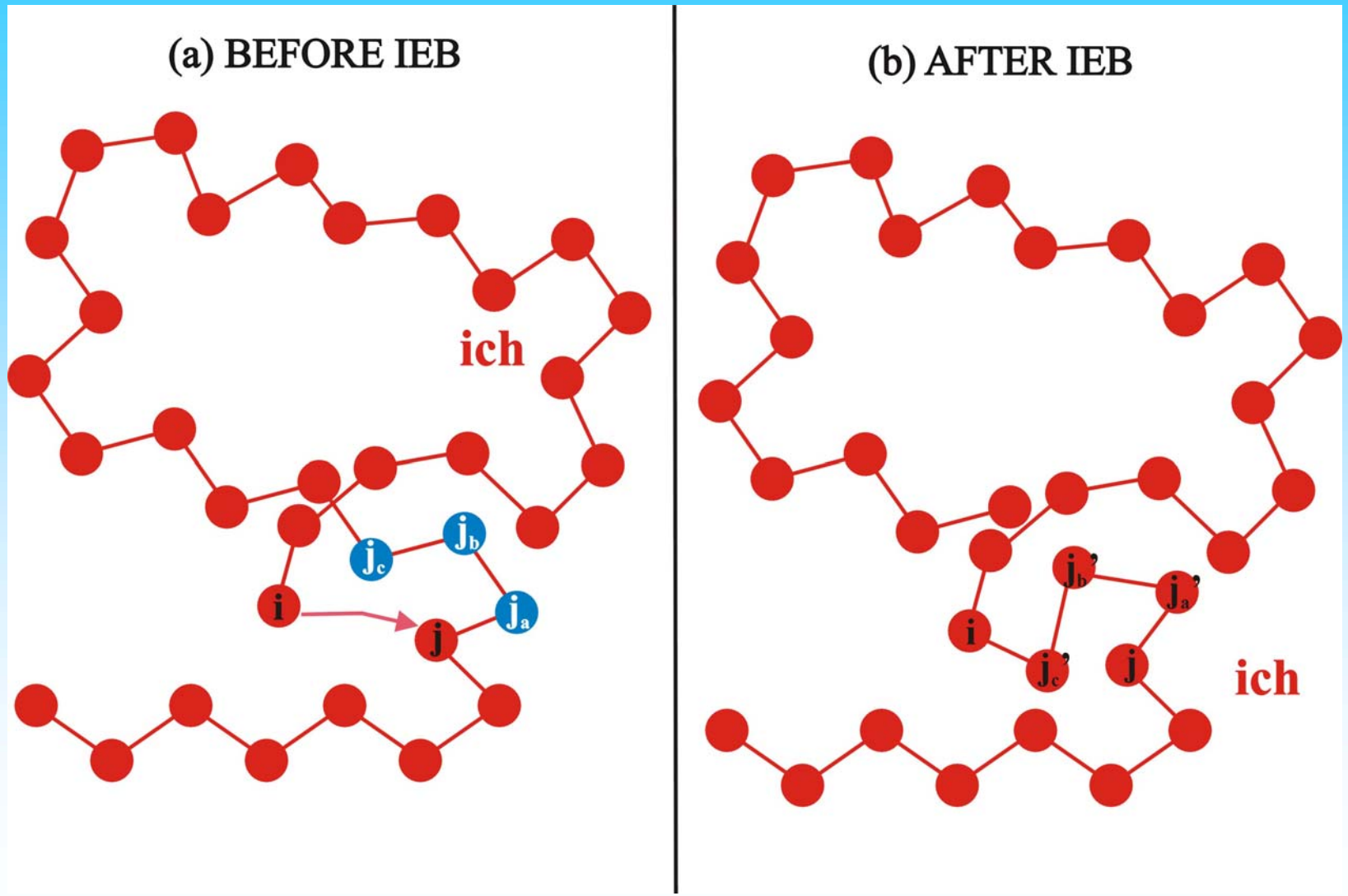


Features

- changes chain **connectivity**
- induces and requires ***polydispersity***
- ***reduced performance*** with **decreasing**
  a) **polydispersity index** and/or
  b) number of chain **ends**

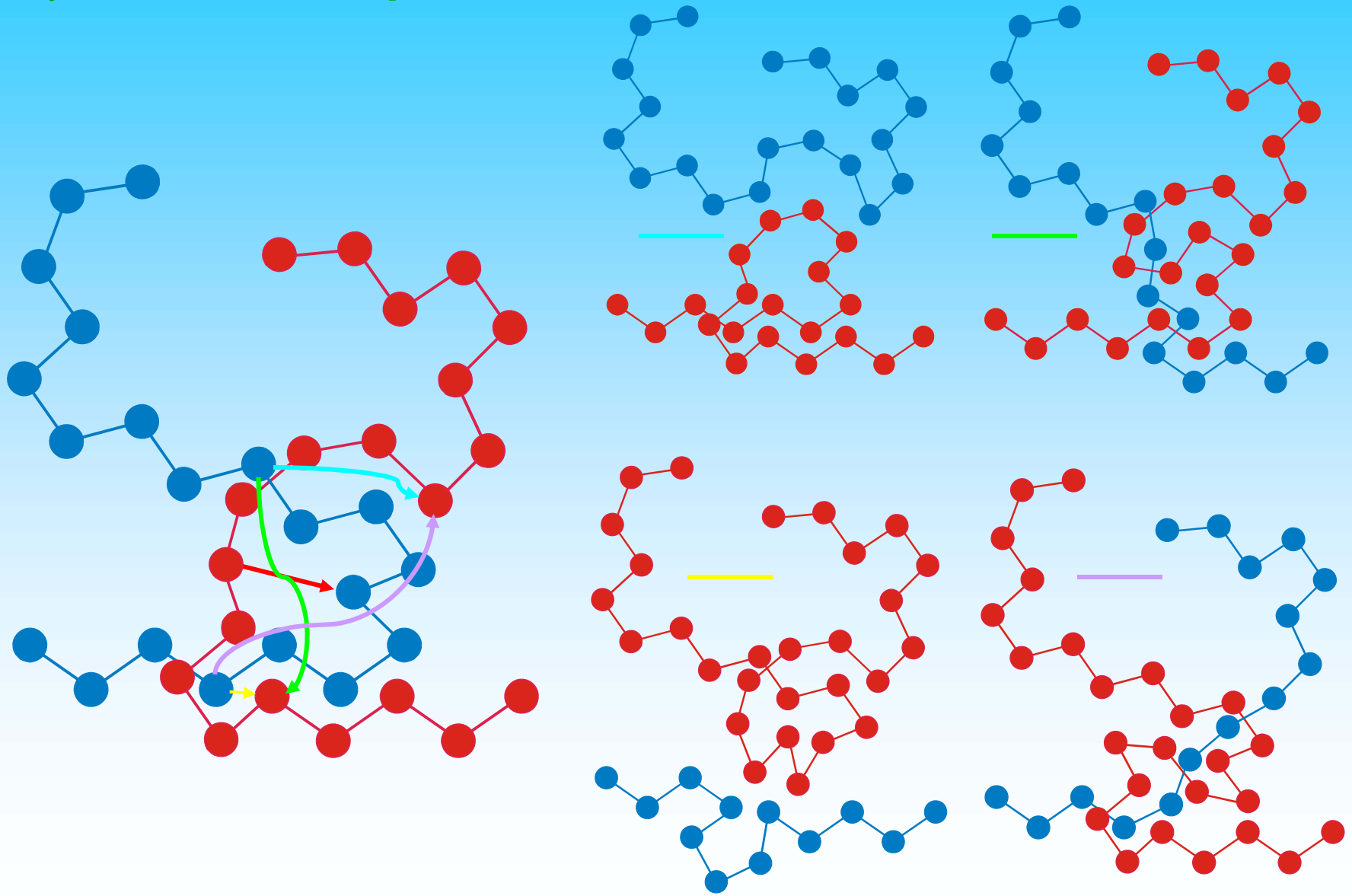
- ***performance increases*** *as* ***chain length increases!***

Self End-Bridging (SEB)



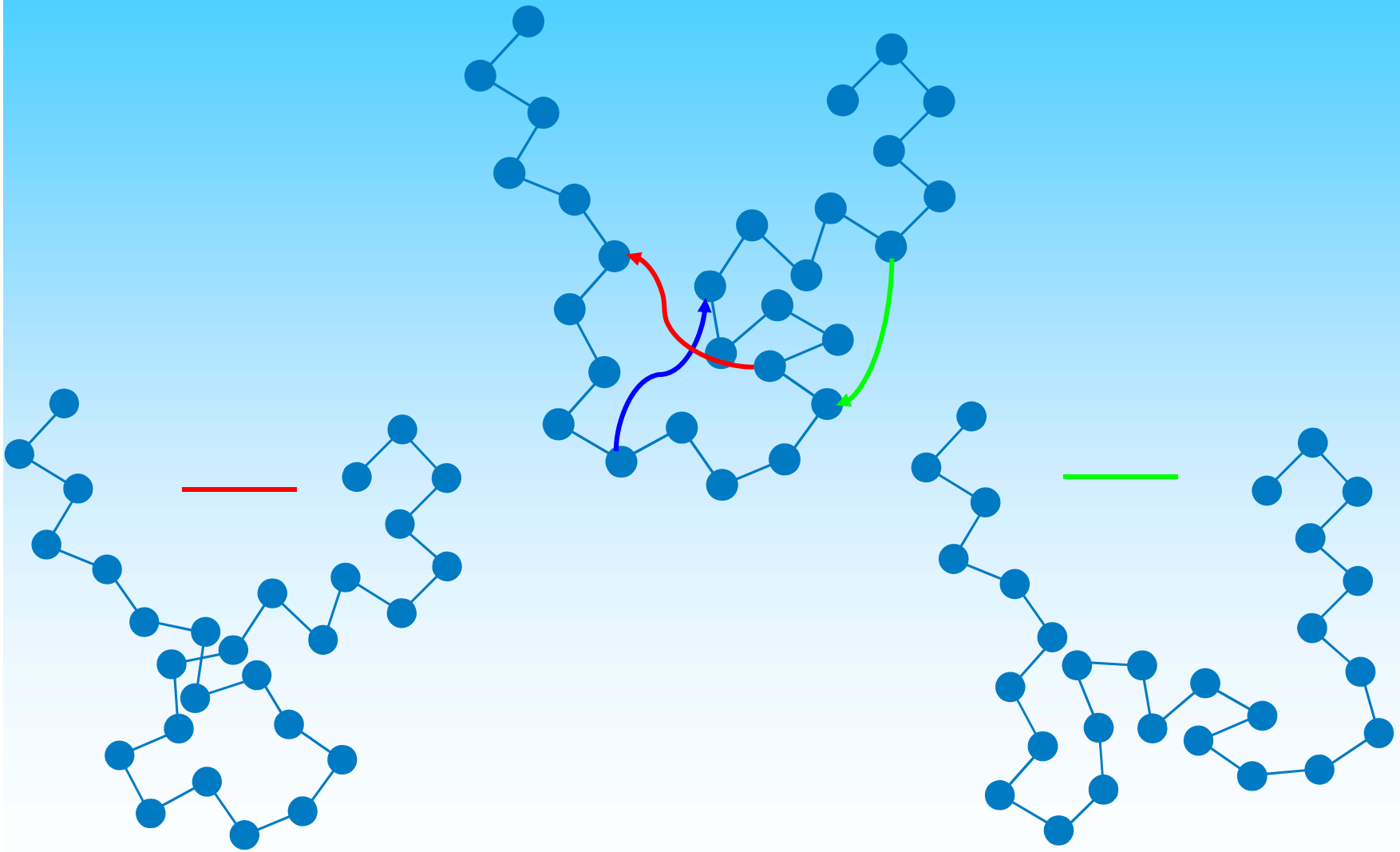
Double Bridging (DB)

[Karayiannis et al., 2002; 2003]



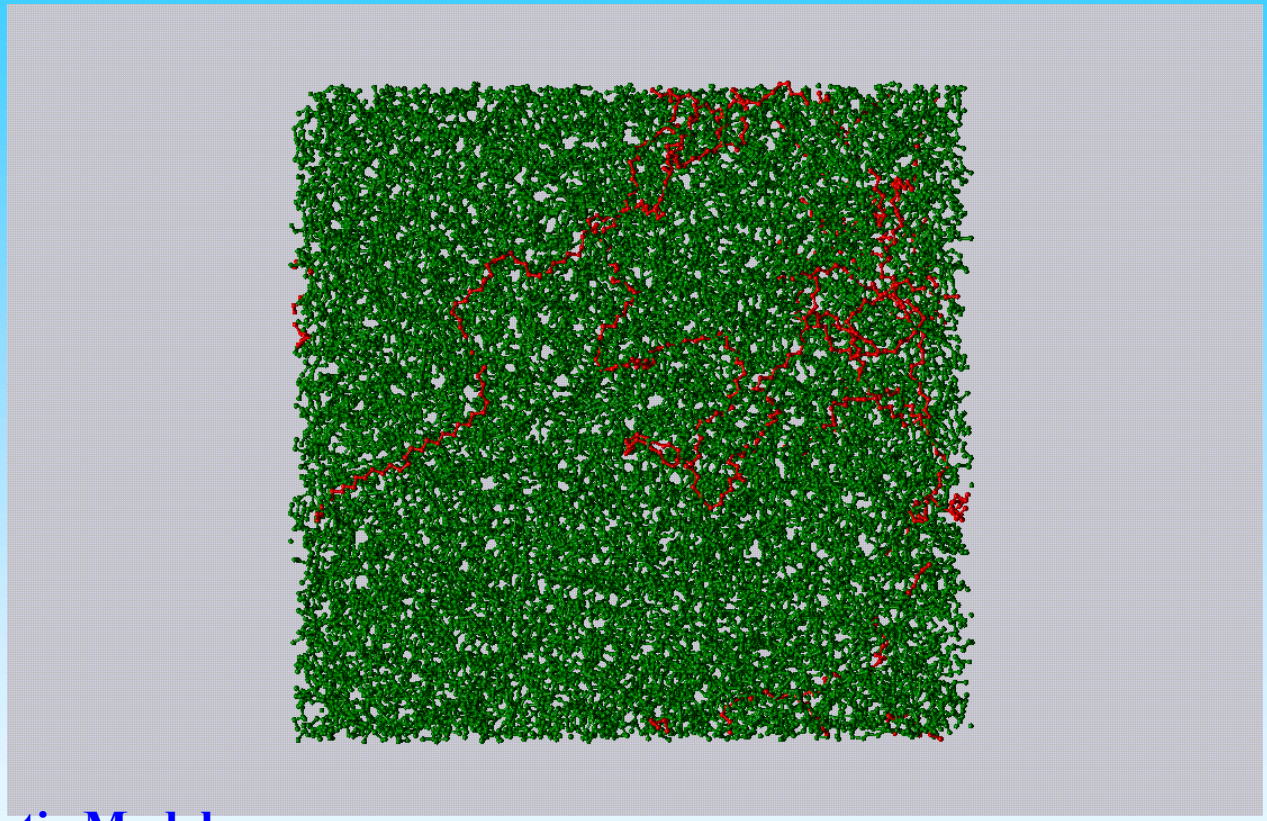
Intramolecular Double Rebridging (IDR)

[Karayiannis et al., 2002]



MC SIMULATION OF LONG LINEAR PE MELTS

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



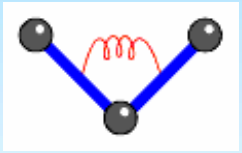
Atomistic Model

- **United atom model:** Each methylene and methyl considered as a single interacting site
- Constant **bond lengths** (*l*=1.54Å)
- 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

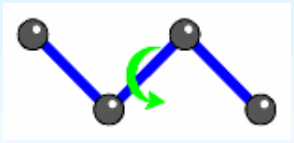
- **United atom description (United atom model - UA)**
- **Groups CH_3, CH_2, CH are considered as spherical interacting sites**
- **Potential force-fields:**
  - **Fixed bond lengths (1.54Å)**

  - **Bond bending potential (TraPPE) [Martin & Siepmann, 1998]**



$$V_{bend}(\theta) = \frac{1}{2} k_\theta (\theta - \theta_o)^2$$

  - **Torsion angle potential (Toxvaerd) [*Toxvaerd*, 1997]**



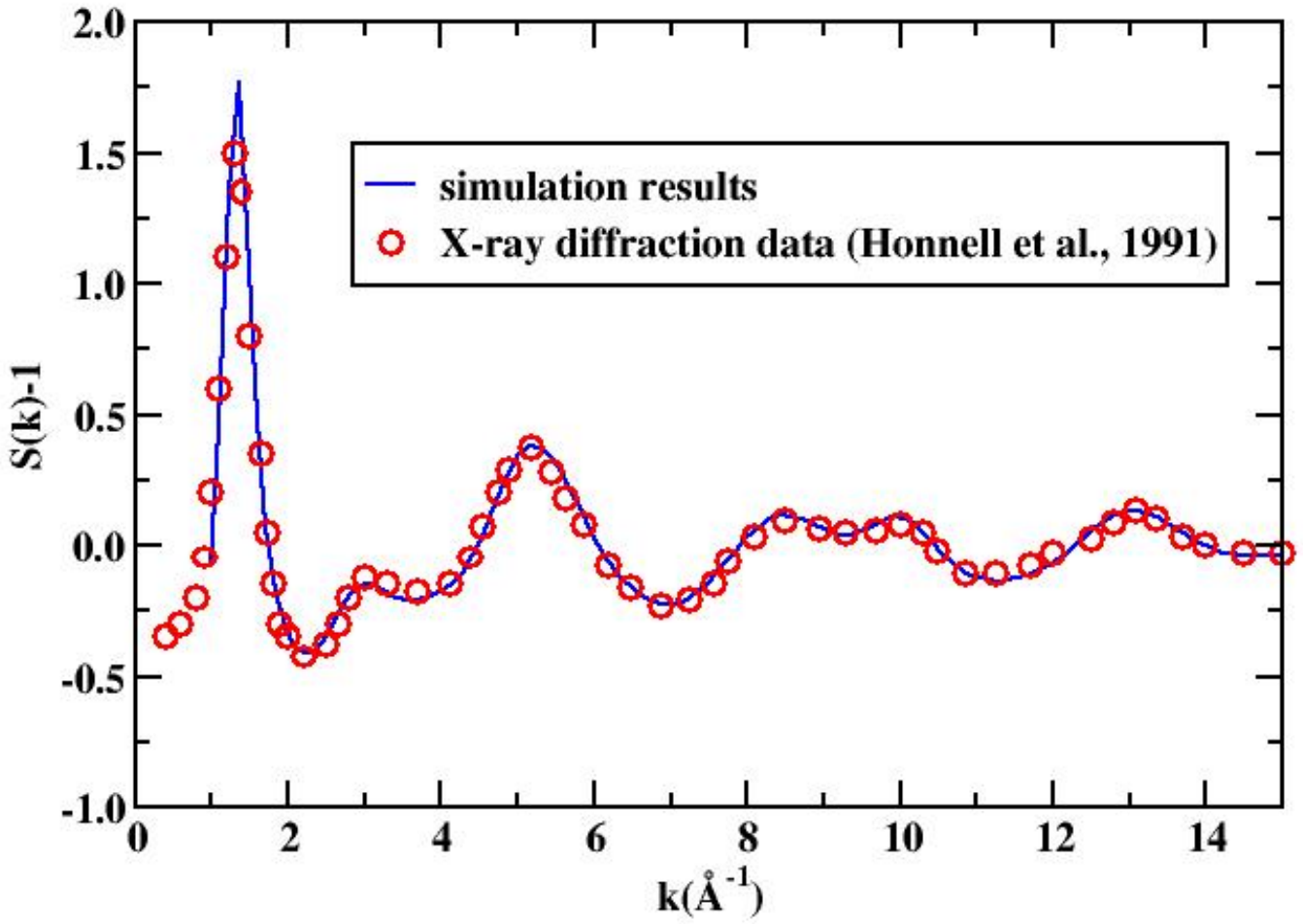
$$V_{tor} = \sum_{i=0}^{8} c_i \cos(\phi)^i$$

  - **Nonbonded potential (Lennard-Jones) (TraPPE)**

$$V_{L-J} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

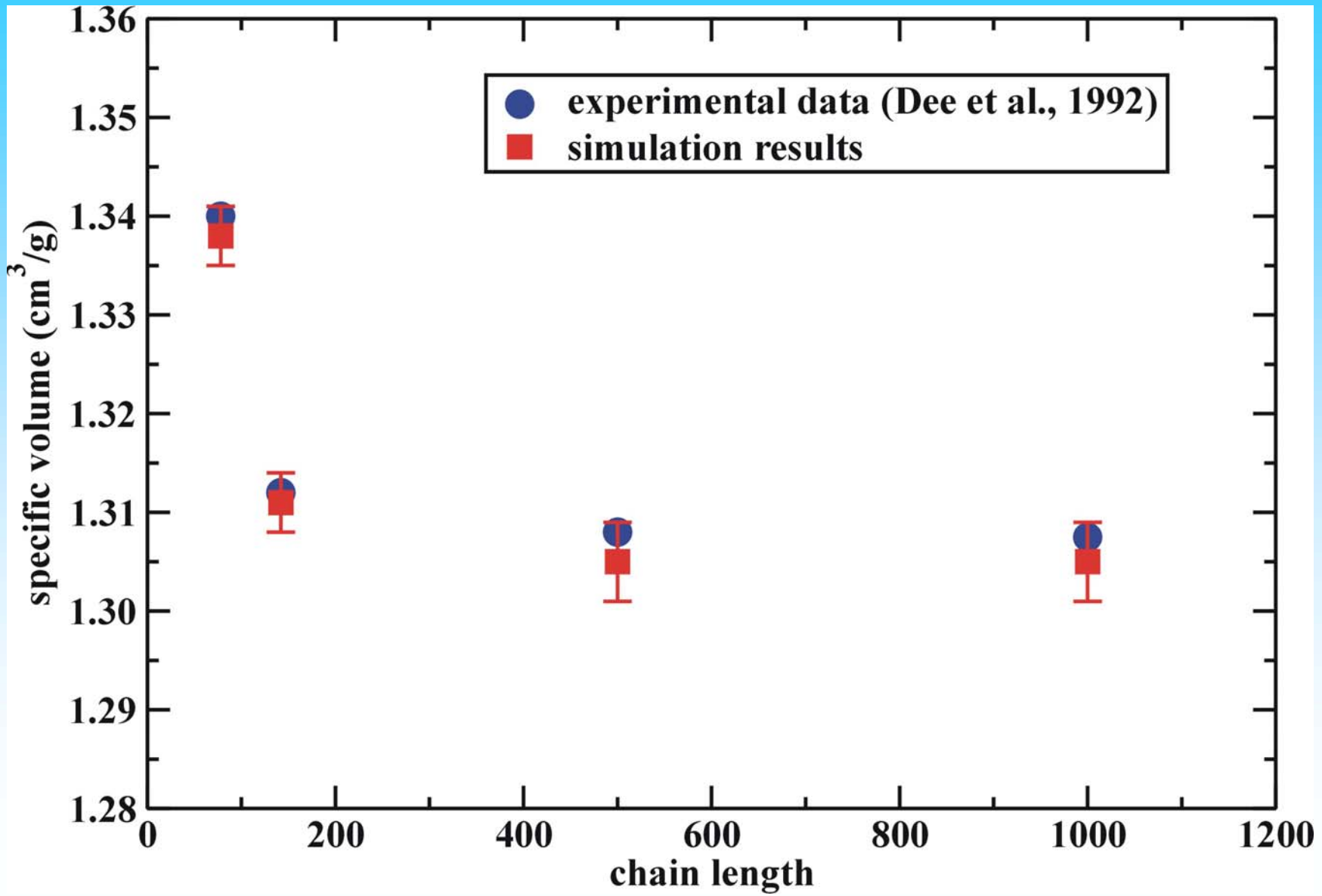
Static structure factor of a Linear Monodisperse PE melt

[C_{1000}, T = 450K, P = 1atm]

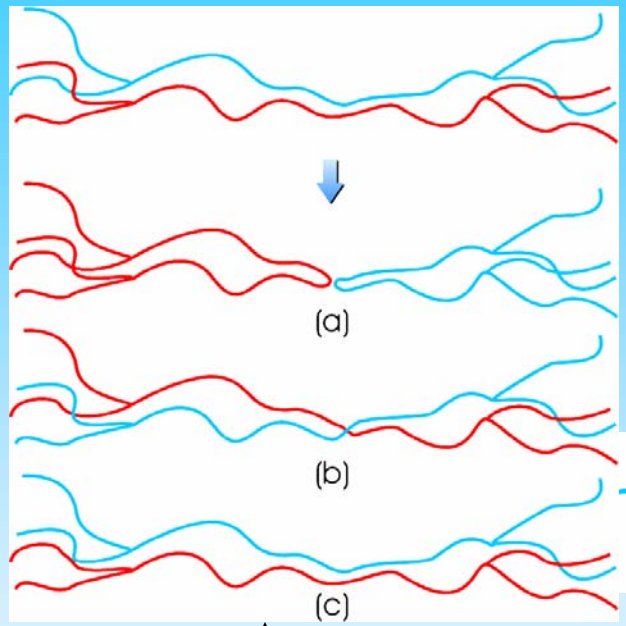


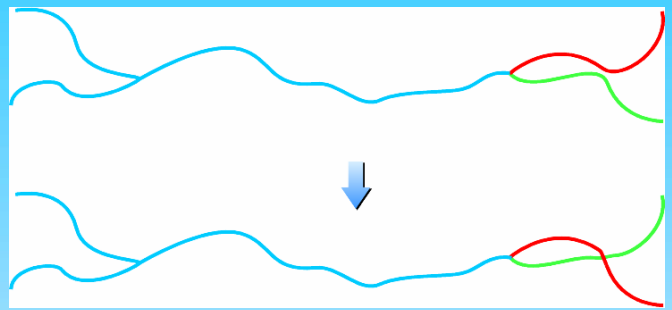
Density of Linear_Monodisperse PE melts

[T = 450K, P = 1atm]



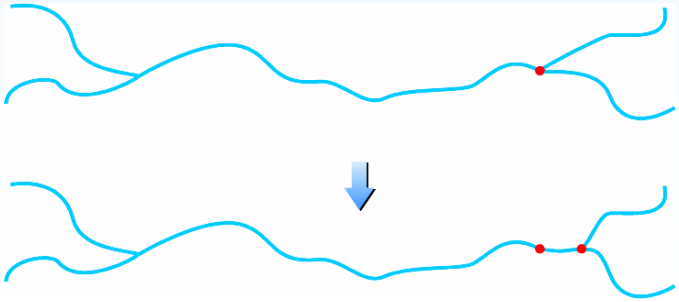
Monte Carlo algorithm has also been extended to H-shaped PE melts



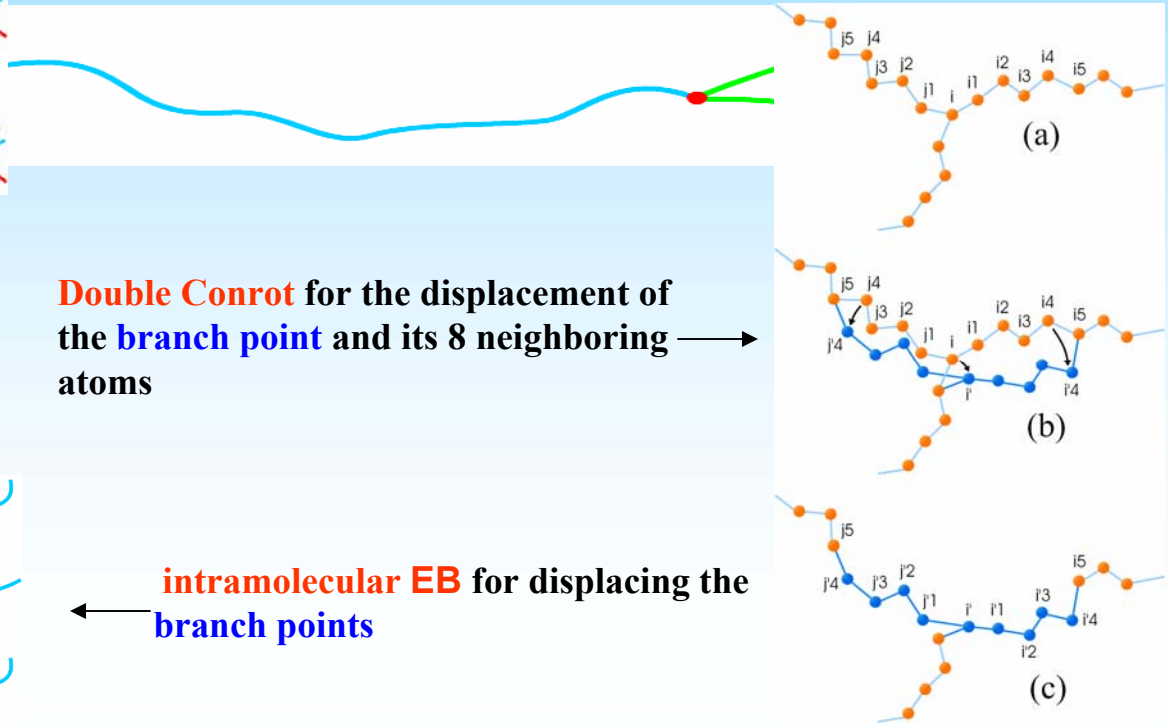


IDR move applies between different branches of the same chain

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

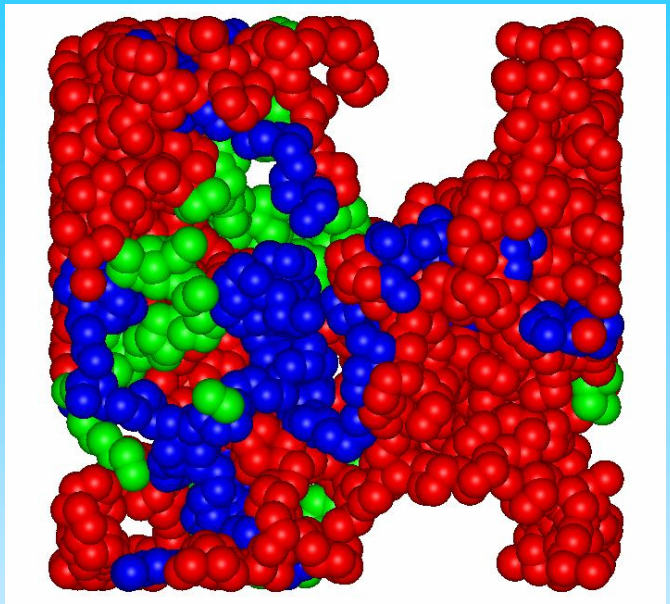


Double Conrot for the displacement of the branch point and its 8 neighboring atoms

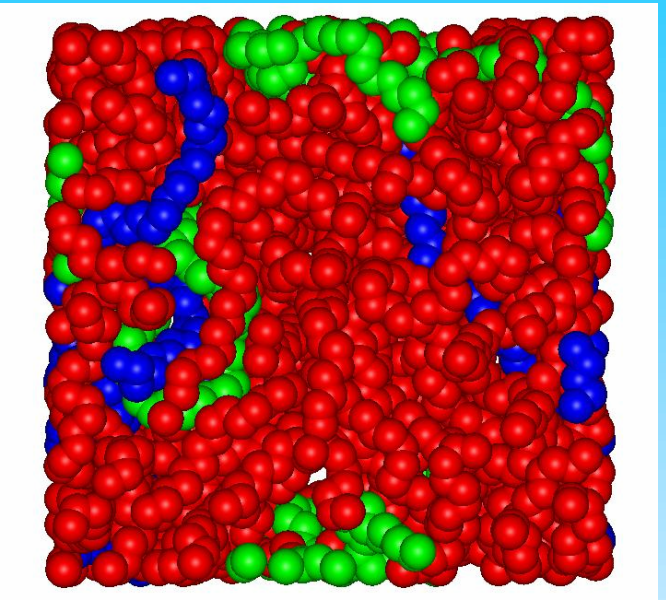


intramolecular EB for displacing the branch points

Extension to Branched Polymers: Atomistic snapshots



(A)



(B)

Typical atomistic snapshots of an H_400_70 system

(A) Before equilibration

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

[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 ⇒ 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**

$$\frac{d\mathbf{x}}{dt} = \mathbf{L}(\mathbf{x}) \cdot \frac{\delta E(\mathbf{x})}{\delta \mathbf{x}} + \mathbf{M}(\mathbf{x}) \cdot \frac{\delta S(\mathbf{x})}{\delta \mathbf{x}}$$

⇒

- E ~ Energy functional
- S ~ Entropy functional
- $\mathbf{L}$ ~ Reversible matrix
- $\mathbf{M}$ ~ **Dissipative matrix**

- **Degeneracy conditions**

$$\mathbf{L}(\mathbf{x}) \cdot \frac{\delta S(\mathbf{x})}{\delta \mathbf{x}} = 0 \qquad \mathbf{M}(\mathbf{x}) \cdot \frac{\delta E(\mathbf{x})}{\delta \mathbf{x}} = 0$$

- **Energy and Entropy functional**

$$E(\mathbf{x}) = \int \left[\frac{u(\mathbf{r})^2}{2\rho(\mathbf{r})} + \varepsilon(\mathbf{r}) \right] d\mathbf{r} \; ; \quad S(\mathbf{x}) = \int s\big(\rho(\mathbf{r}), \varepsilon(\mathbf{r}), \mathbf{X}(\mathbf{r})\big)\, d\mathbf{r}$$

- **Thermodynamic state variables, x**

$$\mathbf{x} = \{\rho(\mathbf{r}),\ \mathbf{u}(\mathbf{r}),\ \varepsilon(\mathbf{r}),\ \mathbf{X}(\mathbf{r})\}$$

⇒

- ρ ~ mass density
- $\mathbf{u}$ ~ momentum density
- ε ~ internal energy density
- $\mathbf{X}$ ~ **structural variables**

GENERIC MC

	Energy = field strength × extensive variable		
Thermal	U	T	S
Mechanical	U	P	V
Material	U	μ	N
Deformation	U	$k_B T\boldsymbol{\alpha}$	$N\tilde{\mathbf{c}} \equiv N\dfrac{\langle 3\mathbf{RR}\rangle}{\langle R^2\rangle_{eq}}$

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

$$\tilde{\mathbf{c}} = \frac{3\langle \mathbf{RR}\rangle}{\langle R^2\rangle_{eq}}$$ ~ Conformation tensor

- Fundamental thermodynamic function of nonequilibrium system

$$U(S,V,N,N\tilde{\mathbf{c}}) = TS - PV + \mu N + k_B T\boldsymbol{\alpha} : N\tilde{\mathbf{c}}$$

FROM THE POINT OF VIEW OF STATISTICAL MECHANICS

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

$$P = \rho^2 \left[\frac{\partial}{\partial \rho} \frac{\Delta A}{N_{ch}} \left(\rho, T, \mathbf{C} \right) \right]_{T,\mathbf{C}} \frac{N_A}{M}$$

$$\alpha = \frac{1}{k_B T} \left[\frac{\partial}{\partial \mathbf{C}} \frac{\Delta A}{N_{ch}} (\rho, T, \mathbf{C}) \right]_{\rho,T}$$

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

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

3. The corresponding generalized statistical ensemble is [N_{ch}nPTμ*α]:

N_{ch}, total number of chains
n, total number of atoms
P, pressure
T, temperature
μ*, reduced chemical potentials (to control the MW distribution)
α, tensorial filed

How to choose the field α for a given shear flow rate $\nabla \mathbf{u}$

$$\rho \sim \exp\left[-\frac{1}{k_B T}\left(-k_B T \boldsymbol{\alpha} : (N\tilde{\mathbf{c}}) + U(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n)\right)\right]$$

UCM:

$$\lambda_H \dot{\boldsymbol{\tau}}_{(1)} + \boldsymbol{\tau} = \eta\, \dot{\boldsymbol{\gamma}}$$

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

Giesekus:

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

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

PTT:

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

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

$$Y(tr\boldsymbol{\tau}) = \exp\left(\frac{\varepsilon}{G} tr\boldsymbol{\tau}\right) \cong \mathbf{I} + \frac{\varepsilon}{G} tr\boldsymbol{\tau}$$

Remark 1: **All these single conformation tensor models have the form**

$$\boxed{\begin{array}{l}\boldsymbol{\tau} = 2(1-\xi)\mathbf{C}\cdot\dfrac{\partial A}{\partial \mathbf{C}} \\ \dfrac{\partial \mathbf{C}}{\partial t} + \mathbf{u}\cdot\nabla\mathbf{C} - (\nabla\mathbf{u})^{T}\cdot\mathbf{C} - \mathbf{C}\cdot(\nabla\mathbf{u}) + \dfrac{\xi}{2}\left(\mathbf{C}\cdot\dot{\boldsymbol{\gamma}} + \dot{\boldsymbol{\gamma}}\cdot\mathbf{C}\right) = -\mathbf{R} : \dfrac{\partial A}{\partial \mathbf{C}}\end{array}}$$

Remark 2: **One can solve for the field α by inverting the above equation**

Application: steady simple shear flow

$$\nabla\upsilon = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad \tilde{\mathbf{c}} = \begin{bmatrix} \tilde{c}_{xx} & \tilde{c}_{xy} & 0 \\ \tilde{c}_{xy} & \tilde{c}_{yy} & 0 \\ 0 & 0 & \tilde{c}_{zz} \end{bmatrix}$$

$$\Rightarrow \quad \boldsymbol{\alpha} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ \alpha_{xy} & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{bmatrix} \quad \boldsymbol{\alpha} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ \alpha_{xy} & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{bmatrix} \quad \boldsymbol{\alpha} = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ \alpha_{xy} & \alpha_{yy} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

Examples of α from known viscoelastic models

UCM

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

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

Giesekus Model

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

$$(1-2\beta)\tilde{c}_{yy} + \beta(\tilde{c}_{xy}^2 + \tilde{c}_{yy}^2) = 1-\beta$$

$$(1-2\beta)\tilde{c}_{xy} - \lambda\dot{\gamma}\,\tilde{c}_{yy} + \beta(\tilde{c}_{xx}\tilde{c}_{xy} + \tilde{c}_{xy}\tilde{c}_{yy}) = 0$$

$$(1-2\beta)\tilde{c}_{xx} - 2\lambda\dot{\gamma}\,\tilde{c}_{xy} + \beta(\tilde{c}_{xx}^2 + \tilde{c}_{xy}^2) = 1-\beta$$

$$\tilde{c}_{zz} = 1$$

Remark: The field α is model-dependent

Idea: Define α 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** $\mathbf{x}=\{\rho(\mathbf{r}), \mathbf{u}(\mathbf{r}), \varepsilon(\mathbf{r}), \tilde{\mathbf{c}}(\mathbf{r})\}$
- **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, ρ = 0.7438 g/cm^3 ; Rouse time, $\tau_R \approx 0.5$ ns**
  - **Five different states in a broad range: 0.43 ≤ De ≤106**

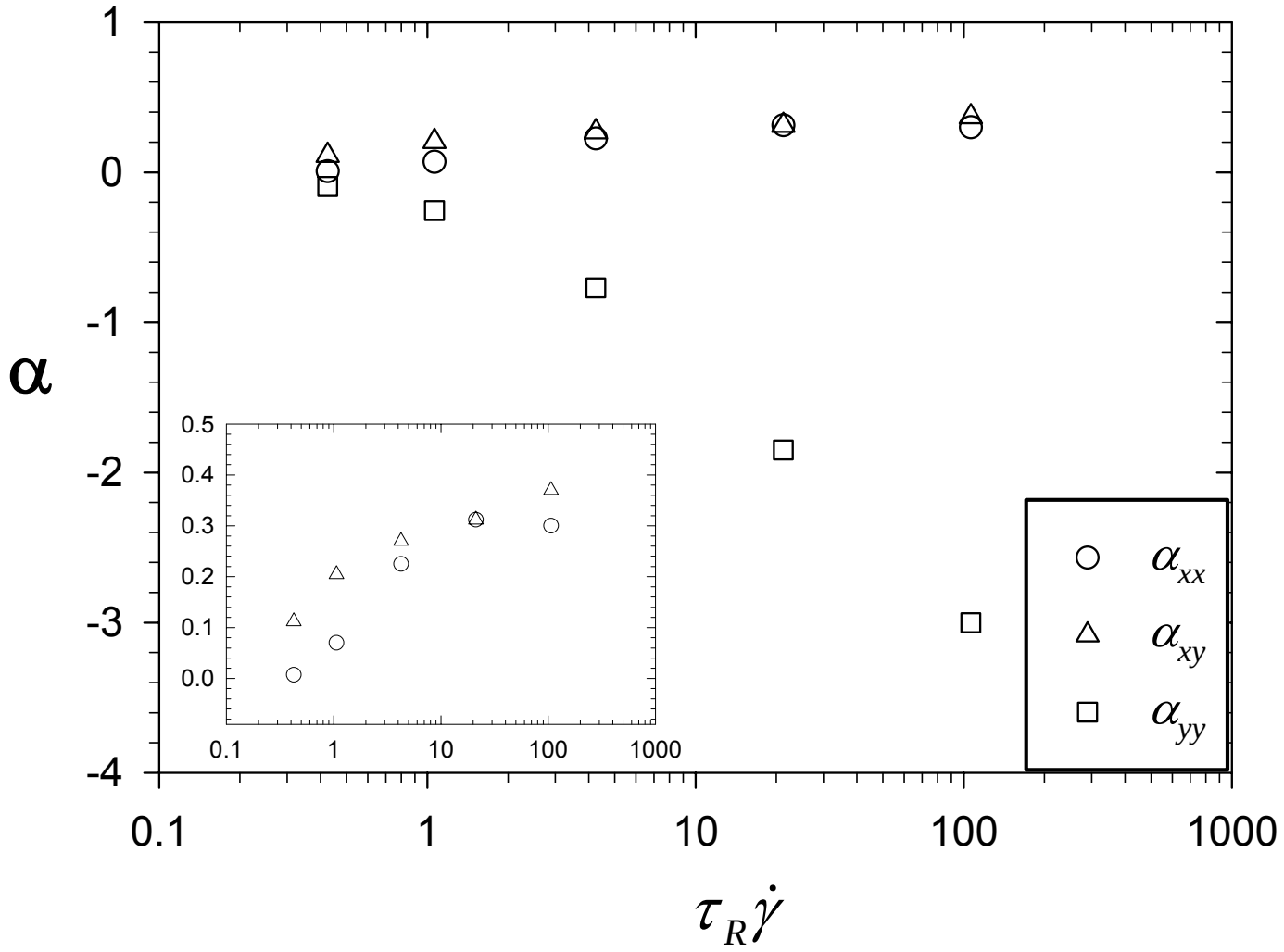
- **Potential model**
  - **TraPPE (with flexible or fixed bond lengths)**

- **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**

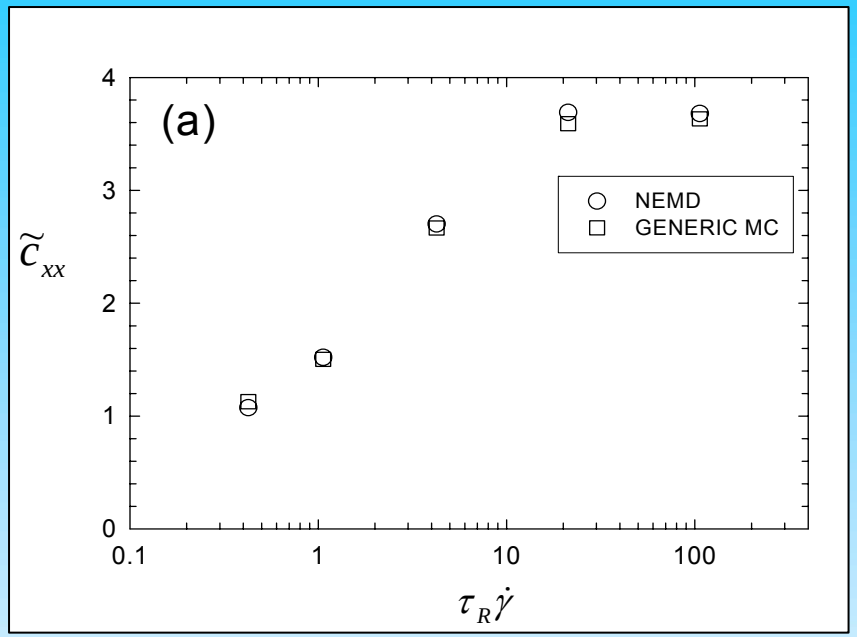
- **GENERIC MC simulations**
  - **Total 500 million cycles for all the shear rate**
  - **Initial values of α using the Giesekus model**
  - **6 to 8 iterations were sufficient for reproducing the non-equilibrium state**
  - **one iteration took approximately 4~5 days using 2.2 GHz Opteron CPUs**

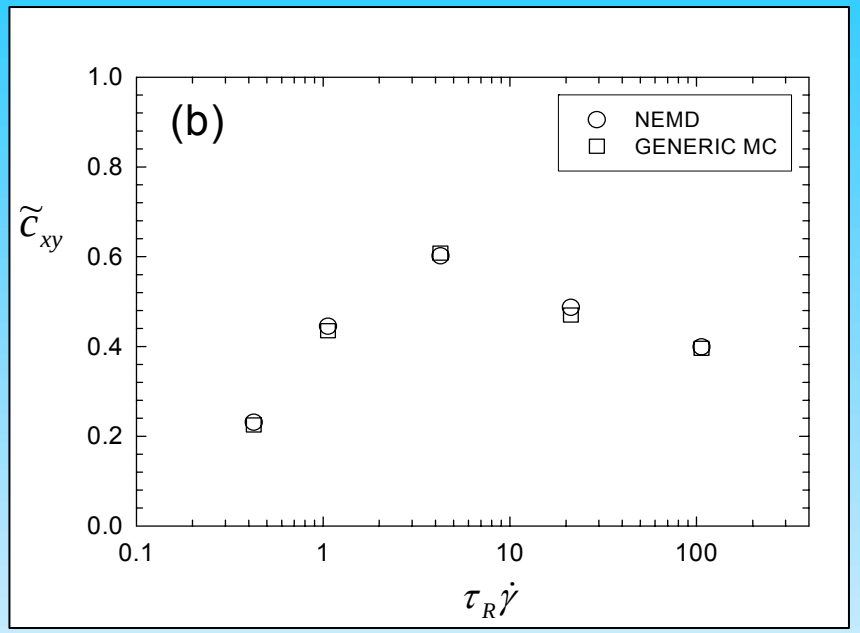
Thermodynamic field α vs. Deborah number De

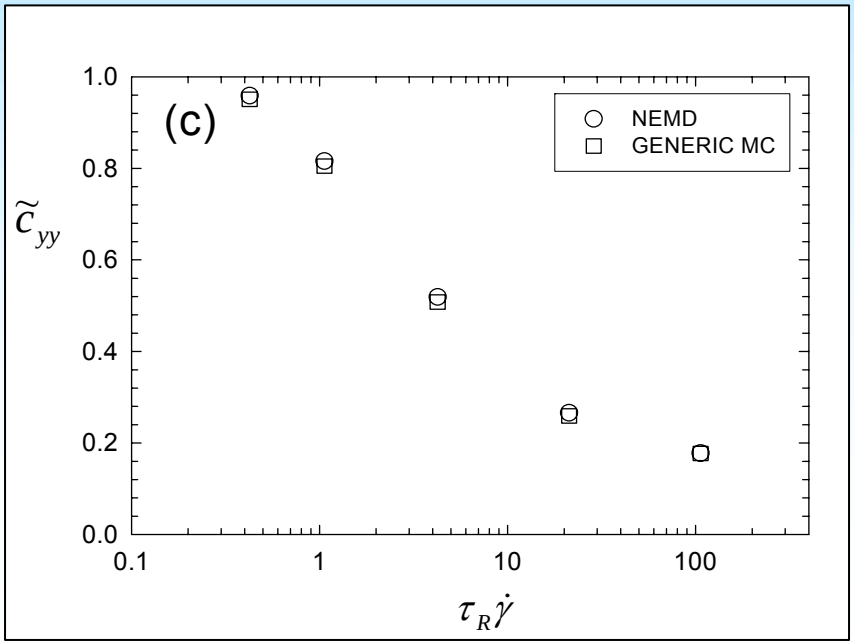
$$\alpha = \begin{bmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ \alpha_{xy} & \alpha_{yy} & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

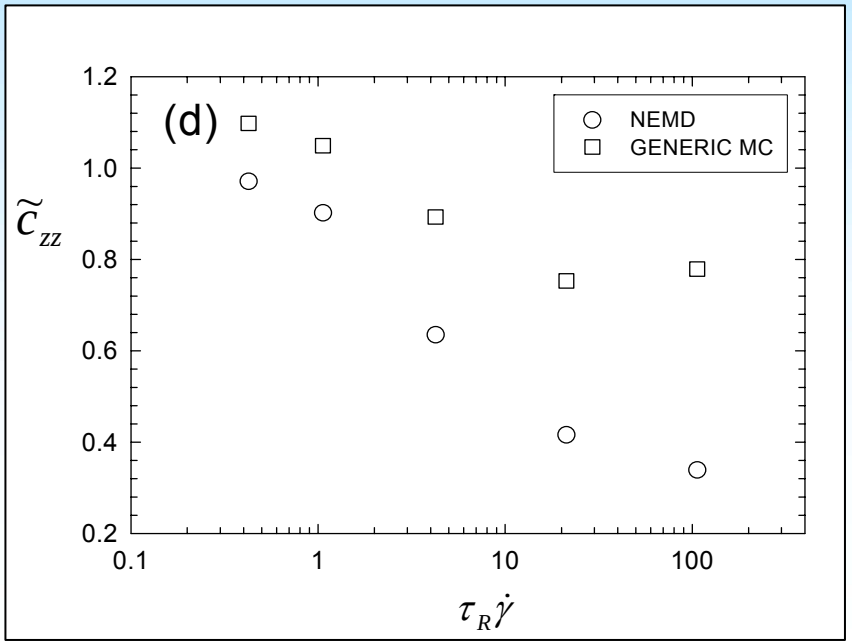


Comparison of $\tilde{c}$ between GENERIC MC and NEMD









A symmetry relation

- **Elastic stress**

$$\tau_{\alpha\beta} = -2\tilde{c}_{\alpha\gamma}\frac{\delta A(\tilde{\mathbf{c}})}{\delta \tilde{c}_{\gamma\varepsilon}} = -2nk_BT\tilde{c}_{\alpha\gamma}\alpha_{\beta\gamma}$$

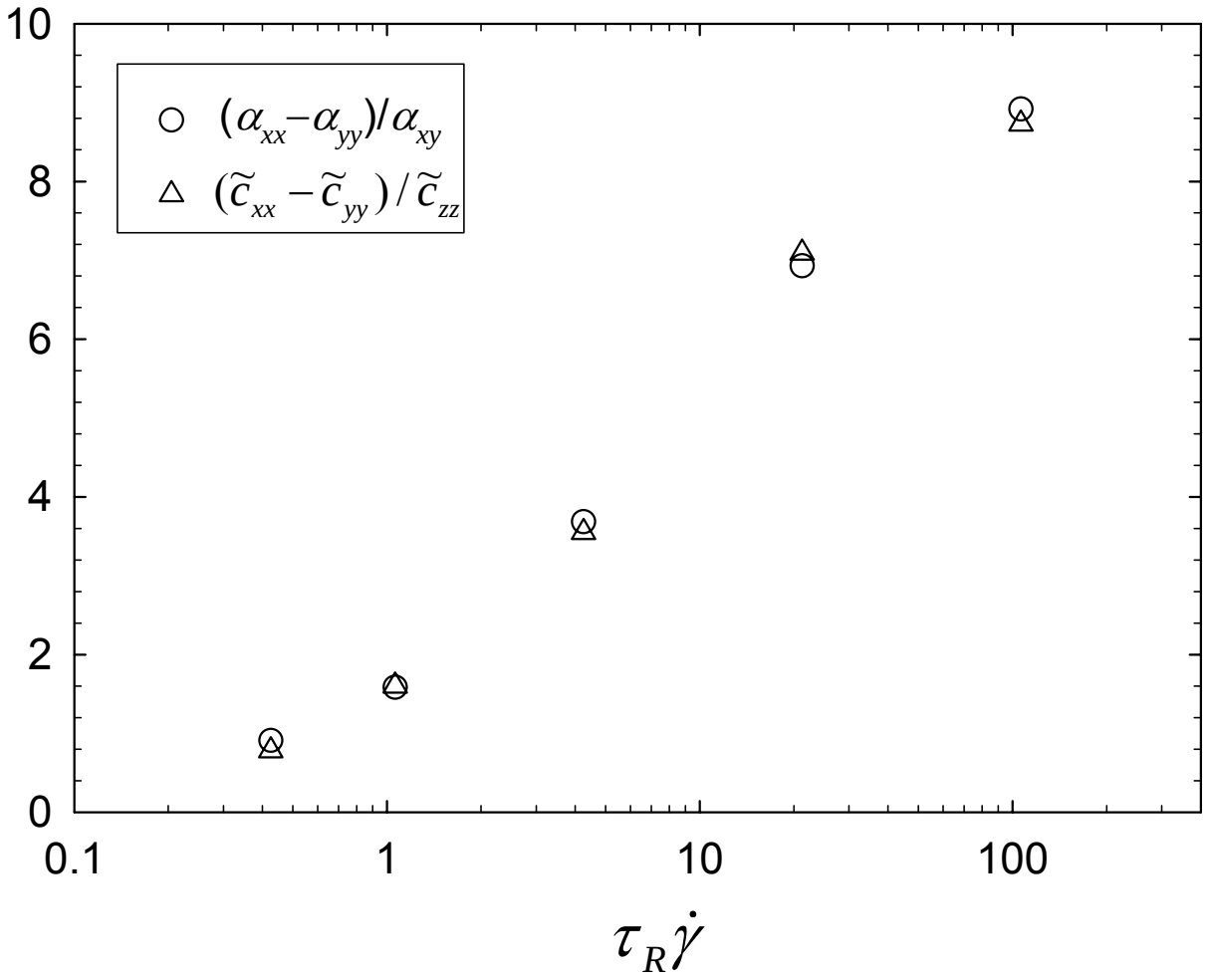
and

$$\nabla\mathbf{v} = \begin{bmatrix} 0 & 0 & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \Longrightarrow \tau_{xy} = \tau_{yx}\,;\ \tilde{c}_{xy} = \tilde{c}_{yx}\,;\alpha_{xy} = \alpha_{yx}$$

$$\Rightarrow \quad \frac{\alpha_{xx} - \alpha_{yy}}{\alpha_{xy}} = \frac{\tilde{c}_{xx} - \tilde{c}_{yy}}{\tilde{c}_{xy}}$$

does it hold?

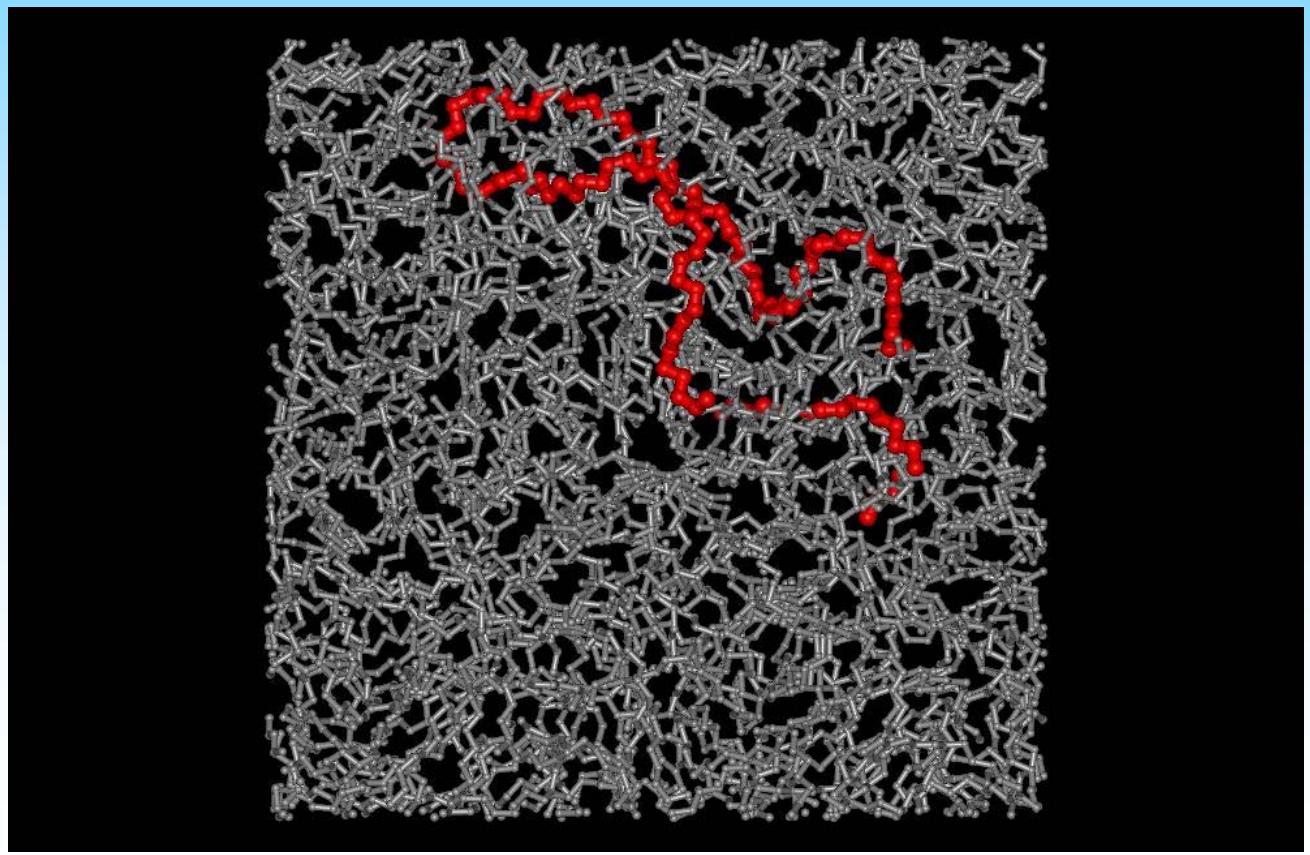
$$(\alpha_{xx} - \alpha_{yy}) / \alpha_{xy} \stackrel{?}{=} (\tilde{c}_{xx} - \tilde{c}_{yy}) / \tilde{c}_{xy}$$



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 α and De as a function of chain length so that α 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 α 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

- $$\Lambda_{\alpha\beta\gamma\varepsilon} = \frac{1}{2nk_s\lambda_H}\left(\frac{k_s}{k_BT}\right)\left[(1-\beta)\left(\tilde{c}_{\alpha\gamma}\delta_{\beta\varepsilon} + \tilde{c}_{\alpha\varepsilon}\delta_{\beta\gamma} + \tilde{c}_{\beta\gamma}\delta_{\alpha\varepsilon} + \tilde{c}_{\beta\varepsilon}\delta_{\alpha\gamma}\right) + 2\beta\left(\frac{b-\frac{1}{3}\mathrm{tr}\,\tilde{\mathbf{c}}}{b-\mathrm{tr}\,\tilde{\mathbf{c}}}\right)\left(\tilde{c}_{\alpha\gamma}\tilde{c}_{\beta\varepsilon} + \tilde{c}_{\alpha\varepsilon}\tilde{c}_{\beta\gamma}\right)\right]$$

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

$$\Rightarrow \quad \hat{\tilde{c}}_{\alpha\beta} = -\Lambda_{\alpha\beta\lambda\varepsilon}\frac{\delta A(\tilde{\mathbf{c}})}{\delta\tilde{c}_{\gamma\varepsilon}} \;; \qquad \tau_{\alpha\beta} = \tau_{\alpha\beta}^{(el)} = -2c_{\alpha\gamma}\frac{\delta A(\tilde{\mathbf{c}})}{\delta\tilde{c}_{\gamma\varepsilon}}$$

$$\hat{\tilde{c}}_{\alpha\beta} = -\frac{1}{\lambda_H}\left[(1-\beta)\delta_{\alpha\gamma} + \beta\left(\frac{b-\frac{1}{3}\mathrm{tr}\,\tilde{\mathbf{c}}}{b-\mathrm{tr}\,\tilde{\mathbf{c}}}\right)\tilde{c}_{\alpha\gamma}\right]\left[\left(\frac{b-\frac{1}{3}\mathrm{tr}\,\tilde{\mathbf{c}}}{b-\mathrm{tr}\,\tilde{\mathbf{c}}}\right)\tilde{c}_{\gamma\beta} - \delta_{\gamma\beta}\right]$$

$$\tau_{\alpha\beta} = -nk_BT\left[\left(\frac{b-\frac{1}{3}\mathrm{tr}\,\tilde{\mathbf{c}}}{b-\mathrm{tr}\,\tilde{\mathbf{c}}}\right)\tilde{c}_{\alpha\beta} - \delta_{\alpha\beta}\right]$$

Thermodynamic admissibility of the Modified FENE-Cohen+Giesekus Model

- $$\Lambda_{\alpha\beta\gamma\varepsilon} = \frac{1}{2nk_s\lambda_H}\left(\frac{k_s}{k_B T}\right)\left[(1-\beta)\left(\tilde{c}_{\alpha\gamma}\delta_{\beta\varepsilon} + \tilde{c}_{\alpha\varepsilon}\delta_{\beta\gamma} + \tilde{c}_{\beta\gamma}\delta_{\alpha\varepsilon} + \tilde{c}_{\beta\varepsilon}\delta_{\alpha\gamma}\right) + 2\beta\left(\frac{b-\frac{1}{3}\mathrm{tr}\,\tilde{\mathbf{c}}}{b-\mathrm{tr}\,\tilde{\mathbf{c}}}\right)\left(\tilde{c}_{\alpha\gamma}\tilde{c}_{\beta\varepsilon} + \tilde{c}_{\alpha\varepsilon}\tilde{c}_{\beta\gamma}\right)\right]$$

- $$A(\tilde{\mathbf{c}}) = \int d^3x \frac{1}{2} nk_B T\left[\frac{1}{3}\mathrm{tr}\,\tilde{\mathbf{c}} - \frac{2}{3}b\ln\left(1-\frac{\mathrm{tr}\,\tilde{\mathbf{c}}}{b}\right) - \ln\det(\tilde{\mathbf{c}})\right]$$

$$\Rightarrow \quad \frac{\delta A(\tilde{\mathbf{c}})}{\delta \tilde{c}_{\alpha\beta}}\Lambda_{\alpha\beta\gamma\varepsilon}\frac{\delta A(\tilde{\mathbf{c}})}{\delta \tilde{c}_{\gamma\varepsilon}} \propto \sum_{i=1}^{3}\frac{1}{\lambda_i}\left(\xi\lambda_i - 1\right)^2\left[\beta\xi\lambda_i + (1-\beta)\right] \geq 0$$

where $$\xi = \frac{b-\frac{1}{3}\mathrm{tr}\,\tilde{\mathbf{c}}}{b-\mathrm{tr}\,\tilde{\mathbf{c}}} \geq 1$$

$\Leftrightarrow$ The range for thermodynamic admissibility is $0 \leq \beta \leq 1$

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