Modeling Strong Extensional Flows of Polymer Solutions and Melts

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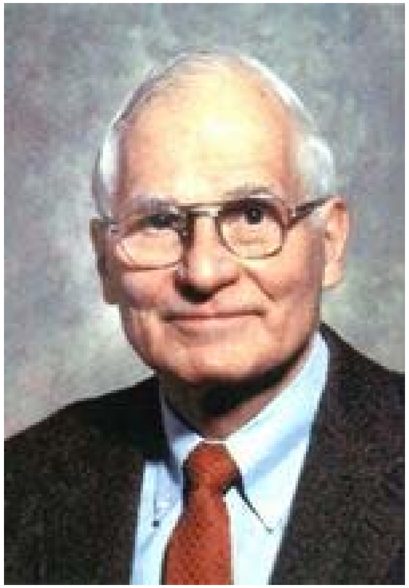
CSCAMM Workshop
Multiscale Modeling and Simulation of Complex Fluids
April 19, 2007

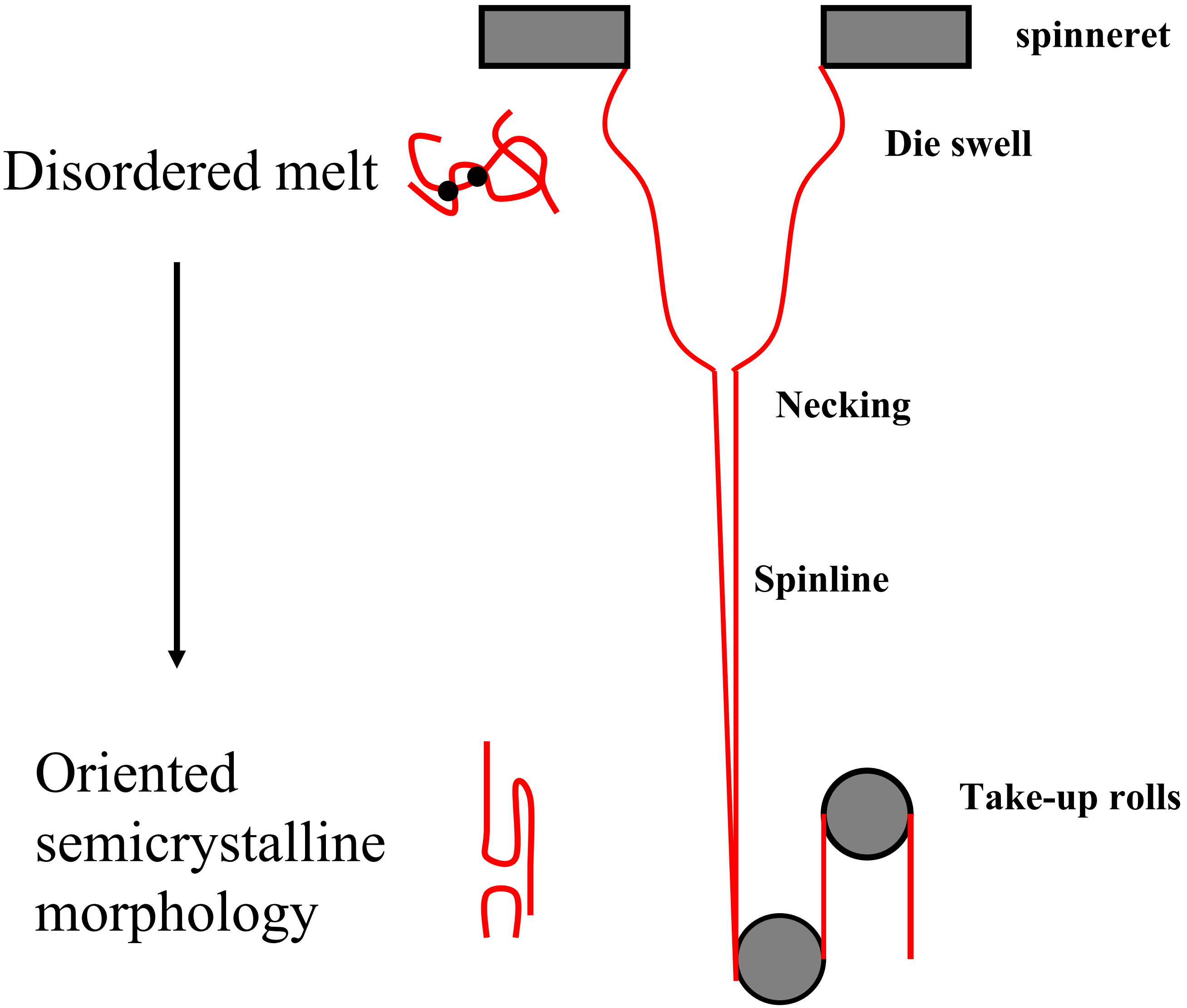
Acknowledgements:
Dr. Joydeep Mukherjee, Department of Chemical Engineering, University of Michigan



Art Metzner, 1927 - 2006

Commemorative Symposium: May 14, 2007, Dept. of Chem. Engrg., Univ. of Delaware

Fiber Spinning of Semicrystalline Polymer Melts



spinneret

Die swell

Disordered melt

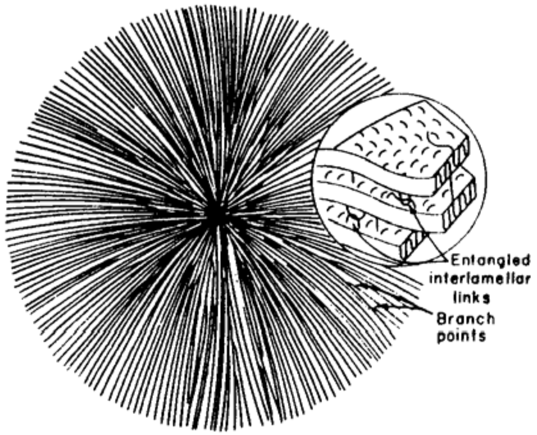
Necking

Spinline

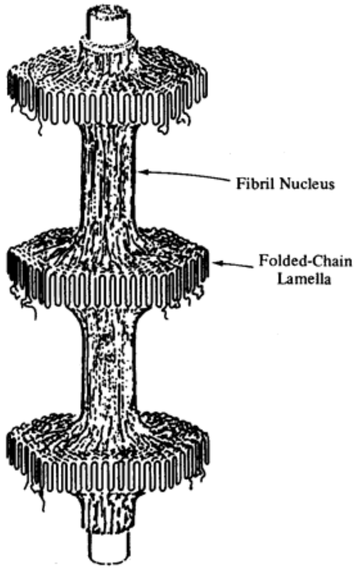
Oriented semicrystalline morphology

Take-up rolls

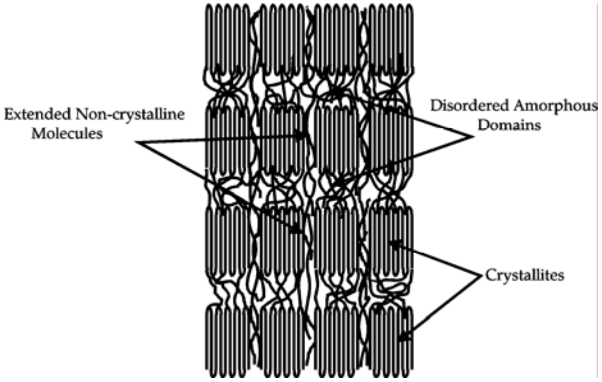
Semicrystalline Morphologies in Polymers



Spherulite[1]



Shish-kebab[2]



Fibrillar[3]

Most of the continuum models have a high degree of empiricism and lack capability to predict semicrystalline morphology.

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[1] A. Keller, G.R. Lester and L.B. Morgan, *Phil. Trans. Roy. Soc. (London)* **A247** 1 (1954)

[2] A. Keller and M.J. Machin, *J. Macromol. Sci. Phys.* **B1** 41 (1967)

[3] D.C. Prevorsek, P.J. Harget, R.K. Sharma and A.C. Reimschuessel, *J. Macromol. Sci. Phys.* **B8** 127 (1973)

Micro-Macro Hierarchical Approach[1]

Processing conditions

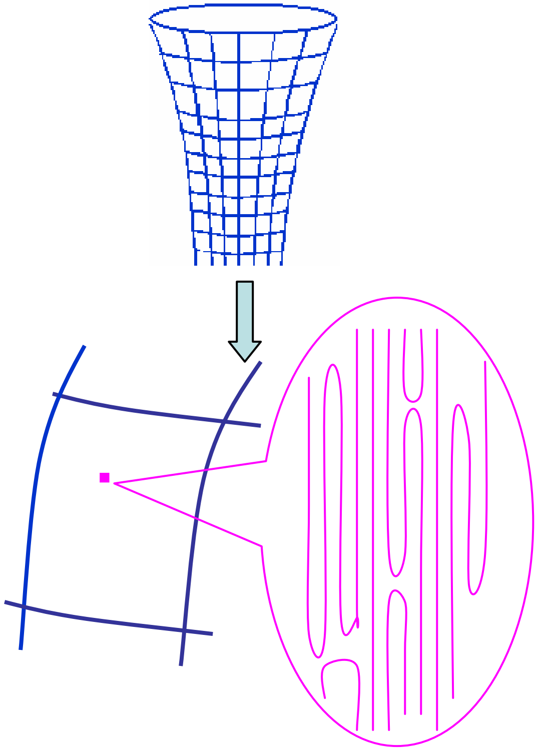
- Temperature
- Take-up roll speed

Macroscopic Model:

- Amorphous melt rheology and chain deformation
- Nonequilibrium thermodynamic potentials

Microscopic Simulations

- Chain conformations and microscopic thermodynamic information under the influence of flow deformation for different semicrystalline morphologies using a microscopic model



Predictions:

Morphology

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[1] Mukherjee, Wilson , Beris, Flow-induced non-equilibrium thermodynamics of lamellar semicrystalline polymers, J. Non-Newt. Fluid Mech., 120 (1-3): 225-240 (2004).

Outline

- Objective: Examine/improve the internal consistency in micro-macro modeling following a hierarchical approach applied to a dense amorphous linear polymer system

- Microscopic modeling

    - Lattice subdivision-based Monte Carlo method

- Macroscopic modeling

    - Conformation tensor based models using Non-Equilibrium Thermodynamics

- Microscopic modeling under non-equilibrium conditions

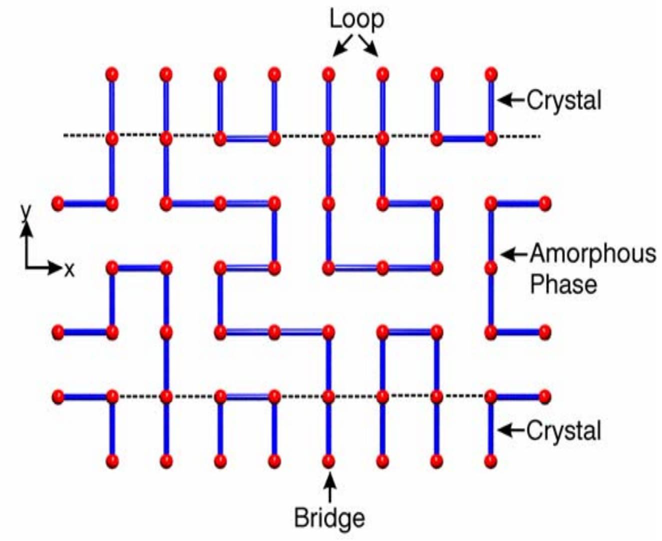
- Conclusions

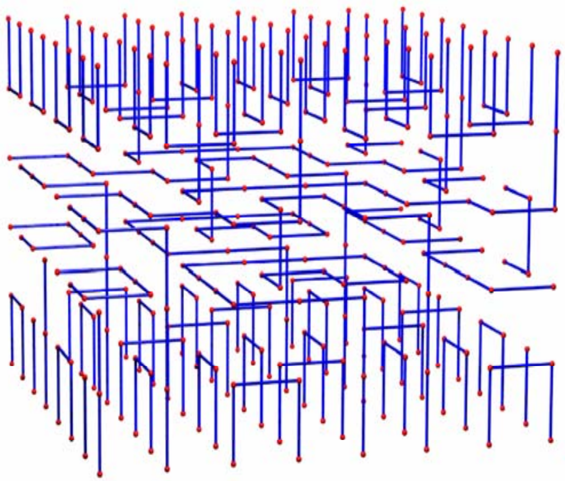
Microscopic Modeling: Lattice Models

- Originally developed by Flory and Yoon[1]
- Has been found to be useful in the study of dense semicrystalline polymers
- Various lattice based approaches:
  - Random walk models
  - Exact enumeration methods
  - Monte Carlo methods
  - Mean-field models

2

Layer 1





[1] Flory and Yoon, *Polymer* **18** (1977), pp. 509-513

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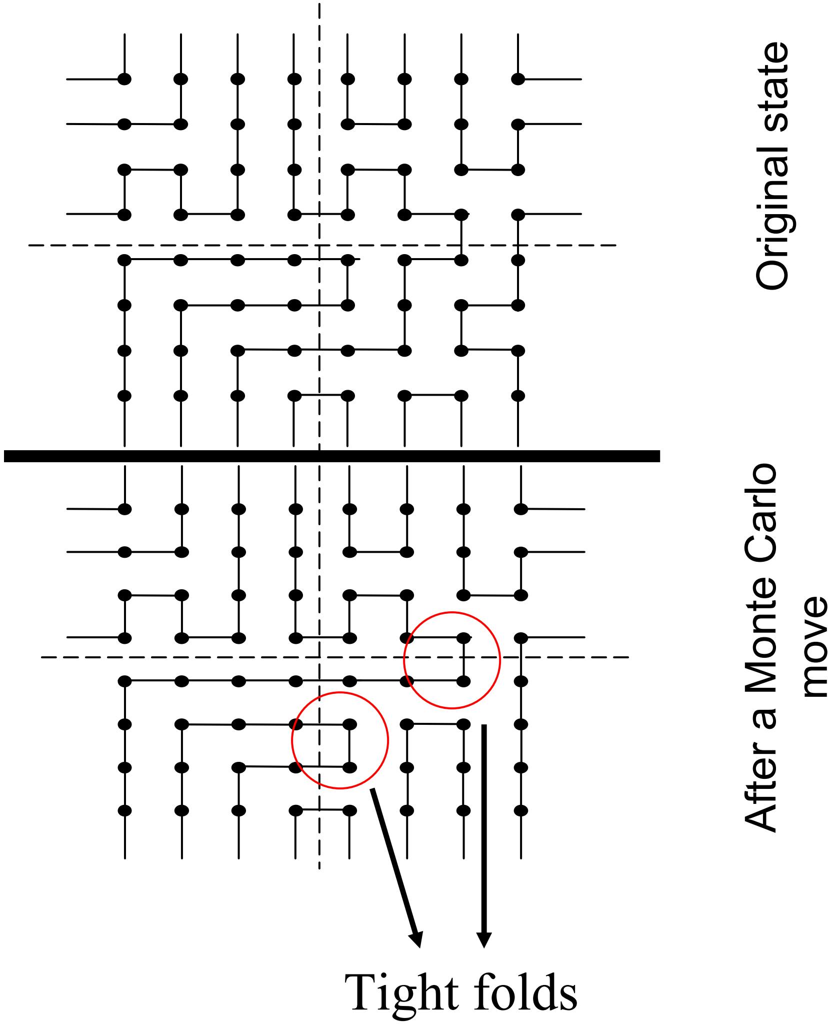
Lattice-based Metropolis Monte Carlo Scheme

- A modular lattice subdivision approach.
- At any Monte Carlo step perform any of Monte Carlo moves:
  - Internal sublattice optimization
  - Isomerization
- Accept the new state with a probability

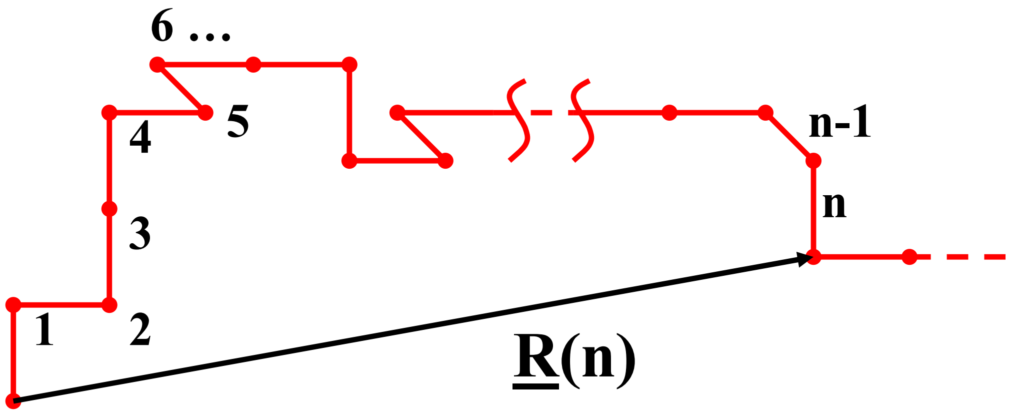
$$p \propto \exp\left(-E_\eta \times N_{tight\ folds}\right)$$

E_η energetic penalty on tight folds non-dimensionalized with respect to the Boltzmann factor k_BT



Initial Macroscopic Modeling of the Dense Amorphous Polymer Phase: Phan-Thien Tanner Model[2]

- Based on a network model
- Can also be described from bracket formulation of non-equilibrium thermodynamics [3]
- The internal structure is described by the conformation tensor, $\underline{\underline{c}}$,the second moment of the end-to-end n-segment chain distance.



$$\underline{\underline{c}}(n) = \langle \underline{R}(n)\underline{R}(n) \rangle$$

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[2] Phan-Thien N, Tanner R.I., J.Non-Newtonian Fluid Mech.,2(1977) 353-365

[3]A.N. Beris, B.J. Edwards, Thermodynamics of Flowing Systems, Oxford University Press, New York, 1994

Phan-Thien Tanner (PTT)Model

Constitutive equation

$$\breve{\underline{\underline{\mathbf{c}}}}^{*} = -\frac{1}{\lambda(\underline{\underline{\mathbf{c}}}^{*})}\left(\underline{\underline{\mathbf{c}}}^{*}-\underline{\underline{\mathbf{1}}}\right)$$

$$\underline{\underline{\boldsymbol{\sigma}}} = G_0\left(\underline{\underline{\mathbf{c}}}^{*}-1\right)$$

η - extensional viscosity

λ - relaxation time

G - elastic modulus

- ➢ Internal structure dependent relaxation time

$$\frac{1}{\lambda(\underline{\underline{\mathbf{c}}}^{*})} = \frac{1}{\lambda_0}\exp\left(\alpha\left(\mathrm{tr}(\underline{\underline{\mathbf{c}}}^{*})-3\right)\right)$$

λ_0 - zero shear rate relaxation time

$\alpha \sim 0.05$ for PE

Non-equilibrium thermodynamic information

$$A^{*} = \frac{M}{2}\left[\mathrm{tr}\left(\underline{\underline{\mathbf{c}}}^{*}\right)-\log\left(\det\left(\underline{\underline{\mathbf{c}}}^{*}\right)\right)\right]$$

$$\frac{\delta A^{*}}{\delta \underline{\underline{\mathbf{c}}}^{*}} = \frac{M}{2}\left(\underline{\underline{\mathrm{I}}}-\left(\underline{\underline{\mathbf{c}}}^{*}\right)^{-1}\right)$$

A^{*}- free energy of the system (non-dimensionalized by $k_B T$)

M- total number of entanglements in the system

Hamiltonian Functional Formalism*

*Beris and Edwards, Thermodynamics of Flowing Systems, Oxford UP, 1994

- For any arbitrary functional F, its time evolution can be described as the sum of two contributions:
  - a reversible one, represented by a Poisson bracket:
    - {F,H}
  - an irreversible one, represented by a dissipative bracket:
    - [F,H]
- The final dynamic equations are recovered through a direct comparison with the expression derived by differentiation by parts:

$$dF/dt = \{F,H\} + [F,H] = \int \delta F/\delta \mathbf{x} \cdot d\mathbf{x}/dt \, dV$$

Advantages of Hamiltonian Formalism (1)

- It only requires knowledge of the following:
  - A set of macroscopic variables, taken uniformly as volume densities. The include, in addition to the equilibrium thermodynamic ones (the component mass density, ρ_i, for every component i, the entropy density si), the momentum density, $\rho\mathbf{v}$, and any additional structural parameter, again expressed as a density
  - The total energy of the system or any suitable Lagrange transform of it, typically the total Helmholtz free energy, expressed as a functional of all other densities with the temperature substituting for the entropy density
  - The Poisson bracket, {F,H}
  - The dissipation bracket, [F,H]

Advantages of Hamiltonian Formalism (2)

A set of macroscopic variables can easily be assumed depending on the physics that we want to incorporate to the problem

The total Helmholtz free energy can also easily be constructed as the sum of kinetic energy plus an extended thermodynamic free energy that typically includes an easily derived expression (in terms of the structural parameters) in addition to a standard equilibrium expression

The Poisson bracket, {F,H} is rarely needed by itself: only when an equation is put together for the first time characteristic of the variables involved in this system; otherwise, its effect is probably already known from previous work: it corresponds to a standard reversible dynamics. For viscoelastic flows, this corresponds to the terms defining an upper convected derivative

The dissipation bracket, [F,H] is the only one to contain major new information and is typically where our maximum ignorance lies. Barren any other information (say, by comparison against a microscopic theory) the main information that we can use is a linear irreversible thermodynamics expression: according to that, the dissipation bracket becomes a bilinear functional in terms of all the nonequilibrium Hamiltonian gradients with an additional nonlinear (in H) correction with respect to $\delta F/\delta s$ (entropy correction) that can be easily calculated so that the conservation of the total energy is satisfied: [H,H] = 0.

Final Equations for Single Conformation Viscoelasticity

- For an isothermal system, we get the standard dynamics for a viscoelastic medium (together with the divergence-free velocity constraint):

$$\rho \frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{v} = -\nabla p + \eta_s \Delta \mathbf{v} + \nabla \cdot \mathbf{T}^T$$

$$\frac{\mathrm{D}}{\mathrm{Dt}} \mathbf{c} - \nabla \mathbf{v}^T \cdot \mathbf{c} - \mathbf{c} \cdot \nabla \mathbf{v} = -\frac{\xi}{2}\left(\dot{\boldsymbol{\gamma}} \cdot \mathbf{c} + \mathbf{c} \cdot \dot{\boldsymbol{\gamma}}\right) - \boldsymbol{\Lambda} : \frac{\partial a}{\partial \mathbf{c}}$$

$$\mathbf{T}^T = 2(1-\xi)\mathbf{c} \cdot \frac{\partial a}{\partial \mathbf{c}}$$

Key Question: Consistency with the Underlying Microscopic Physics

- Approach:
  - Solve the Continuum Macroscopic Model for a well defined flow to obtain:
    - Structural information: Conformation Tensor, **c**
    - Thermodynamic information: (Non-equilibrium) Free Energy, A and Free Energy potentials, δA/δ**c**
  - For the given flow, and the given potentials, solve directly for the corresponding microscopic structure
    - Use a specially developed Non-Equilibrium Monte-Carlo approach applied to a 3d Lattice model with full periodicity
  - Attest on the consistency through a direct comparison of the microscopic/macroscopic results
  - Interpret results and suggest improvements to the macroscopic model repeating the procedure if necessary

Uniaxial Extensional flow for PTT

Solve the equations for uniaxial extensional flow at steady state

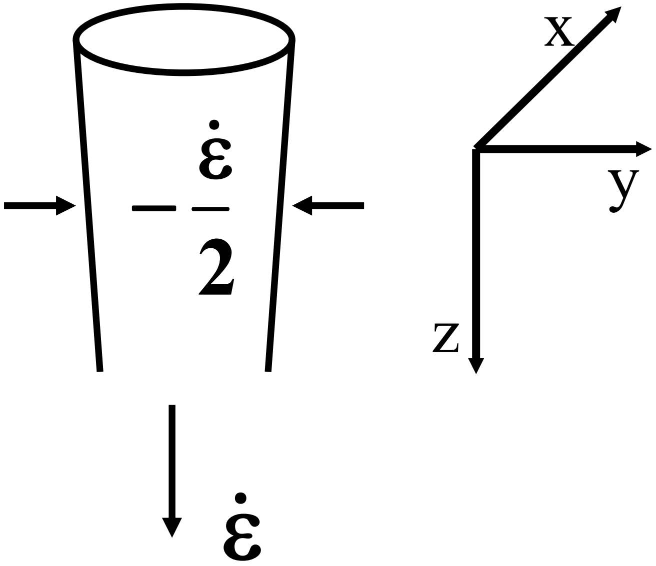
Diagonal Conformation tensor

$$\underline{\underline{\mathbf{c}}}^* = \begin{bmatrix} c^*_{xx} & 0 & 0 \\ 0 & c^*_{xx} = c^*_{yy} & 0 \\ 0 & 0 & c^*_{zz} \end{bmatrix}$$

$$c^*_{xx} = \frac{1}{1+\mathrm{We}^*} \text{ and } c^*_{zz} = \frac{1}{1-2\mathrm{We}^*},$$

where, $\mathrm{We}^* < 0.5$

We^* is the <u>Weissenberg number</u> $= \dfrac{\lambda(\underline{\underline{\mathbf{c}}}^*)}{\dot{\varepsilon}^{-1}}$



Non-equilibrium thermodynamic potentials

$$\frac{\delta A^*}{\delta c^*_{xx}} = \frac{\delta A^*}{\delta c^*_{yy}} = -\frac{M}{2}\mathrm{We}^*;\ \frac{\delta A^*}{\delta c^*_{zz}} = M\mathrm{We}^*$$

→ **Macro-micro bridges**

Notice that at equilibrium ($\mathrm{We}^* \sim 0$), these potentials go to zero!

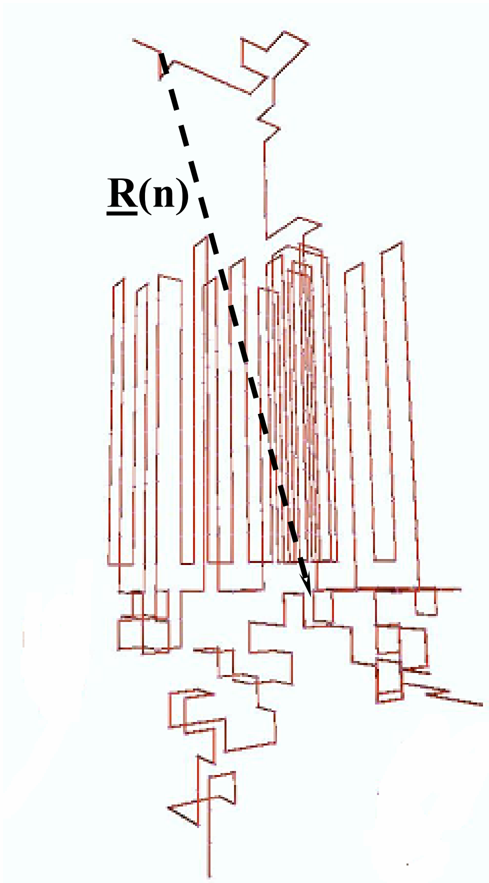
Non-equilibrium Thermodynamic Bias

Need to formulate the proper non-equilibrium thermodynamic guidance to drive the microscopic simulations

Ansatz:

Accept the new microstate with a probability

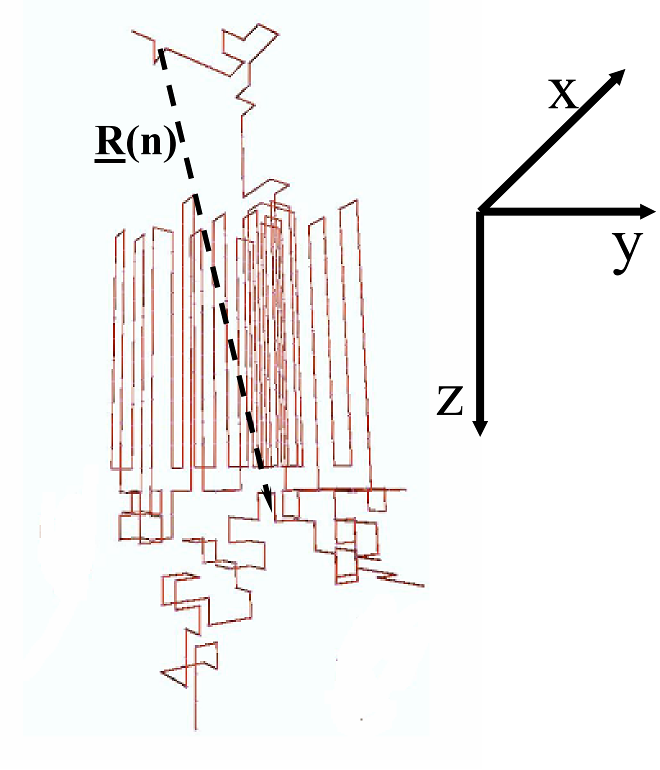
$$p \propto \exp\left\{ \underbrace{\frac{\delta A^{*}}{\delta \underline{\underline{\mathbf{c}}}^{*}} :< \underline{\mathbf{R}}\,\underline{\mathbf{R}} >^{*}}_{\text{Non-equilibrium forcing term}} \right\}$$



Evaluation of the Non-equilibrium Bias

1. *Evaluate the non-equilibrium thermodynamic potential from Macroscopic model (PTT) :*

$$\frac{\delta A^*}{\delta c^*_{xx}} = \frac{\delta A^*}{\delta c^*_{yy}} = -\frac{M}{2}We^*; \quad \frac{\delta A^*}{\delta c^*_{zz}} = MWe^*$$



2. *Use it to evaluate the Non-equilibrium forcing term*

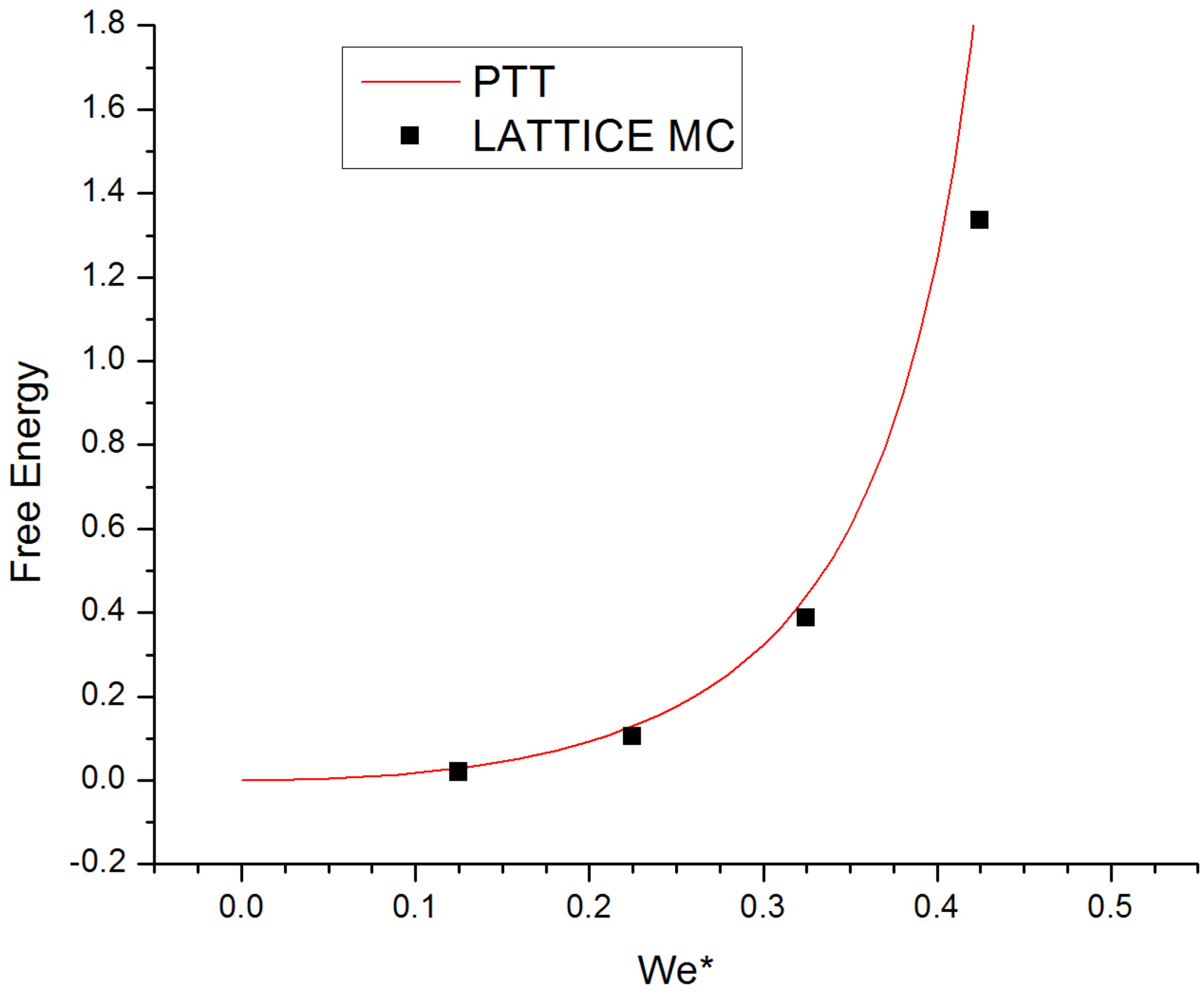
$$\frac{\delta A^*}{\delta \underline{\underline{\mathbf{c}}}^*} : \langle \underline{\mathbf{R}}\,\underline{\mathbf{R}} \rangle^* \quad \text{where} \quad \langle \underline{\mathbf{R}}\,\underline{\mathbf{R}} \rangle^* = \frac{\langle \underline{\mathbf{R}}\,\underline{\mathbf{R}} \rangle}{(n/1.845)},$$

N_e : entanglement length (typically 100 lattice chain segments for polyethylene).

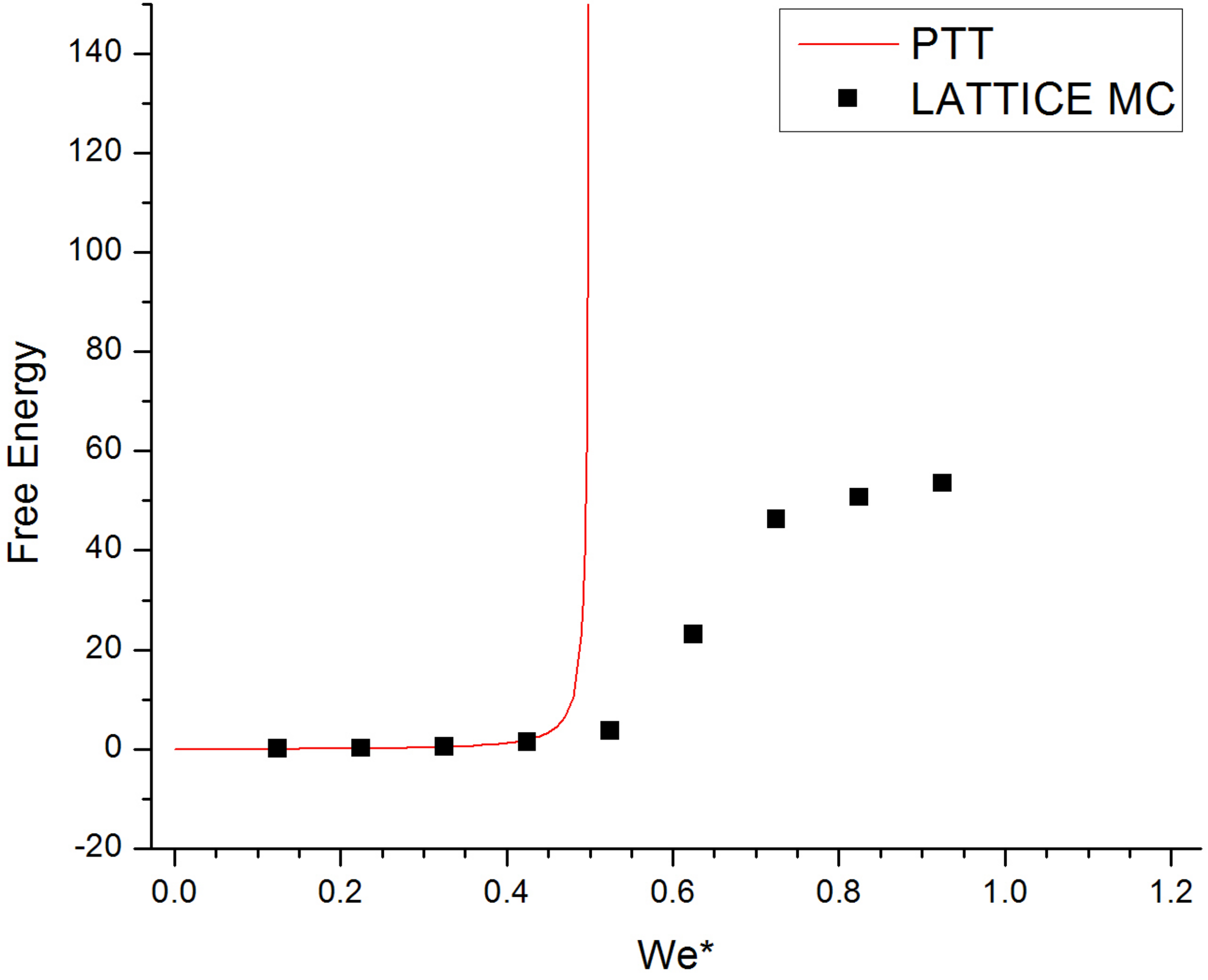
For N_e segment chain, $n = N_e$, we have

$$\therefore \frac{\delta A^*}{\delta \underline{\underline{\mathbf{c}}}^*} : \langle \underline{\mathbf{R}}\,\underline{\mathbf{R}} \rangle^* = 1.845 \times We^* \left(\frac{1}{N_e^2} \sum_{\text{all possible multisegment selections of length } N_e} \left(R_z^2 - \frac{R_x^2 + R_y^2}{2} \right) \right)$$

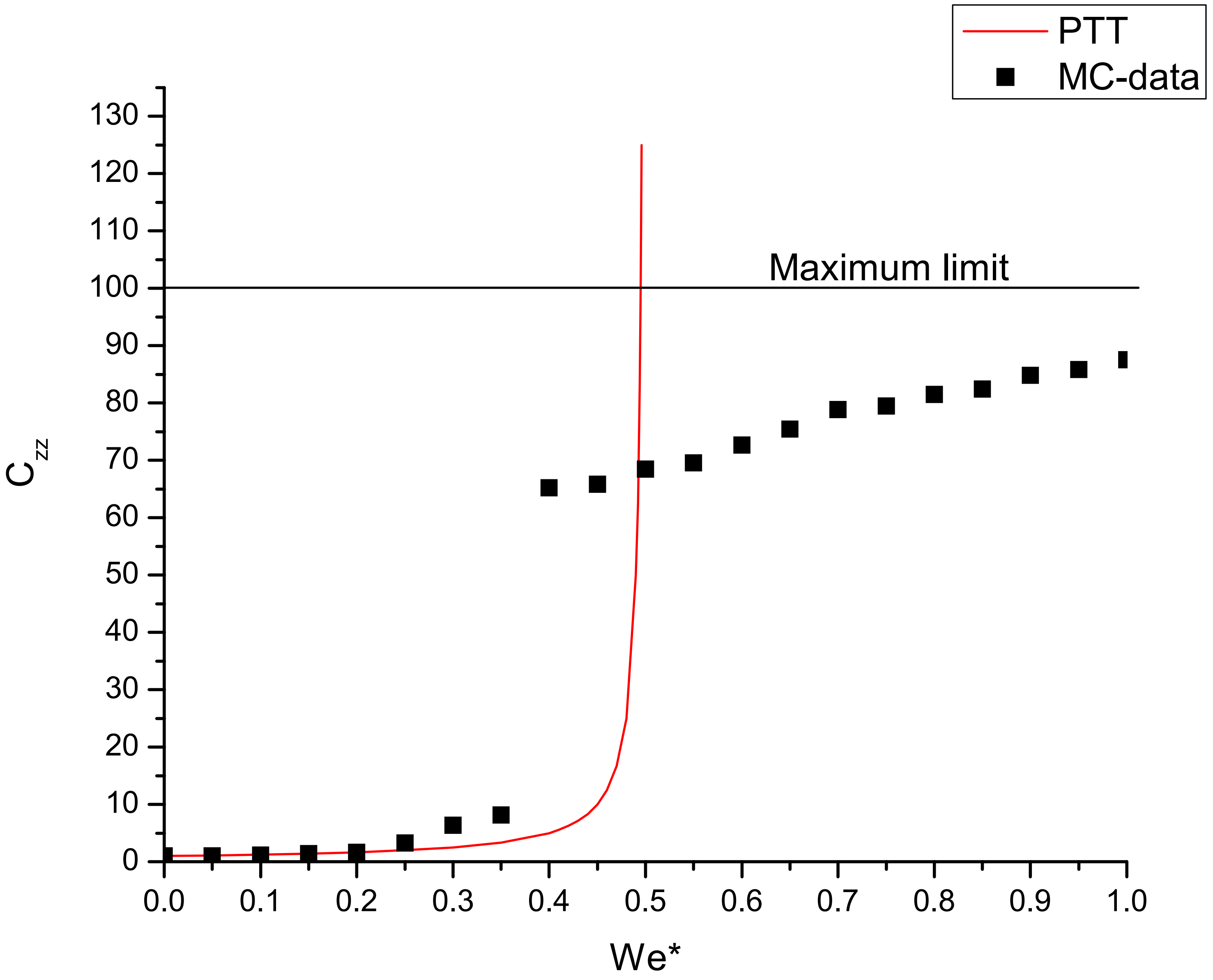
Consistency at low We* between Microscopic and PTT Models



Serious Qualitative Inconsistency at higher We*



Inconsistencies in C_{zz} at high We^* between PTT and MC



Modified FENE-P/PTT Model

Constitutive equation

$$\breve{\underline{\underline{\mathbf{c}}}}^* = -\frac{1}{\lambda(\underline{\underline{\mathbf{c}}}^*)}\left(f\underline{\underline{\mathbf{c}}}^* - \underline{\underline{\mathbf{1}}}\right); \qquad f = \frac{L^2-3}{L^2-\mathrm{tr}\underline{\underline{\mathbf{c}}}^*}$$

$$\underline{\underline{\boldsymbol{\sigma}}} = G_0\left(f\underline{\underline{\mathbf{c}}}^* - 1\right)$$

L - extensibility parameter

λ - relaxation time

G_0 - elastic modulus

- Internal structure dependent relaxation time

$$\frac{1}{\lambda(\underline{\underline{\mathbf{c}}}^*)} = \frac{1}{\lambda_0}\exp\left(\alpha(\mathrm{tr}(\underline{\underline{\mathbf{c}}}^*)-3)\right)$$

λ_0 - zero shear rate relaxation time

$\alpha \sim 0.05$ for PE

Non-equilibrium thermodynamic information

$$A^* = \frac{M}{2}\left[(L^2-3)\log(f(\underline{\underline{\mathbf{c}}}^*)) - \log\left(\det\left(\underline{\underline{\mathbf{c}}}^*\right)\right)\right] \equiv Ma_f^*$$

$$\frac{\delta A^*}{\delta\underline{\underline{\mathbf{c}}}^*} = \frac{M}{2}\left(f\left(\underline{\underline{\mathbf{c}}}^*\right)\underline{\underline{\mathrm{I}}} - \left(\underline{\underline{\mathbf{c}}}^*\right)^{-1}\right)$$

A^*- free energy of the system (non-dimensionalized by k_BT)

M- total number of entanglements in the system

Uniaxial Extensional flow for FENE-P/PTT

Solve the equations for uniaxial extensional flow at steady state

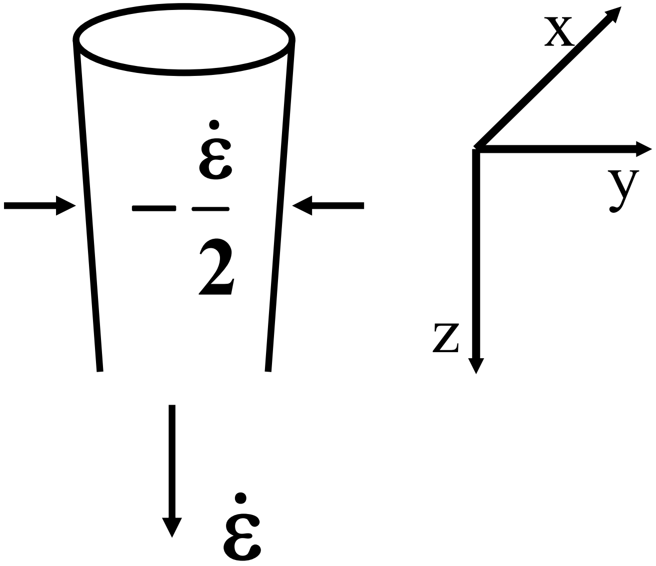
Diagonal Conformation tensor

$$\underline{\underline{\mathbf{c}}}^* = \begin{bmatrix} c_{xx}^* & 0 & 0 \\ 0 & c_{xx}^* = c_{yy}^* & 0 \\ 0 & 0 & c_{zz}^* \end{bmatrix}$$

$$c_{xx}^* = \frac{1}{f + We^*} \text{ and } c_{zz}^* = \frac{1}{f - 2We^*},$$

$$\text{where, } We^* \text{ is unrestricted!}$$

$$We^* \text{is the } \underline{\text{Weissenberg number}} = \frac{\lambda(\underline{\underline{\mathbf{c}}}^*)}{\dot{\varepsilon}^{-1}}$$



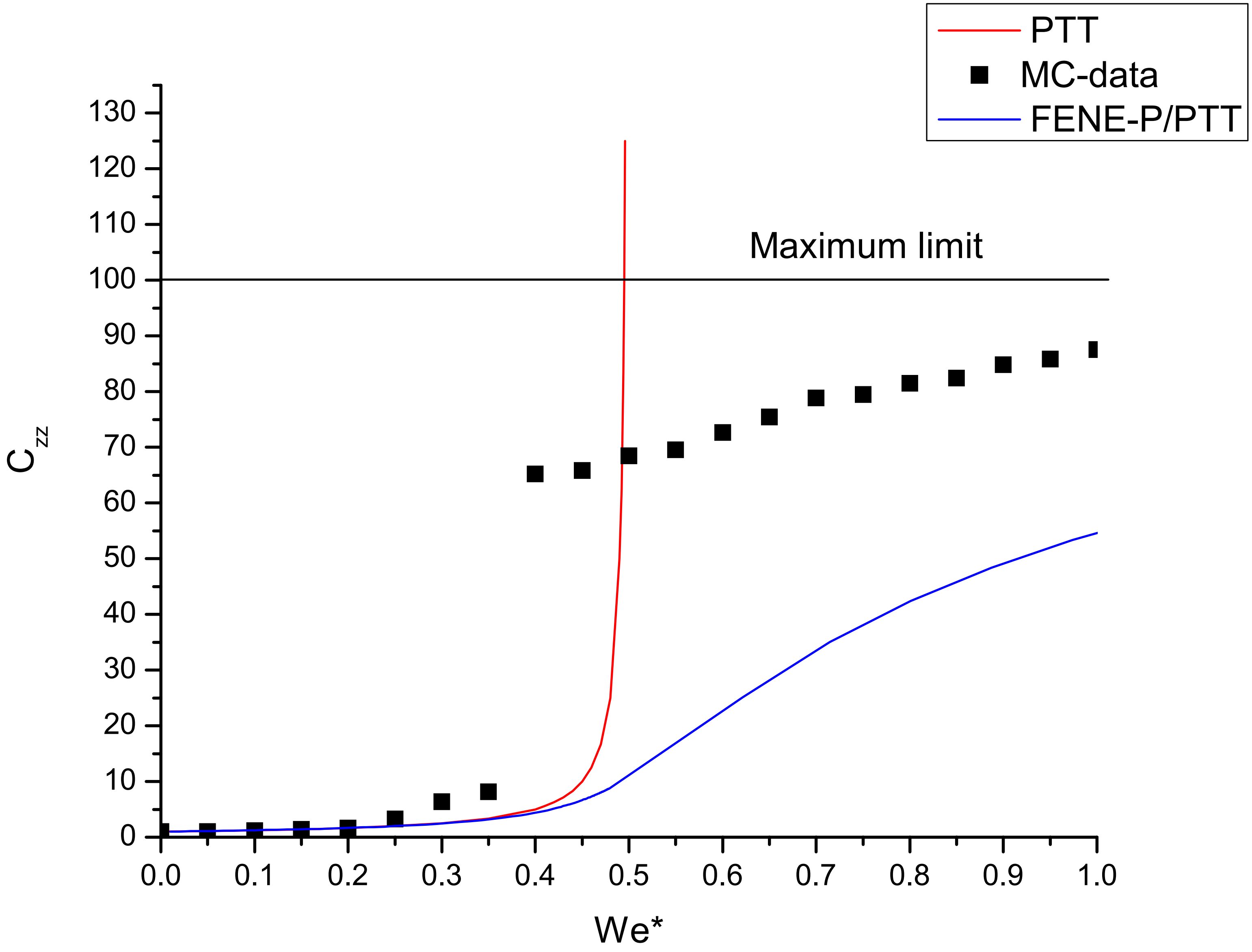
Same Non-equilibrium thermodynamic potentials as before!

$$\frac{\delta A^*}{\delta c_{xx}^*} = \frac{\delta A^*}{\delta c_{yy}^*} = -\frac{M}{2} We^*; \quad \frac{\delta A^*}{\delta c_{zz}^*} = M We^*$$

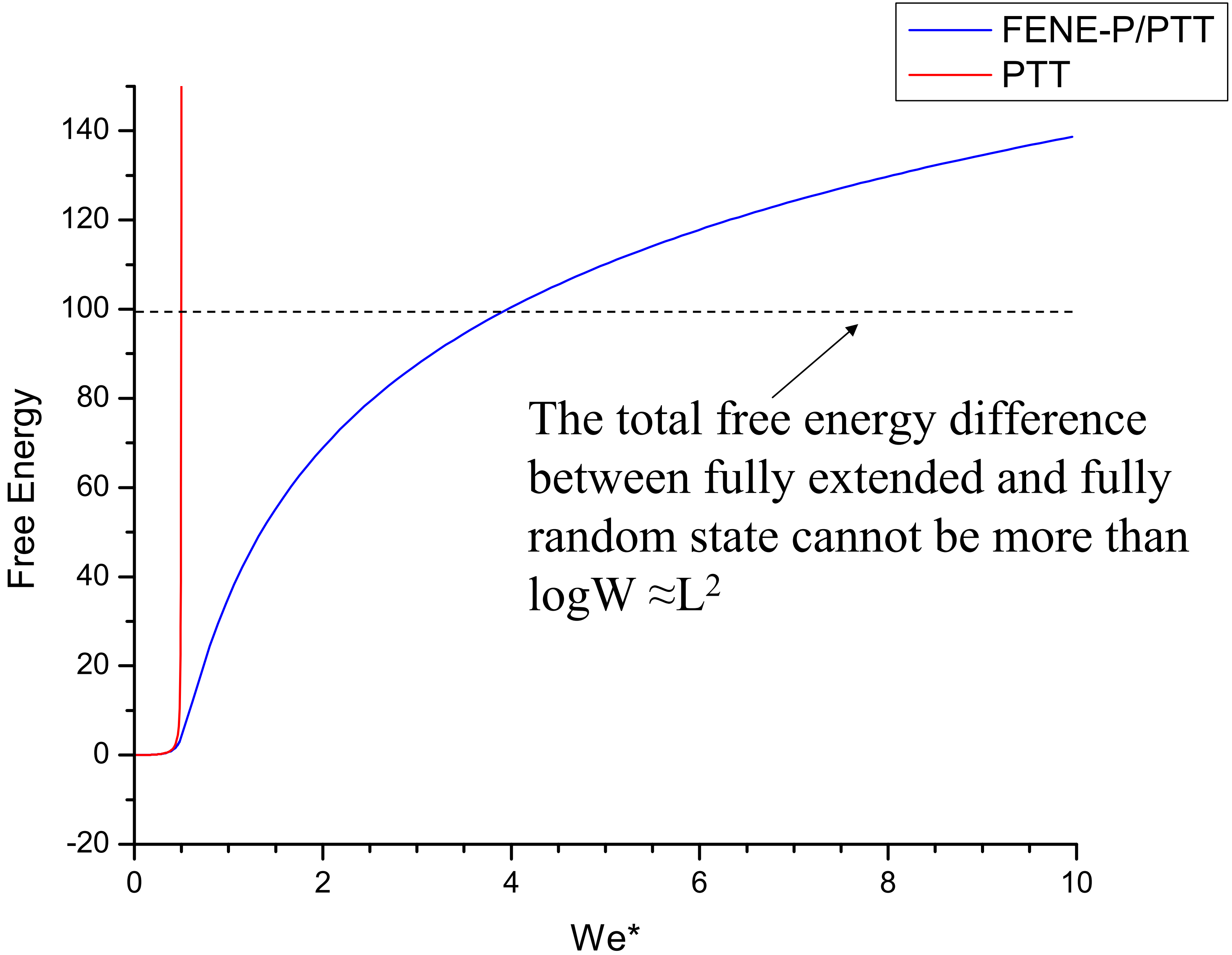
→ **Macro-micro bridges**

This model is also compatible to the same microscopic simulations!

Comparison between FENE-P/PTT, PTT and MC



Inconsistencies in the free energy



The total free energy difference between fully extended and fully random state cannot be more than $\log W \approx L^2$

Bounded Free Energy FENE-PB/PTT Model

Constitutive equation

$$\breve{\underline{\underline{\mathbf{c}}}}^* = -\frac{B}{\lambda(\underline{\underline{\mathbf{c}}}^*)}\left(f\underline{\underline{\mathbf{c}}}^* - \underline{\underline{\mathbf{1}}}\right); \qquad f = \frac{L^2 - 3}{L^2 - \mathrm{tr}\,\underline{\underline{\mathbf{c}}}^*}$$

$$\underline{\underline{\boldsymbol{\sigma}}} = G_0 B\left(f\underline{\underline{\mathbf{c}}}^* - 1\right); \qquad B = \left(\frac{L^2}{a_f^* + L^2}\right)^2$$

L - extensibility parameter

λ - relaxation time

G_0 - elastic modulus

- Internal structure dependent relaxation time

$$\frac{1}{\lambda(\underline{\underline{\mathbf{c}}}^*)} = \frac{1}{\lambda_0}\exp\left(\alpha(\mathrm{tr}(\underline{\underline{\mathbf{c}}}^*) - 3)\right)$$

λ_0 - zero shear rate relaxation time

$\alpha \sim 0.05$ for PE

Non-equilibrium thermodynamic information

$$A^* = M\left[{(L^2 a_f^*)}\big/{(L^2 + a_f^*)}\right]$$

$$\frac{\delta A^*}{\delta \underline{\underline{\mathbf{c}}}^*} = \frac{M}{2}B\left(f\left(\underline{\underline{\mathbf{c}}}^*\right)\underline{\underline{\mathbf{I}}} - \left(\underline{\underline{\mathbf{c}}}^*\right)^{-1}\right)$$

A^*- free energy of the system (non-dimensionalized by $k_B T$)

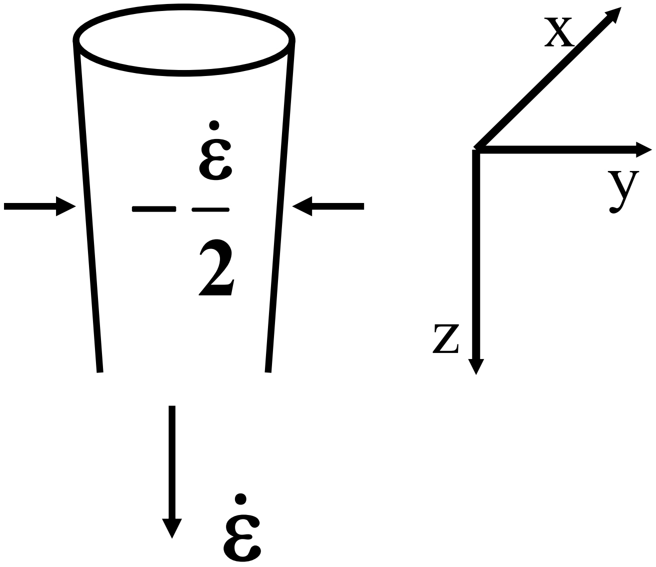
M- total number of entanglements in the system

Uniaxial Extensional flow for FENE-PB/PTT

Solve the equations for uniaxial extensional flow at steady state

Diagonal Conformation tensor

$$\underline{\underline{\mathbf{c}}}^* = \begin{bmatrix} c^*_{xx} & 0 & 0 \\ 0 & c^*_{xx} = c^*_{yy} & 0 \\ 0 & 0 & c^*_{zz} \end{bmatrix}$$



$$c^*_{xx} = \frac{B}{Bf + We^*} \text{ and } c^*_{zz} = \frac{B}{Bf - 2We^*},$$

where, We^* is (as before) unrestricted!

We^* is the Weissenberg number $= \dfrac{\lambda(\underline{\underline{\mathbf{c}}}^*)}{\dot{\varepsilon}^{-1}}$

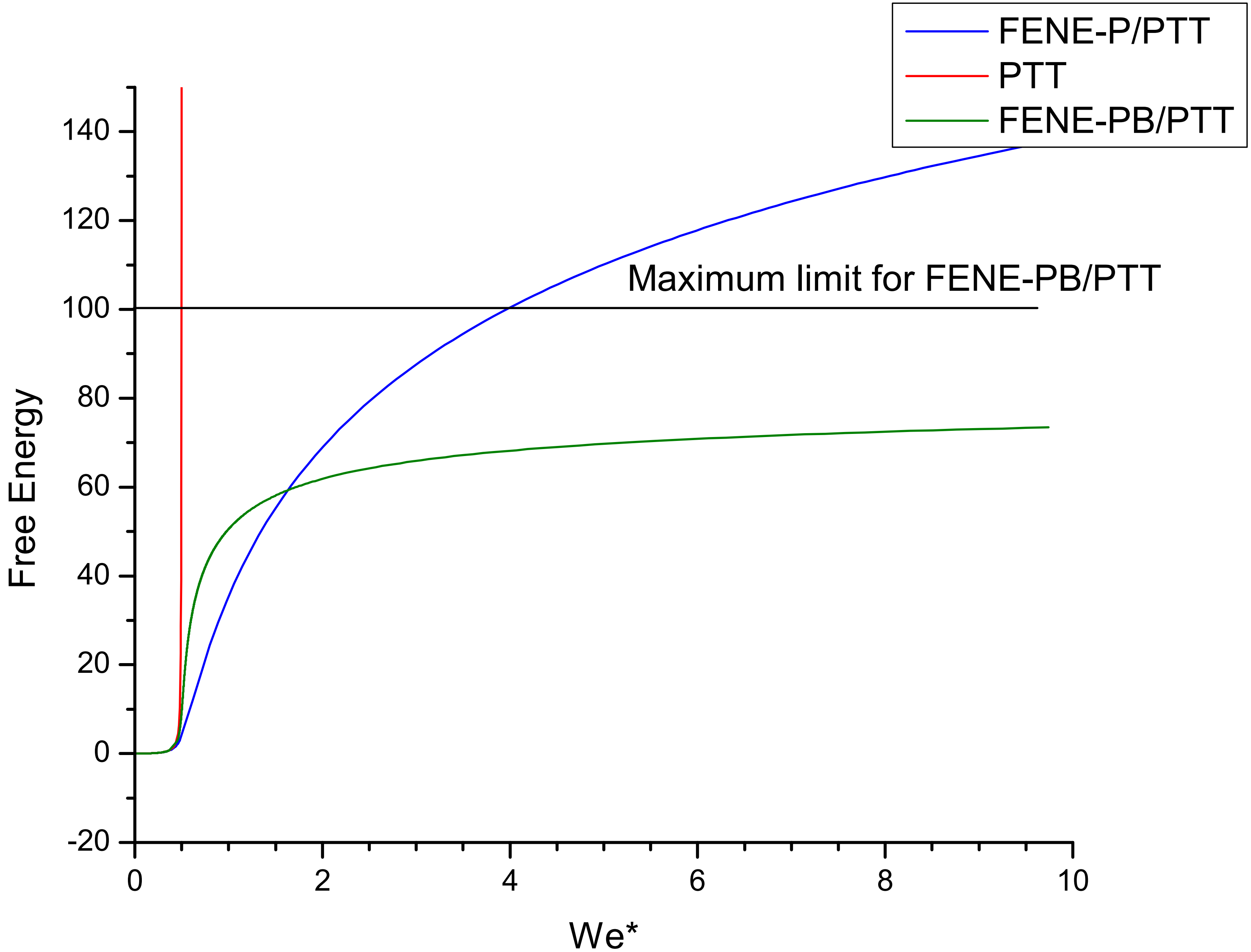
Same Non-equilibrium thermodynamic potentials as before!

$$\frac{\delta A^*}{\delta c^*_{xx}} = \frac{\delta A^*}{\delta c^*_{yy}} = -\frac{M}{2} We^*; \quad \frac{\delta A^*}{\delta c^*_{zz}} = M We^*$$

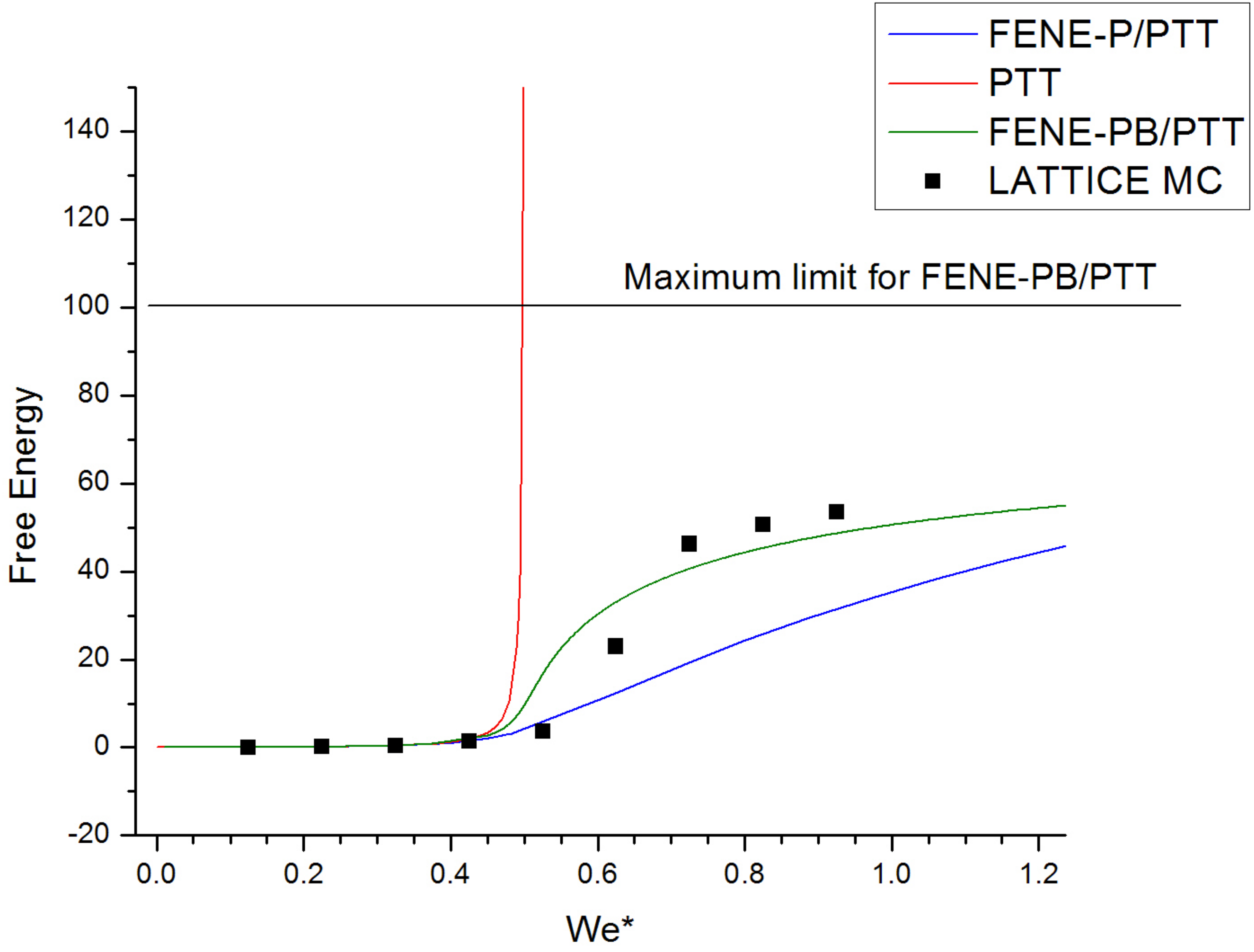
→ **Macro-micro bridges**

The microscopic simulations are also compatible to this model!

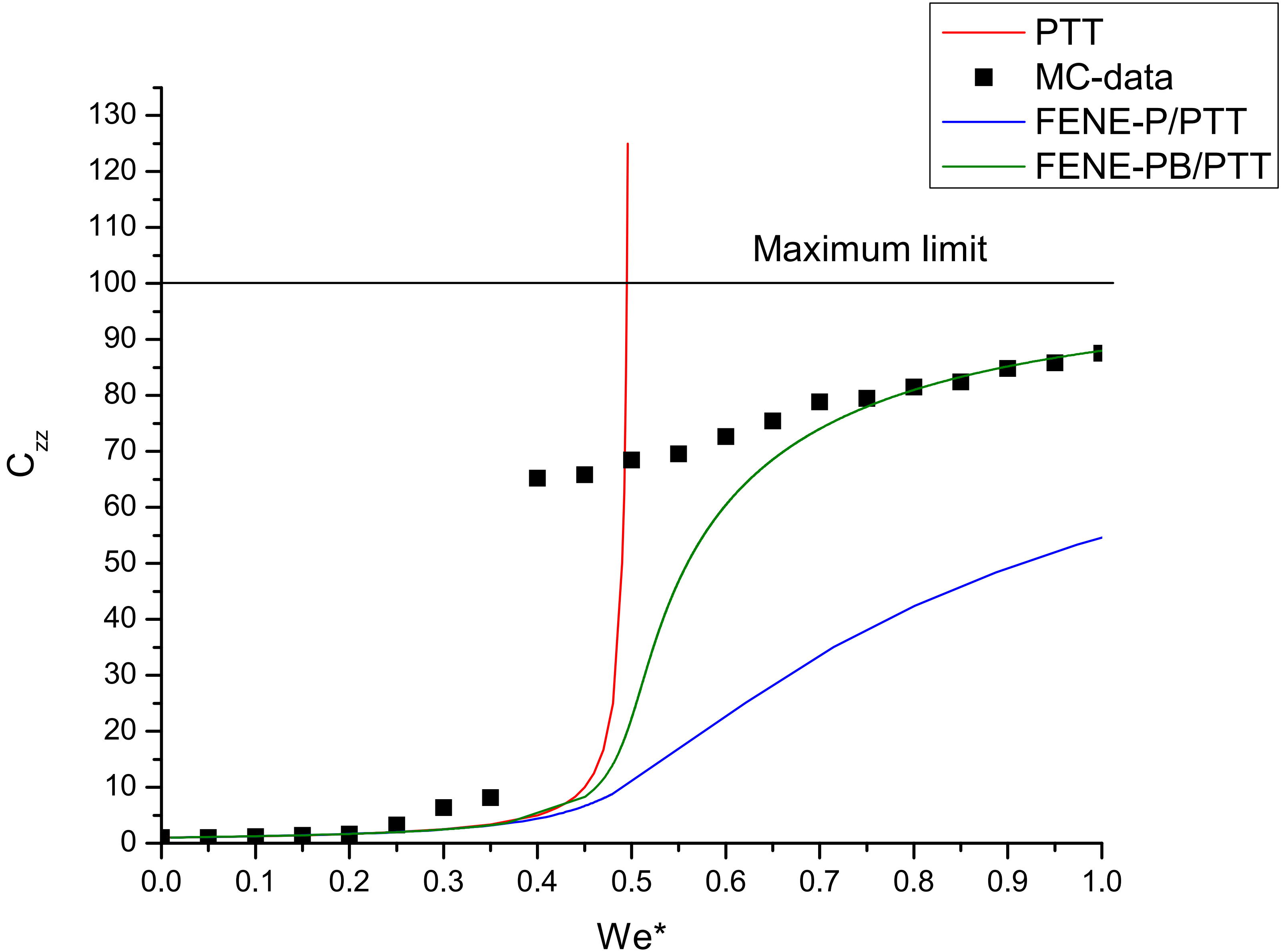
FENE-PB/PTT has always a finite free energy



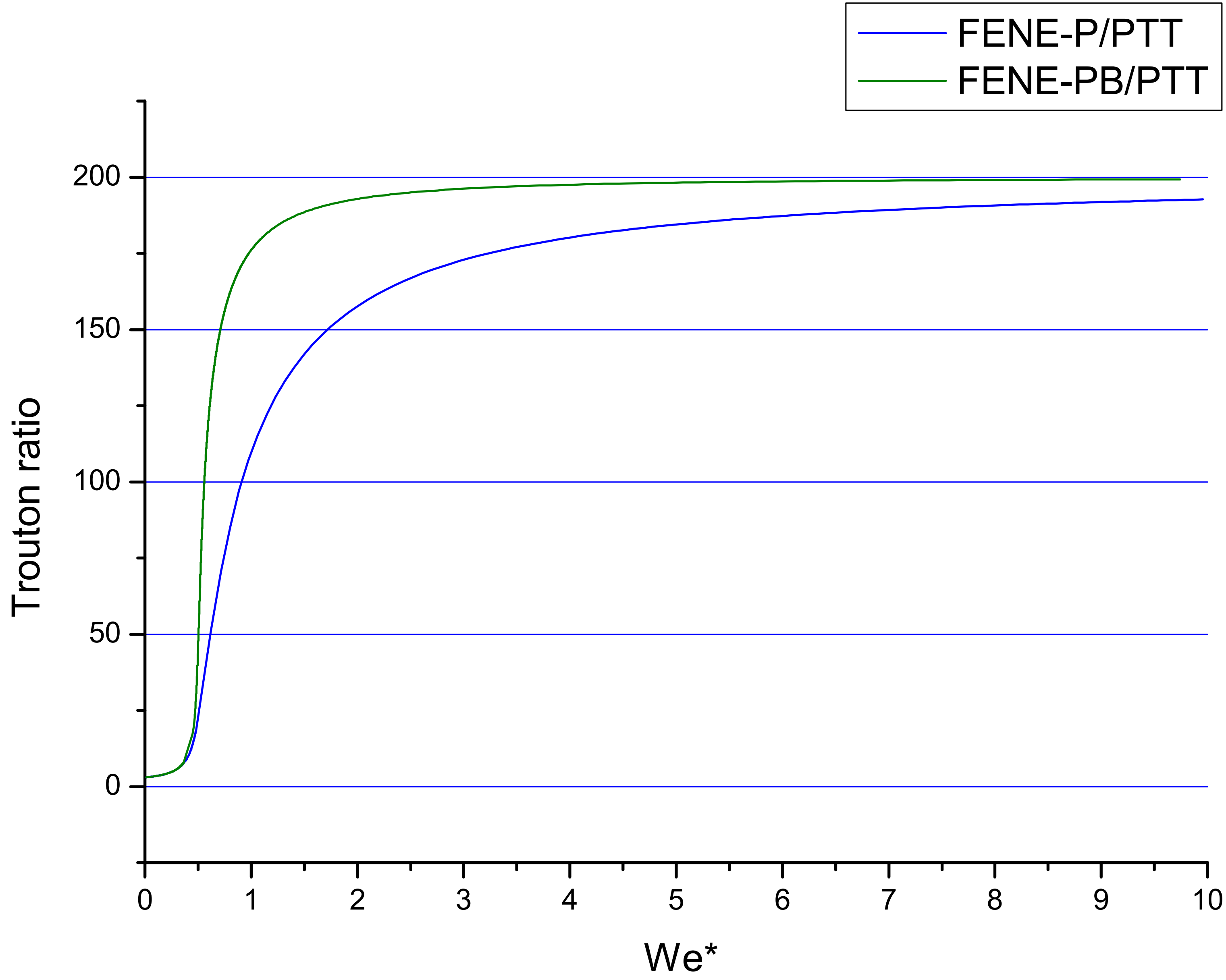
There is good agreement between FENE-PB/PTT and MC



There is also consistency in C_{zz} between FENE-PB/PTT and MC



Extensional viscosity properties of the modified models are also realistic



Conclusions

- Efficient 3-D lattice-subdivision based Monte Carlo simulations have enabled us to check for microscopic consistency various continuum viscoelastic models for dense linear polymer models.

- Previous models have shown to be defective at high levels of molecular extension. A new phenomenological model has been developed (FENE-PB/PTT) that is consistent to finite levels on both the molecular extension and the total free energy.

- Preliminary results show that the new model captures well the sudden changes accompanying the coil-to-stretch transition at high extensions.

Acknowledgements

Dr. Joydeep Mukherjee

Dr. Stevan Wilson

Randy Oswald

Brian Snyder

Funding:

- NSF GOALI (Materials processing and manufacturing division).

- Dupont-Nylon

Evaluating Microscopic Thermodynamic Information

$A^*(E_\eta, We^*)$ can be evaluated incrementally close to static equilibrium as:

$$A^*(E_\eta, We^*) = \underbrace{A^*(E_\eta, We^* = 0)}_{\text{Equilibrium}} + \int_0^{We^*} \frac{\partial A^*(E_\eta, We^*)}{\partial We^*} \, dWe^*$$

Now we calculate $\frac{\partial A^*}{\partial We^*}$ from the relationship of A^* with $A^*_{\text{expanded}} = A^* - \frac{\partial A^*}{\partial \mathbf{c}^*} : \mathbf{c}^*$ and the fact that in the MC we calculate $A^*_{\text{expanded}} = -\log Z = -\log\left(\sum_{\text{i-microstate}} \exp\left(\frac{\delta A^*}{\delta \underline{\underline{c}}^*} :< \underline{R}\,\underline{R} >_i^* \right)\right)$

$$\text{==>} \qquad \frac{\partial A^*}{\partial We^*} = \frac{\partial}{\partial We^*}\left(A^*_{\text{expanded}} + \frac{\partial A^*}{\partial \mathbf{c}^*} :< \mathbf{RR} >^* \right) =$$

$$-\frac{\partial}{\partial We^*}\left(\frac{\partial A^*}{\partial \mathbf{c}^*}\right) :< \mathbf{RR} >^* + \frac{\partial}{\partial We^*}\left(\frac{\partial A^*}{\partial \mathbf{c}^*}\right) :< \mathbf{RR} >^* + \frac{\partial A^*}{\partial \mathbf{c}^*} : \frac{\partial}{\partial We^*} < \mathbf{RR} >^* =$$

$$\frac{\partial A^*}{\partial \mathbf{c}^*} : \frac{\partial}{\partial We^*} < \mathbf{RR} >^*$$