Molecular models for polymer rheology

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Zero-shear viscosity of linear polymer melts

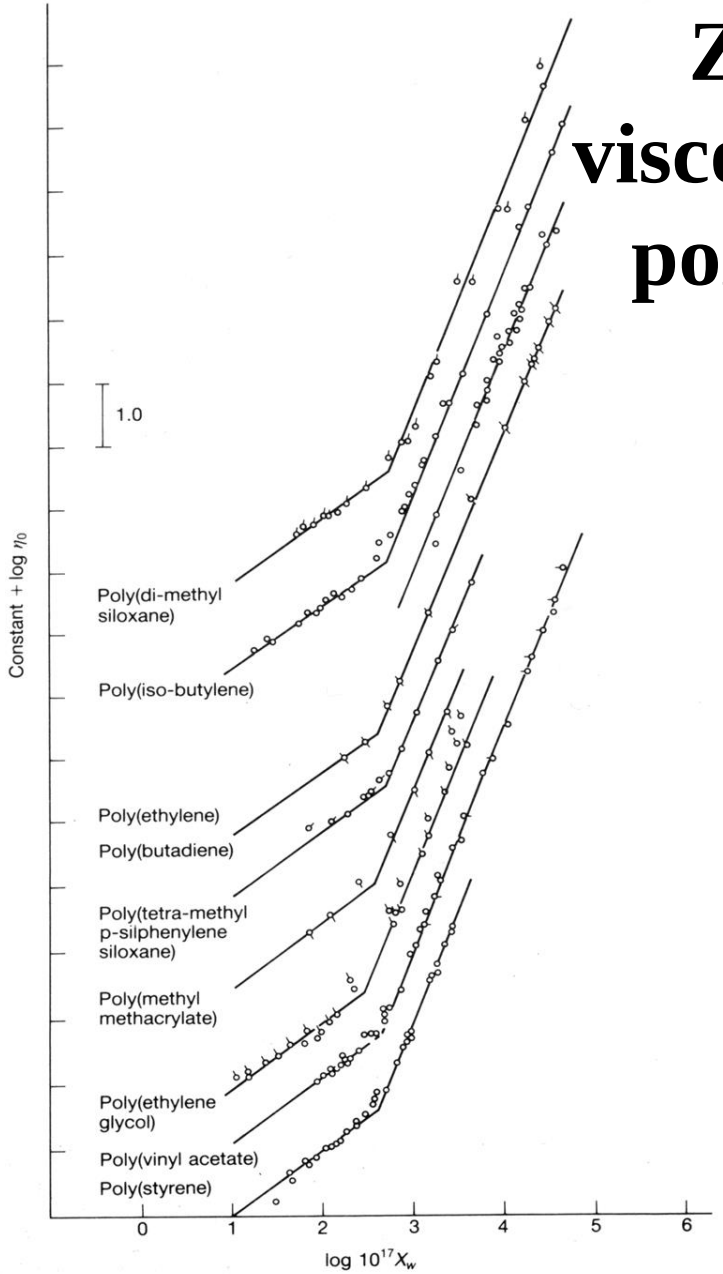
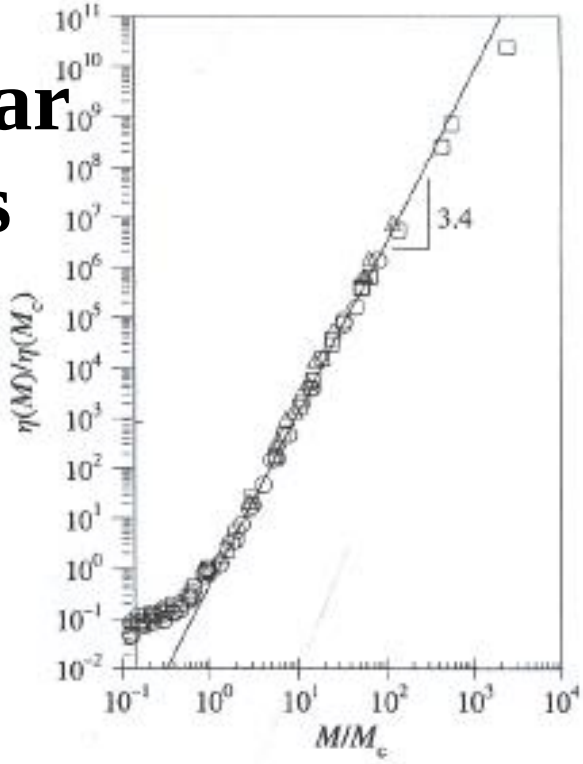


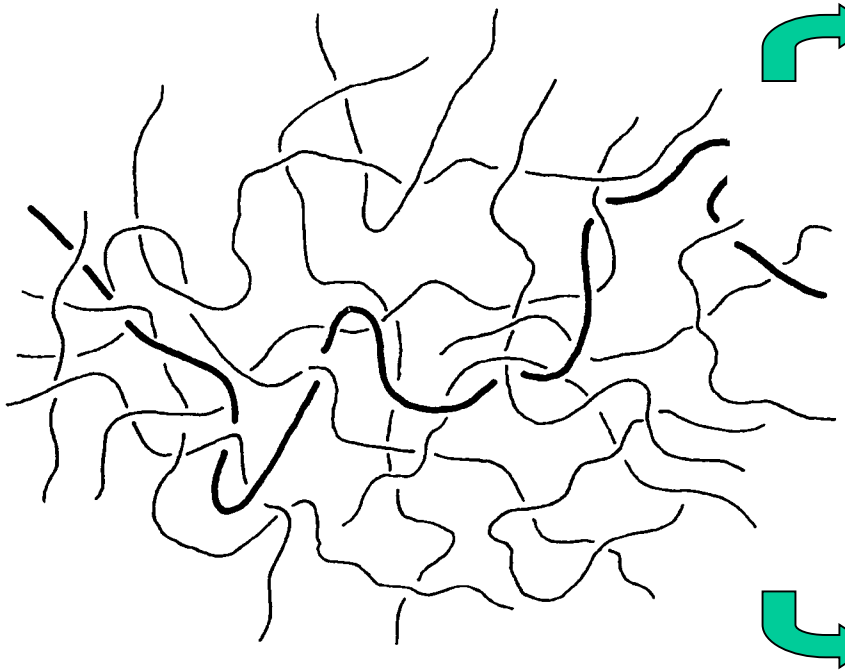
Fig. 7.6. Steady-state viscosity of various polymers in melt, where X_w is a parameter proportional to M_w. The curves are shifted vertically so as not to overlap each other. Reproduced from ref. 33.

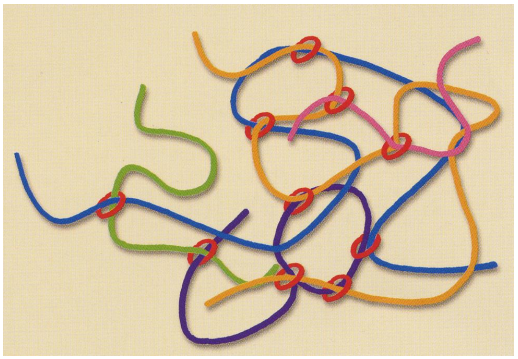


Molar mass dependence of viscosity for polymer melts reduced by their critical molar mass. Open circles are polyisobutylene with $M_c = 14\,000\ \mathrm{g\,mol^{-1}}$, from T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.* **70**, 2384 (1948) and *J. Phys. Chem.* **55**, 221 (1951). Open squares are polybutadiene with $M_c = 6700\ \mathrm{g\,mol^{-1}}$, from R. H. Colby *et al.*, *Macromolecules* **20**, 2226 (1987). Open triangles are hydrogenated polybutadiene with $M_c = 8100\ \mathrm{g\,mol^{-1}}$, from D. S. Pearson *et al.*, *Macromolecules* **27**, 711 (1994).

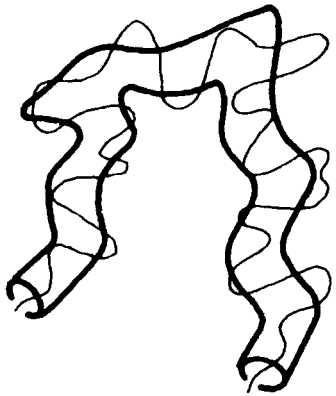
Polymers with entanglements

(melts or solutions)



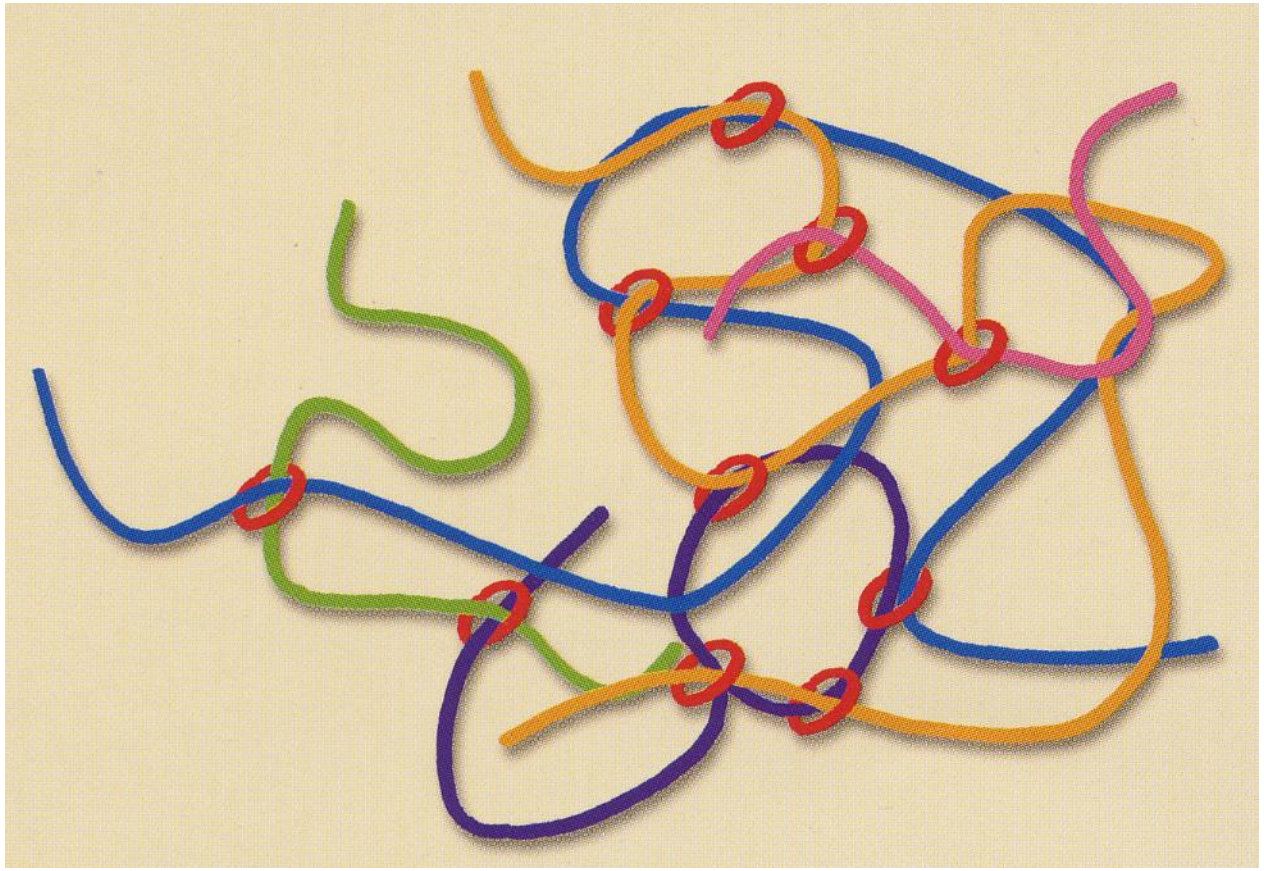


Many-chain simulations



Single-chain models

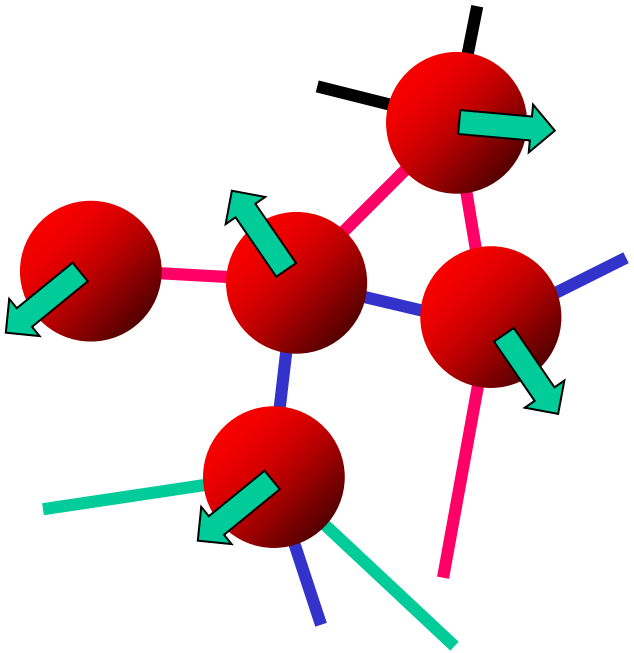
3D sliplink model



Primitive Chain Network Model

J. Chem. Phys 2001, …, *Macromolecules 2012*

Coarse-graining at $M_e \sim M_c$ level



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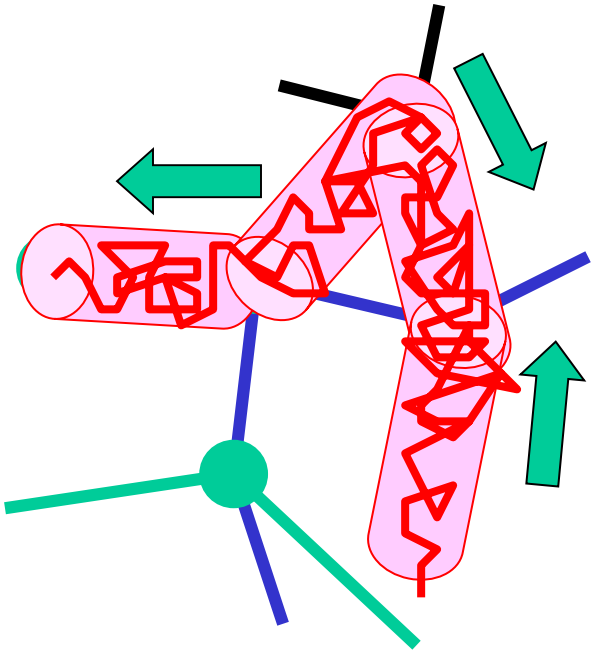


3D motion of nodes

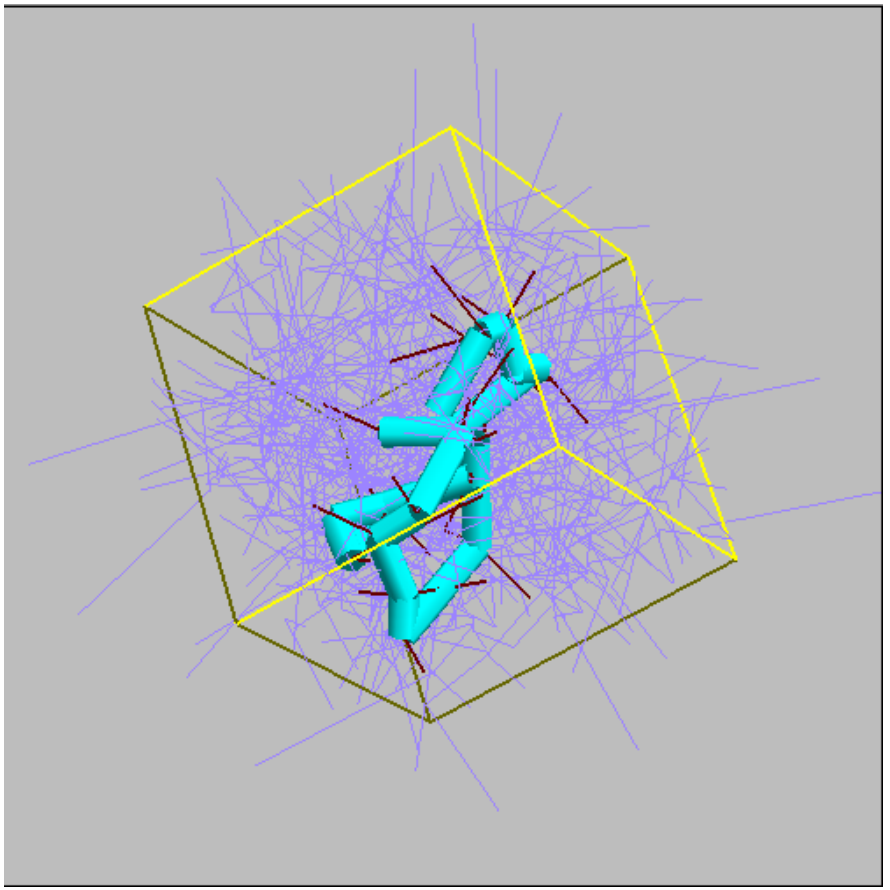
1D monomer sliding inside tube

Code: NAPLES

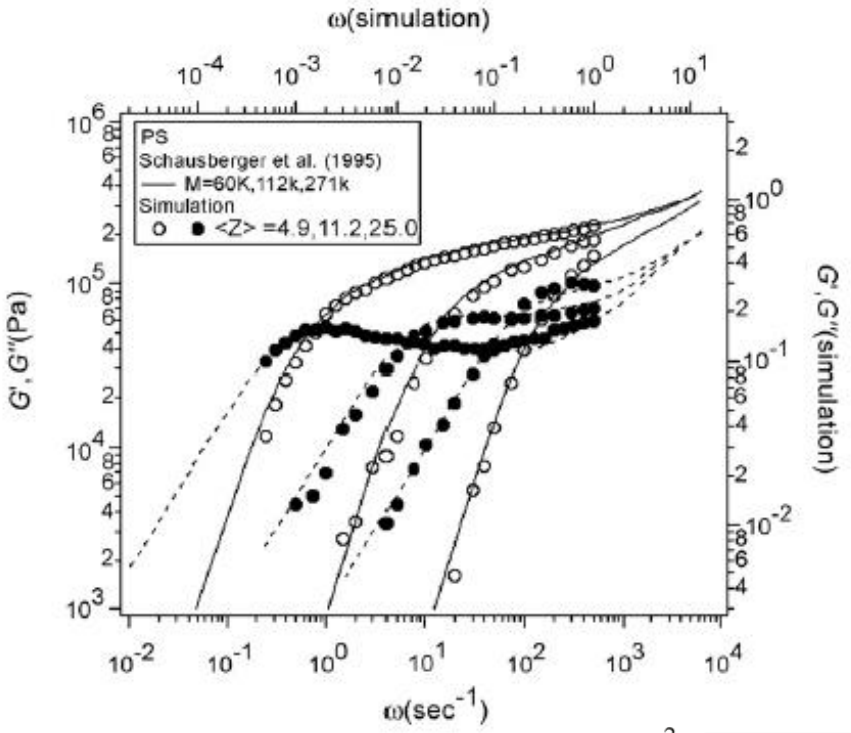
(New Algorithm for Polymeric Liquids Entangled and Strained)

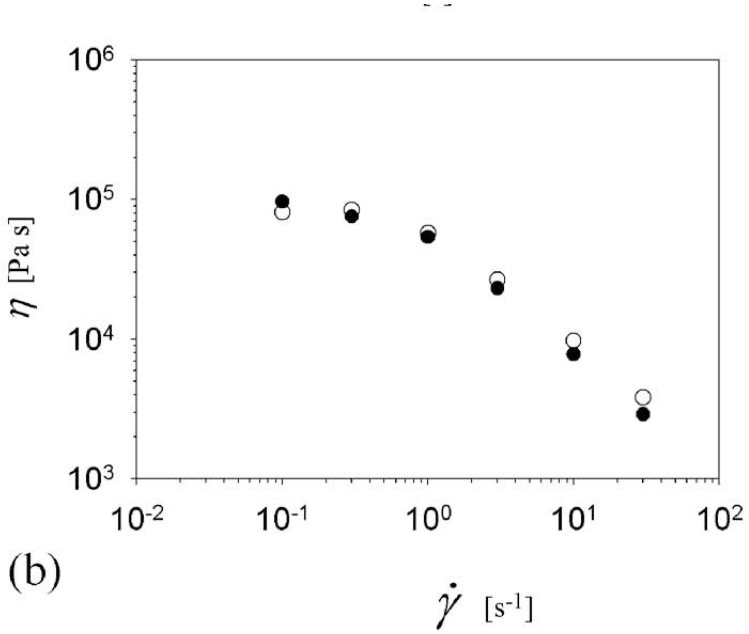
Z=10
(corresponding to PS of M~70,000)

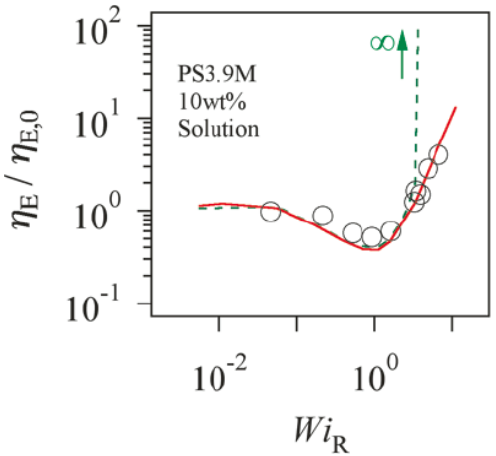
Number of molecules 512

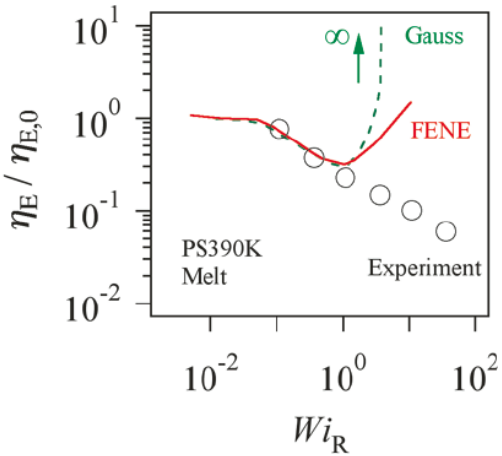


Typical results for PS





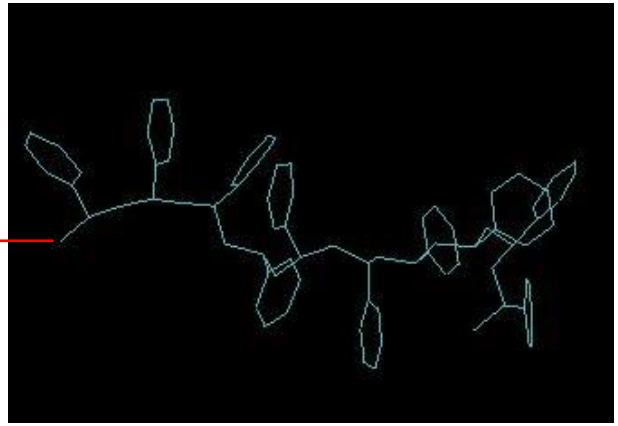




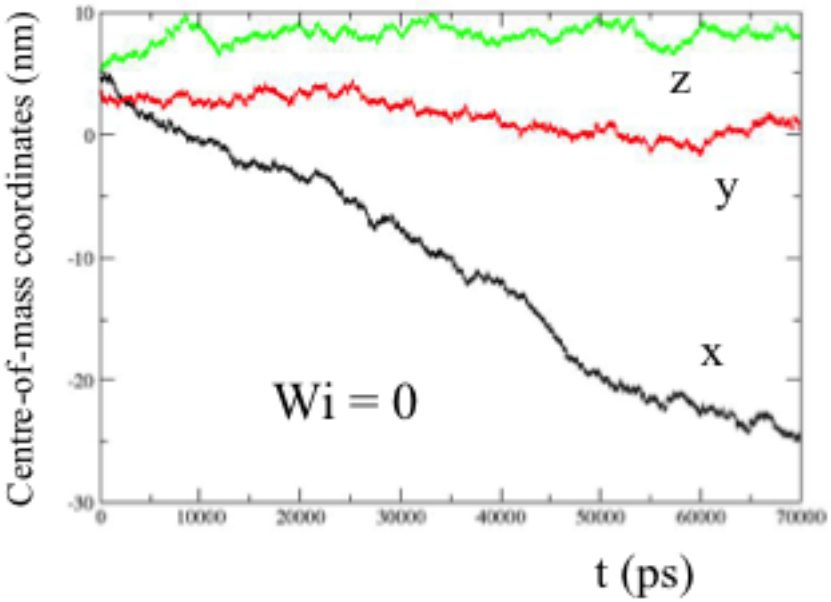
Flow-induced friction change

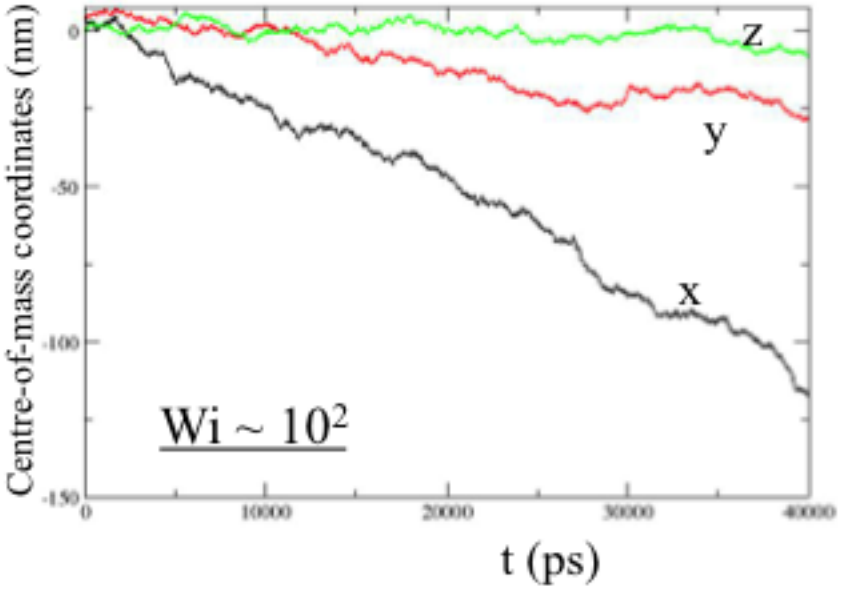
Molecular Dynamics

F_x



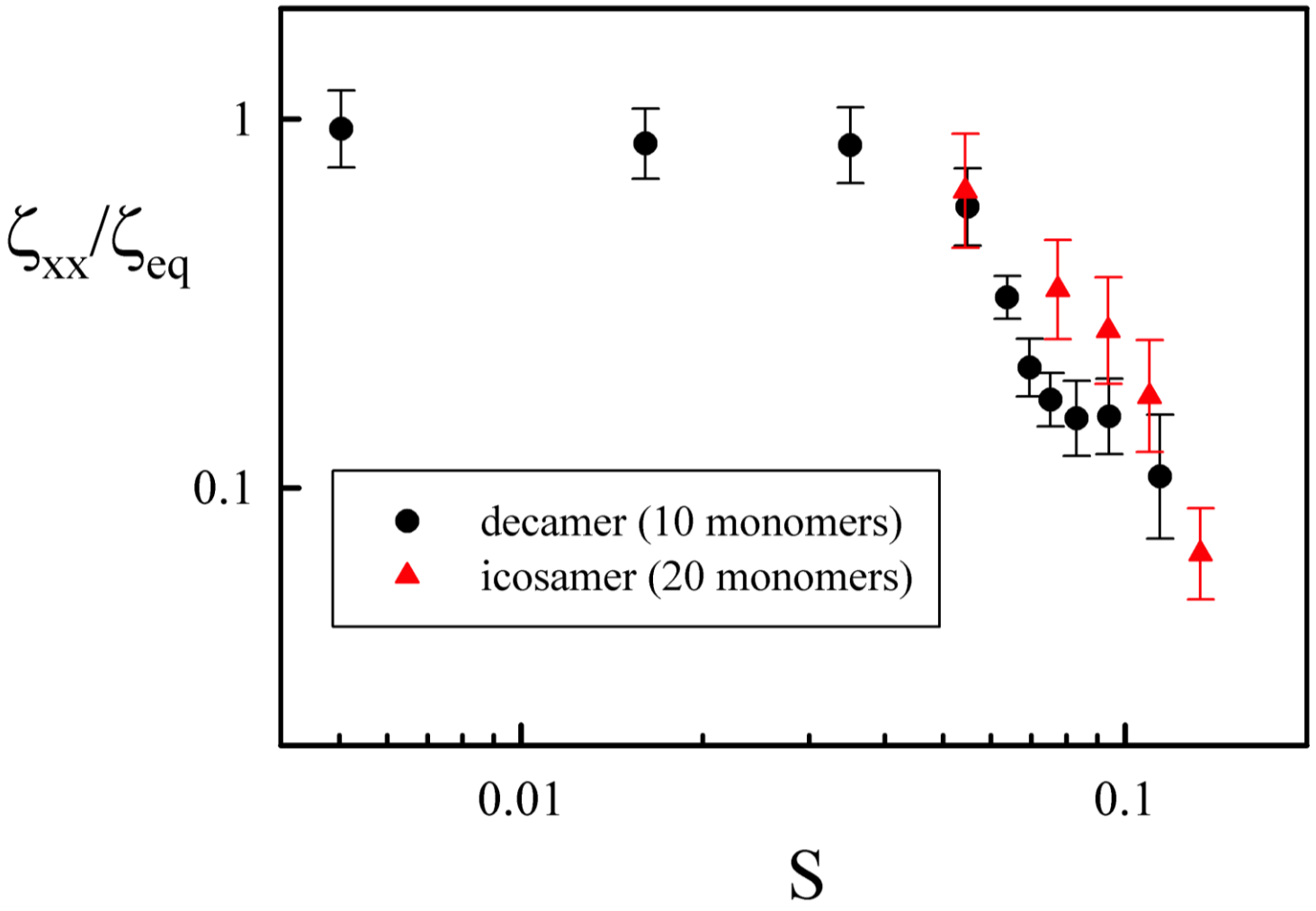
PS decamer



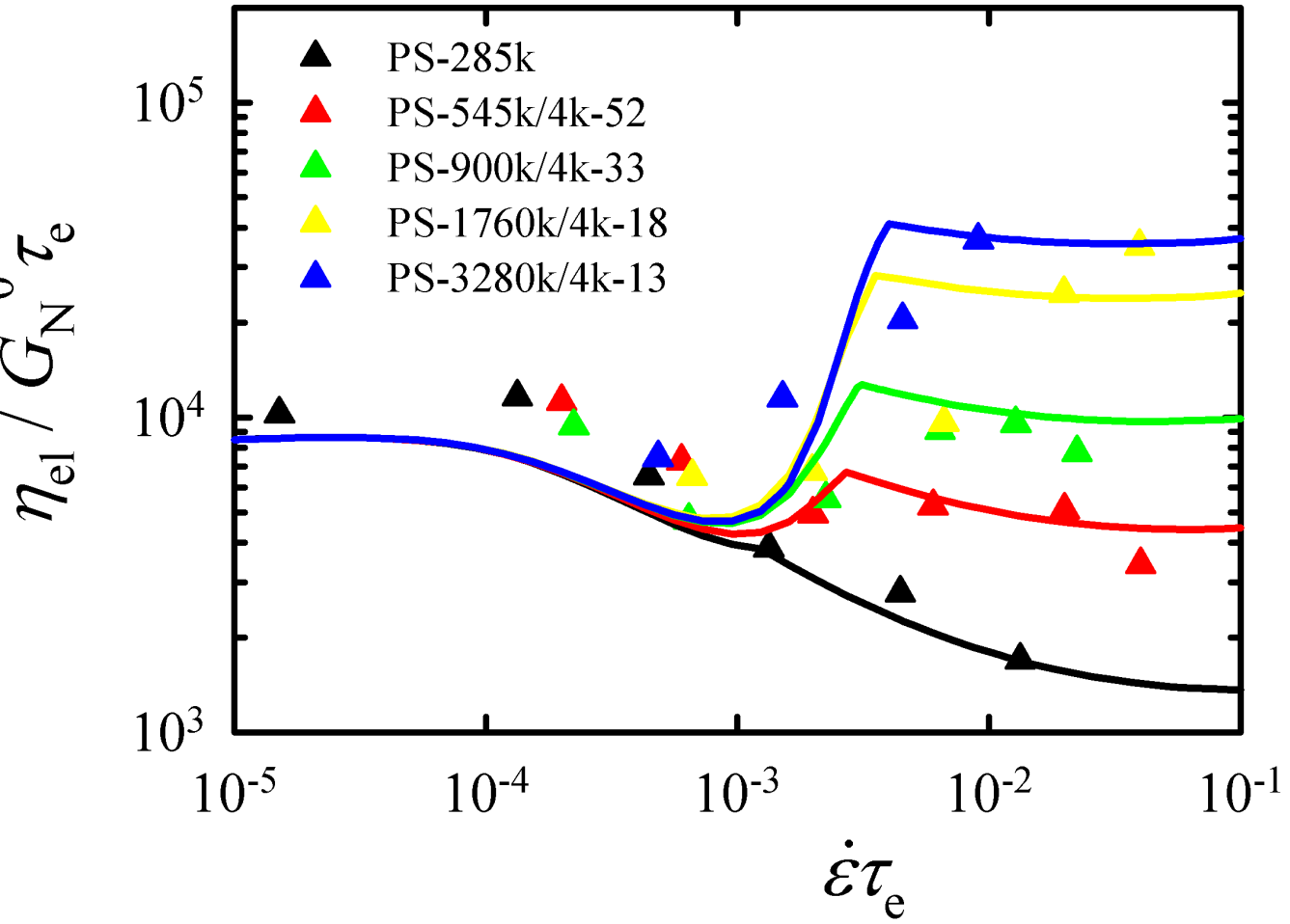


The average slope gives the velocity, and the friction coefficient is the ratio force/velocity

NEMD results



Single-chain model predictions with friction reduction



Friction reduction effects become increasingly dominant with increasing polymer concentration.

A new stochastic simulation for the rheology of telechelic associating polymers

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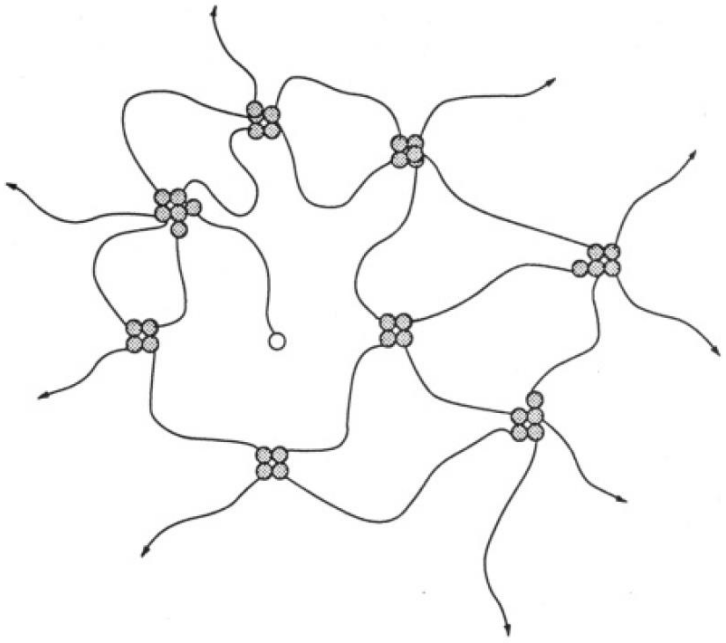
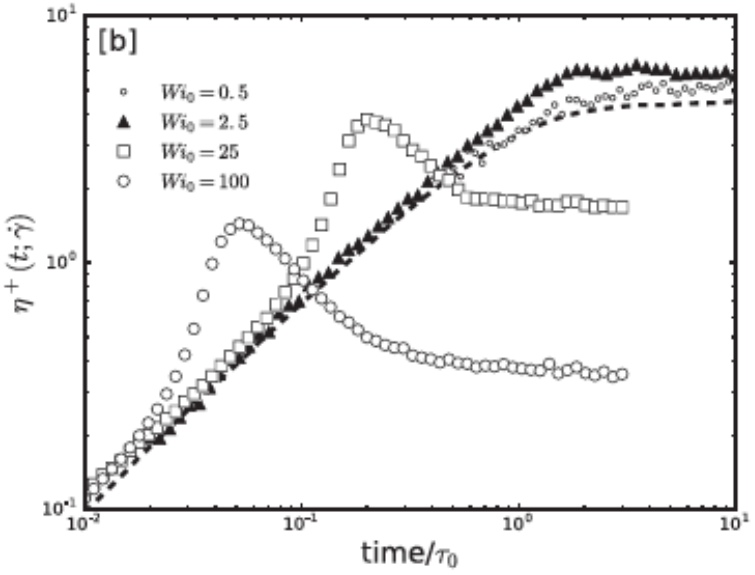
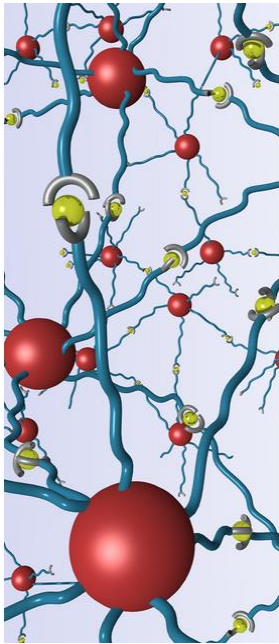
Abstract

We here suggest a new Brownian dynamics algorithm for telechelic associating polymers with the aim of better understanding the complex rheological behavior of these systems and in particular of hydrophobically modified ethoxylated urethane solutions showing strain hardening in shear startup and significant deviations from the Cox–Merz rule (including shear thickening phenomena). Several molecular mechanisms have indeed been suggested to explain such a complex behavior, ranging from finite extensible nonlinear elasticity (FENE) effects, shear-induced increased association, and, very recently, flow-induced repulsive interactions between colliding flower-like micelles. The preliminary results here reported (only exploring a limited range of the wide parameter space) appear to suggest that FENE effects are mostly responsible for strain hardening, while deviations from the Cox–Merz rule are due to the persistence of bridge chains, as well as, in some cases, to the flow-induced formation of new bridges. In the explored parameter space, no significant role appears to be played by flow-induced collisions between micelles beyond that of preventing network collapse.
[http://dx.doi.org/10.1122/1.4997592]

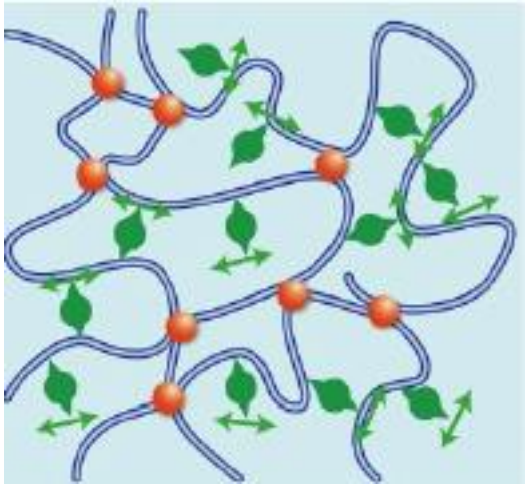




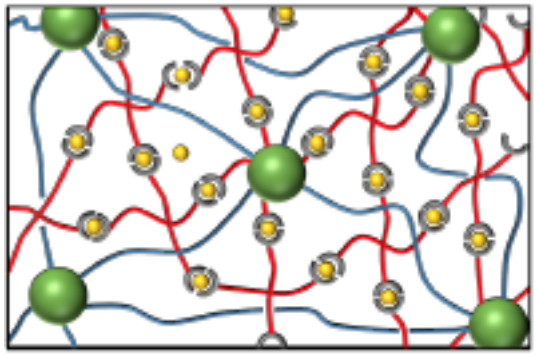


Modelling the nonlinear rheology of reversible DDNs

Single networks with dual crosslinks



Double networks



Here again we will resort to Brownian dynamics simulations of 3D networks