Basic principles of coarse-grained molecular simulations

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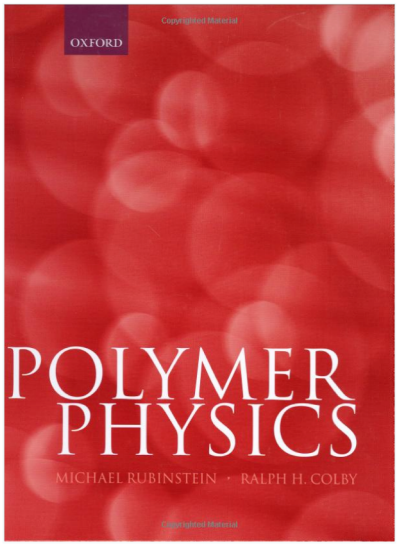
Computer simulations in polymer physics

(Colby and Rubinstein, 2003)



- «Simulations occupy an important intermediate position between theory and experiments»

- «They can provide valuable tests of assumptions and predictions of theoretical models as well as attempt to mimic experimental systems, such as polymer solutions, melts and networks»

The two main approaches

- **Molecular dynamics (MD)**

- **Monte Carlo (MC)**

MC

- Random sampling of different possible states

- Useful for equilibrium dynamics only, i.e., for linear rheology

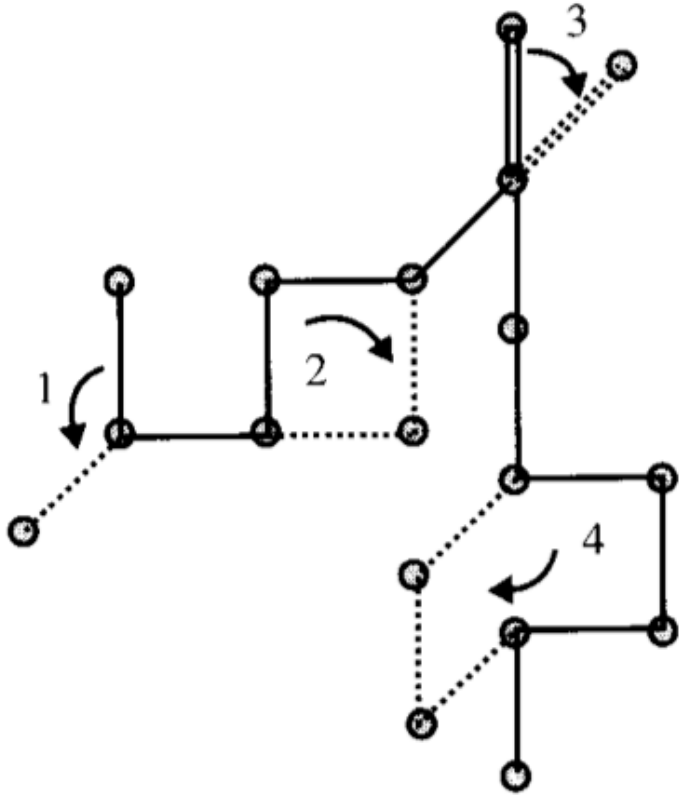
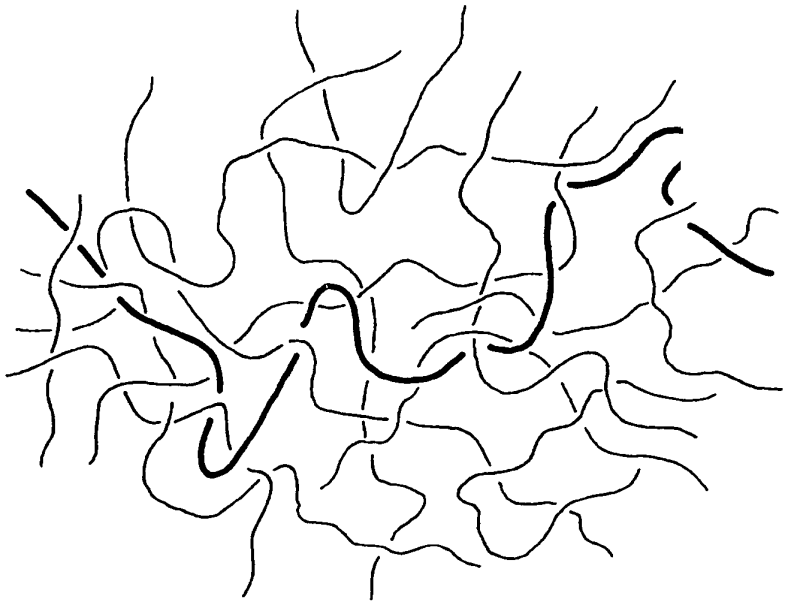


Fig. 9.31
Typical moves in a dynamic Monte Carlo simulation: (1) end flip, (2) corner move, (3) kink jump, and (4) crankshaft move. The solid lines are bonds in one of many possible configurations and the dotted lines are potential new bond positions.

MC for entangled polymers



Topological constraint due to chain uncrossability

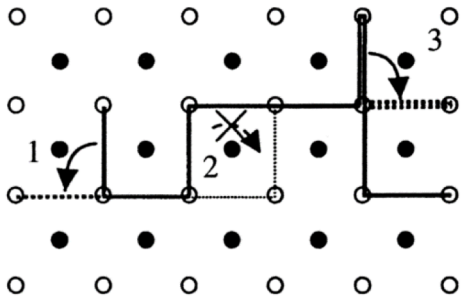
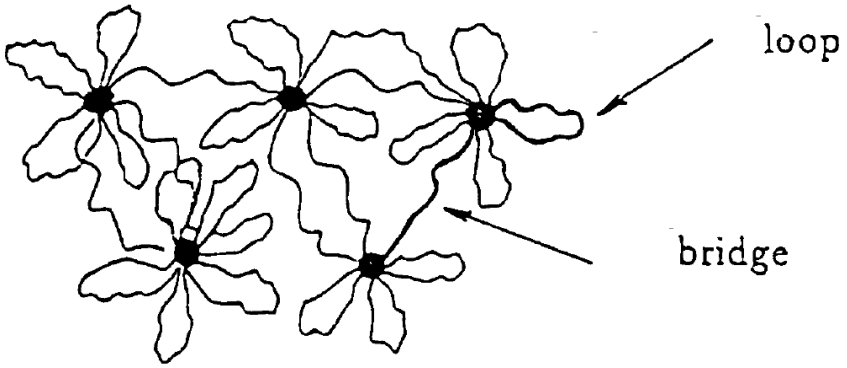


Fig. 9.32
Evans–Edwards model on a two-dimensional square lattice. Corner flips (move 2) cross obstacles and are forbidden. End flips (move 1) and kink flips (move 3) satisfy topological constraints and are allowed.

Not all moves are allowed

MC – network of telechelic polymers



- If states have different energies E, transition probability are proportional to the Boltzmann factor

$$P_i \sim \exp\left(-\frac{E_i}{kT}\right)$$

The loop status has a lower energy than the bridge, and therefore is more probable

Detailed balance

At equilibrium, the number of transitions (per unit time) from any state i to any j is on average equal to the number of transitions (per unit time) from j to i

$$P_i g_{i\to j} p_{i\to j} = P_j g_{j\to i} p_{j\to i}$$

with g the transition attempt probability and p the acceptance probability

In Metropolis algorithm:

$$g_{j\to i} = g_{i\to j}$$

Molecular dynamics (MD)

Numerical integration of Newton's equations of motion, $\boldsymbol{F} = m\boldsymbol{a}$, for a system of particles. Particles follow deterministic trajectories in space for a well-defined set of interaction potentials between them.

If particle=atoms, we need bond-bending and bond-stretching C-C potentials, but also non-bonded interaction potentials.

Small time steps (10^{-15}s) are required, often not compatible with polymer relaxation times (even longer than 1s)

Angewandte Nobel Lectures

Molecular Modeling

DOI: 10.1002/anie.201403691

Birth and Future of Multiscale Modeling for Macromolecular Systems (Nobel Lecture)**

*Michael Levitt**

coarse-grained models · hybrid QM/MM models · molecular potential energy · Nobel lecture · protein dynamics in water

(Biophysicist, 2013 Nobel Prize in Chemistry, for the development of multiscale models for complex chemical systems)

YEAR	COST	SPEED	MEMORY	SIZE
1967	$40x10^6	0.1 MH$_3$	1 MB	HALL
2013	$4000	1 GH$_3$	10 GB	LAPTOP
CHANGE	10000	10000	10000	10000

10^4 improvement in all aspects

Periodic boundary conditions (PBC)

Surface effects and/or finite-size effects are «by-passed» by densely filling the space with identical copies of the simulation box

As particls leave the simulation box from one side they re-enter it from the opposite side

Implementing PBC

1. Applying periodic boundary conditions to particle positions

- **Simple:**

```
routine periodic_boundary_positions
do i=1,N
  if (x(i) >= Lx) x(i)=x(i)-Lx
  if (x(i) <  0 ) x(i)=x(i)+Lx
  if (y(i) >= Ly) y(i)=y(i)-Ly
  if (y(i) <  0 ) y(i)=y(i)+Ly
enddo
end routine
```

or:

```
routine periodic_boundary_positions_with_nint
do i=1,N
  x(i) = x(i)-Lx*nint(x(i)/Lx-0.5)
  y(i) = y(i)-Ly*nint(y(i)/Ly-0.5)
enddo
end routine
```

Johan Padding

TU/e Technische Universiteit Eindhoven University of Technology

Force fields and open source codes

- Accurate interaction potentials from quantum-chemical calculations have been tuned to achieve maximum agreement with experimental thermodynamic data (phase transition)

- Whole industry revolving around obtaining such interaction potentials, known as force fields

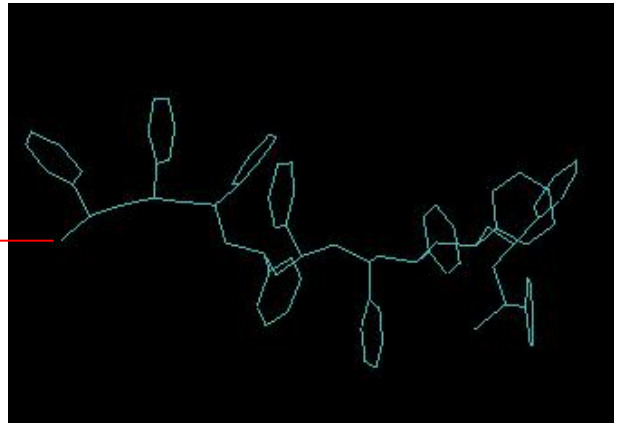
- Many open souce codes;
  1. GROMACS
  2. LAMMPS
  3. NAMD
  4. ESPRESSO
  5. AMBER
  6. …

My MD experience

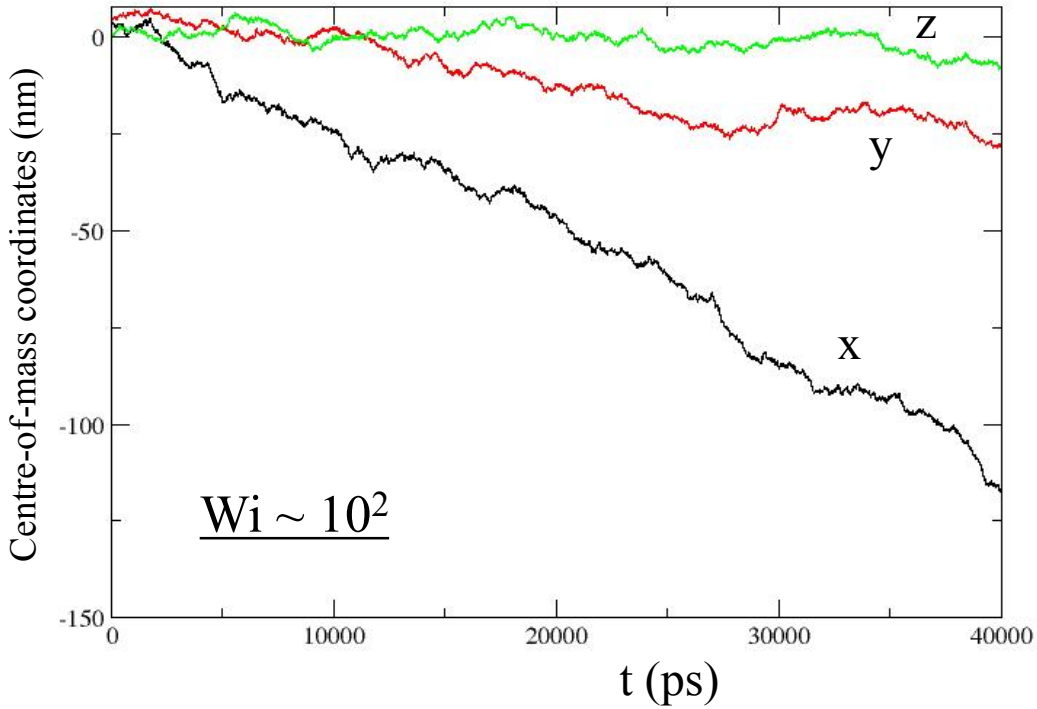
Flow-induced friction change

MD with Gromacs +
Trappe force-field

F_x



PS decamer

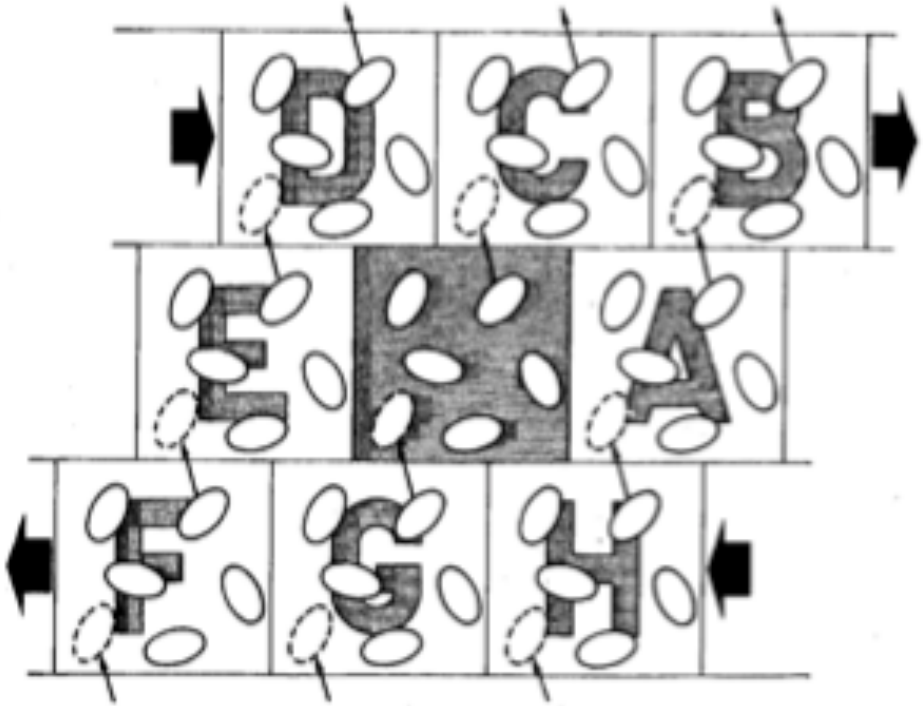


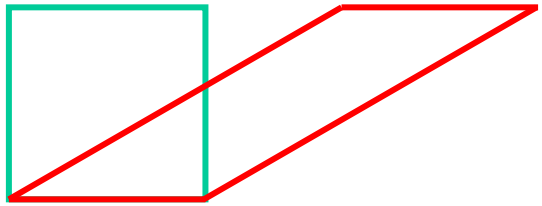
The average slope gives the velocity v_x, hence the friction coefficient:

$$\zeta = \frac{F_x}{v_x}$$

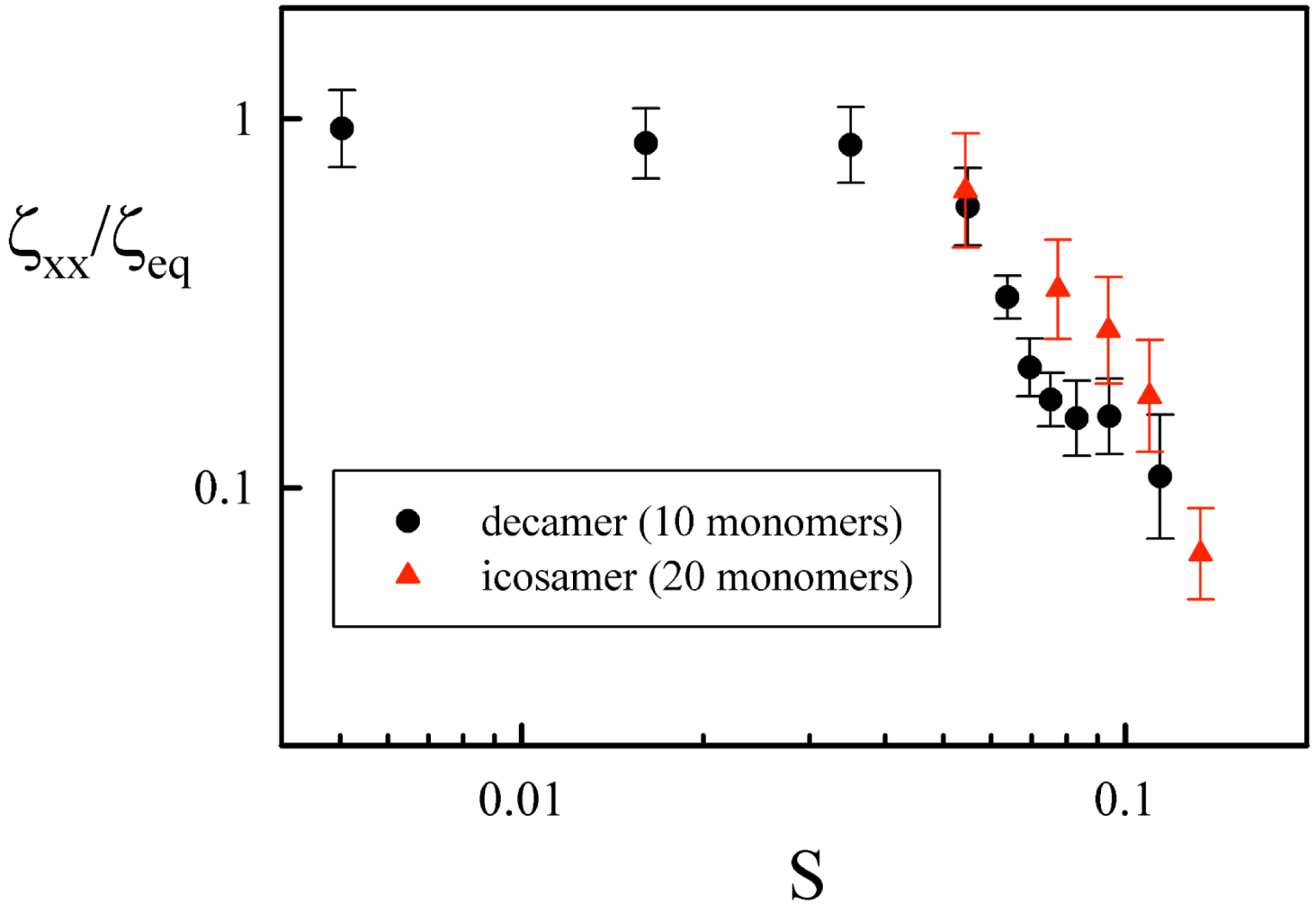
Non-Equilibrium Molecular Dynamics (NEMD)

It is more convenient to account for a shear flow by shifting the cubic boxes, rather than deforming the box since the steady shear can then be maintained without the box angles becoming extremely acute



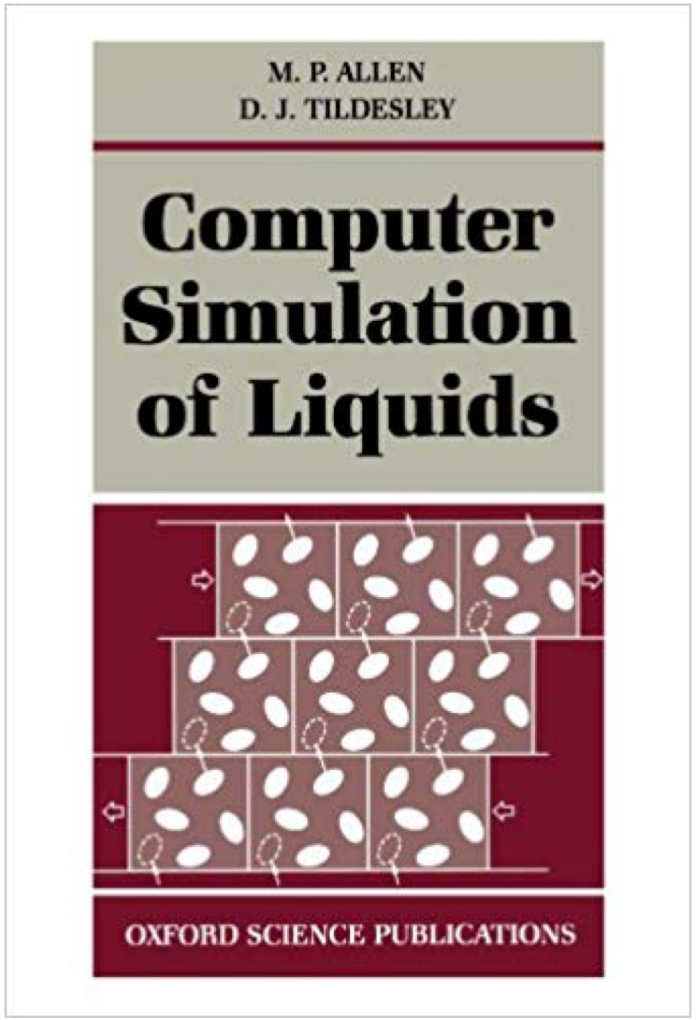


NEMD results

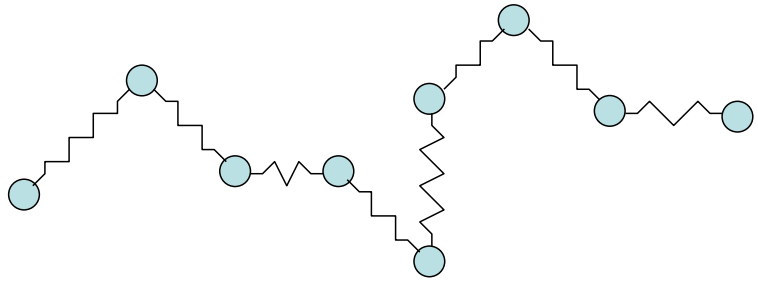


Macromolecules 2012

For more necessary details …



Coarse-grained molecular dynamics



- particles=beads
- intra-chain potentials=springs (chain connectivity)
- inter-chain potentials=*e.g.*, excluded volume (to enforce uncrossability)
- collisions with surrounding particles (solvent/polymer): random forces+viscous friction
- No longer deterministic: Brownian dynamics

Coarse-grained modeling

From Wikipedia, the free encyclopedia

Coarse-grained modeling, **coarse-grained models**, aim at simulating the behaviour of complex systems using their coarse-grained (simplified) representation. Coarse-grained models are widely used for molecular modeling of biomolecules[1][2] at various granularity levels. A wide range of coarse-grained models have been proposed. They are usually dedicated to computational modeling of specific molecules: proteins,[1][2] nucleic acids,[3][4] lipid membranes,[2][5] carbohydrates[6] or water.[7] In these models, molecules are represented by individual atoms and pseudo-atoms (that replace the group of atoms), or pseudo-atoms only. By decreasing the degrees of freedom much longer simulation times can be studied than using classical atomistic models. Coarse-grained models have found practical applications in: protein structure prediction, prediction of protein interactions and molecular dynamics simulations of protein folding.[1]

In 2013, the Nobel Prize in Chemistry has been awarded "for the development of multiscale models for complex chemical systems" to Michael Levitt, Ariel Warshel, and Martin Karplus. Their early works on coarse-grained protein modeling[8][9] have been recognized by the Nobel Prize Committee as an important step in studies of large macromolecular systems.[10] Coarse-grained models are presently often used as components of multiscale modeling protocols in combination with atomistic resolution models.[1] Atomistic resolution models alone are presently not efficient enough to handle large system sizes and simulation timescales.[1][2]

Brownian dynamics

9.1 Introduction

The simulation techniques we shall describe in this chapter are not motivated in quite the same way as those treated in previous chapters. The problem we wish to address is timescale separation, which occurs when one form of motion in the system is much faster than another. This can be a serious problem in MD, and similar difficulties arise in MC simulations. The short time-steps needed to handle the fast motion and the very long runs needed to allow evolution of the slower modes make the simulations very expensive. This is especially irritating if the fast motions are not of great interest in themselves. In some cases (Sections 3.4, 4.7) it is possible to replace such fast degrees of freedom by rigid constraints, but this is not always feasible. Consider the simulation of a large molecule (e.g. a protein) or a collection of heavy ions in a solvent. Even though the motion of the solvent molecules is of little interest, they will be present in large numbers, and they will make a full MD simulation very expensive. In such a case, an approximate approach may be adopted. The solvent particles are omitted from the simulation, and their effects upon the solute represented by a combination of random forces and frictional terms. Newton's equations of motion are thus replaced by some kind of Langevin equation.

Kremer & Grest simulations

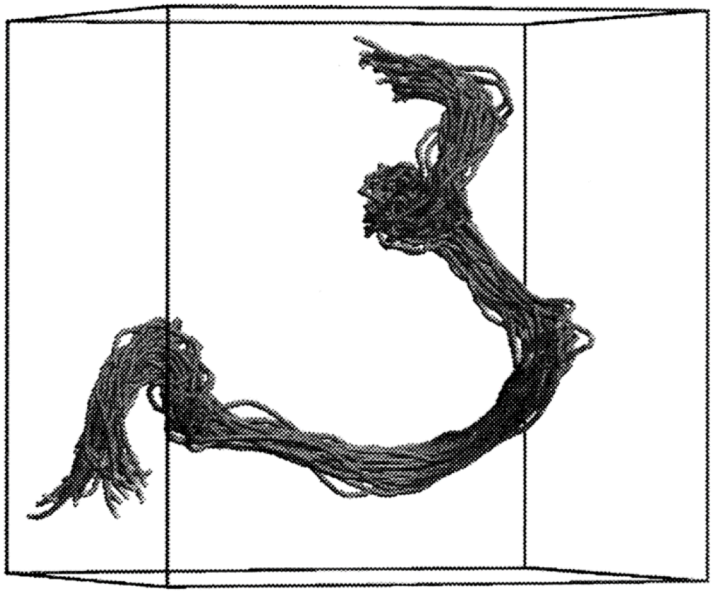


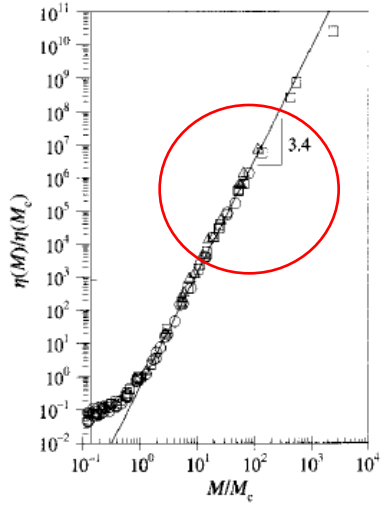
Fig. 9.29
Molecular dynamics simulation of a chain with $N = 400$ monomers in an entangled polymer melt. Forty configurations of the chain are shown at equally spaced time intervals up to the Rouse time of the chain. Picture courtesy of G. S. Grest based on data from K. Kremer and G. S. Grest, *J. Chem. Phys.* **92**, 5057 (1990).

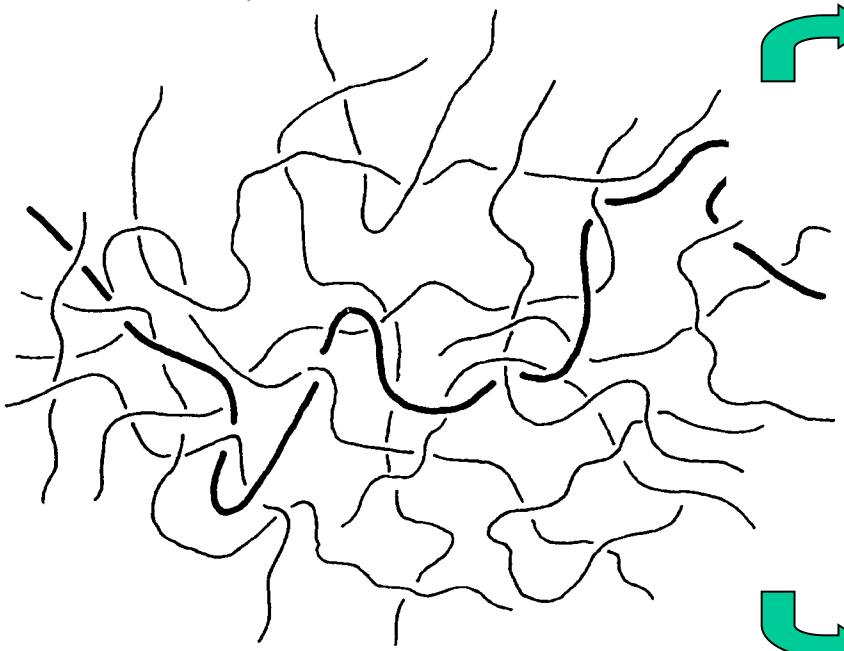
In entangled polymers, coarse-graining is limited by need of fulfilling topological constraints

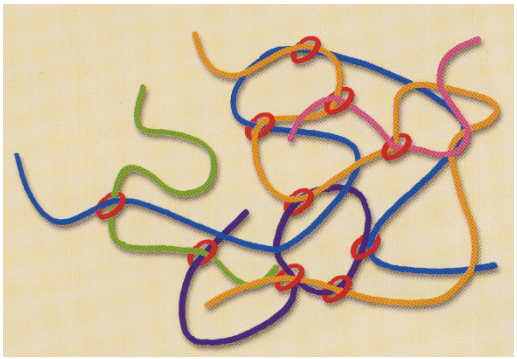
Computations (for entangled polymers) are still proibitive

Polymers with entanglements

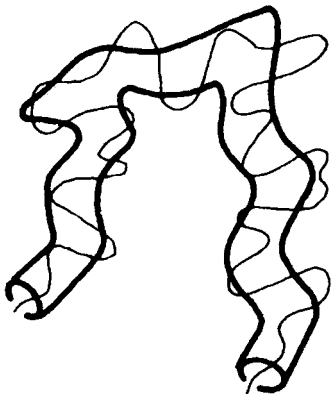
(melts or solutions)







Many-chain simulations

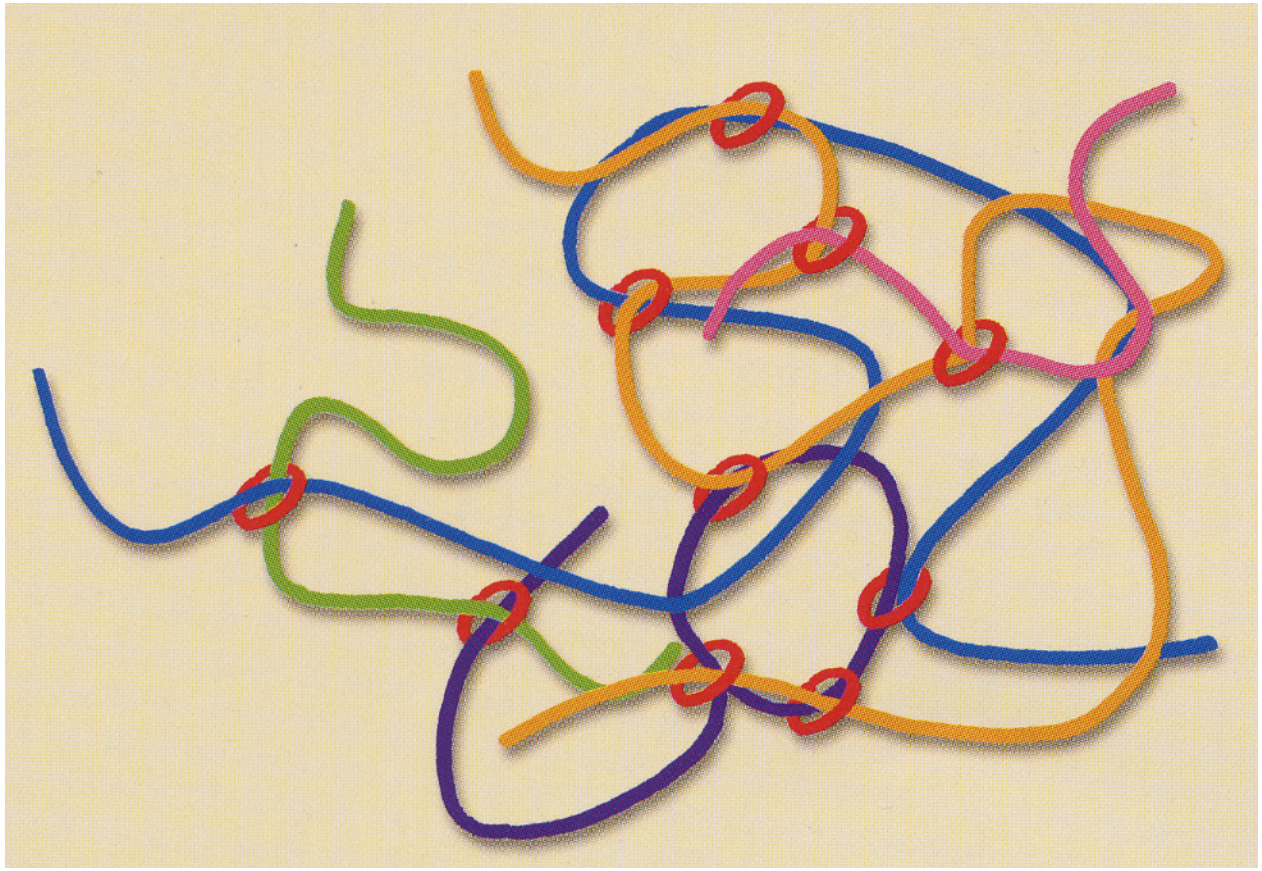


Single chain in a tube

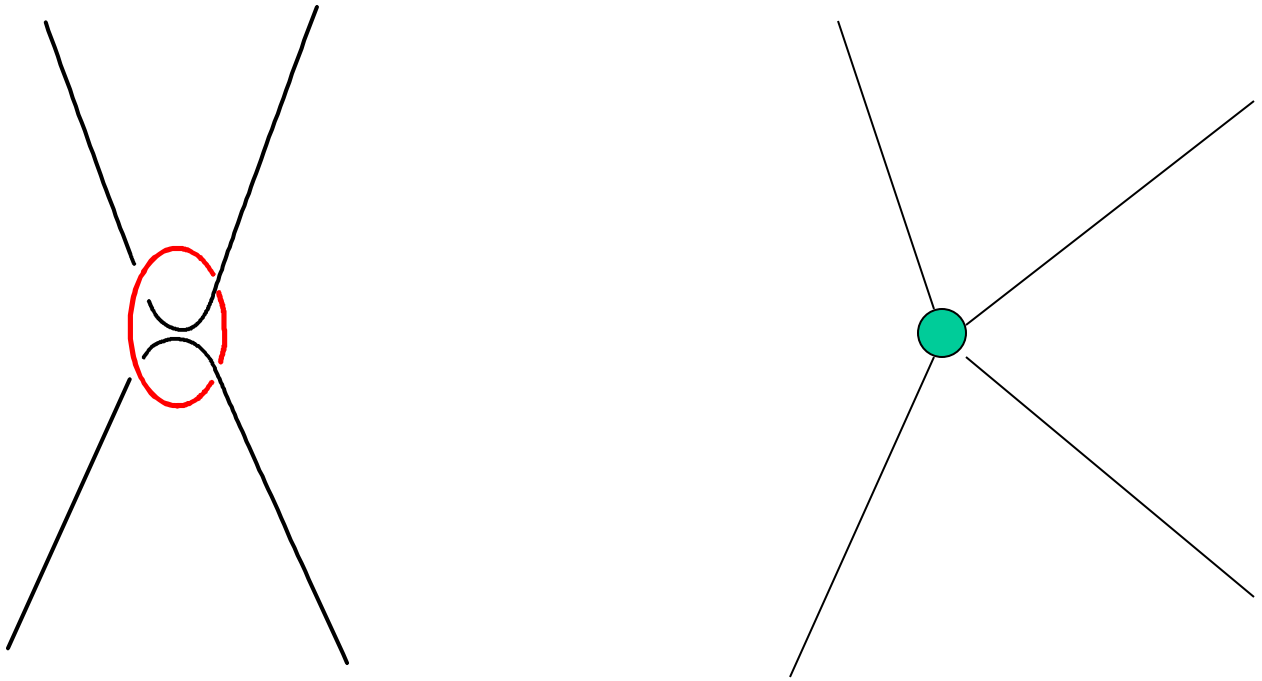
“Efficient” Brownian simulations

- Hua, Schieber (1998): Bead-spring chain in an affine tube. Constraint release is accounted for through virtual coupling between chain pairs.
- Takimoto, Tasaki, Doi (2000): Reptating chain in affine tube, with single-mode stretch and contour-length fluctuations. Constraint release as above. (Extension to branched with Larson.)

3D sliplink model



Entanglements (or sliplinks) *vs.* crosslinks

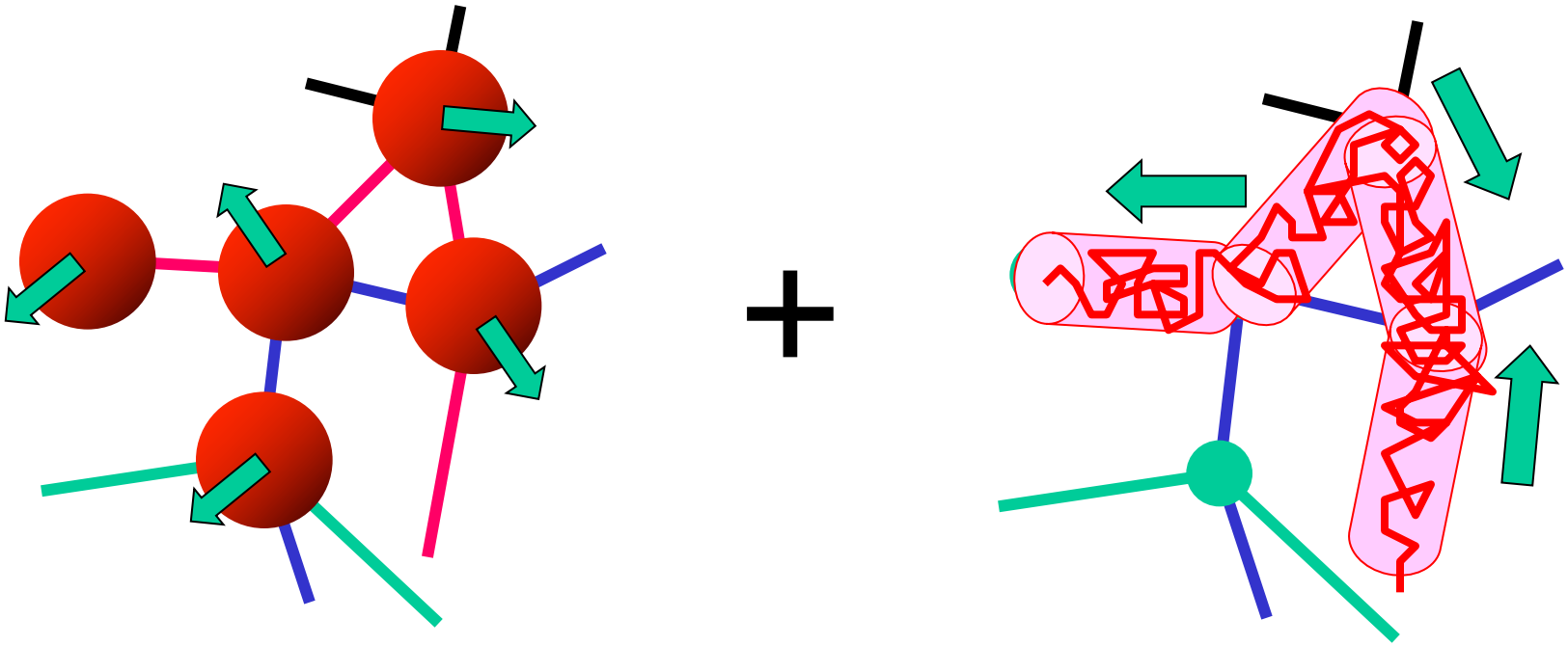


Monomers can slide through the sliplink

Primitive Chain Network Model

Masubuchi *et al*. (JCP 2001)

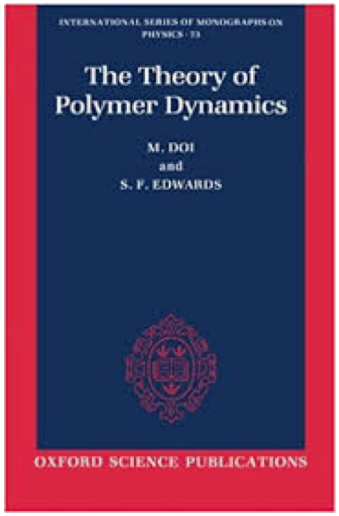
Coarse-graining at M_e level



3D motion of nodes

1D monomer sliding inside tube

Brownian motion

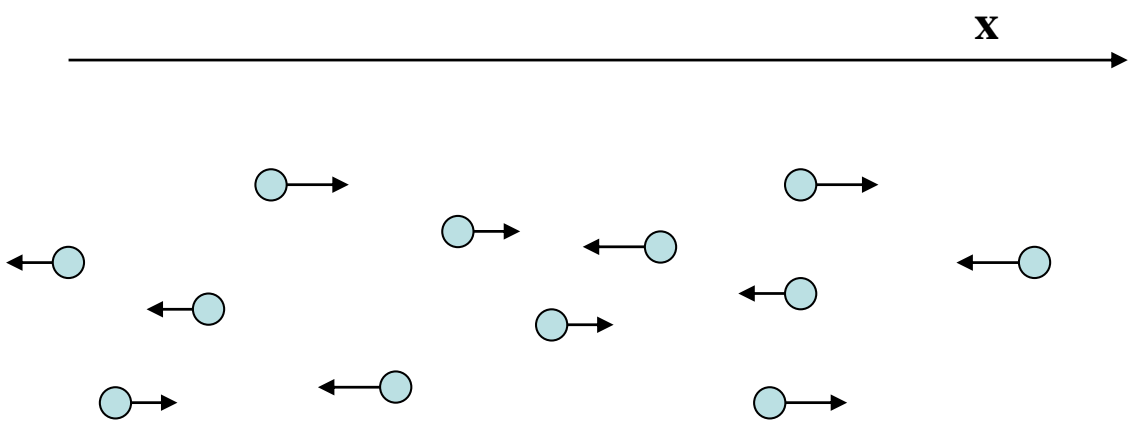


Polymers in solutions incessantly change both their shape and position randomly by thermal agitation. This Brownian motion dominates various time-dependent phenomena in polymer solutions such as viscoelasticity, diffusion, birefringence, and dynamic light scattering, which are to be discussed in subsequent chapters. In this chapter, we study the basic theory of Brownian motion. Since the general aspects of the theory of Brownian motion have already been discussed in many articles,[1–3] we shall limit the discussion to topics which will be useful in the application to polymer solutions and suspensions.

In principle, Brownian motion can be discussed starting from the dynamical equation of motion of the Brownian particle and the fluid molecules. However, this microscopic approach is not useful for calculating the various dynamical quantities we are interested in. Here we take a phenomenological approach, regarding Brownian motion as a kind of stochastic process, and construct a phenomenological equation describing Brownian motion based on known macroscopic laws. This approach, originated by Einstein,[4] is limited by several conditions, such as that the time-scale and the length-scale under consideration are much longer than those characteristic of solvent molecules, and that a linear relation holds between fluxes and forces. For polymer solutions and suspensions, these conditions are normally satisfied without any problems, and the theory we shall describe in this chapter can be regarded as a general base for describing their dynamics.

The phenomenological equation for Brownian motion has two seemingly different, but essentially the same, forms—the Smoluchowski equation and the Langevin equation. The Smoluchowski equation is derived from the generalization of the diffusion equation and has a clear relevance to the thermodynamics of irreversible processes. The Langevin equation, on the other hand, has no direct relationship to thermodynamics, but is capable of describing wider classes of stochastic processes.[2] We shall first study the Smoluchowski equation, and then consider its equivalence to the Langevin equation.

The simplest dynamics:
Brownian particles with 1 degree of freedom



Distribution function of interest = particle concentration = c

Balance equation
(number of particles is conserved)

$$\frac{\partial c}{\partial t} = -\frac{\partial N_x}{\partial x}$$

Free particles (force free)

Flux is due to Brownian motion (diffusion) only. Hence:

$$N_x = -D\frac{\partial c}{\partial x}$$

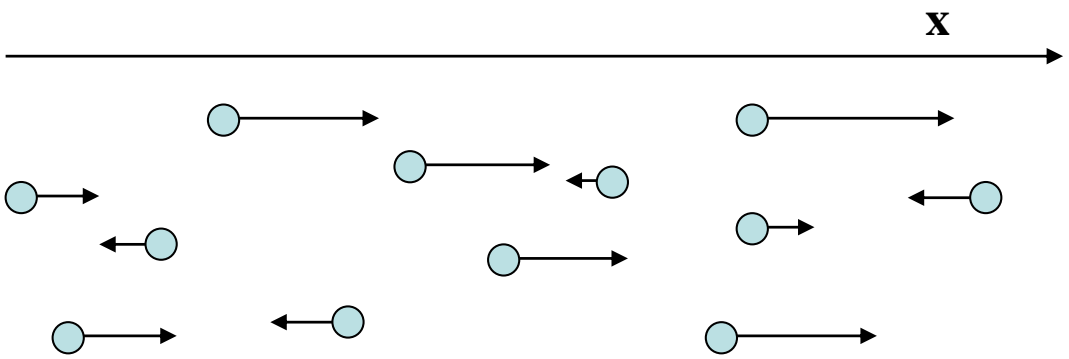
where D = [m^2/s] is the diffusion coefficient.

Putting N_x in the balance equation, the well known diffusion equation is obtained:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)$$

Particles in a force field

Suppose now that the particles are in a field of force that moves them, e.g., towards the right side



If v_x is the particle velocity due to the force field, to the diffusion flux we must add the term:

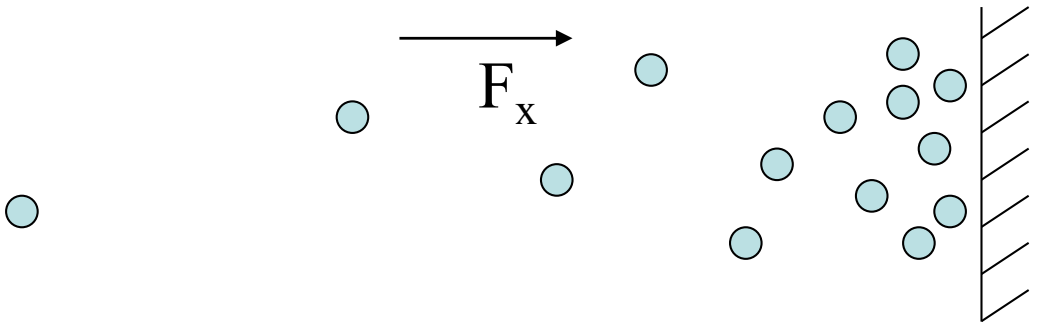
$$N_x = c\, v_x = c\frac{F_x}{\zeta}$$

where ζ is the friction coefficient of a particle

Substituting into the balance equation, we now obtain:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x} - c\frac{F_x}{\zeta} \right)$$

Let's analyze the equilibrium condition, when the flux vanishes (e.g., in the presence of a wall)



The equation becomes

$$D\frac{dc}{dx} - c\frac{F_x}{\zeta} = 0$$

which is rewritten:

$$\frac{dc}{c} = \frac{F_x\, dx}{\zeta D} = -\frac{dE}{\zeta D}$$

where E is the energy of the force field. Integration gives:

$$c = c_0 \exp\left(-\frac{E}{\zeta D}\right)$$

where c_0 is the concentration where energy is zero (e.g. on the wall)
Comparison with Boltzmann equation:

Equilibrium distribution proportional to $\exp(-E/kT)$

gives Einstein formula:

$$D = \frac{kT}{\zeta}$$

Using Einstein equation linking to one another the diffusion and friction coefficients, the *c* equation becomes:

$$\frac{\partial c}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial c}{\partial x} + c\frac{\partial}{\partial x}\left(\frac{E}{kT}\right)\right]$$

(where we have assumed that *D* does not vary with x).

Finaly assume that the Brownian particles are immersed in a solvent moving with velocity v_x. Obviously, particles are also convected, and the *complete* c equation is obtained:

$$\frac{\partial c}{\partial t} = D\frac{\partial}{\partial x}\left[\frac{\partial c}{\partial x} + c\frac{\partial}{\partial x}\left(\frac{E}{kT}\right)\right] - \frac{\partial}{\partial x}\left(c\, v_x\right)$$

The 3D equation

Generalization to more degrees of freedom is straightforward. Balance becomes:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{N}$$

Accounting for all 3 possible contributions to the flux **N**, the general equation becomes:

$$\frac{\partial c}{\partial t} = D\nabla \cdot \left[\nabla c + c\nabla\left(\frac{E}{kT} \right) \right] - \nabla \cdot (c\,\mathbf{v})$$

diffusion force convection

The Langevin equation

An alternative description is to write a force balance on the Brownian particle

$$\zeta \frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{\partial U}{\partial x} + f(t)$$

with $f(t)$ the Brownian force arising from the random collision of the surrounding molecules. Since we do not know the precise time-dependence of f, we regard it as a stochastic variable with a plausible distribution $\Psi[f(t)]$.

It can be shown (see Appendix 3.II DE) that if f is Gaussian with moments

$$\langle f(t) \rangle = 0, \qquad \langle f(t) f(t') \rangle = 2\zeta k_B T \, \delta(t - t')$$

Then the distribution of $x(t)$ determined by the Langevin equation satisfies the Smoluchowski equation

Let's check it for a free particle (U=0)

The Langevin equation reads

$$\zeta \frac{\mathrm{d}x}{\mathrm{d}t} = f(t)$$

If the particle was at x' at t=0, its position at t is

$$x(t) = x' + \frac{1}{\zeta}\int_0^t \mathrm{d}t' f(t')$$

i.e., $x(t)$-x' is a linear combination of Gaussian variables, and hence $x(t)$ is Gaussian (see Appendix 2.I DE)

$$\Psi(x,t) = (2\pi B)^{-1/2} \exp\left(-\frac{(x-A)^2}{2B}\right) \qquad A = \langle x(t)\rangle, \qquad B = \langle (x(t)-A)^2\rangle$$

Those moments are easily calculated

$$A = x' + \frac{1}{\zeta}\int_0^t \mathrm{d}t' \langle f(t')\rangle = x'$$

$$B = \left\langle \left(\frac{1}{\zeta}\int_0^t \mathrm{d}t' f(t')\right)\left(\frac{1}{\zeta}\int_0^t \mathrm{d}t'' f(t'')\right)\right\rangle$$

$$= \frac{1}{\zeta^2}\int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \langle f(t')f(t'')\rangle$$

$$= \frac{2k_B T}{\zeta}\int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' \, \delta(t'-t'') = \frac{2k_B T}{\zeta} t$$

and hence

$$\Psi(x,t) = (4\pi D t)^{-1/2} \exp\left(-\frac{(x-x')^2}{4Dt}\right)$$

Smoluchowski approach

The Smoluchowski equation is

$$\frac{\partial \Psi}{\partial t} = D \frac{\partial^2}{\partial x^2} \Psi$$

with B.C.'s

$t = 0, \Psi(x,t) = \delta(x - x'); \; x = \pm\infty, \Psi(x,t) = 0$

Since there is no characteristic length, this PDE can be easily solved by reducing it to an ODE by introducing the nondimensional similarity variable $\xi = x/\sqrt{4Dt}$ (see classical Transport Phenomena books).

The solution is:

$$\Psi(x, t) = (4\pi Dt)^{-1/2} \exp\left(-\frac{(x - x')^2}{4Dt}\right)$$

If D depends on x …

… an additional term must be added to the Langevin equation

$$\zeta \frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{\partial U}{\partial x} + f(t) + \frac{\zeta}{2}\frac{\partial D}{\partial x}$$

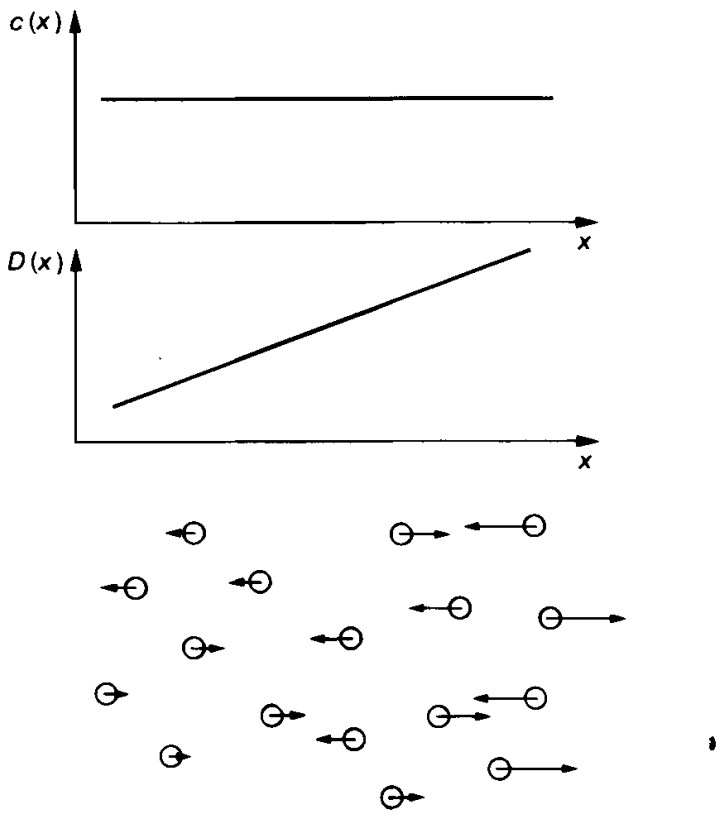
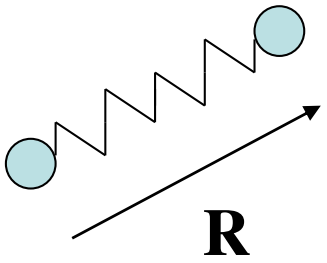


Fig. 3.2. Explanation for the term $\partial D/\partial x$ in eqn (3.38). Consider the equilibrium state for the case of $U = 0$ and $\partial D/\partial x > 0$. The random force $f(t)$ in eqn (3.38) causes displacement of individual particles as shown by the arrows: the particles on the right are more mobile than those on the left. This creates a net flux of particles toward the negative direction. To compensate for this, the term $\partial D/\partial x$ is needed.

The simplest molecular model of polymer viscoelasticity. The "dumbbell" model



Two friction beads connected by a spring

End-to-end vector distribution function: $\Psi(\mathbf{R}, t)$

$$\frac{\partial \psi}{\partial t} = D \frac{\partial}{\partial \mathbf{R}} \cdot \left[\frac{\partial \psi}{\partial \mathbf{R}} + \psi \frac{\partial}{\partial \mathbf{R}} \left(\frac{E}{kT} \right) \right] - \frac{\partial}{\partial \mathbf{R}} \cdot \left(\psi \mathbf{k} \cdot \mathbf{R} \right)$$

diffusion $D = kT/\zeta$

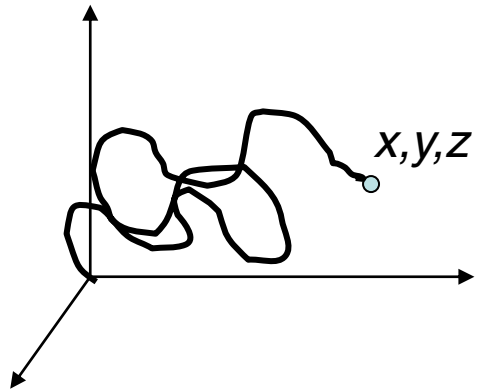
spring

convection due to velocity gradient **k**

Smoluchowski equation or Fokker-Planck equation

- Solution of the Smoluchowski equation is seldom analytic, though an analytic solution may become possible after some approximation is introduced. Numerical solution is the alternative.
- Once Ψ is obtained, all averages can be calculated, among them the average that corresponds to the stress tensor.
- Sometimes, the partial differential equation for Ψ is transformed (by a suitable integration over the whole space of the coordinates) into a much simpler ordinary time-differential equation for the stress tensor, usually through simplifications called "closure approximations".

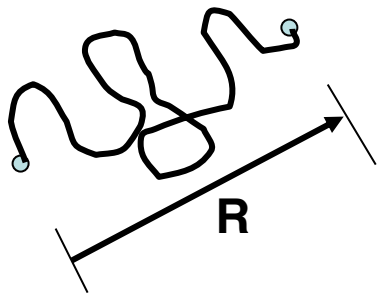
Elastic force in a Gaussian chain



$$P(x,y,z) = C\exp\left(-\frac{3}{2}\frac{x^2+y^2+z^2}{R_0^2}\right)$$

$$S = k\ln P = -\frac{3}{2}k\frac{x^2+y^2+z^2}{R_0^2} + k\ln C = -\frac{3}{2}k\frac{\mathbf{R}^2}{R_0^2} + k\ln C$$

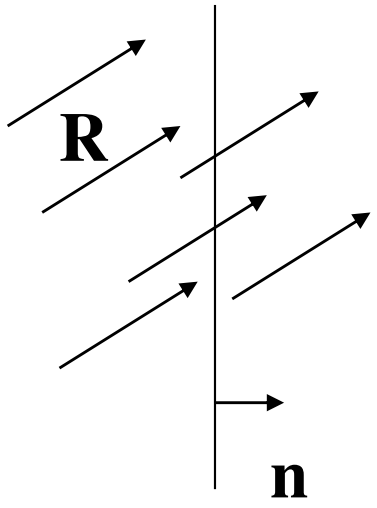
$$E = U - TS;\quad \mathbf{F} = -\frac{\partial E}{\partial \mathbf{R}} = T\frac{\partial S}{\partial \mathbf{R}}$$



$$\mathbf{F} = -\frac{3kT}{R_0^2}\mathbf{R}$$

The stress tensor **T** (for dumbbells)

Assume temporarily that all chains have the same end-to-end vector **R**



If ν is number of chain per unit volume, chains being cut per unit area are $\nu(\mathbf{R}\cdot\mathbf{n})$

If **F** is the force in each spring, the total force across unit area is $\nu\mathbf{FR}\cdot\mathbf{n}$. Hence:

$$\mathbf{T} = \nu\mathbf{FR}$$

In reality, because of distribution, it is: $\mathbf{T} = \nu \langle \mathbf{FR} \rangle$

Linear force: $\mathbf{F}=(3kT/R_0^2)\mathbf{R}$

$$\mathbf{T} = \frac{3\nu kT}{R_0^2}\langle \mathbf{RR} \rangle$$

$$\langle \mathbf{RR} \rangle = \int \mathbf{RR}\psi(\mathbf{R})d^3R$$

where $\psi(\mathbf{R})$ is the distribution function of end-to-end vector

At equilibrium, $\psi(\mathbf{R})$ is isotropic and Gaussian.

Dynamic problem = find $\psi(\mathbf{R}, t)$, from which $<\mathbf{RR}>$ as a function of time t, hence $\mathbf{T}(t)$

Recall that for a linear force: $\mathbf{T} = \frac{3\nu kT}{R_0^2}\langle \mathbf{RR} \rangle$

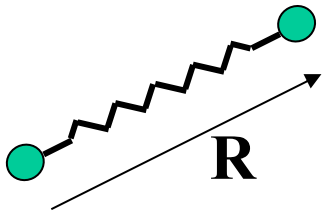
where: $\langle \mathbf{RR} \rangle = \int \mathbf{RR}\psi(\mathbf{R}) d^3R$

$$\frac{\partial \psi}{\partial t} = D\frac{\partial}{\partial \mathbf{R}} \cdot \left[\frac{\partial \psi}{\partial \mathbf{R}} + \psi \frac{\partial}{\partial \mathbf{R}} \left(\frac{E}{kT} \right) \right] - \frac{\partial}{\partial \mathbf{R}} \cdot (\psi \mathbf{k} \cdot \mathbf{R})$$

Multiplying **RR** to all terms, and integrating over **R** space

$$\frac{d}{dt}\langle \mathbf{RR} \rangle = 2D\mathbf{I} - \frac{6D}{R_0^2}\langle \mathbf{RR} \rangle + \mathbf{k} \cdot \langle \mathbf{RR} \rangle + \langle \mathbf{RR} \rangle \cdot \mathbf{k}^T$$

Langevin approach



- Placing the origin in one bead, a force balance on the other bead reads

$$\zeta\,(\mathbf{v} - d\mathbf{R}/dt) - H\mathbf{R} + \boldsymbol{f} = \mathbf{0}$$

  where the 3 terms are friction, spring ($H=3kT/R_0^2$), and Brownian force, respectively
- The velocity **v** is calculated from the assigned velocity gradient **k** as:

$$\mathbf{v} = \mathbf{k} \cdot \mathbf{R}$$

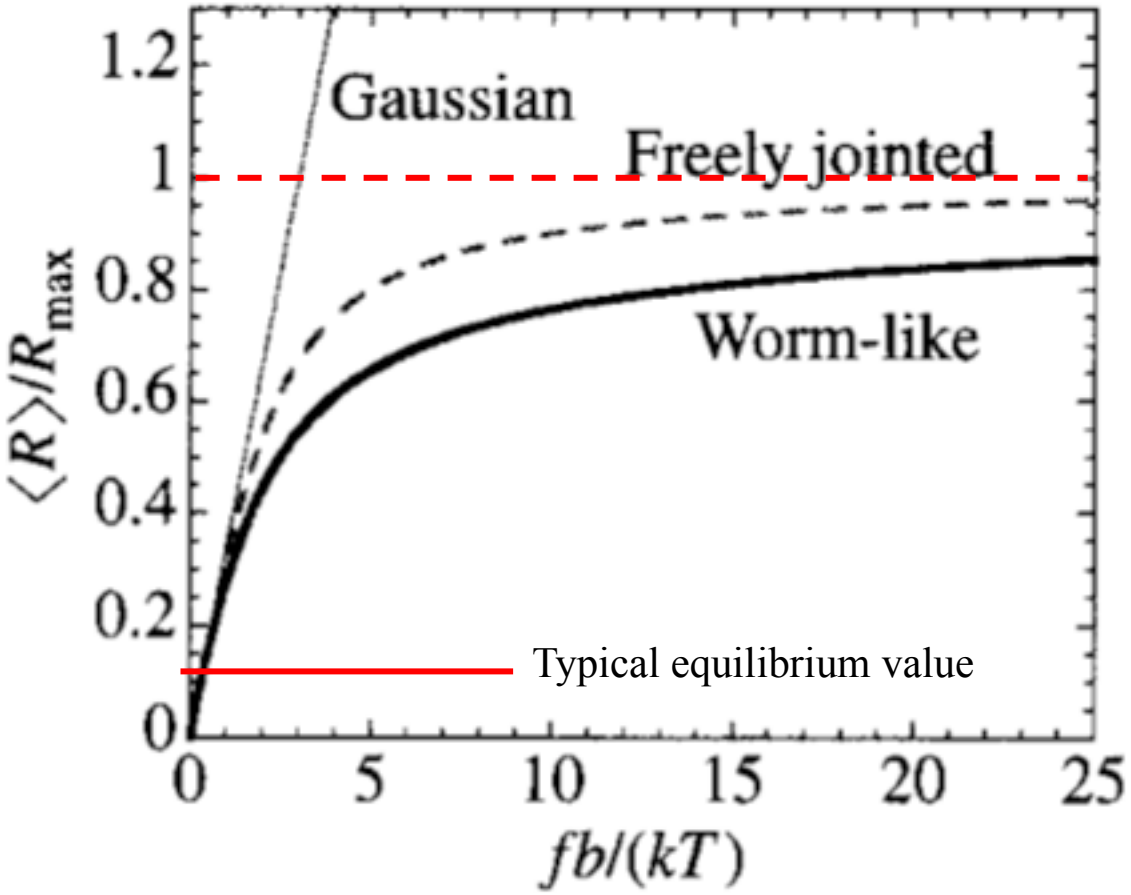
Numerical solution

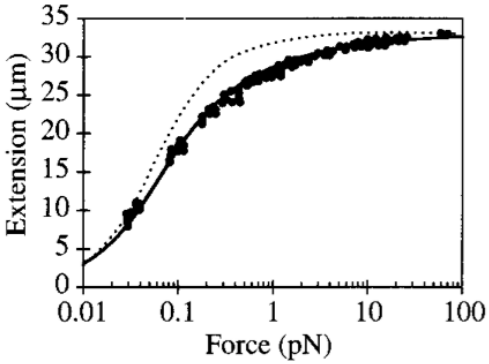
- Given an initial value to **R**, the equation (d**R**/dt = …) is integrated numerically.
- For constant (or zero) **k**, the initial condition is eventually forgotten, and steady-state (or equilibrium) properties can be obtained from time averages.
- Simulations of time-dependent processes require a genuine initial condition for a large population of dumbbells, typically the equilibrium state (itself obtained by pre-running with **k** = **0**).
- Averaging over the dumbbell population gives the stress as a function of time.

Take-home message

- For the dumbbell case, the Smoluchoswki approach is preferred since we can analytically determine rheologically-relevant observable in view of the equation linearity
- If, for instance, we want to account for finite extensibility effects of the polymer chain, the force becomes nonlinear and the Langevin approach is preferred …

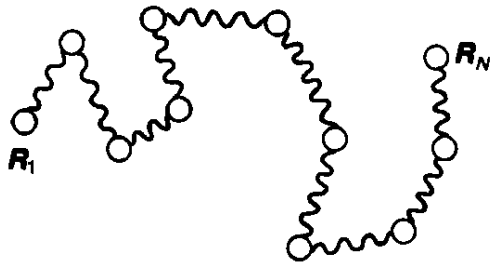
Finite extensibility





Comparison of experimental force for 97 kilobase λ-DNA dimers with the worm-like chain model [solid curve is Eq. (2.119) with $R_{max} = 33\,\mu m$ and $b = 100\,nm$]. The dotted curve corresponds to the Langevin function of the freely jointed chain model

Rouse model



- Smoluchoswki approach

$$\frac{\partial \Psi}{\partial t} = \sum_n \frac{\partial}{\partial \boldsymbol{R}_n} \cdot \boldsymbol{H}_{nm} \cdot \left[k_B T \frac{\partial \Psi}{\partial \boldsymbol{R}_m} + \frac{\partial U}{\partial \boldsymbol{R}_m} \Psi \right]$$

- Langevin approach

$$\frac{\partial}{\partial t} \boldsymbol{R}_n(t) = \sum_m \boldsymbol{H}_{nm} \cdot \left(-\frac{\partial U}{\partial \boldsymbol{R}_m} + f_m(t) \right) + \tfrac{1}{2} k_B T \sum_m \frac{\partial}{\partial \boldsymbol{R}_m} \cdot \boldsymbol{H}_{nm}$$

In the Rouse model, the excluded volume interaction and the hydrodynamic interaction are disregarded and the mobility tensor and the interaction potential are written as

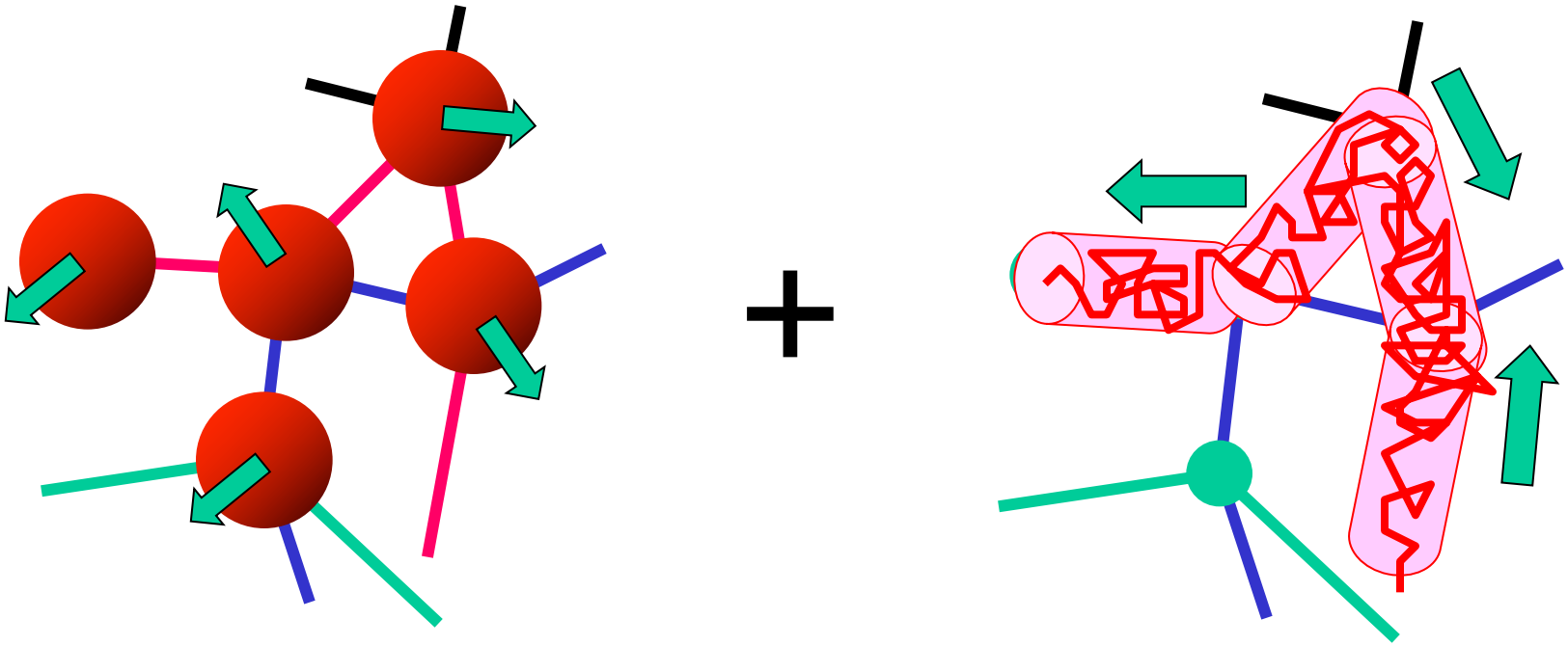
$$\boldsymbol{H}_{nm} = \frac{\boldsymbol{I}}{\zeta} \delta_{nm} \qquad U = \frac{k}{2} \sum_{n=2}^{N} (\boldsymbol{R}_n - \boldsymbol{R}_{n-1})^2 \qquad k = \frac{3 k_B T}{b^2}$$

Here again, for Gaussian linear chains an analytical solution can be obtained. In all other cases (FENE chain, anisotropic friction, …), numerical methods are neeeded, and the Langevin approach is preferred.

Primitive Chain Network Model

Masubuchi *et al*. (JCP 2001)

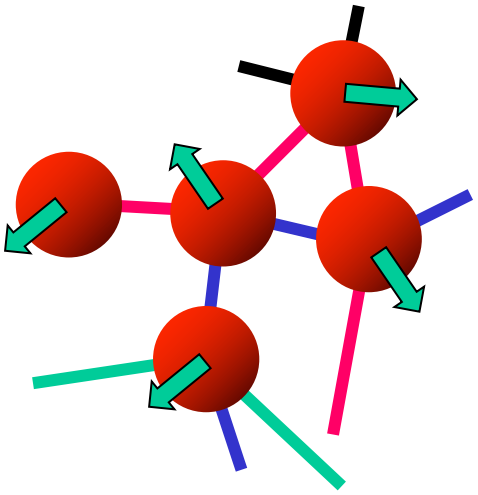
Coarse-graining at M_e level



3D motion of nodes

1D monomer sliding inside tube

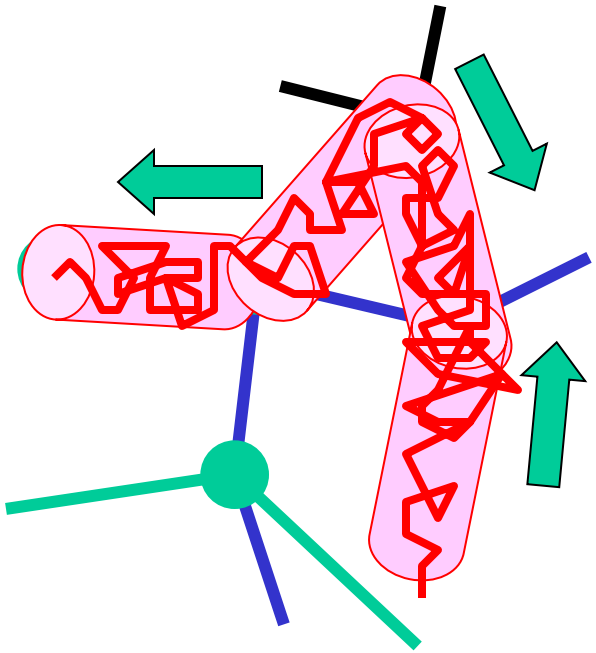
Equation of motion for nodes



$$2\zeta\dot{\mathbf{R}} = \frac{3kT}{b^2}\sum_i \frac{\mathbf{r}_i}{n_i} - \nabla\mu + \mathbf{F}$$

$$\mu = kT \ln \rho_{node}$$

Equation for monomer sliding

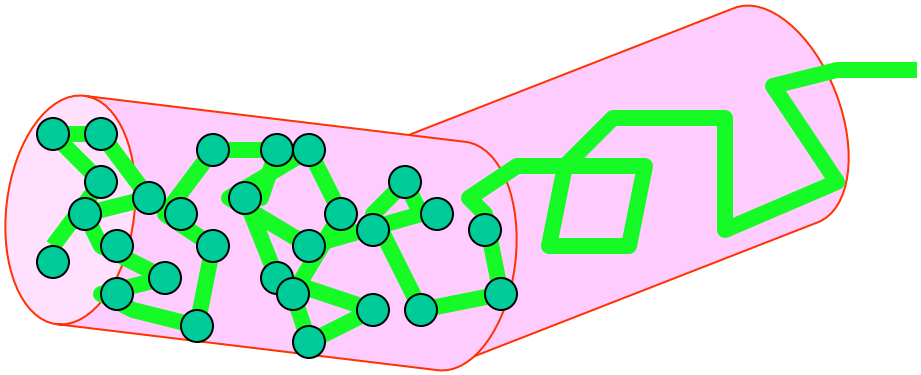


$$\zeta \frac{\dot{n}}{\rho_m} = \frac{3kT}{b^2}\left(\left.\frac{r}{n}\right|_{i+1} - \left.\frac{r}{n}\right|_{i} \right) + f$$

Monomer linear density

$$\rho_m = \frac{1}{2}\left(\left.\frac{n}{r}\right|_{i} + \left.\frac{n}{r}\right|_{i+1} \right)$$

Chain end hooking and unhooking



n monomers in the end segment

$$n < n_o/2 \qquad \text{unhooking}$$

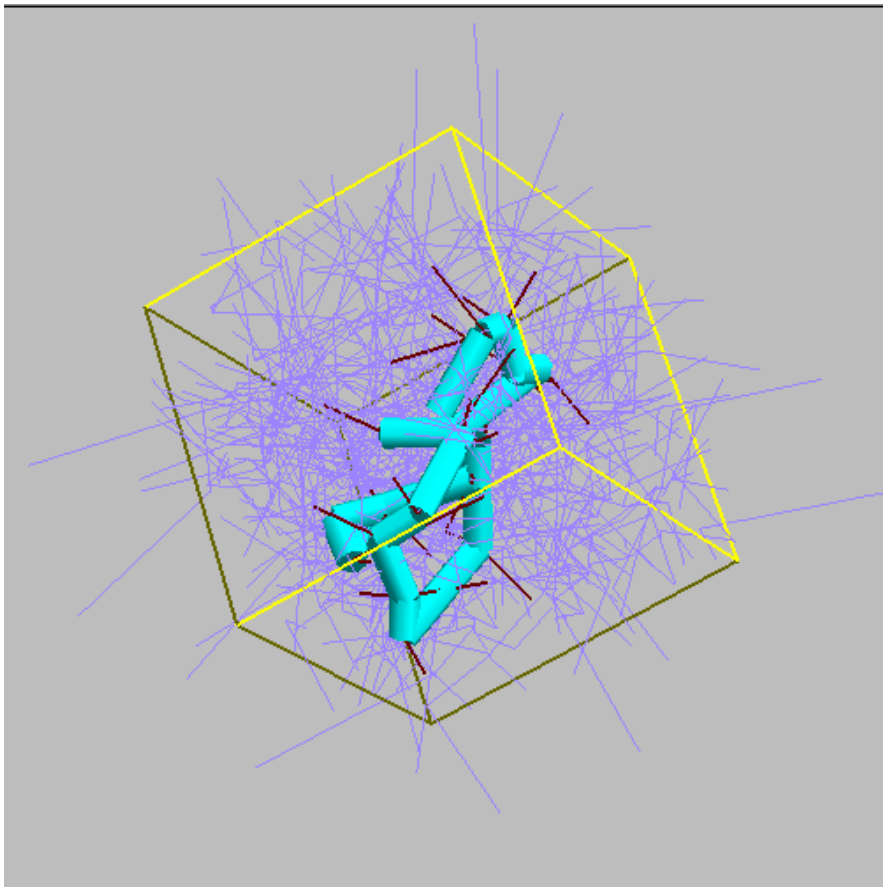
$$n > n_o + n_o/2 \qquad \text{hooking}$$

Code: NAPLES

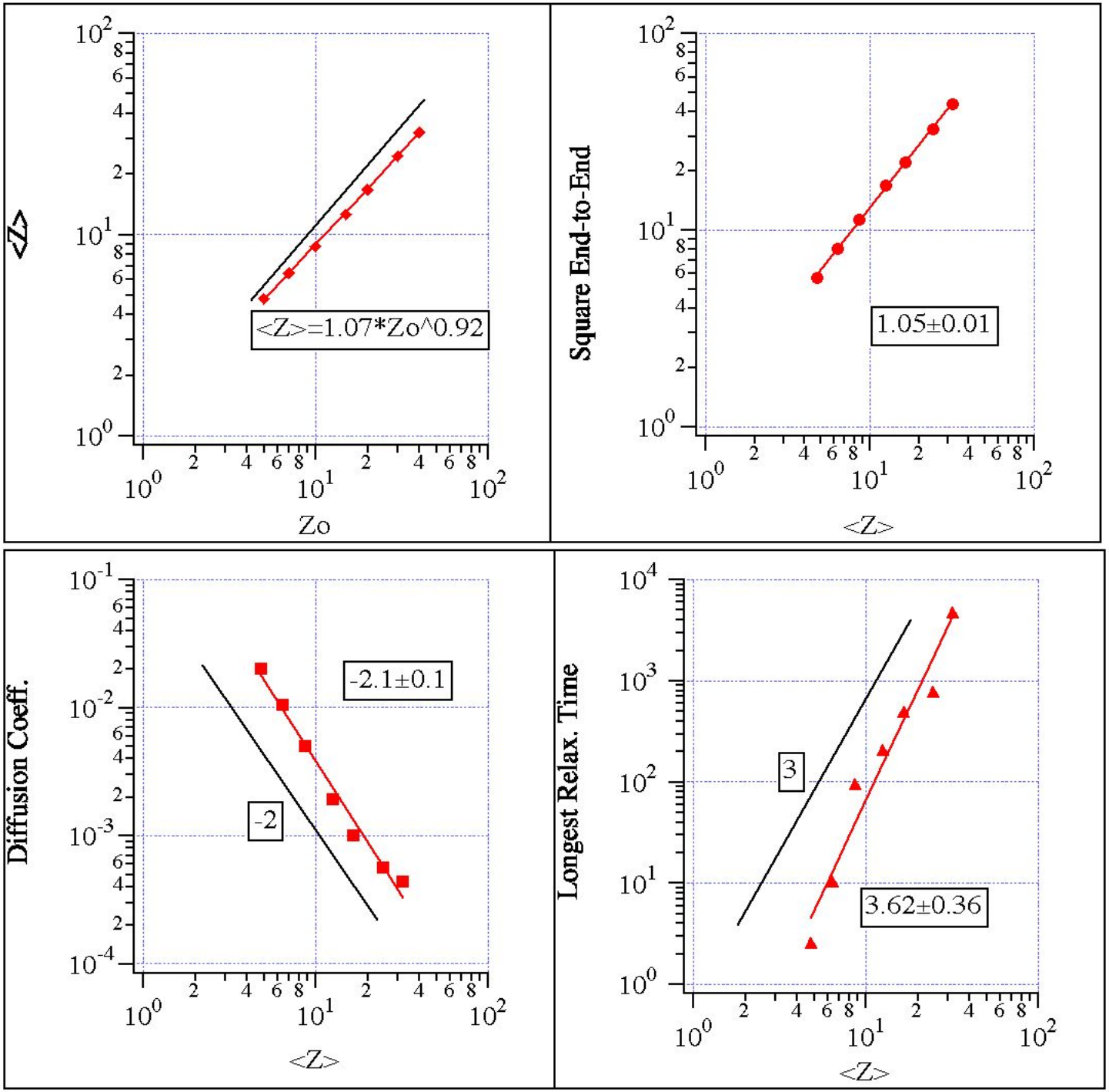
(New Algorithm for Polymeric Liquids Entangled and Strained)

A chain with Z=10
(corresponding to PS of
M~170,000)

Number of molecules ~500



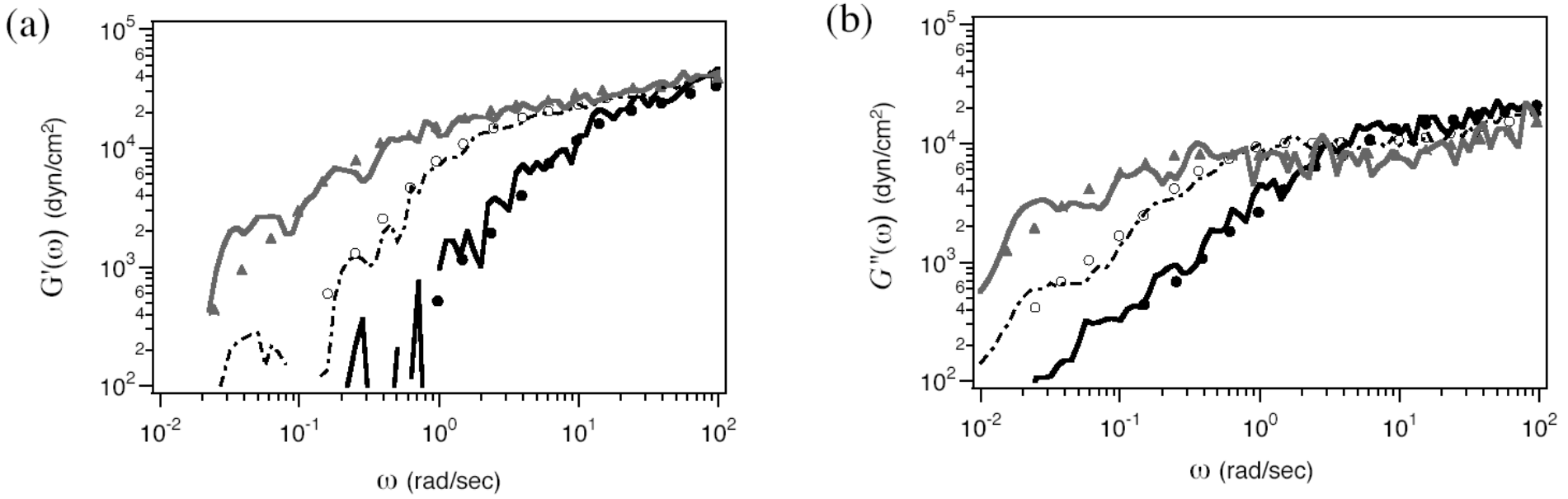
(developed with Y. Masubuchi, Nagoya University)


<Z>
Zo
<Z>=1.07*Zo^0.92
Square End-to-End
<Z>
1.05±0.01
Diffusion Coeff.
<Z>
-2.1±0.1
-2
Longest Relax. Time
<Z>
3
3.62±0.36

Comparison with G'-G" solution data at several M

Masubuchi, Iannirubertо, Greco, Marrucci

JCP 2003



Only 2 shift factors.

Number of entanglements is obtained from vertical shift (modulus).

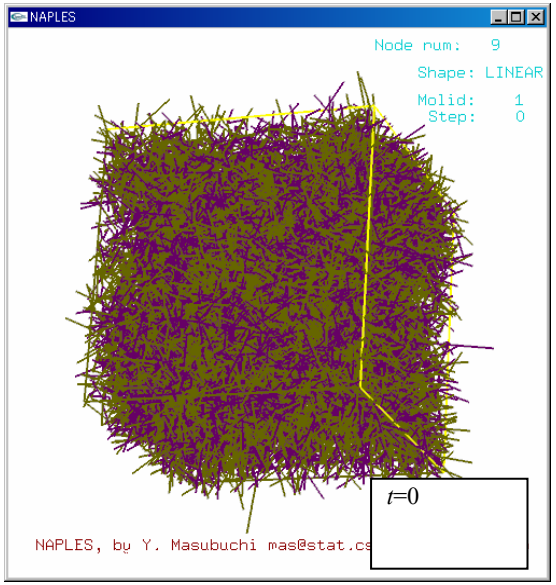
Polymer blends

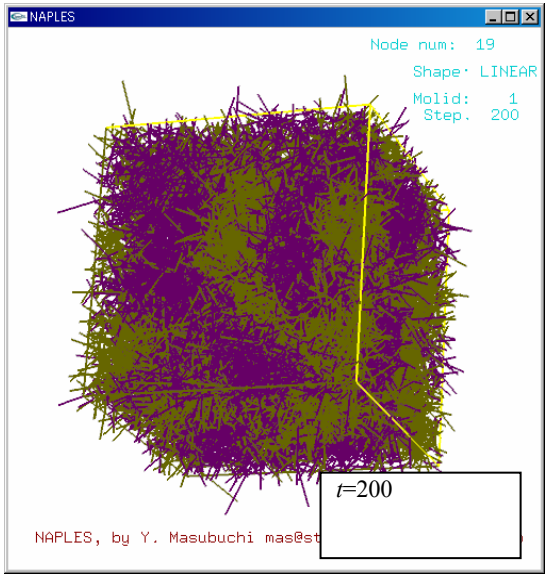
$$\left(\zeta_\alpha + \zeta_\beta\right)\dot{\mathbf{R}} = 3kT\left[\frac{1}{b_\alpha^2}\left(\frac{\mathbf{r}_i}{n_i} - \frac{\mathbf{r}_{i-1}}{n_{i-1}}\right)_\alpha + \frac{1}{b_\beta^2}\left(\frac{\mathbf{r}_j}{n_j} - \frac{\mathbf{r}_{j-1}}{n_{j-1}}\right)_\beta\right] - \nabla\left(n_{0\alpha}\mu_\alpha + n_{0\beta}\mu_\beta\right) + \mathbf{F}$$

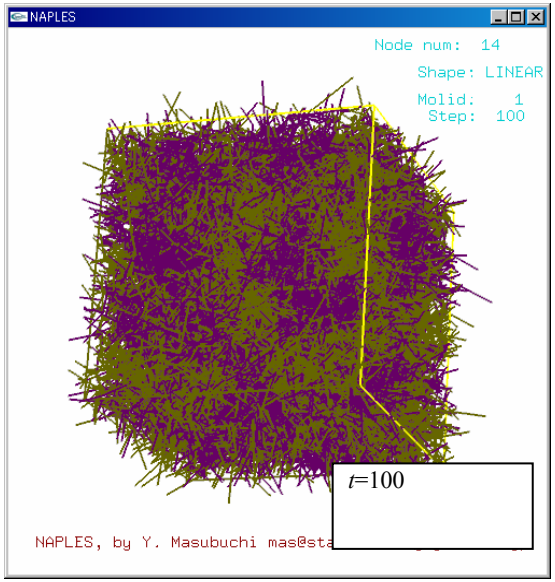
$$\zeta_\alpha \frac{\dot{n}}{\rho_m} = \frac{3kT}{b_\alpha^2}\left(\frac{r_i}{n_i} - \frac{r_{i-1}}{n_{i-1}}\right)_\alpha - n_{0\alpha}\nabla\mu_\alpha + f$$

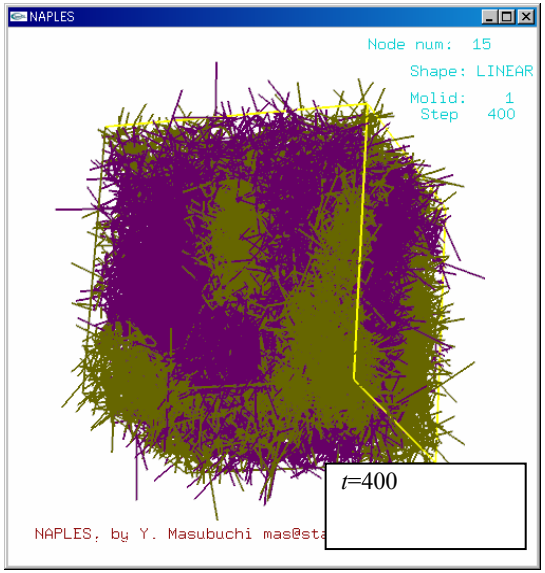
Chemical potential also includes Flory-Huggins contribution

Phase separation dynamics

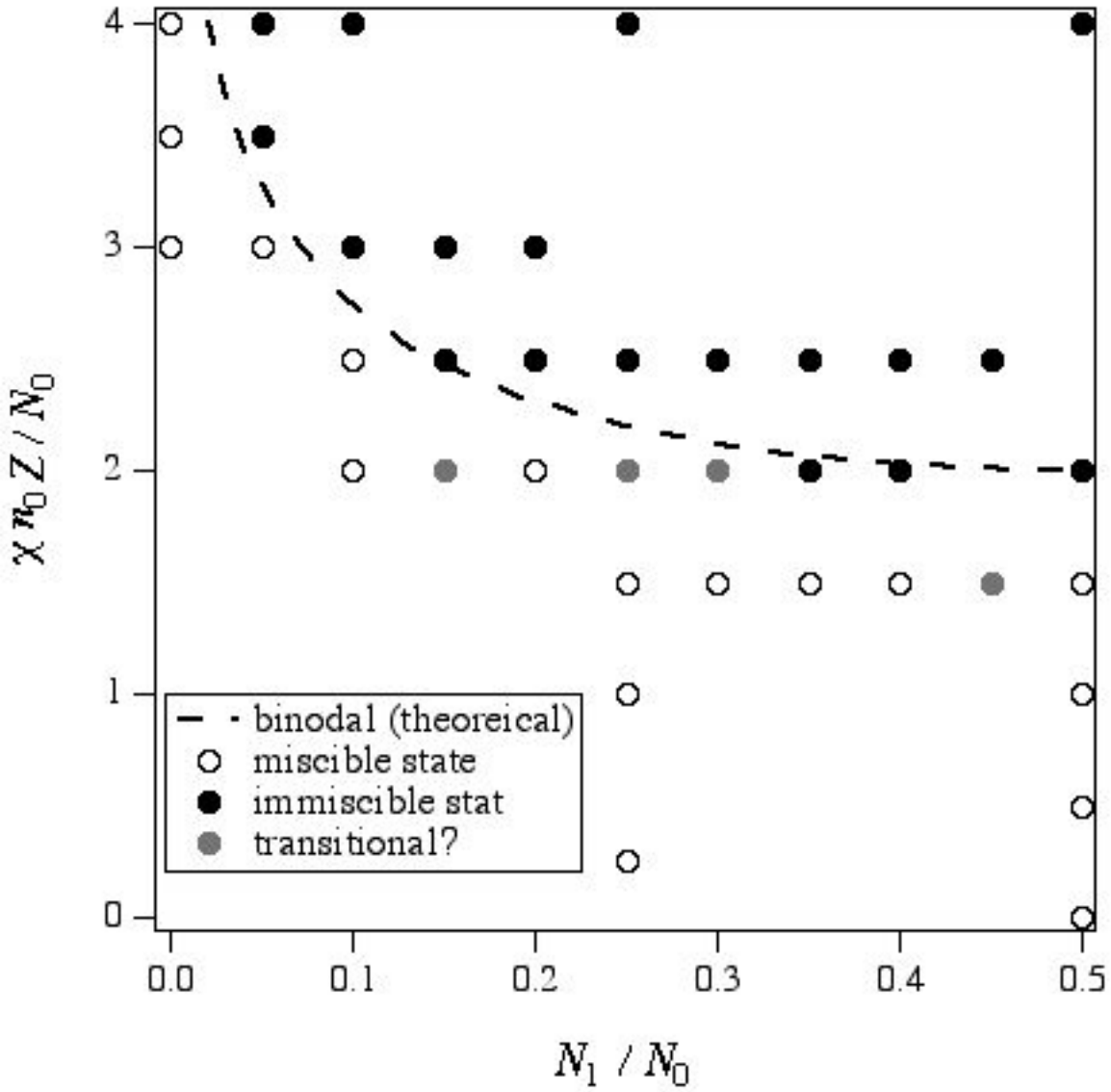




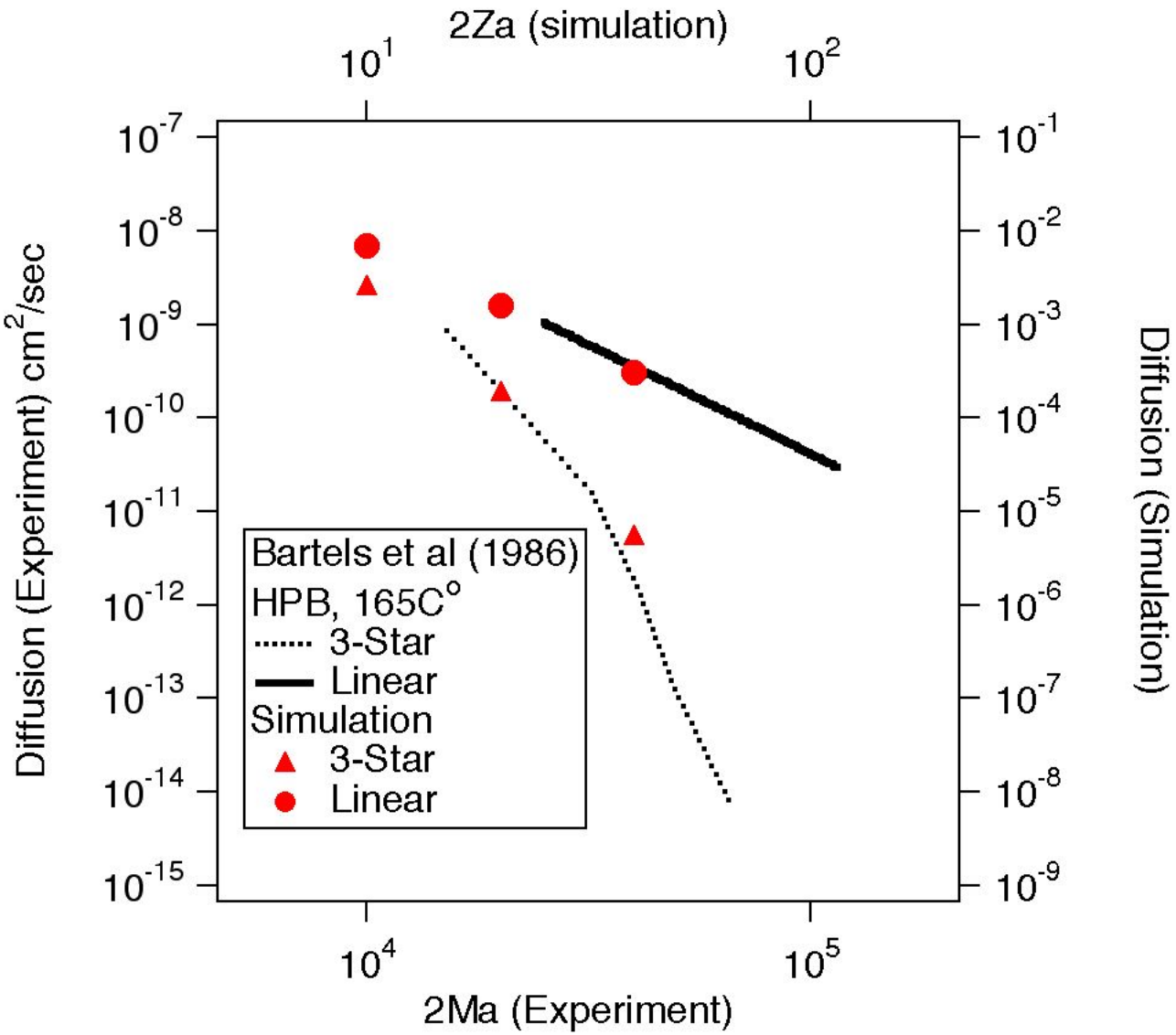




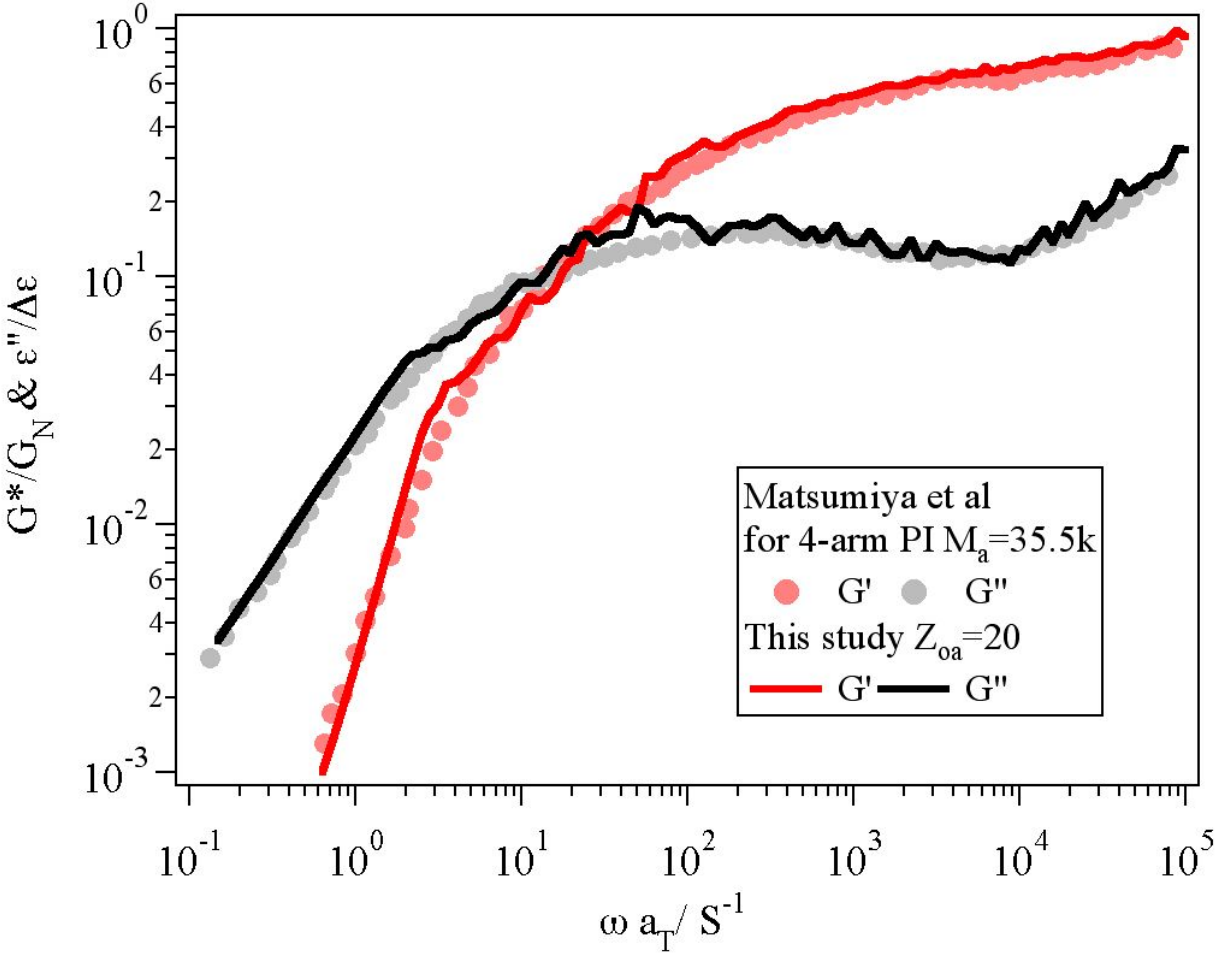
Phase diagram



Star polymers



LVE for 4-arm Star

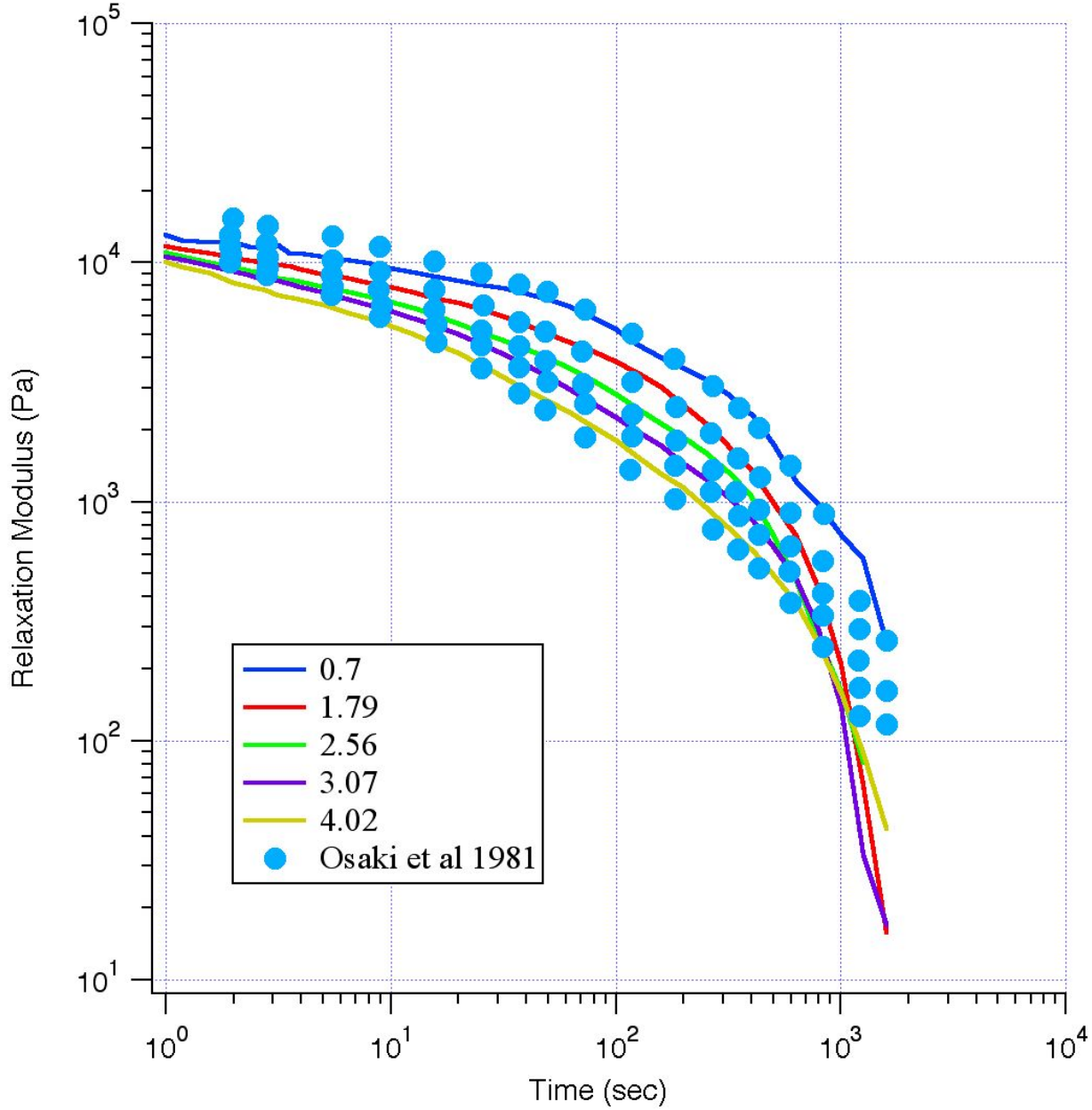


Non-equilibrium simulations

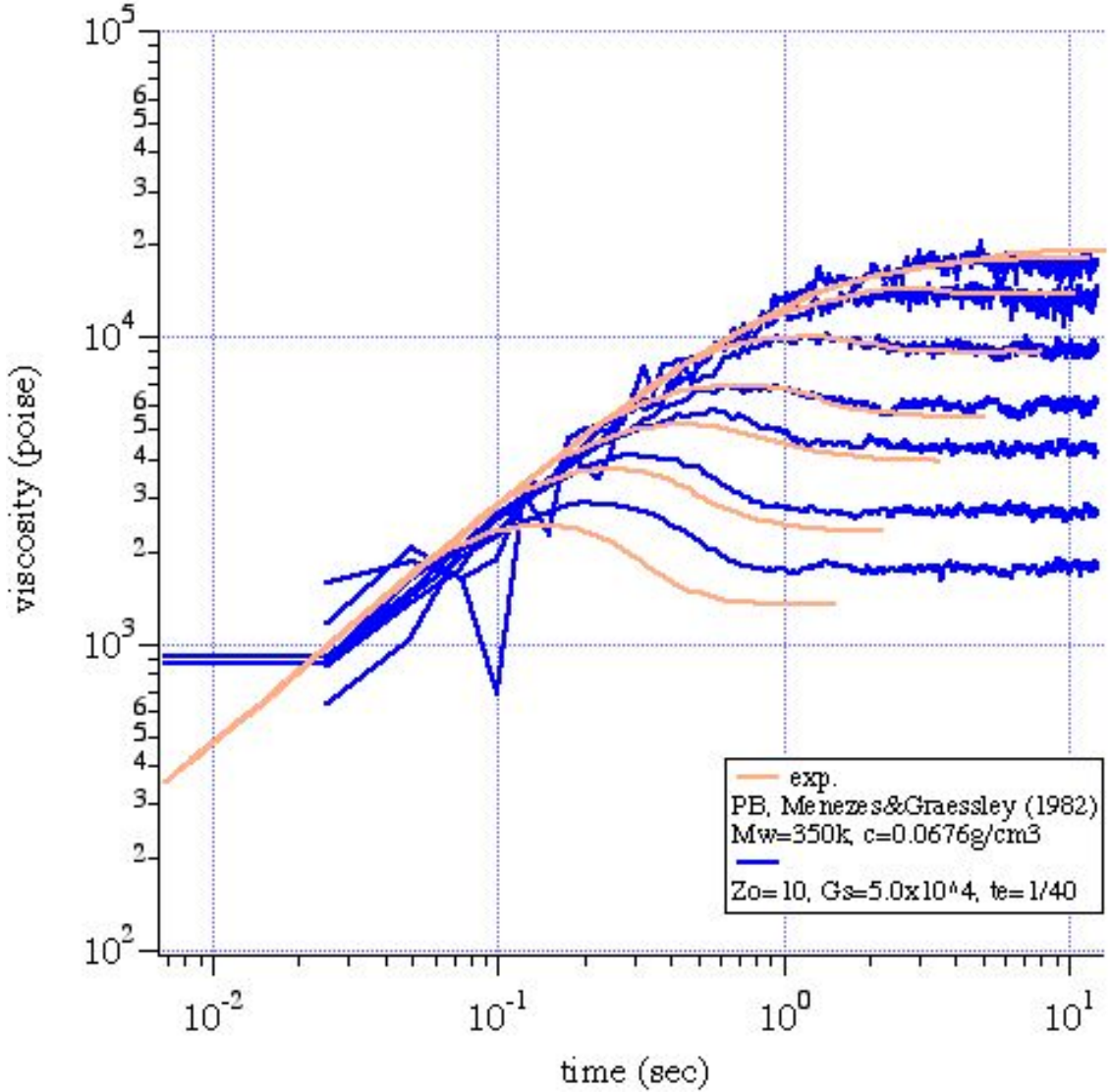
$$2\zeta\left(\dot{\mathbf{R}} - \mathbf{k}\cdot\mathbf{R}\right) = \frac{3kT}{b^2}\sum_i \frac{\mathbf{r}_i}{n_i} - \nabla\mu + \mathbf{F}$$

Periodic boxes are also displaced according to velocity gradient **k**

Step strain


Relaxation Modulus (Pa)
Time (sec)
10^5
10^4
10^3
10^2
10^1
10^0
10^1
10^2
10^3
10^4
0.7
1.79
2.56
3.07
4.02
Osaki et al 1981

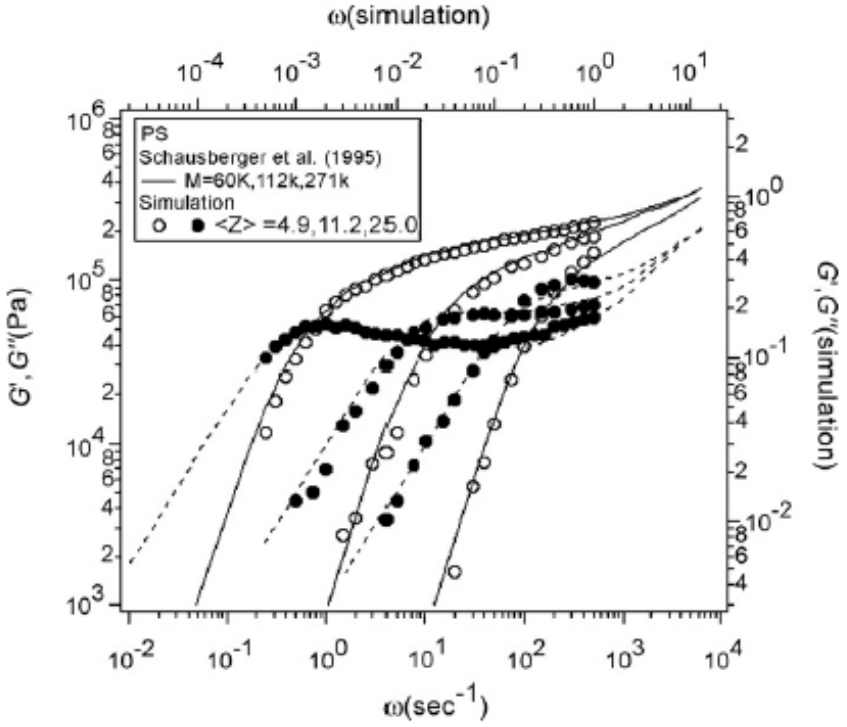
Shear flow start-up

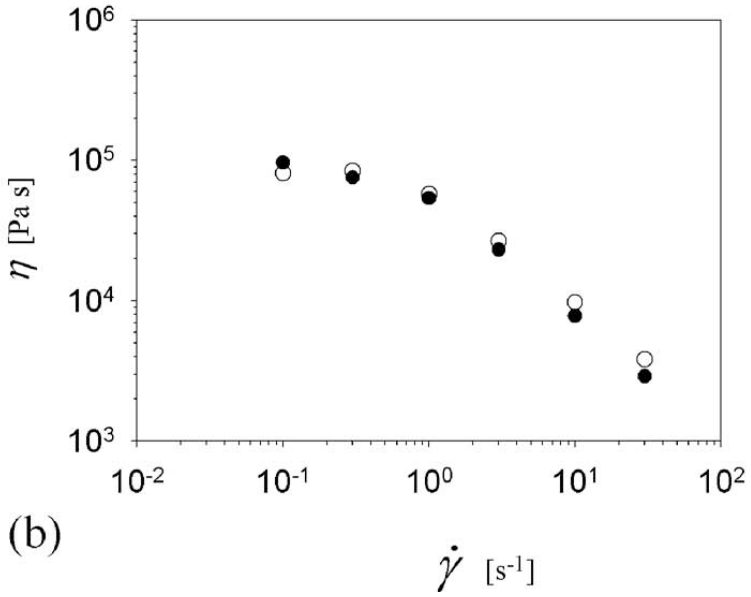


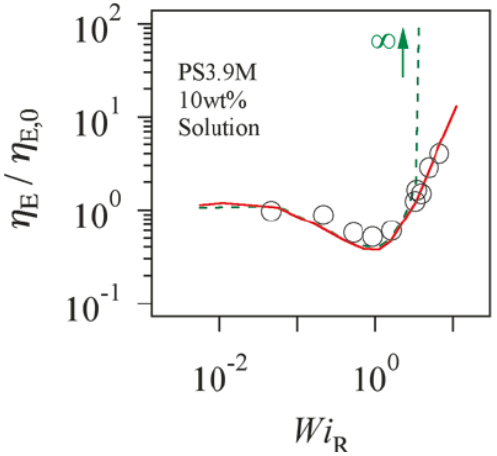
Time and modulus scales from LVE already shown

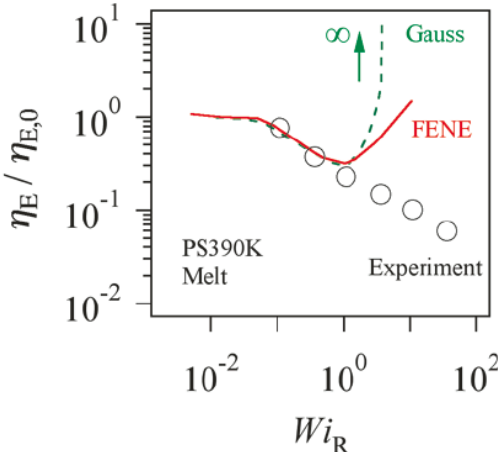
No adjustable parameters

Rheology: comparison with PS data



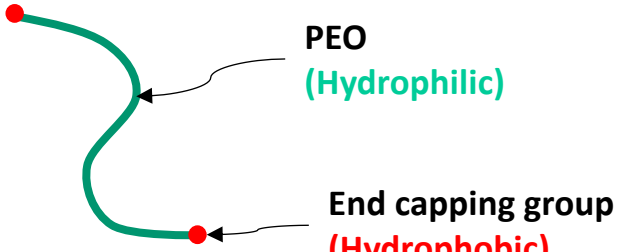


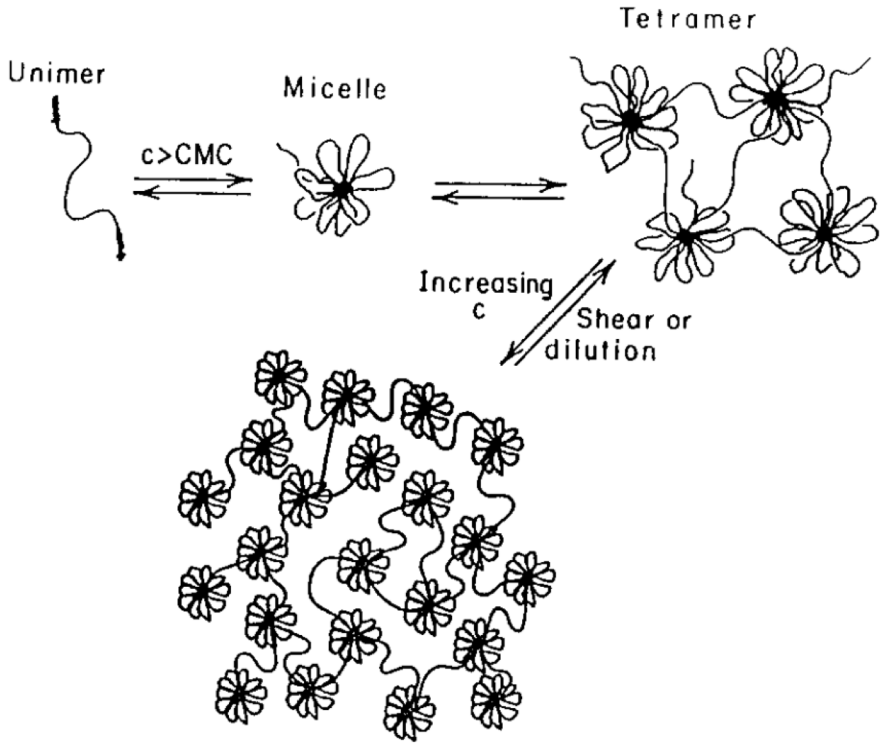




Very successful in linear and nonlinear shear ..., but large discrepancies in fast extensional flows of entangled melts

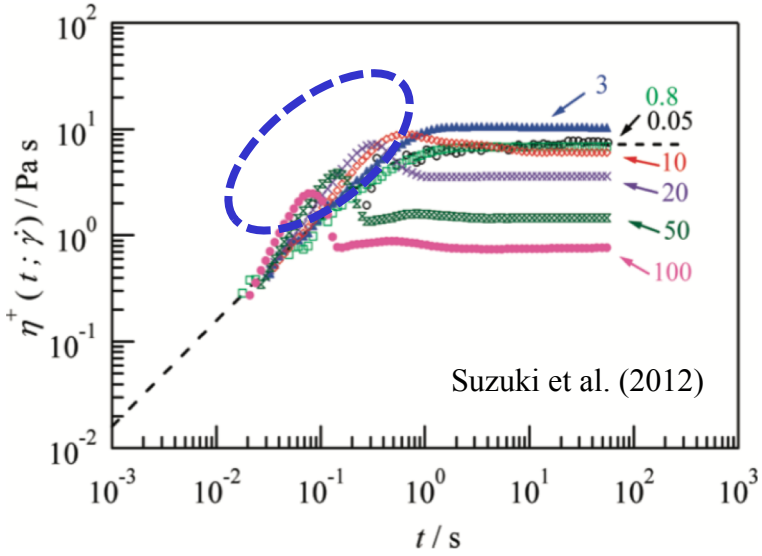
Associating Telechelic Polymers

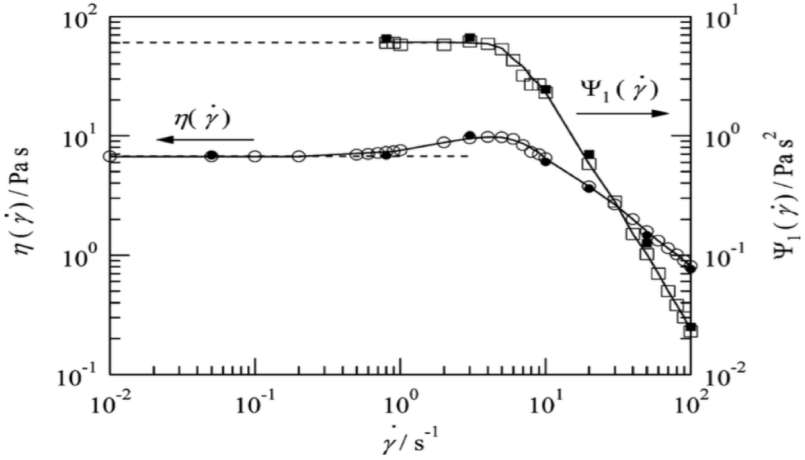




Xu et al. (1996)

Strain-hardening in shear startup





Shear thickening in $\eta(\dot\gamma)$

No thickening in $\Psi_1(\dot\gamma)$

Mixed Langevin-MC scheme

$$\frac{1}{\zeta_k}\left(\frac{\partial \mathbf{r}_k}{\partial t} - \boldsymbol{\kappa}\cdot\mathbf{r}_k\right) = \sum_i \mathbf{F}_{ik}^{(rep)} + \sum_{i\in\mathscr{C}_k} \mathbf{F}_{ik}^{(el)} + \mathbf{F}_k^{(Br)}$$

Fixed Connectivity

+

Dissociation

$$P_{ij}^{dissoc} = \min\{1, \beta_{ij}\delta t\}$$

dissociation probability

$$\beta_{ij} = \beta(\mathbf{r}_{ij}) \equiv \beta_0 \exp\left(\frac{F(\mathbf{r}_{ij})l}{k_B T}\right)$$

Classical detachment frequency

Association

$$P_{ij}^{assoc} = \exp\left(-\frac{U(\mathbf{r}_{ij})}{k_B T}\right)$$

Boltzmann distribution

$$F_j(n) = \frac{1}{Z_j}\sum_{i=1}^{n} P_{ij}^{assoc}$$

Normalized cumulated distribution function