THEORY GROUP

Max-Planck-Institut für Polymerforschung
Max Planck Institute for Polymer Research

Introduction to

Computer Simulations of Soft Matter

Methodologies and Applications

Boulder July, 19-20, 2012

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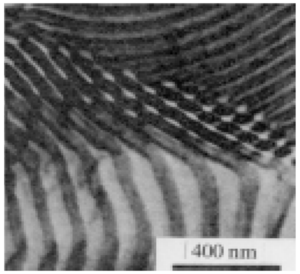
Max Planck Institute for Polymer Research, Mainz

Overview

- Simulations, general considerations
- Monte Carlo (MC)
  - Basics
  - Application to Polymers (single chains, many chains systems
  - methods
  - Molecular Dynamics(MD)
  - Basics
  - Ensembles
  - Application to Polymers
  - Example: Melt of linear and ring polymers
  - Simple membrane models
- (DPD and Lattice Boltzmann)
- Multiscale Techniques

Time and length scales



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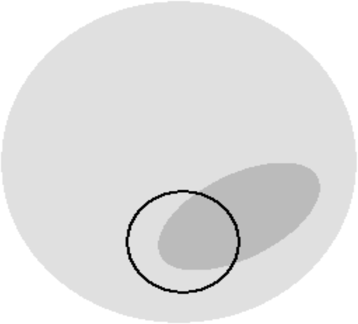

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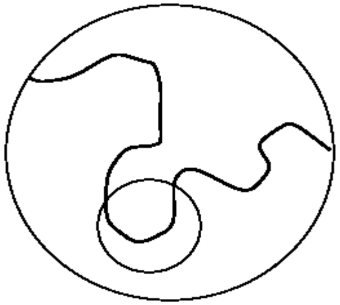
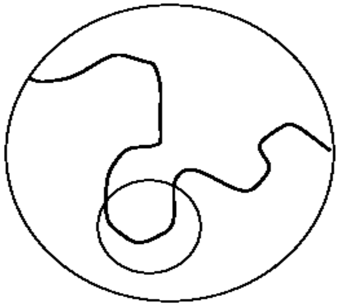


Properties

Macroscopic
domains etc.

Semi macroscopic
L ≅ 100Å - 1000Å
T ≅ 0 (1 sec)

Mesoscopic
L ≅ 10Å - 50Å
$T \cong 10^{-8} - 10^{-4}$ sec
Entropy dominates



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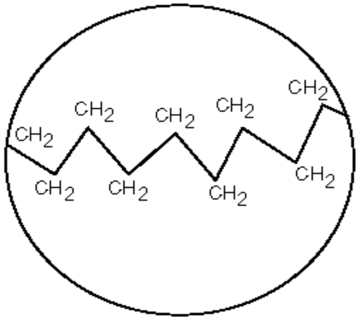

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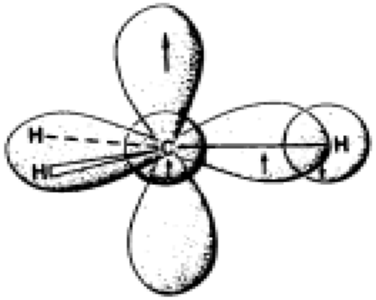


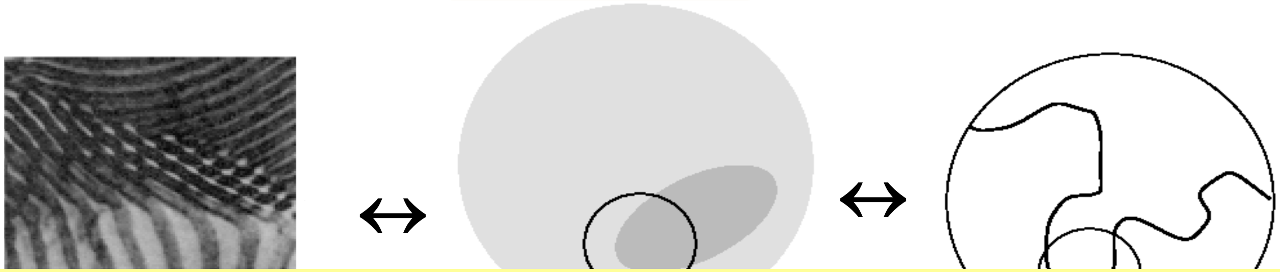
Mesoscopic
L ≅ 10Å - 50Å
$T \cong 10^{-8} - 10^{-4}$ sec
Entropy dominates

Microscopic
L ≅ 1Å - 3Å
$T \cong 10^{-13}$ sec
Energy dominates

(Sub)atomic
electronic structure
chemical reactions
excited states

generic/universal *** **chemistry specific**

Time and length scales



Pro

Ansatz: integrate equations of motion of a classical atomistic model

timestep ≈ 10^{-15} sec
global relaxation time O(1s)
still "small" system ≈ 10^{6} atoms

⇒ At least 10^{21} integration time steps

In most cases neither useful, nor possible

Use alternative options, employ universality, focus on question to be solved

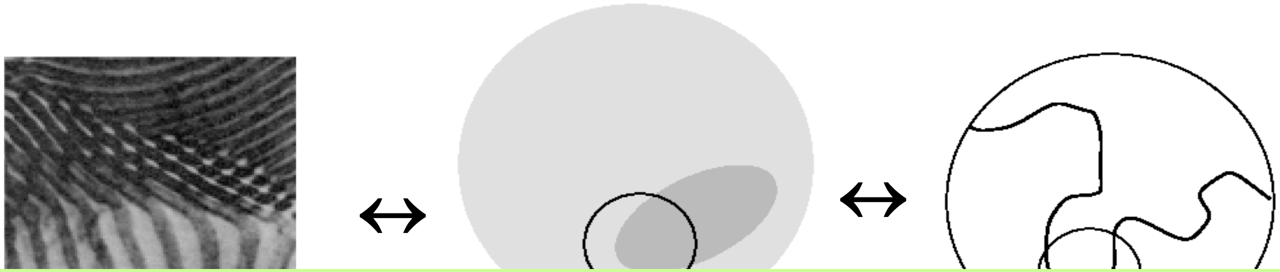
L ≅ 10A - 50A
T ≅ 10^{-8} - 10^{-4} sec
Entropy dominates

L ≅ 1A - 3A
T ≅ 10^{-13} sec
Energy dominates

electronic structure
chemical reactions
excited states

generic/universal *** **chemistry specific**

Time and length scales



General Advise:

- Models should be as simple as possible, taken the question one asks into account
- Use theory information as much as possible

- Avoid conserved extensive quantities, when possible (causes transport issues, slow)
- Try to beat natural slow dynamics for faster averaging (cannot be used to study dynamics)

Pro

L ≅ 10A - 50A
T ≅ 10^{-8} - 10^{-4} sec
Entropy dominates

L ≅ 1A - 3A
T ≅ 10^{-13} sec
Energy dominates

electronic structure
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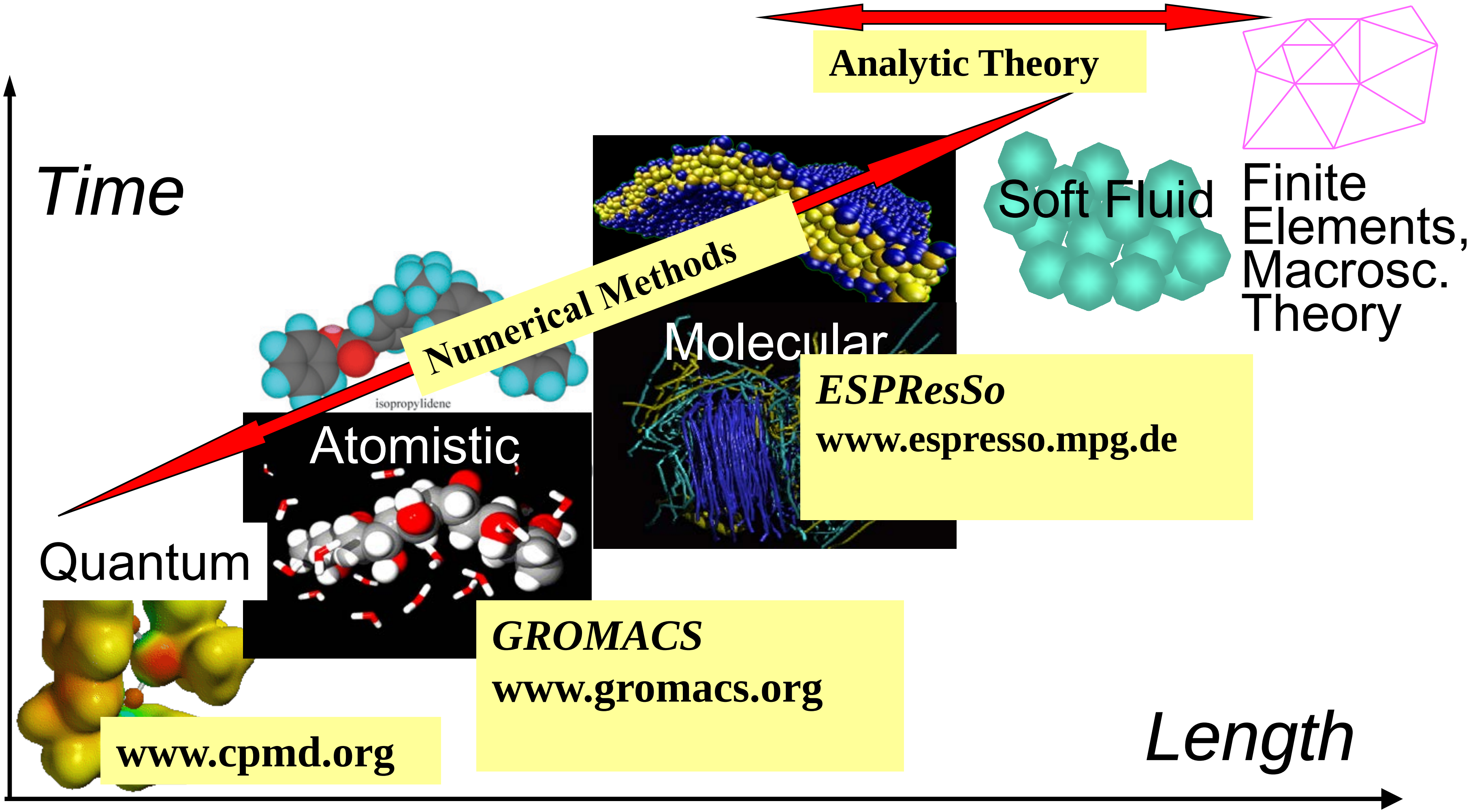
excited states

generic/universal *** **chemistry specific**

Soft Matter Theory: Comprehensive Understanding of Physical and Chemical Properties



Analytic Theory

Time

Numerical Methods

Soft Fluid

Finite Elements, Macrosc. Theory

Molecular

ESPResSo
www.espresso.mpg.de

Atomistic

Quantum

GROMACS
www.gromacs.org

www.cpmd.org

Length

Local Chemical Properties ⇔ Scaling Behavior of Nanostructures
Energy Dominance ⇔ Entropy Dominance of Properties

Simulations, general considerations

Pure MD
(Newton’s eq., Liouville Eq.)

↓

MD coupled to Noise
(Fokker Planck Eq.)

↓

Brownian Dynamics
(Smoluchowski Eq.)

↓

Force Biased MC

↓

Pure MC

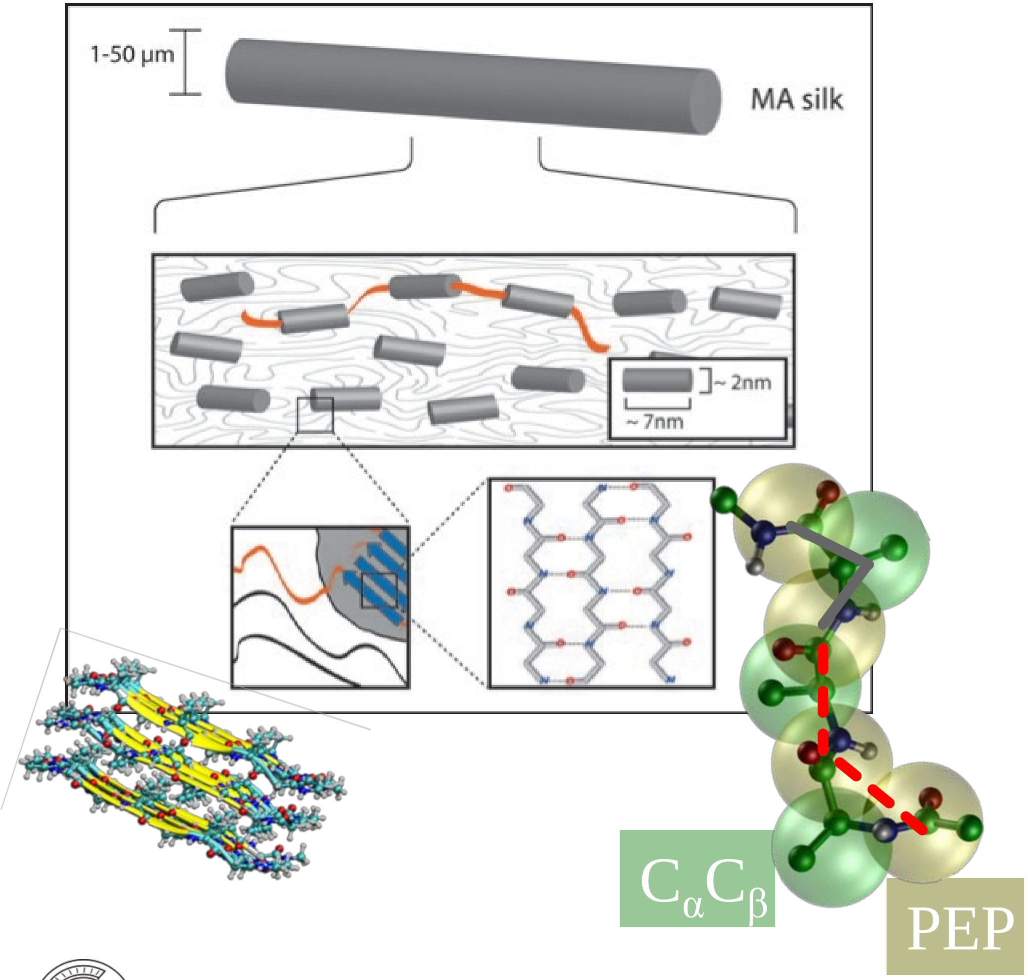
Deterministic dynamics

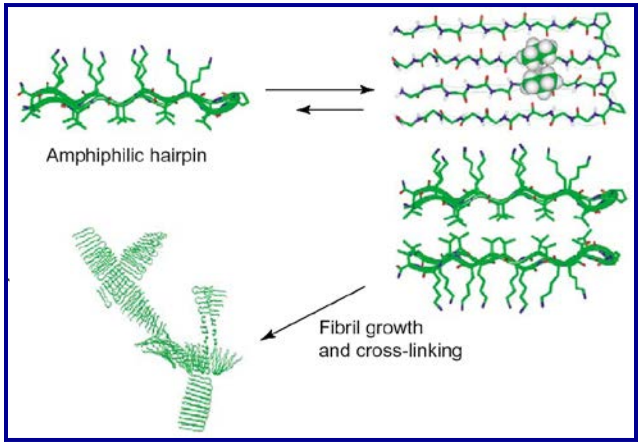
↓

Stochastic dynamics

Simulations, general considerations

Alanine-rich regions in silk proteins





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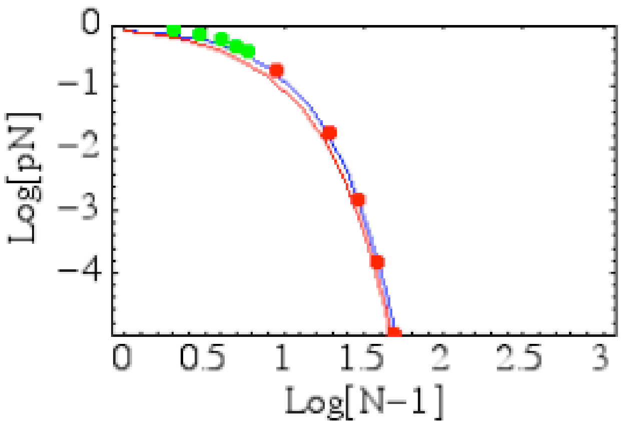
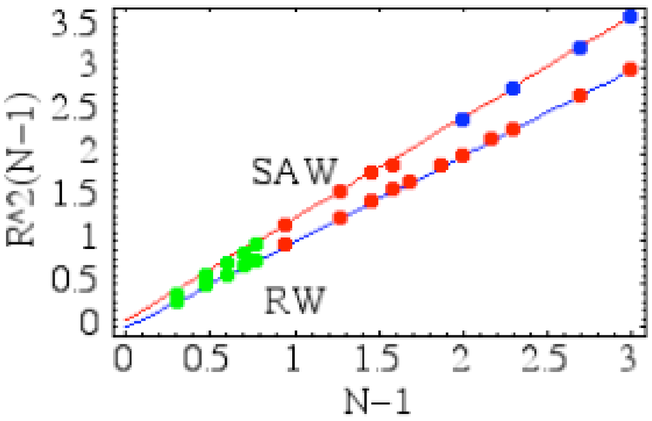
exact enumeration, simple sampling, pivot

- Ratio of number of RW / SAW configurations
- Average size of SAWs

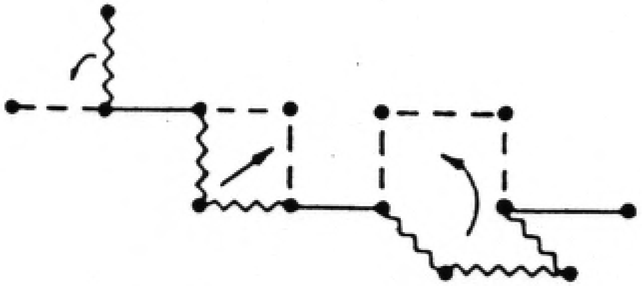
100.	259.568
200.	601.917
500.	1786.96
1000.	4060.73



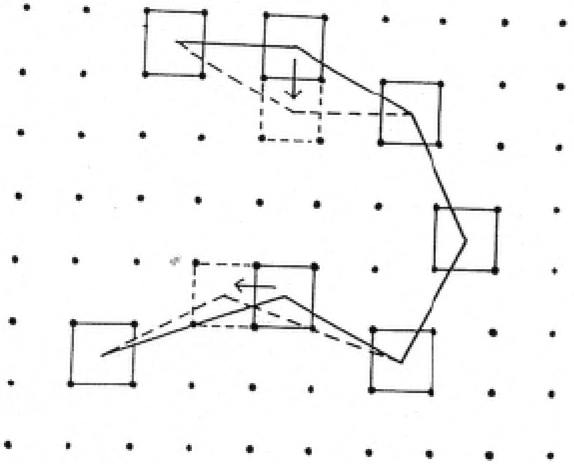


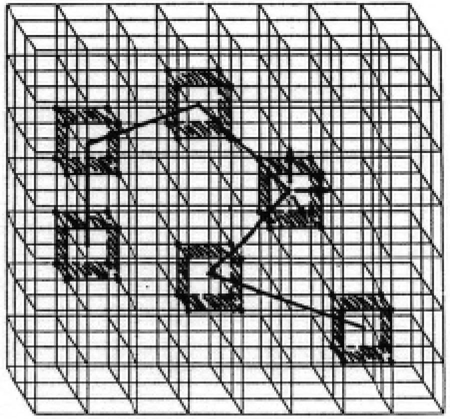
$$\left\langle R^2 \right\rangle \propto N^{2\nu}$$

Simulations, general considerations
MC models/moves for Rouse Dynamics



Generate “new” bonds inside chain:
Mimics Rouse coupling to heat bath





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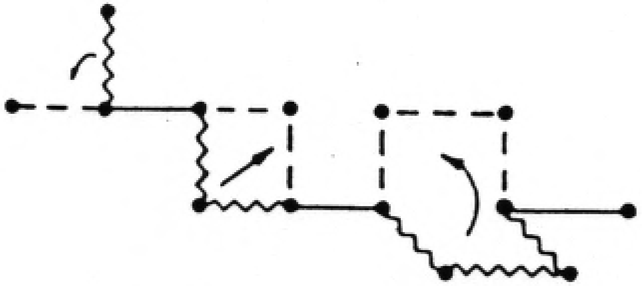
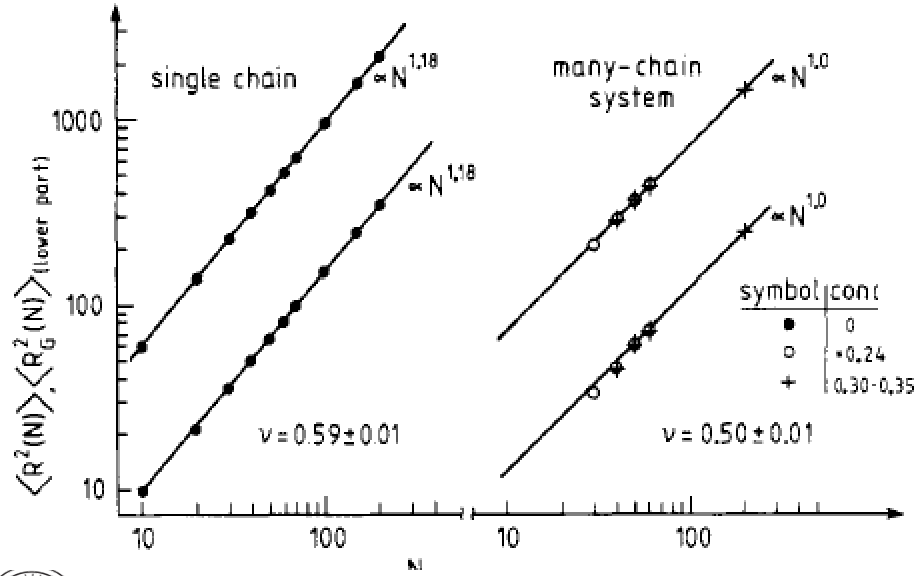
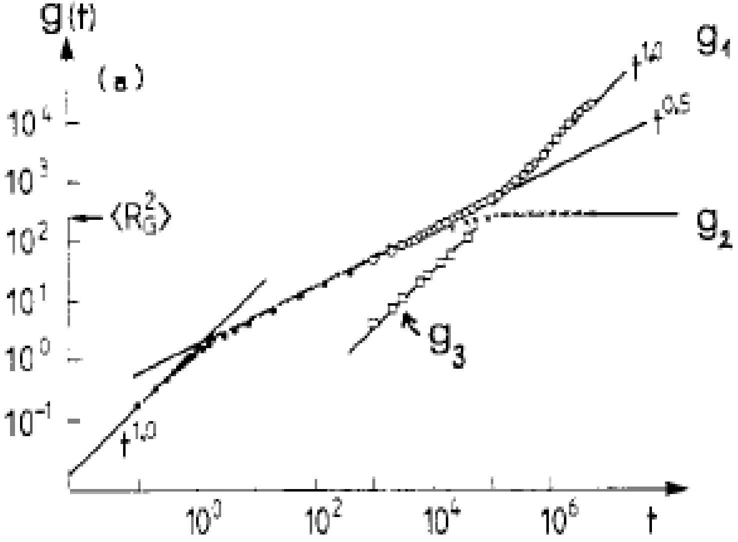


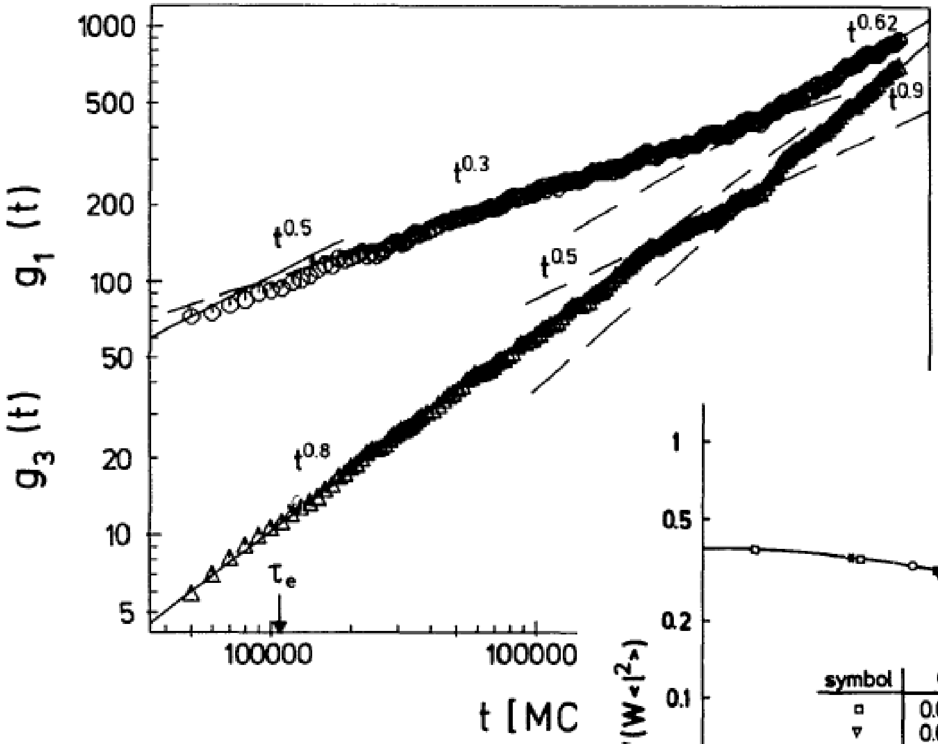


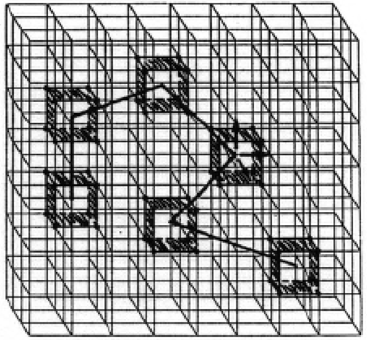
Diamond lattice data

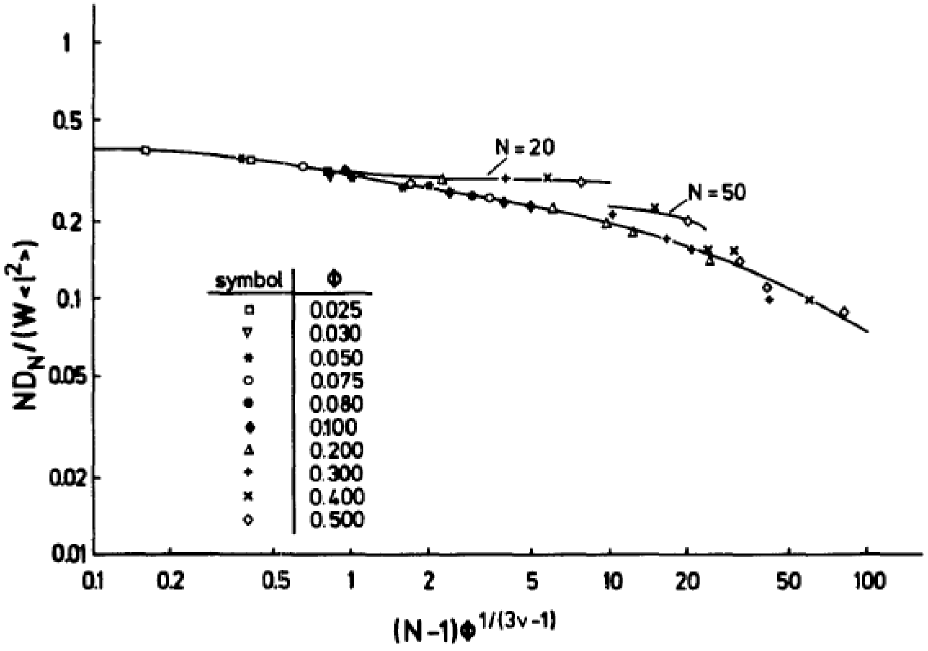


Simulations, general considerations
MC models/moves for Rouse Dynamics

Bond fluctuation model





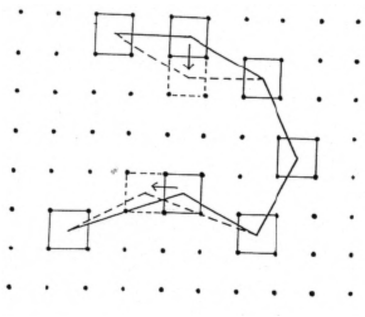


symbol	Φ
□	0.025
▽	0.030
✱	0.050
○	0.075
●	0.080
◆	0.100
△	0.200
+	0.300
×	0.400
◇	0.500

FIG. 9. Scaling plot of $ND_N/(W\langle l^2\rangle)$ vs the rescaled chain length $\tilde{N} \equiv (N-1)[\langle l^2\rangle^{3/2}\phi]^{1/(3\nu-1)}$ for the values of the volume fraction ϕ as indicated in the figure.

JCP 1991

Simulations, general considerations
MC models/moves for Rouse Dynamics



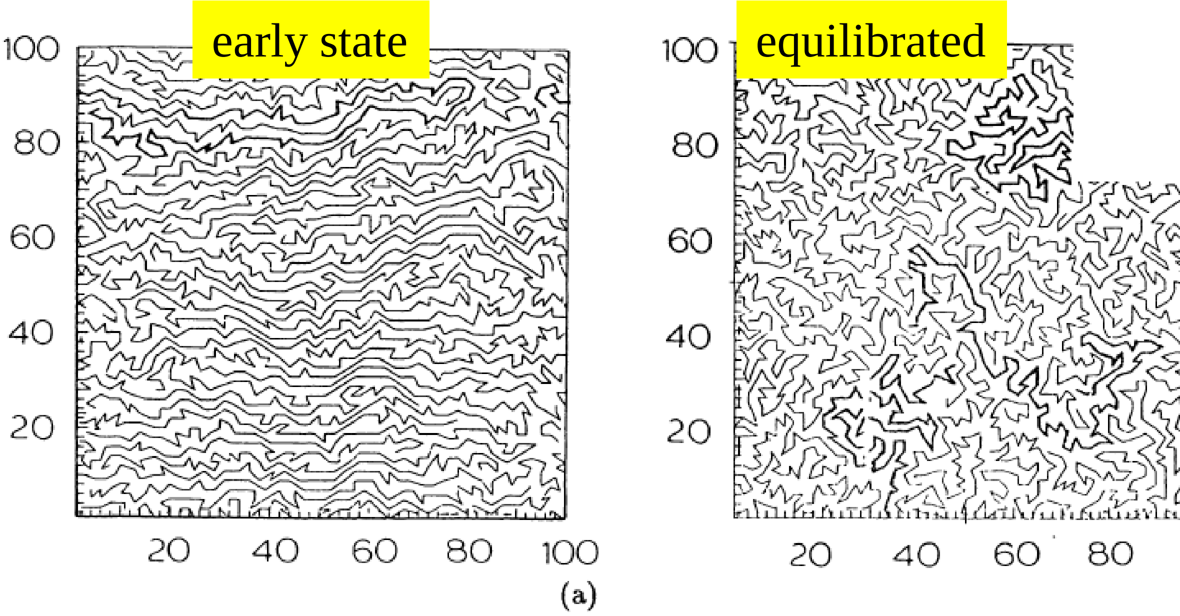
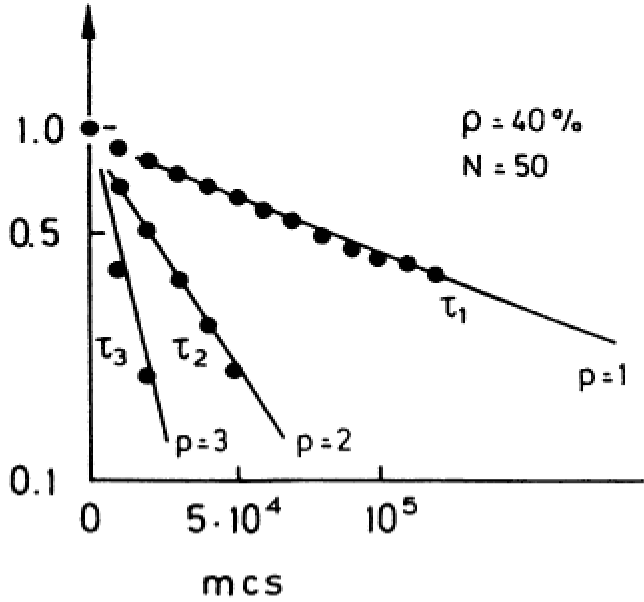


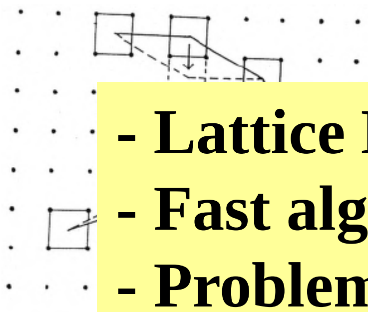
Fig. 2. — (a) Snapshot configuration of a $\rho = 0.8$, $N = 100$ system a short time after the initial state. The internested structure is clearly displayed. (b) Snapshot configuration of the structure of figure 2a, where the system was almost equilibrated.

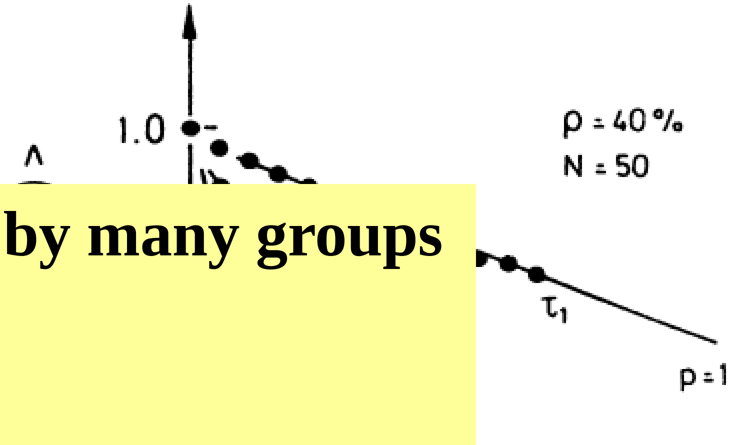


J. Phys. France **51** (1990) 915–932

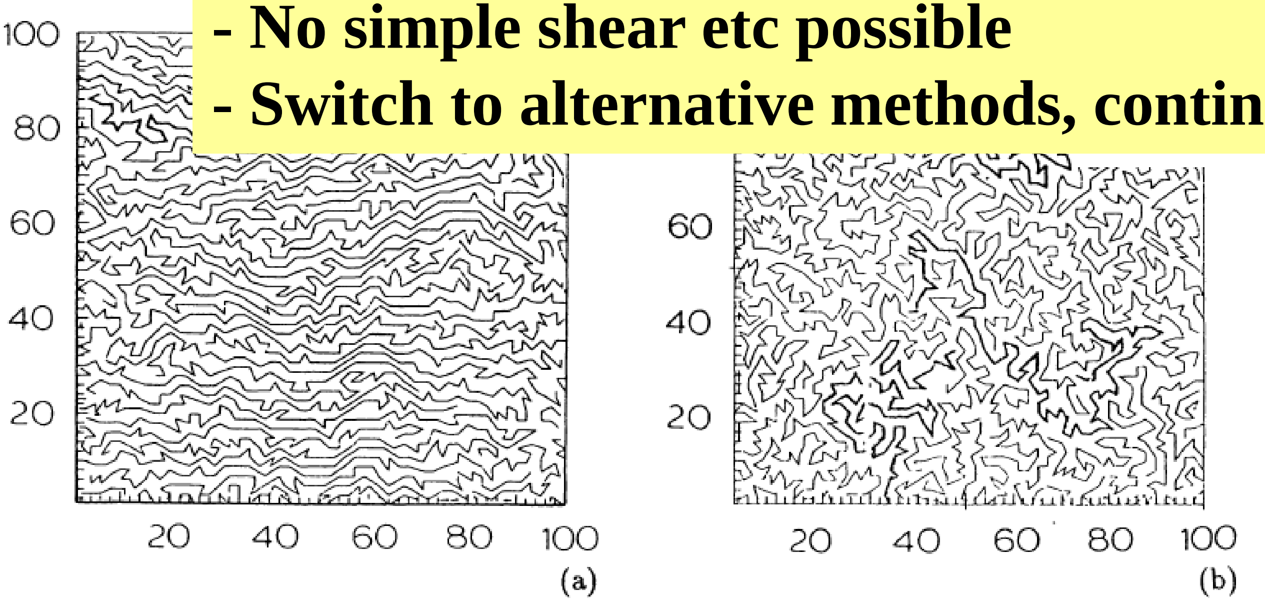
ond fluctuation model

Simulations, general considerations
MC models/moves for Rouse Dynamics





- **Lattice MC methods still used by many groups**
- **Fast algorithms**
- **Problems at high densities**
- **No simple shear etc possible**
- **Switch to alternative methods, continuum**



(a) (b)

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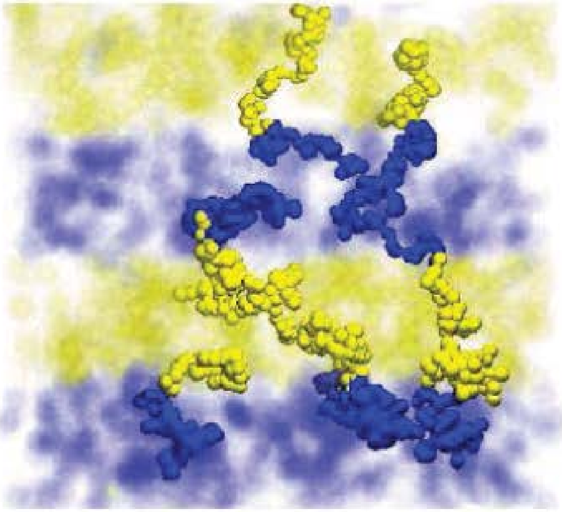
Hybrid methods: SCF + MC

(Mueller, Daoulas, de Pablo, Schmid)



calculate the instantaneous, fluctuating and spatially varying density

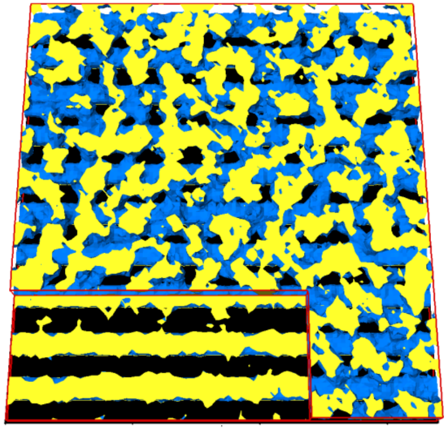
re-calculate the external fields from the fluctuating densities using

$$w_A = iw_+ + w_- = -\frac{\chi_o N}{2}\left[\phi_A - \phi_B\right] + \kappa_o N \left[\phi_A + \phi_B - 1\right]$$

$$w_B = iw_+ - w_- = +\frac{\chi_o N}{2}\left[\phi_A - \phi_B\right] + \kappa_o N \left[\phi_A + \phi_B - 1\right]$$

MC or BD simulation of single chain molecules in fluctuating, external fields

M. Müller, K. Daoulas et al: Coupling SCF calculations to particle based Monte Carlo



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Basic Idea: Integrate Newton’s equations of motion for a collection of N classical particles

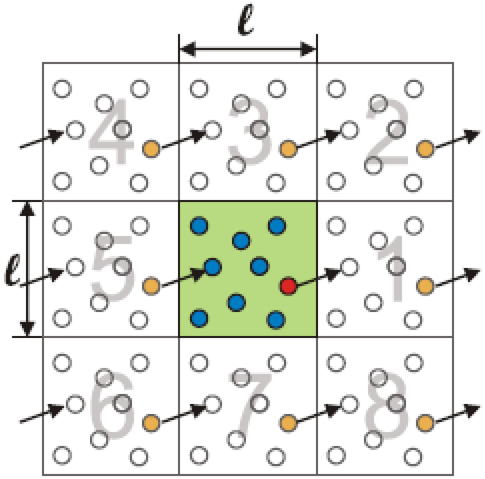

Figure 2.1: All replicated in three dimensions.

Integrate equations of motion:
Microcanonical, “NVE Ensemble”

$$m_i \ddot{\vec{r}}_i = \vec{F}_i(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_{N-1}, \vec{r}_N)$$

$$\dot{\vec{r}}_i = \frac{\partial \mathcal{H}}{\partial \vec{p}_i} \, , \quad \dot{\vec{p}}_i = -\frac{\partial \mathcal{H}}{\partial \vec{r}_i}$$

Interaction potential e.g. LJ

$$U_{LJ}\,(r_{ij}) = \{(\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^{6}\}$$

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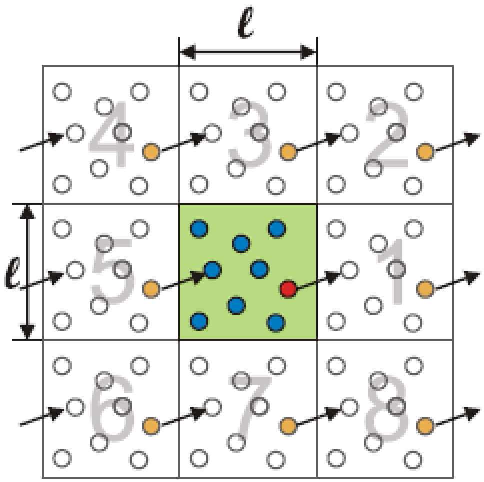


Figure 2.1: All replicated in three dimensions.

Integrate equations of motion:
Velocity Verlet, symplectic

$$\vec{r}(t+\Delta t) = \vec{r}_i(t) + \frac{\Delta t}{m_i}\vec{p}_i(t) + \frac{\Delta t^2}{2m_i}\vec{F}_i(t) + \mathcal{O}(\Delta t^3)$$

$$\vec{p}(t+\Delta t) = \vec{p}_i(t) + \Delta t\, \vec{F}_i(t) + \frac{\Delta t^2}{2}\dot{\vec{F}}_i(t) + \mathcal{O}(\Delta t^3)$$

$$\vec{F}(t+\Delta t) = \vec{F}_i(t) + \Delta t\, \dot{\vec{F}}_i(t) + \mathcal{O}(\Delta t^2)$$

$$\boxed{\begin{aligned}\vec{r}(t+\Delta t) &= \vec{r}_i(t) + \frac{\Delta t}{m_i}\vec{p}_i(t) + \frac{\Delta t^2}{2m_i}\vec{F}_i(t) + \mathcal{O}(\Delta t^3)\\ \vec{p}(t+\Delta t) &= \vec{p}_i(t) + \frac{\Delta t}{2}\left(\vec{F}_i(t) + \vec{F}_i(t+\Delta t)\right) + \mathcal{O}(\Delta t^3)\end{aligned}}$$

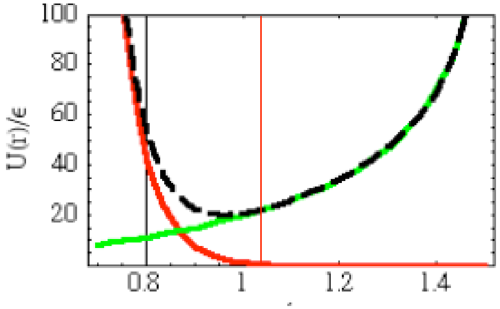
Interaction potential e.g. LJ

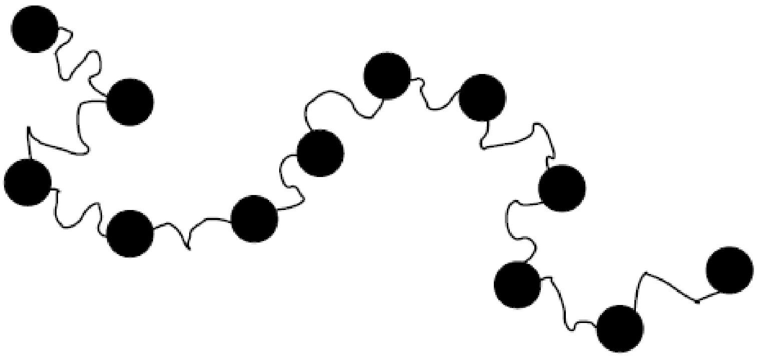
$$U_{LJ}\,(r_{ij}) = \{(\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^{6}\,\}$$

Variants of integration scheme, cf books by Frenkel and Smit, Allen and Tildesley

Simulations, general considerations

MD of single, isolated chain in space??





Bead-Bead interaction

$$U_{ij}^{0}=\begin{cases}4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12}-\left(\frac{\sigma}{r_{ij}}\right)^{6}+\frac{1}{4}\right], & r_{ij}\leqslant\sigma 2^{1/6}\\ 0, & r_{ij}>\sigma 2^{1/6}\ ,\end{cases}$$

Plus FENE spring for bonds

$$U_{ij}^{\mathrm{ch}}=\begin{cases}-0.5kR_0^2\ln[1-(r_{ij}/R_0)^2], & r_{ij}\leqslant R_0\\ 0, & r_{ij}>R_0\ ,\end{cases}$$

Simulations, general considerations

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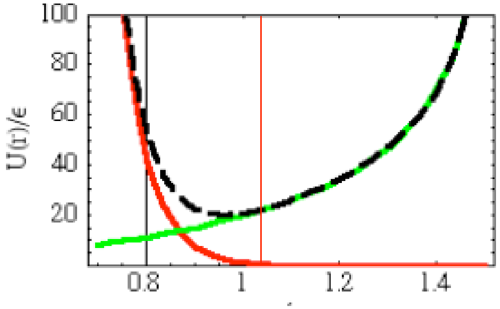

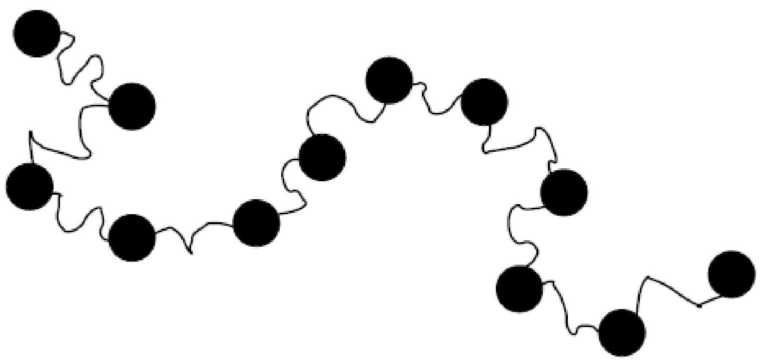

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NVE Ensemble integration:

Never equilibrates, Rouse modes do not couple strongly enough

Need noise term needed!

$$\ddot{\mathbf{r}}_i=-\nabla U_i-\Gamma\dot{\mathbf{r}}_i+\mathbf{W}_i(t)$$

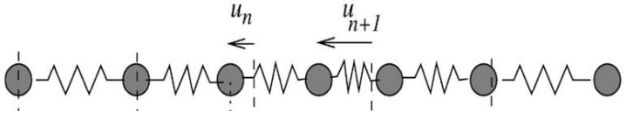
$$\langle\mathbf{W}_i(t)\cdot\mathbf{W}_j(t')\rangle=\delta_{ij}\delta(t-t')6k_BT\Gamma$$

→ **Fermi-Pasta-Ulam Problem**

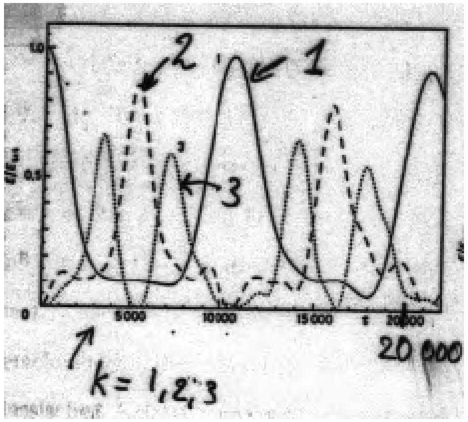
FPU Problem

weakly anharmonic chain in d=1,
with periodic boundary conditions

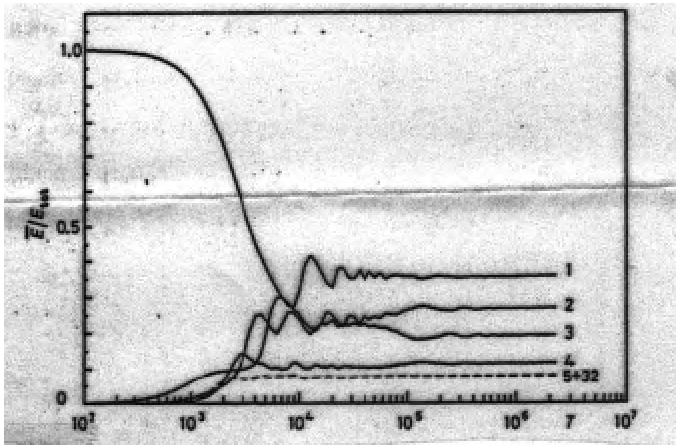
E/N =0.7, r=3, α=0.1

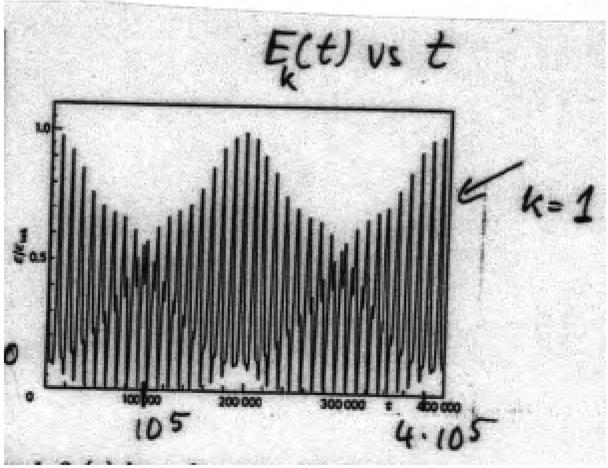


Short time



Long time





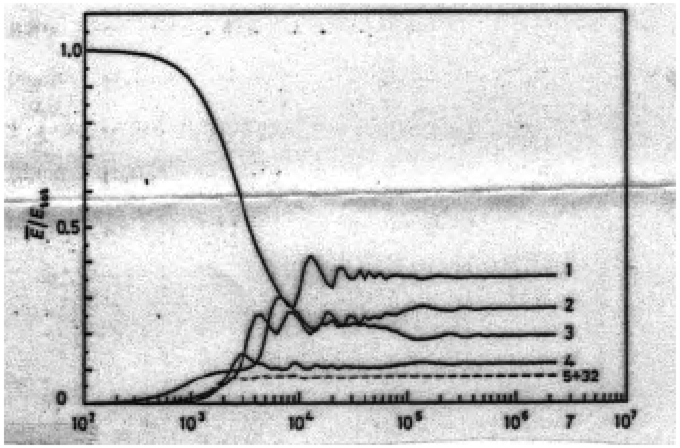
No equilibration!

Applies also to harmonic crystal

FPU Problem

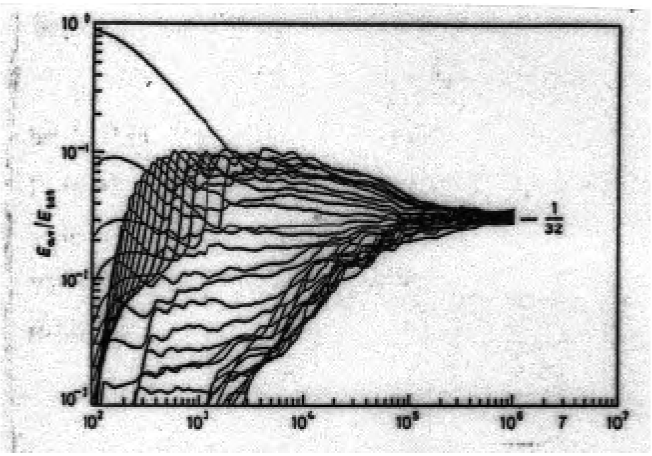
weakly anharmonic chain in d=1,
with periodic boundary conditions

E/N =0.7, r=3, α=0.1



non ergodic

E/N =1.2, r=3, α=0.1



ergodic

E/N =1.0, r=3, α=0.1, most probably border line non ergodic - ergodic

For ergodicity need (strongly) mixing modes!

Simulations, general considerations
FPU Problem

FPU Hamiltonian for $\alpha=0$ integrable,
phase space is a N-dimesional manifold of the general 2N-dimensional phase space

for $\alpha\neq0$ not integrable anymore, however there is NO analytical expression, of α_{min}, for which modes properly mix and make system ergodic

Fast equilibrating MD has strongly mixing modes, thus chaotic dynamics

Intrinsically instable, not deterministic for longer times

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Fast equilibrating MD has strongly mixing modes, thus chaotic dynamics

➡ **Intrinsically instable, not deterministic for longer times**

➡ **Need stabilization, coupling to a thermostat -> NVT, canonical ensemble**

MD – Ensembles

Integrating Newton’s equations
=> microcanonical (NVE)
➡ **stability issues for long runs…**

MD plus Thermostat
=> Canonical Ensemble, NVT
two options: local vs global coupling
➡ **possible consequences for dynamics**

MD plus Barostat
=> constant pressure Ensemble, NPE,
usually with Thermostat, NPT

Application:
Polymer melts and networks

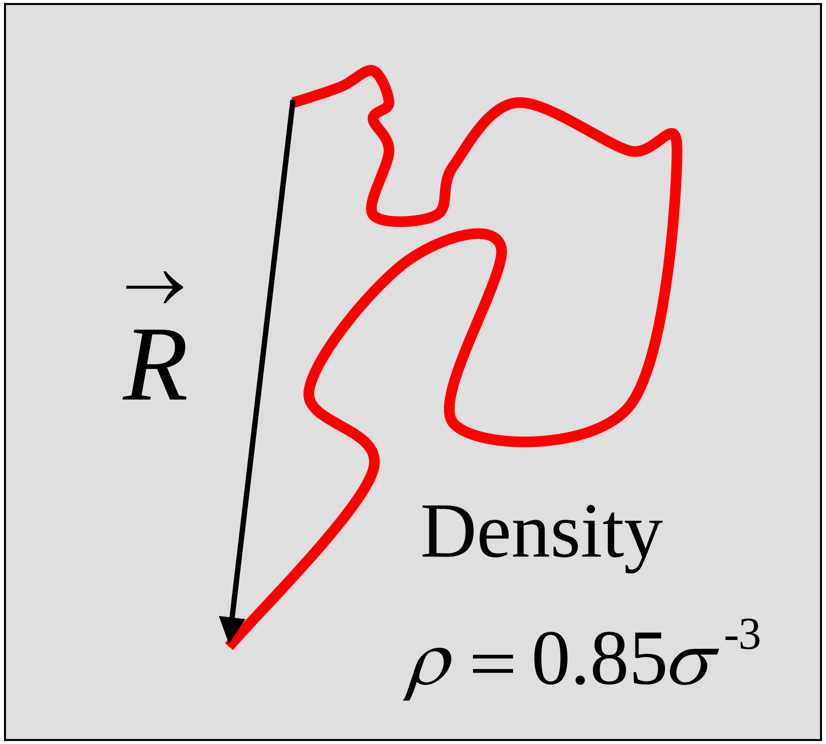
- how to generate an equilibrated polymer melt?

- role of topological constraints

- ring polymers vs open chains

Bead-spring model

K.K & G.S. Grest



Density

$$\rho = 0.85\sigma^{-3}$$

Dense monomeric liquid

Flexible chains

$$\langle R^2 \rangle \approx c_\infty b^2 (N-1) = l_K L$$

$$c_\infty = 1.7$$

$$b = 0.97\sigma$$

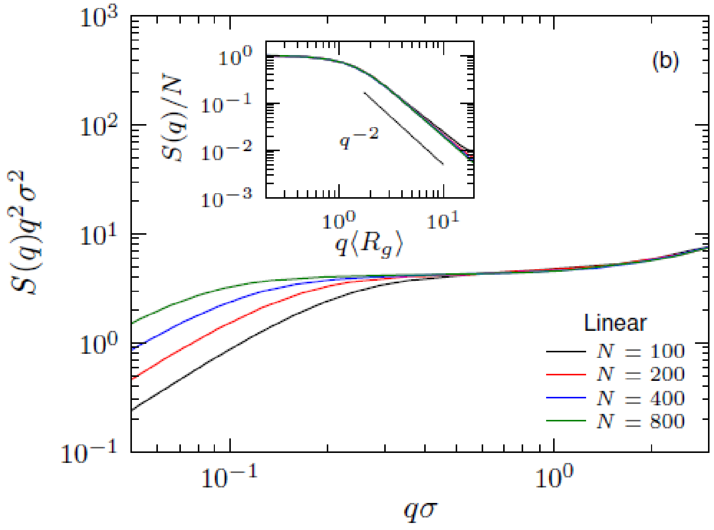
$$l_K = c_\infty b, \qquad L = (N-1)b$$

Equilibration of initial melt

Auhl et al JCP, 2003

Max-Planck-Institut für Polymerforschung
Max Planck Institute for Polymer Research

- **Run a short chain melt to equilibrium by “brute force” and/or algorithm with global moves**
- **This is the “reference” system for longer chain melts!**



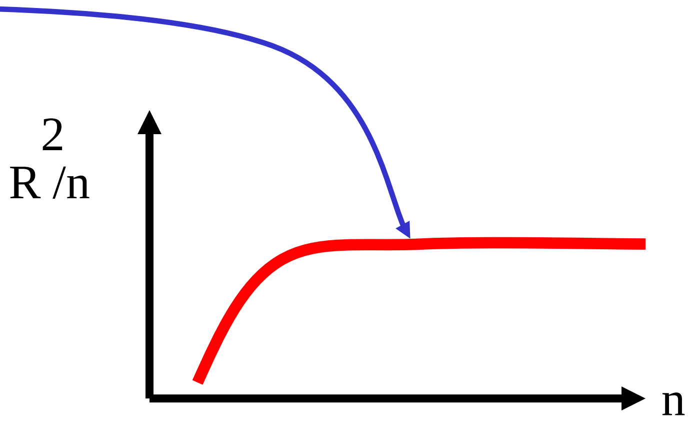
typically $N = O(N_e)$

$$\langle R^2(N)\rangle = l_K N$$

Create **Target Function**

$$\langle R^2(n)\rangle = \langle (r_i - r_{i+n})^2\rangle$$

$$\langle R^2(n)\rangle \propto \begin{cases} n^2, & nl < l_k \\ n, & nl > l_k \end{cases}$$



Equilibration of initial melt

- **Create random walks with “correct” statistics by Monte Carlo procedure (e.g. NRRWs)**

$$\left\langle R^2(N) \right\rangle = l_K N$$

*** Position walks randomly in space**
*** Move walks around by random procedure (translation, rotation, inflection) to minimize density fluctuations**
*** replace/exchange walks randomly to reduce density fluctuations**
*** Slowly increase excluded volume**
*** Control target functions permanently**
*** Eventually complement by double-bridging moves**

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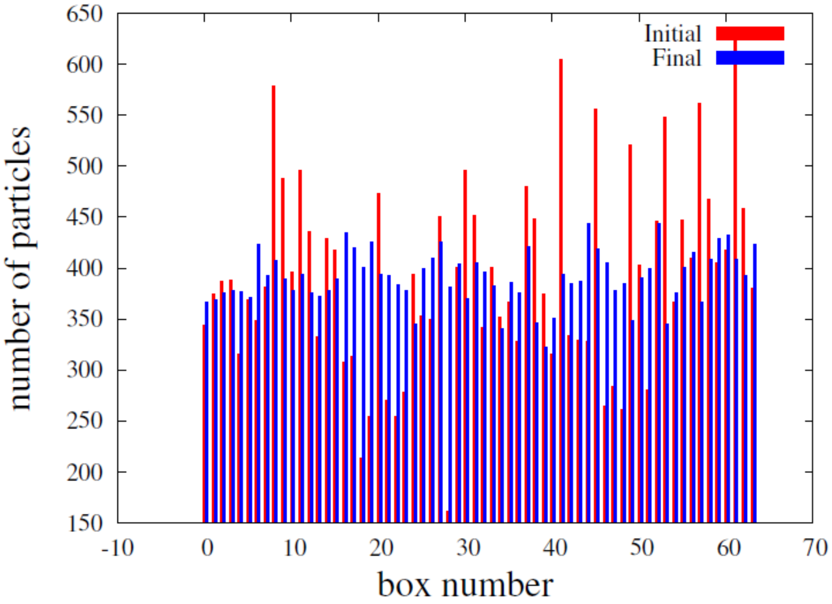
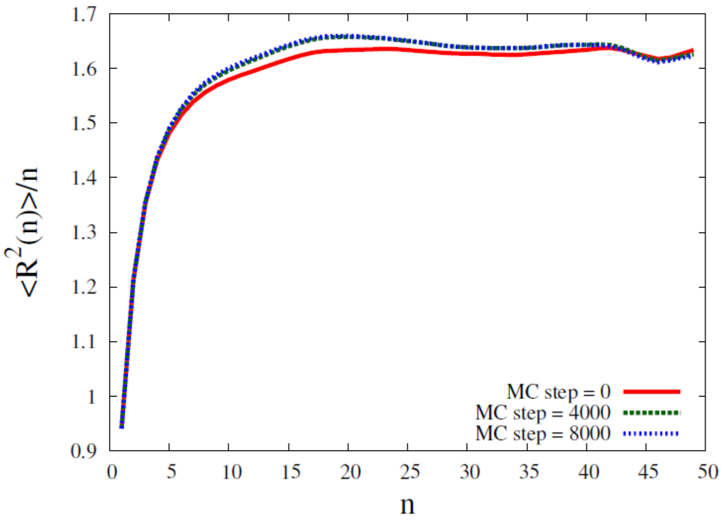
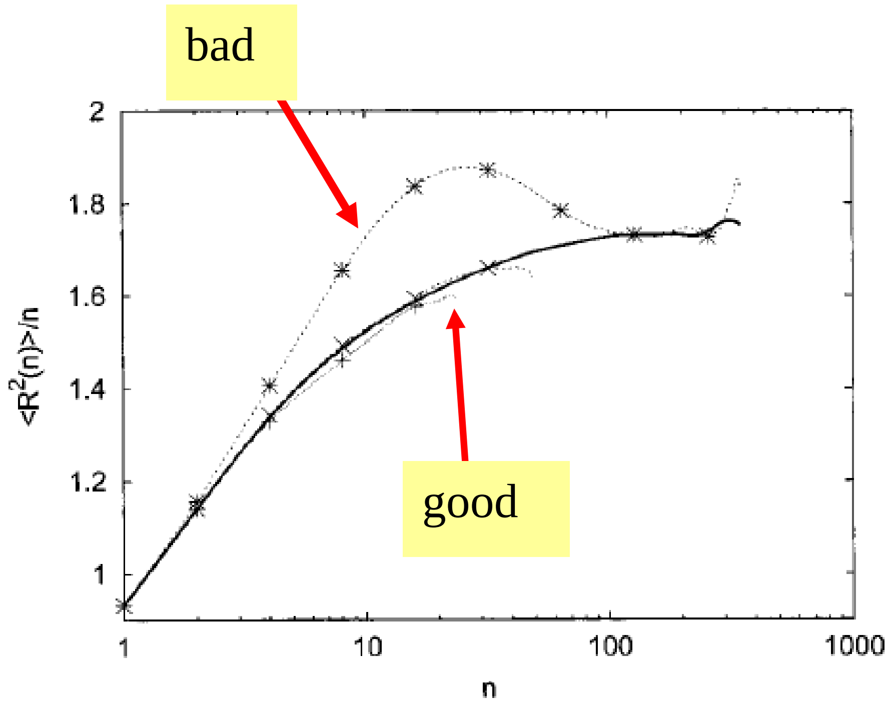
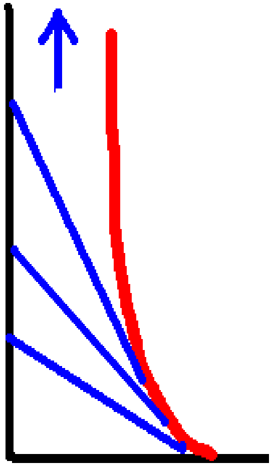




* Slowly increase excluded volume
* Control target functions permanently
* Eventually complement by double-bridging moves

MD runs plus very slow insertions of the excluded volume





Equilibration of initial melt

$$\left\langle R^2(n)\right\rangle = \left\langle (r_i - r_{i+n})^2\right\rangle$$

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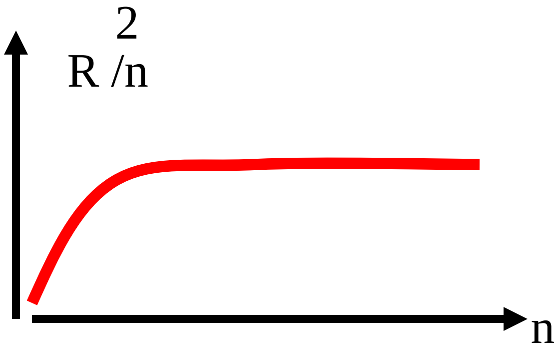
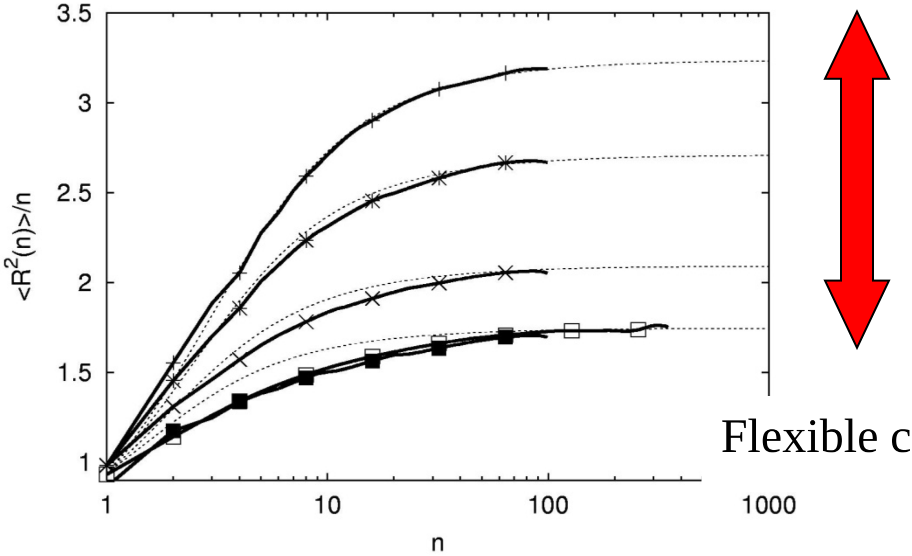
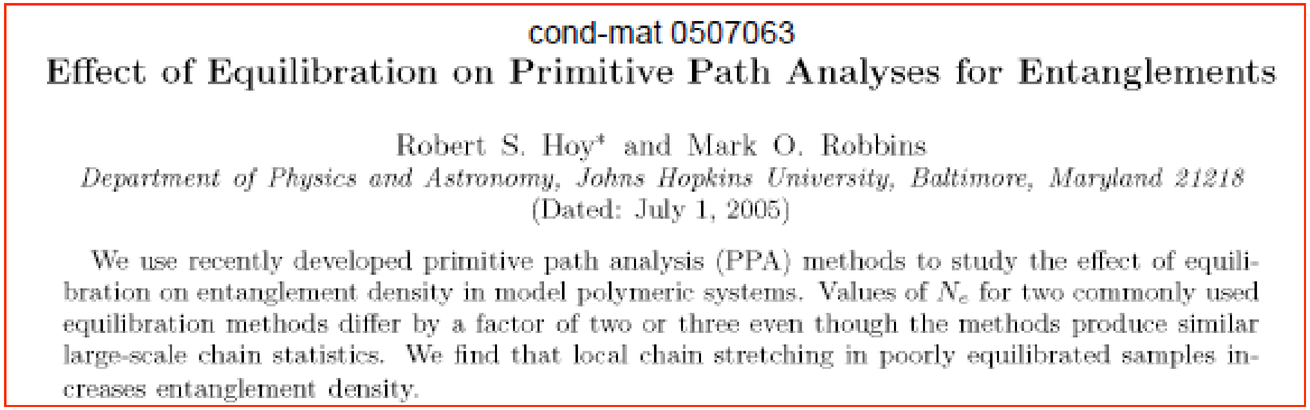


Stiff chains



Flexible chains

Equilibration of initial melt: ABSOLUTELY CRUCIAL

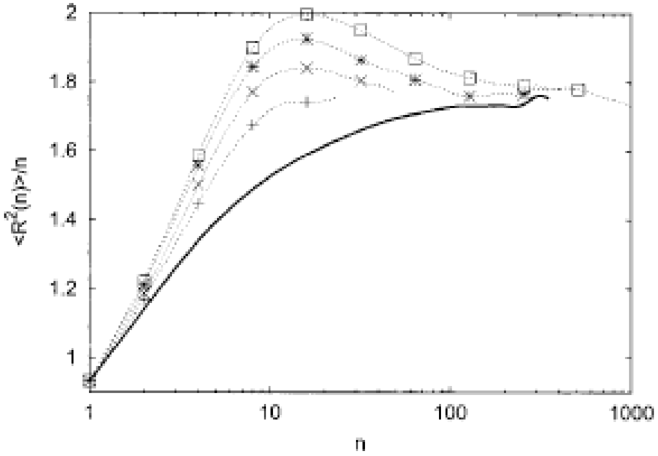


cond-mat 0507063

Effect of Equilibration on Primitive Path Analyses for Entanglements

Robert S. Hoy* and Mark O. Robbins
Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland 21218
(Dated: July 1, 2005)

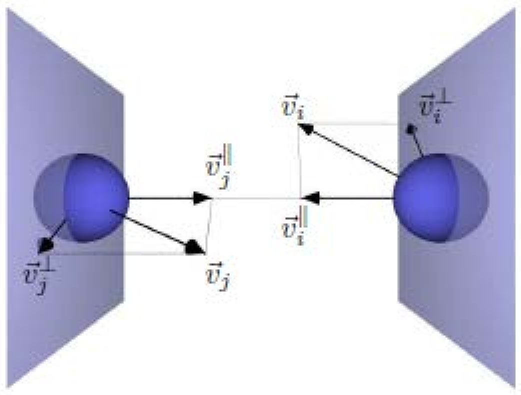
We use recently developed primitive path analysis (PPA) methods to study the effect of equilibration on entanglement density in model polymeric systems. Values of N_e for two commonly used equilibration methods differ by a factor of two or three even though the methods produce similar large-scale chain statistics. We find that local chain stretching in poorly equilibrated samples increases entanglement density.

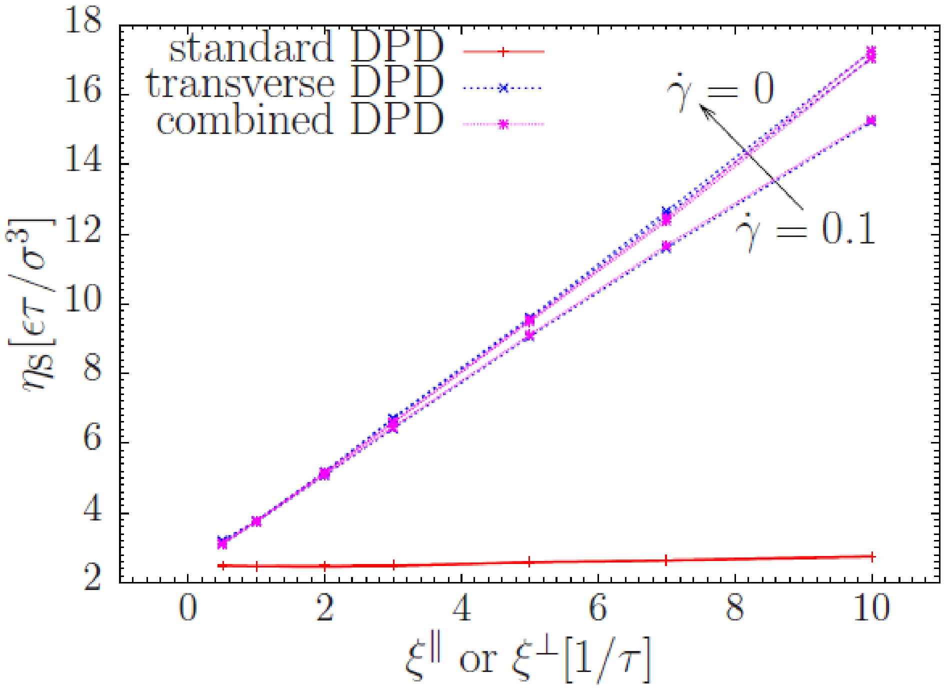


fast pushoff leads to
chain stretching on
intermediate length scales

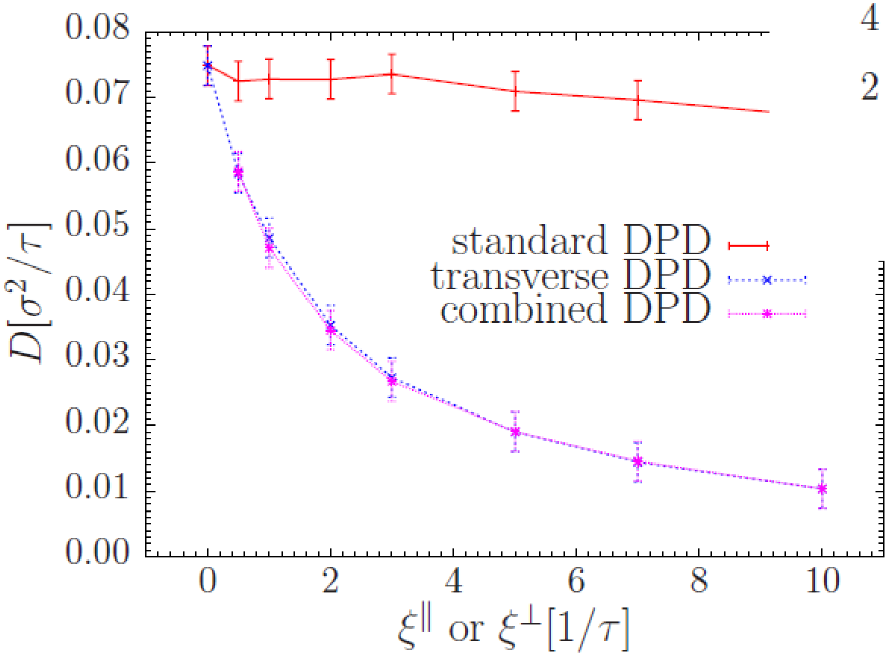
R. Auhl, R. Everaers, G. S. Grest, K. Kremer & S. Plimpton,
J. Chem. Phys. (2003)

DPD: Dissipative Particle Dynamics





shear viscosity



diffusion

General Literature

Reviews

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- C. Peter, K. Kremer, Introductory Lecture for FD 144 Faraday Discuss., **144**, 9 (2010)

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- Frenkel and Smit, “Understanding Molecular Simulations”, Academic Press, 2002
- Allen and Tildesley, “Computer Simulatiosn of Liquids”, Clarendon Press, 1989
- G. Voth, ed., “Coarse-Graining of Condensed Phase and Biomolecular Systems”, Taylor and Francis, 2009