Introduction to

Computer Simulations of Soft Matter
Methodologies and Applications
Boulder July, 19-20, 2012

K. Kremer
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

(Macroscopic) domains etc.

- Length scale: $L \approx 10\text{ Å} - 50\text{ Å}$
- Time scale: $T \approx 10^{-8} - 10^{-4}\text{ sec}$
- Energy dominates

(Semi macroscopic)

- Length scale: $L \approx 100\text{ Å} - 1000\text{ Å}$
- Time scale: $T \approx 0 (1\text{ sec})$
- Entropy dominates

(Mesoscopic)

- Length scale: $L \approx 10\text{ Å} - 50\text{ Å}$
- Time scale: $T \approx 10^{-8} - 10^{-4}\text{ sec}$
- Entropy dominates

(Microscopic)

- Length scale: $L \approx 1\text{ Å} - 3\text{ Å}$
- Time scale: $T \approx 10^{-13}\text{ sec}$
- Energy dominates

(Sub)atomic electric structure

- Chemical reactions
- Excited states

Properties

- Generic/universal
- Chemistry specific

***
Time and length scales

**Ansatz:** Integrate equations of motion of a classical atomistic model

- timestep $\approx 10^{-15}$ sec
- global relaxation time $O(1s)$
- still “small” system $\approx 10^6$ atoms

$\Rightarrow$ 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

- $L \approx 10A - 50A$
- $T \approx 10^{-8} - 10^{-4}$ sec
- Entropy dominates

- $L \approx 1A - 5A$
- $T \approx 10^{-13}$ sec
- Energy dominates

generic/universal $***$ chemistry specific
Time and length scales

Subatomic electronic structure ↔ chemical reactions ↔ excited states

Microscopic
\[ L \cong 1\text{Å} - 3\text{Å} \]
\[ T \cong 10^{-13} \text{sec} \]
Energy dominates

Mesoscopic
\[ L \cong 10\text{Å} - 50\text{Å} \]
\[ T \cong 10^{-8} - 10^{-4} \text{sec} \]
Entropy dominates

Semi macroscopic
\[ L \cong 100\text{Å} - 1000\text{Å} \]
\[ T \cong 0 (1 \text{sec}) \]

Macroscopic

generic/universal *** chemistry specific

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)
Soft Matter Theory: Comprehensive Understanding of Physical and Chemical Properties

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

Time

Quantum

Atomistic

Numerical Methods

Soft Fluid

Finite Elements, Macrosc. Theory

Analytic Theory

Finite Elements, Macrosc. Theory

www.gromacs.org

www.cpmd.org

www.espresso.mpg.de

GROMACS

www.gromacs.org

ESPResSo

www.espresso.mpg.de
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
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
exact enumeration, simple sampling, pivot

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

<table>
<thead>
<tr>
<th>Value</th>
<th>Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>259.568</td>
</tr>
<tr>
<td>200</td>
<td>601.917</td>
</tr>
<tr>
<td>500</td>
<td>1786.96</td>
</tr>
<tr>
<td>1000</td>
<td>4060.73</td>
</tr>
</tbody>
</table>

\[
\langle R^2 \rangle \propto N^{2\nu}
\]
Simulations, general considerations
MC models/moves for Rouse Dynamics

Generate “new” bonds inside chain: Mimics Rouse coupling to heat bath
Simulations, general considerations
MC models/moves for Rouse Dynamics

Diamond lattice data
Simulations, general considerations
MC models/moves for Rouse Dynamics

Bond fluctuation model

FIG. 9. Scaling plot of $N^2 \langle \xi^2 \rangle / W(\xi^2)$ vs the rescaled chain length $\bar{N} = (N - 1)/(\xi^2)^{1/3}$ for the values of the volume fraction $\phi$ as indicated in the figure.
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.
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

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

**Bond fluctuation model**
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

\[
\begin{align*}
    w_A &= iw_+ + w_- = -\frac{\chi_0 N}{2} [\phi_A - \phi_B] + \kappa_0 N [\phi_A + \phi_B - 1] \\
    w_B &= iw_+ - w_- = +\frac{\chi_0 N}{2} [\phi_A - \phi_B] + \kappa_0 N [\phi_A + \phi_B - 1]
\end{align*}
\]

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

Integrate equations of motion: Microcanonical, “NVE Ensemble”

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

\[ \dot{p}_i = \frac{\partial H}{\partial \dot{r}_i}, \quad \dot{r}_i = -\frac{\partial H}{\partial p_i} \]

Interaction potential e.g. LJ

\[ U_{LJ} (r_{ij}) = \left\{ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right\} \]
Basic Idea: Integrate Newton’s equations of motion for a collection of N classical particles

Integrate equations of motion:
Velocity Verlet, symplectic

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

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

\[ \vec{F}(t + \Delta t) = \vec{F}_i(t) + \Delta t \ddot{\vec{F}}_i(t) + \mathcal{O}(\Delta t^2) \]

Interaction potential e.g. LJ

\[ U_{LJ}(r_{ij}) = \left\{ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right\} \]

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

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

Plus FENE spring for bonds

\[
U_{ij}^{ch} = \begin{cases} 
-0.5kR_0^2 \ln \left[ 1 - \left( \frac{r_{ij}}{R_0} \right)^2 \right], & r_{ij} \leq R_0 \\
0, & r_{ij} > R_0
\end{cases}
\]
Simulations, general considerations

MD of single, isolated chain in space??

Bead-Bead interaction

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

Plus FENE spring for bonds

\[ U_{ij}^{ch} = \begin{cases} 
-0.5kR_0^2 \ln \left( 1 - \left( \frac{r_{ij}}{R_0} \right)^2 \right), & r_{ij} \leq R_0 \\
0, & r_{ij} > R_0
\end{cases} \]

NVE Ensemble integration:

Never equilibrates, Rouse modes do not couple strongly enough

Need noise term needed!

\[ \ddot{r}_i = -\nabla U_i - \Gamma \dot{r}_i + \mathbf{w}_i(t) \]

\[ \langle \mathbf{w}_i(t) \cdot \mathbf{w}_j(t') \rangle = \delta_{ij} \delta(t - t') 6k_B T \Gamma \]

Fermi-Pasta-Ulam Problem
FPU Problem

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

$E/N = 0.7, r=3, \alpha=0.1$

Short time

No equilibration!

Applies also to harmonic crystal
FPU Problem

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

$E/N = 0.7$, $r=3$, $\alpha=0.1$

non ergodic

$E/N = 1.2$, $r=3$, $\alpha=0.1$

ergodic

$E/N = 1.0$, $r=3$, $\alpha=0.1$, 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 $N$-dimensional manifold of the general $2N$-dimensional phase space

for $\alpha\neq 0$ not integrable anymore, however there is NO analytical expression, of $\alpha_{\text{min}}$, 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
Simulations, general considerations
FPU Problem

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

for $\alpha \neq 0$ not integrable anymore, however there is NO analytical expression, of $\alpha_{\text{min}}$, 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

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

Dense monomeric liquid
Flexible chains

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

\begin{align*}
  c_\infty &= 1.7 \\
  b &= 0.97 \sigma \\
  l_K &= c_\infty b, \quad L = (N - 1)b
\end{align*}

Density
\[ \rho = 0.85 \sigma^{-3} \]
Equilibration of initial melt
Auhl et al JCP, 2003

• 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 \( N = O(N_e) \)

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

Create Target Function

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

\[
\left\langle R^2(n) \right\rangle \propto \left\{ \begin{array}{c}
\frac{n^2}{n}, & nl < l_k \\
, & n, nl > l_k
\end{array} \right.
\]
Equilibration of initial melt

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

\[ \langle R^2(N) \rangle = l_K N \]

* 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
Equilibration of initial melt

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

\[ \langle R^2(N) \rangle = l_k N \]

- 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

MD runs plus very slow insertions of the excluded volume
Equilibration of initial melt

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

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

Stiff chains

Flexible chains
Equilibration of initial melt: ABSOLUTELY CRUCIAL

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 $N_c$ 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,
DPD: Dissipative Particle Dynamics

Shear viscosity

Diffusion

\[ \eta \propto \frac{\sigma^2}{\tau} \]

\[ D \propto \frac{\sigma^2}{\tau} \]
General Literature

Reviews
- S. J. Marrink et al, Biochimica Biophysica Acta, 2008, general review on lipid models and membranes
- C. Peter, K. Kremer, Introductory Lecture for FD 144 Faraday Discuss., 144, 9 (2010)

Books: