Molecular Dynamics (MD) Simulations of Polymer Crystallization and Melting

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Outline

- Introduction and Motivation
- Methods and Computational Details
- Results and Discussions
  - Cooling/Heating cycles
  - Self-seeding and Precursor states
Introduction: Polymers

Polyethylene:

\[\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{ or } \left(\text{CH}_2\right)_n\]

Plastics: *semi-crystalline* polymers

*non-equilibrium* structure

crystalline part: folded straight chains (*stems*)

strong hysteresis in crystallization-melting
Introduction: Polymer Crystallization/Melting

Non-equilibrium and complex phenomenon.

Internal (folding) and external order (crystal formation) are coupled - kinetic pathways are important.

Simulations have to explore kinetic and thermodynamic properties.

Molecular dynamics

Particular emphasis on nucleation

Melting of non-equilibrium structures leads to reorganization and morphological transitions (morphogenesis)
Non-equilibrium and complex phenomenon.

Internal (folding) and external order (crystal formation) are coupled - kinetic pathways are important.

How do polymer chains change their confirmations from randomly coiled structures (melt) to folded stems (crystal)?

Particular emphasis on nucleation

Melting of non-equilibrium structures leads to reorganization and morphological transitions (morphogenesis)
Simulations on different length scales

**Ab initio**
- Explicit electrons

**All atom**
- Atomistic Force Field

**Mesoscopic**
- Coarse-Grained, particle- or molecule-based

**Macroscopic**
- Material modeling

- 2-20 Å: Quantum Chemistry
- 1-10 nm
- 5-50 nm
- 10-100 nm
- > 100 nm

**Methods**
- CPMD
- Atomistic Molecular Dynamics
- Mesoscopic Molecular Dynamics
- DPD: Dissipative Particle Dynamics
- Finite Elements

DPD: Dissipative Particle Dynamics, for simulation of phase separation
Molecular Dynamics (MD) Simulation

Basic idea:

Newton’s equations of motion

\[ \frac{d^2 r_i}{dt^2} = \frac{F_i}{m_i} \]

\[ F_i = -\nabla_{r_i} V(r_1, \ldots, r_N) \]

Numerically solve them from \( t \) to \( t+\Delta t, \ t+2\Delta t, \ldots \) (trajectory)

Temperature and Pressure are calculated and controlled by thermostat and barostat

\[ K = \frac{3}{2} N k_B T \]

\[ PV = N k_B T + \frac{1}{D} \left\langle \sum_{i=1}^{N} r_i \cdot F_i \right\rangle \]

No artificial assumption of dynamics

Slow (need powerful computers)
Force field (potential)

Different interactions:

- **Connectivity**
  \[ V_{bond} = \frac{1}{2} k_r (r - r_0)^2 \]
  Harmonic springs or constraints

- **Angular potential**
  \[ V_{ang} = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \]
  Harmonic angular potential

- **Torsional potential**
  \[ V_{tor} = \sum_{\alpha=1}^{3} \frac{1}{2} k_\phi^\alpha (1 - \cos(\alpha \phi - \phi_0)) \]
  Dihedral potential

- **Excluded volume**
  \[ V_{nb} = 4 \varepsilon_{ab} \left[ \left( \frac{\sigma_{ab}}{r_{ab}} \right)^{12} - \left( \frac{\sigma_{ab}}{r_{ab}} \right)^6 \right] \]
  Lennard-Jones + electrostatic effects

(a) All-atom model  (b) United-atom model  (c) Coarse-grained model
The CG-PVA model involves a process called coarse graining. It starts with an atomistic model of poly(vinyl alcohol), which is then simplified into a mesoscopic model. This process is illustrated by the figure, showing effective potentials criterium: conservation of liquid structure.

Atomistic force field: (atoms, bonds, angles, torsions)
- 7 particles + 23 potentials

Mesoscopic model: 1 particle + 3 potentials
- Connectivity
- Excluded volume
- Angular rigidity

References:
D. Reith, H. Meyer, and F. Müller-Plathe, Macromolecules 34, 2335 (2001)
Angular potential

Boltzmann Inversion

$P(\theta) \sim \sin \theta e^{-\beta U(\theta)}$

Derive potential

Atomistic Simulations (full line)

CG Simulations (circles)

A posteriori verification: Original angular distribution recovered
CG-PVA with LAMMPS – scaling efficiency

Benchmark on the super computer (deimos) at TU-Dresden

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator):

MD details

- Periodic boundary, NPT ensemble
- Nose-Hoover thermostat, Brendsen barostat
- Integration method: Verlet, dt=0.01 (~16-35fs)
- Reduced units:

<table>
<thead>
<tr>
<th>Unit</th>
<th>reduced</th>
<th>real</th>
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<tr>
<td>Temperature</td>
<td>1</td>
<td>550 K</td>
</tr>
<tr>
<td>mass</td>
<td>1</td>
<td>44 u</td>
</tr>
<tr>
<td>Length</td>
<td>1</td>
<td>0.52 nm</td>
</tr>
<tr>
<td>time</td>
<td>1</td>
<td>~1.6-3.5 ps</td>
</tr>
<tr>
<td>pressure</td>
<td>8</td>
<td>1 atm</td>
</tr>
</tbody>
</table>
Case-1:

**Relaxation and Cooling/Heating Cycles**

200 chains, 500 monomers per chain, $10^5$ total monomers

Cooling and heating using 64 CPUs (deimos): ~300 hours

- **Self-avoiding Random Walk**
- **Relaxation**
  - 1.6e8 MDs
  - ~2.5-5.6 µs

- **Cooling**
  - 2.0e8 MDs
  - ~7.0 µs

- **Heating**
  - 2.0e8 Mds
  - ~7.0 µs
Results of MD  

Peak 1-3: $T=0.85, 0.868, 0.885$

Simulated scattering pattern during cooling

\[ S(\mathbf{q}) = \frac{1}{N} \langle \rho(\mathbf{q})^* \rho(\mathbf{q}) \rangle, \quad \rho(\mathbf{q}) = \int \rho(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} d\mathbf{r} = \sum_{j=1}^{N} e^{-i\mathbf{q} \cdot \mathbf{r}_j}, \]

\[ \rho(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) \]
Snapshots during Heating

4 Micro-Crystalline-Domains (MCD): a-d
Only 'b' and 'c' can be seen in the shown section plan
Arrows: change of conformation
Ellipses: growth of stem length
3D Snapshots of MCD 'b' during heating

T=0.7

T=0.88
During heating

\[ S(q) \]: static structure factor, related to SAXS/WAXS
\[ S_{\text{max}} \]: peak value at low q region

\[ 2\pi/\sigma \]

\[ 2\pi/b_0 \]
Larger system from $T=0.9$ to $0.75$

1000 chains, 1000 coarse atoms per chain, $10^6$ total atoms

Cooling and Heating using 252 CPUs (deimos): ~300 hours

Time

Relaxation

~2.8 µs

Self-seeding

~3 µs

Cooling

~2.6 µs

Heating

~2.7 µs

$T=0.9006(0.9,0.9016)$

$T=0.87$

$T=0.85$

$T=0.8$
Snapshots during cooling
Simulated scattering pattern during cooling
Case-2

Larger system from $T=0.9$ to $0.75$

1000 chains, 1000 coarse atoms per chain, $10^6$ total atoms

![Graph showing relaxation, cooling, heating, and self-seeding times.]

- Relaxation: $\sim 2.8\mu s$
- Cooling: $\sim 2.6\mu s$
- Heating: $\sim 2.7\mu s$
- Self-seeding: $\sim 3\mu s$
Snapshots during self-seeding at $T=0.85$ from $T=0.9006$.
During **self-seeding:**

(a) Crystallinity (%)
- Red line: $\phi_c$
- Green line: $\phi_d(d_c = 7.5)$

(b) Population ($\times 10^4$)
- Red line: $t = 0$
- Green line: $t = 2 \times 10^5$
- Blue line: $t = 4 \times 10^5$
- Black line: $t = 6 \times 10^5$

(c) Radius (R)
- Green line: $d_c = 10$
- Blue line: $d_c = 7.5$

(d) Population ($\times 10$)
- Bars for $n_{fold}$ times 2 to 14.
Folding kinetics of Individual chain during self-seeding

(a) $t = 0.7, 1, 1.5, 3 \times 10^5$

(b) Angle

(c) Domain size

Birth time of a bundle of stems
Slipping and thickening
Precursor state
Semiflexible segments
Stem length Vs. life time \( (\tau = t - t_0) \) during self-seeding:

At precursor states:
\[
d_{tt} \sim c\tau,
\]

At thickening process:
\[
d_{tt} \sim d_0 + \frac{T}{\Delta E} \ln(\tau)
\]
Case-2 Conclusions

- A large single crystal can be obtained by self-seeding.
- There are at least two stages during the crystallization: the precursor states and the following thickening process.
- Three kinetics are observed directly: lateral growth, slipping along chains, and stem thickening.
Thanks

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YOU
for your attention
Definition of stem length ($d_{tt}$) and domain size in time-index face ($S_d$)

$S_d$ reflects the orientational-temporal persistence of segments.

(a) $\theta \geq 150^\circ (tt)$

$\theta < 150^\circ$

(b) $d_{tt}$

(c) $S_d$

$\begin{array}{cccc}
3 & 3 & 0 & 6 \\
3 & 0 & 6 & 6 \\
0 & 6 & 6 & 0 \\
1 & 0 & 6 & 0 \\
\end{array}$
Computer Simulations: MD Vs. MC

**Molecular Dynamics (MD)**

Basic ideas:

Newton's equations of motion

\[
\frac{d^2 r_i}{dt^2} = \frac{F_i}{m_i}
\]

Temperature and Pressure are calculated and controlled by thermostat and barostat

No artificial assumption of dynamics

Slower

(need to compute force)

**Monte Carlo (MC)**

Metropolis Sampling:

\[
p = \min\{1, \exp(-\Delta E/kT)\}
\]

Temperature is a parameter

Need a set of trial states

(artificial assumed pathway, especially for nonequilibrium)

Pressure is unusable even if it can be calculated (slow)

Faster
Self-seeding: thin film experiments

Polymer crystallization -- far from equilibrium

Classical concept (developed for crystallization from solution)

Nucleation on a growth front:

crystal order and lamella grow at the same time

Alternative Concepts (developed after recent experiments in the melt)

Stepwise process (Strobl):

first growth of a mesomorphic layer, then crystal order inside the lamella

Computer simulation: details on molecular scale, conformations of individual chains, easy to control

Case-1 Conclusions

- With very slow heating, the melting and growth of micro crystallized domains can be coexisted during heating, which leads to multiple peaked behavior in endothermal curves.

- The thermal stability of a micro crystallized domain is dependent on the stem length.