Simulating Polymer Systems on GPU

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Polymers adsorbing to substrates

**Applications**
- Protein-membrane interactions
- Heterogeneous catalysis
- Protein microarray (www.arrayit.com) detection of individual molecules (hampered by unspecific binding)
- Steric colloidal stabilisation (paints, inks, pharmaceuticals, food dispersions ...)
- Lubrication

**Experiments**
- Nano Lett. 4, 577 (2004). STM for imaging and manipulating dsDNA
Detailed studies of quantitative properties require microscopic approach based on atomistic models with many fine-tuned parameters.

To get a qualitative overview of the generic behaviour and phase diagrams we use here a coarse-grained approach based on minimalistic models.

Minimalistic (lattice) models:
- Random Walks – Polymers at theta point (1950–1970)
- Self-Interacting Self-Avoiding Random Walks – Polymers in bad (and good) solvent exhibiting also collapsed states (1990–…).
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To get a qualitative overview of the generic behaviour and phase diagrams we use here a coarse-grained approach based on minimalistic models.

Minimalistic (lattice) models:

- Random Walks – Polymers at theta point (1950–1970)
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Simulation strategies

- **Off-lattice** bead-stick or bead-spring models

- **Monte Carlo** computer simulations in **generalized ensembles**:
  - multicanonical
  - parallel tempering
  - ...

- **Sophisticated analysis tools**:
  - microcanonical quantities
  - finite-size scaling
  - ...

**Lattice** protein and polymer adsorption (HP model):
Flat attractive substrate

model setup

\[ V = L_x L_y L_z \]

“grafted” versus “free”

attractive substrate

bead-stick model
substrate attraction strength $\epsilon_s$, temperature $T$

$$E = 4 \sum_{i=1}^{N-2} \sum_{j=i+2}^{N} \left( r_{ij}^{-12} - r_{ij}^{-6} \right) + \frac{1}{4} \sum_{i=1}^{N-2} \left[ 1 - \cos(v_i) \right] + \epsilon_s \sum_{i=1}^{N} \left( \frac{2}{15} z_i^{-9} - z_i^{-3} \right)$$

Flat substrate: Method and observables

Method

- **Multicanonical Monte Carlo** computer simulations ($N = 20$ monomers) and **parallel tempering** ($N = 40$ monomers)

Main observables

- **Energy** $\langle E \rangle$ and its individual contributions
- Associated **heat capacity** $C = \partial \langle E \rangle / \partial T$
- Polymer **center-of-mass** $r_{cm} = N^{-1} \sum_{n=1}^{N} r_n$ (average distance to substrate)
- **Radius of gyration** $\langle R_g \rangle = \left\langle \left[ N^{-1} \sum_{n=1}^{N} (r_n - r_{cm})^2 \right]^{1/2} \right\rangle$ and its components parallel and perpendicular to the substrate
- **Polymer-substrate contacts** $\langle N_S \rangle$ (counted if $z_i \leq 1.5$)
- **Fluctuations** $d\langle O \rangle / dT = (\langle OE \rangle - \langle O \rangle \langle E \rangle) / T^2$
Flat substrate: Canonical observables

Specific heat and radius of gyration for 20mer

\[
c_V(\epsilon_s, T) = \frac{T}{\epsilon_s}
\]

\[
\langle R_{gyr}\rangle(\epsilon_s, T) = \frac{1}{\epsilon_s}
\]
The microcanonical entropy

\[ s(E) = k_B \ln \frac{g(E)}{N} \]

\((Z(\beta) = \sum_E g(E) \exp(-\beta E))\) is a useful signature for first-order like transitions. The Gibbs hull

\[ \mathcal{H}_s(e) = s(e_{\text{ads}}) + e(\partial s/\partial e)_{e=e_{\text{ads}}} \]

is the tangent that touches \(s(e_{\text{ads}})\) and \(s(e_{\text{des}})\). This gives

\[ T_{\text{micro}}^{\text{ads}} = \left( \frac{\partial \mathcal{H}_s}{\partial e} \right)^{-1} = \left( \frac{\partial s}{\partial e} \right)^{-1} = \left( \frac{\partial s}{\partial e} \right)_{e=e_{\text{ads}}}^{-1} = \left( \frac{\partial s}{\partial e} \right)_{e=e_{\text{des}}}^{-1} \]
Curved attractive substrate – Spherical cage

Study influence of
- curved vs flat substrates
- spherical confinement vs half-space

Polymer in spherical cage: Interactions

- Monomer-monomer interaction as before: $12 - 6$ LJ plus (very) weak bending energy
- Monomer-sphere interaction by integrating $12 - 6$ LJ over the surface of the sphere (radius $R_c$):

$$V_s = 4\pi R_c \frac{R_c}{r_i} \left\{ \frac{1}{5} \left[ \left( \frac{1}{r_i - R_c} \right)^{10} - \left( \frac{1}{r_i + R_c} \right)^{10} \right] - \frac{\epsilon}{2} \left[ \left( \frac{1}{r_i - R_c} \right)^{4} - \left( \frac{1}{r_i + R_c} \right)^{4} \right] \right\}$$
Polymer in spherical cage: Phase diagram

Similar to phase diagram for flat substrate:
Polymer grafted to fluctuating attractive membrane

Polymer grafted to dynamically fluctuating membrane

\[ E = E^{\text{mem}} + E^{\text{pol}} + E^{\text{int}} \]

**Membrane:** Elastic \( L_x \times L_y \) mesh with tethering FENE potential between neighboring nodes (plus hard-sphere potential to ensure self-avoidance)

\[ V_{\text{FENE}}^m(r) = -\frac{K}{2} R_m^2 \ln \left\{ 1 - \left[ (r - r_0)/R_m \right]^2 \right\} \]

\[ E^{\text{mem}} = \sum_{k=1}^{L_x-1} \sum_{l=1}^{L_y} V_{\text{FENE}}^m(|r_{k,l} - r_{k+1,l}|) + \sum_{k=1}^{L_x} \sum_{l=1}^{L_y-1} V_{\text{FENE}}^m(|r_{k,l} - r_{k,l+1}|) \]

**Polymer:** Bead-spring model

\[ E^{\text{pol}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V_{\text{LJ}}^{\text{pp}}(|r_i - r_j|) + \sum_{i=1}^{N-1} V_{\text{FENE}}^p(|r_i - r_{i+1}|) \]

\[ V_{\text{LJ}}^{\text{pp}}(r) = 4\epsilon_{\text{pp}} \left[ (\sigma/r)^{12} - (\sigma/r)^6 \right]; \quad V_{\text{FENE}}^p(r) = -\frac{K}{2} R_p^2 \ln \left\{ 1 - [(r - r_0)/R_p]^2 \right\} \]
Polymer-membrane attraction: Between monomers and mesh nodes

\[ V_{pm}^{LJ}(r) = 4\epsilon_{pm} \left[ (\sigma/r)^{12} - (\sigma/r)^{6} \right] \]

Parameters \((\sigma = r_0/2^{1/6}; r_0 = 1)\):

Membrane: \(L_x = L_y = 27; K = 40; R_m = 0.1\)
Polymer: \(N = 13\), grafted at membrane center, \(\epsilon_{pp} = 1; K = 40; R_p = 0.3\)

Membrane-polymer attraction parametrized by \(\epsilon_{pm} \in [0, 1.5]\)

Stiff membrane (flat, static 2d mesh): Slightly different model than in our recent work on polymer adsorption to a flat substrate, so study this case first
- as reference system for fluctuating membrane
- and for comparison with flat substrate

Stiff membrane: Phase diagram

Similar to phase diagram for flat substrate:

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Similar to stiff membrane, but now “embedded” phases:
Fluctuating membrane: “Embedded” phases

Embedded Compact (MC)  Embedded Elongated (ME)

Back-reaction between polymer and membrane fluctuations
Summary and Outlook

- Adsorption phase diagram of generic polymer model
- Morphologies of low-temperature “frozen” conformations
- Generic phase structure robust and similar to flat substrate system
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Outlook

- Use more realistic polymers (add bending energy for semiflexible (bio-)polymers, simulate all-atom models, . . .)
- Improve substrate model (other geometries, patterned surfaces, fluctuating surfaces, better controlled curvature, . . .)
- Use atomistic lipid bilayer membranes . . .
- . . . together with cholesterol, membrane proteins, solvent, and . . .
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- Adsorption phase diagram of generic polymer model
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. . . something for Wroclaw 2022 !!!
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Recent Developments in Computational Physics

29 November – 01 December 2012, ITP, Universität Leipzig
www.physik.uni-leipzig.de/~janke/CompPhys12

See you there?
Bead-Spring Homopolymer Model

Lennard-Jones potential ($\epsilon = 1$, $\sigma = 2^{-1/6}r_0$, $r_0 = 0.7$):

$$E_{\text{LJ}}(r_{ij}) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$

Truncated at $r_c = 2.5\sigma$:

$$E_{\text{LJ}}^{\text{mod}}(r_{ij}) = E_{\text{LJ}}(\min(r_{ij}, r_c)) - E_{\text{LJ}}(r_c)$$

Finitely extensible nonlinear elastic (FENE) anharmonic potential ($R = 0.3$, $K = 40$):

$$E_{\text{FENE}}(r_{ii+1}) = -\frac{K}{2}R^2 \log \left[ 1 - \left( \frac{r_{ii+1} - r_0}{R} \right)^2 \right]$$

Total energy of a conformation $C = (r_1, \ldots, r_N)$:

$$E(C) = \sum_{i<j}^N E_{\text{LJ}}^{\text{mod}}(r_{ij}) + \sum_{i}^{N-1} E_{\text{FENE}}(r_{ii+1})$$
Parallel tempering (replica exchange) Monte Carlo with $n_r$ replicas: Exchange conformations of neighboring replicas $i$ and $i + 1$ with probability

$$p = \min(1, \exp [(E_i - E_{i+1})(\beta_i - \beta_{i+1})])$$
Specific heat of an elastic polymer chain with lengths $N = 13$ and 55. The inset shows the icosahedral structure of the 55mer at low $T$. 

![Graph showing specific heat vs temperature for $N = 13$ and $N = 55$](image)
Radius of Gyration

Temperature derivative of mean squared radius of gyration.

\[ \frac{d}{dT} \left( \frac{\langle r_{\text{gyr}}^2 \rangle}{N^{2/3}} \right) \]

- \( N = 13 \) (red solid line)
- \( N = 55 \) (green dashed line)

Graph showing the temperature derivative of the mean squared radius of gyration for different system sizes. The graph displays a peak at a certain temperature, indicating a phase transition in the system.
GPU: Grid With Thread Blocks and Memory Layout

Grid 1
- Block (0,0)
- Block (0,1)
- Block (0,2)
- Block (0,3)
- Block (1,0)
- Block (1,1)
- Block (1,2)
- Block (1,3)

Grid 2
- Block (0,0)
- Thread (0,0)
- Thread (0,1)
- Thread (0,2)
- Thread (0,3)
- Thread (1,0)
- Thread (1,1)
- Thread (1,2)
- Thread (1,3)
- Thread (2,0)
- Thread (2,1)
- Thread (2,2)
- Thread (2,3)

Memory Layout:
- Texture memory
- Constant memory
- Global memory
- Shared memory
- Local memory
Table: Specifications of the used hardware.

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<th>GPU2</th>
<th>GPU3</th>
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<td>GTX480</td>
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<td>30</td>
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<td>8</td>
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<td>registers per block</td>
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<td>32768</td>
</tr>
</tbody>
</table>
Naive Parallel Tempering Implementation

![Graph showing Naive Parallel Tempering Implementation](image-url)
Improved Parallel Tempering Implementation

\[ \langle t_{\text{GPU}} \rangle [s] \]

\( n_r \)
**Table:** Overview of maximum achieved speed-ups – $\max (S_p(n_r))$ – for the two different GPU implementations, compared to the single-core CPU implementation.

<table>
<thead>
<tr>
<th></th>
<th>naive</th>
<th>improved</th>
</tr>
</thead>
<tbody>
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<td>GPU1</td>
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<tr>
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<td>GPU3</td>
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