Simulating Polymer Systems on GPU

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IMPRS School 2012: *GPU Computing – Methods and Applications in the Natural Sciences*

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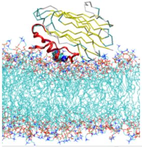
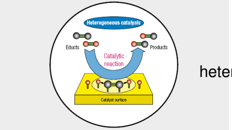
Polymers adsorbing to substrates

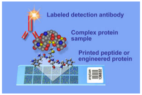
Applications



protein-membrane interactions

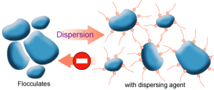


heterogeneous catalysis



protein microarray (www.arrayit.com)

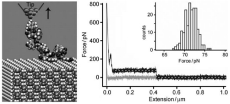
detection of individual molecules (hampered by unspecific binding)



steric colloidal stabilisation (paints, inks, pharmaceuticals, food dispersions . . .)

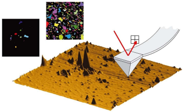
lubrication

Experiments

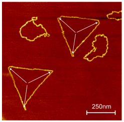


ChemPhysChem **10**, 2795 (2009).

AFM-based single-molecule method, can determine adhesion free energies

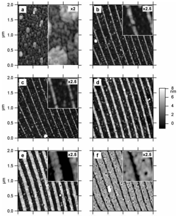


e.g. peptide covered fraction of substrate [Bachmann/Goede/Beck-Sickinger/Grundmann/Irbäck/WJ Angew. Chem. Int. Ed. **49**, 9530 (2010)]



Nano Lett. **4**, 577 (2004).

STM for imaging and manipulating dsDNA



J. Am. Chem. Soc. **127**, 4323 (2005).

antigen 69k adsorbed on alkylsilane stripes printed on a background of oligo(ethylene oxide)

Modeling strategies

- 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-Avoiding Random Walks – Polymers in good solvent (1970–1990)
    E. Eisenriegler, K. Kremer, K. Binder, J. Chem. Phys. **77** (1982) 6296
  - Self-Interacting Self-Avoiding Random Walks – Polymers in bad (and good) solvent exhibiting also collapsed states (1990–. . .)

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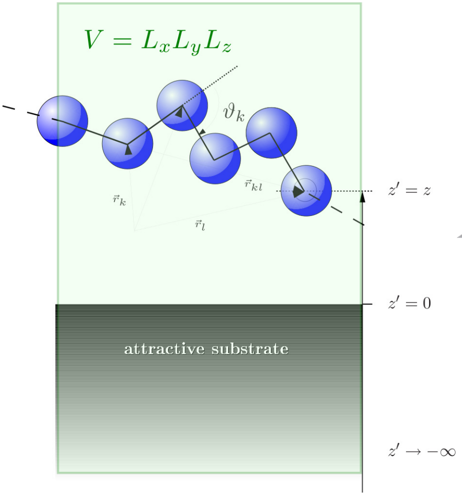
Simulation strategies

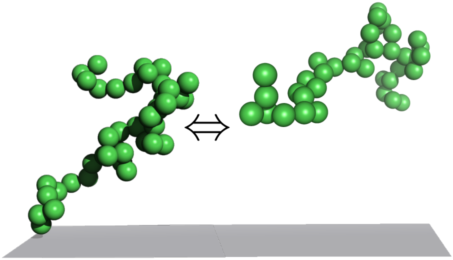
- Off-lattice bead-stick or bead-spring models
- Monte Carlo computer simulations in generalized ensembles:
  - multicanonical
  - parallel tempering
  - ...
- Sophisticated analysis tools:
  - microcanonical quantities
  - finite-size scaling
  - ...

Lattice protein and polymer adsorption (HP model):
M. Bachmann, WJ, Phys. Rev. Lett. **95** (2005) 058102; Phys. Rev. E **73** (2006) 020901(R); Phys. Rev. E **73** (2006) 041802

Flat attractive substrate

model setup

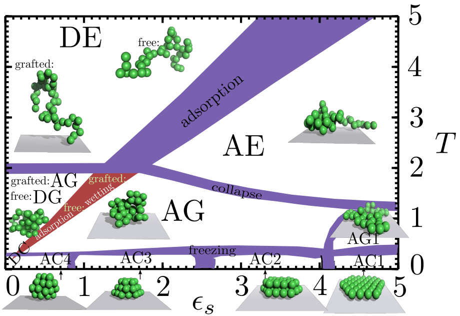




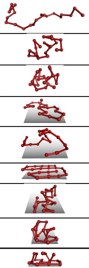
"grafted" versus "free"

bead-stick model

substrate attraction strength ϵ_s, temperature T



pseudophase	typical configuration
DE	
DG	
DC	
AE1	
AE2	
AC1	
AG	
AC2a	
AC2b	



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

M. Möddel, M. Bachmann, WJ, J. Phys. Chem. B **113** (2009) 3314; Phys. Chem. Chem. Phys. **12** (2010) 11548; Macromolecules **44** (2011) 9013

Flat substrate: Method and observables

Method

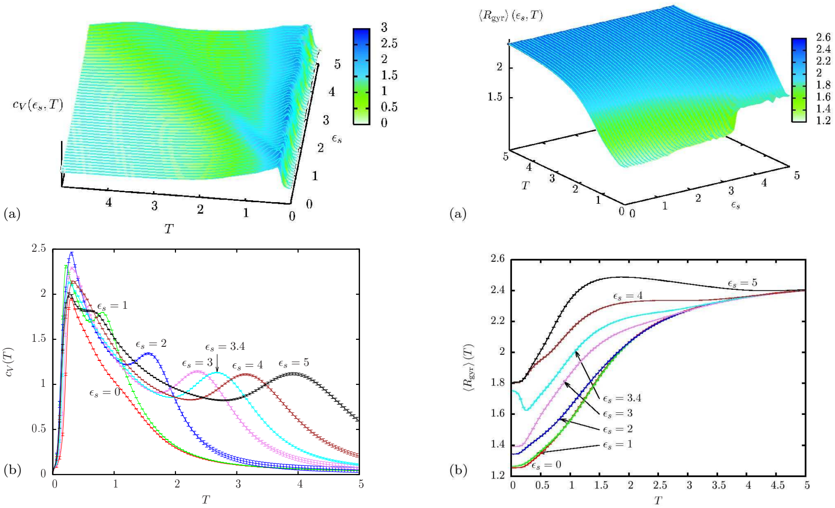
- Multicanonical Monte Carlo computer simulations ($N = 20$ monomers) and parallel tempering ($N = 40$ monomers)

Main observables

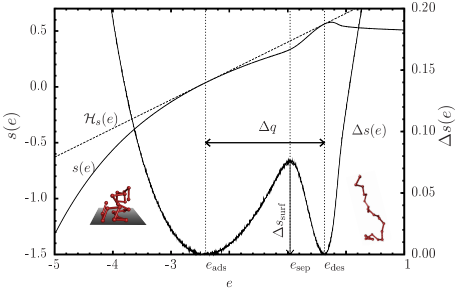
- Energy $\langle E \rangle$ and its individual contributions
- Associated heat capacity $C = \partial \langle E \rangle / \partial T$
- Polymer center-of-mass $\mathbf{r}_{\rm cm} = N^{-1} \sum_{n=1}^{N} \mathbf{r}_n$ (average distance to substrate)
- Radius of gyration $\langle R_{\rm g} \rangle = \langle \left[N^{-1} \sum_{n=1}^{N} (\mathbf{r}_n - \mathbf{r}_{\rm cm})^2 \right]^{1/2} \rangle$ 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



Flat substrate: Microcanonical observables



The microcanonical entropy

$$s(E) = k_B \ln g(E)/N$$

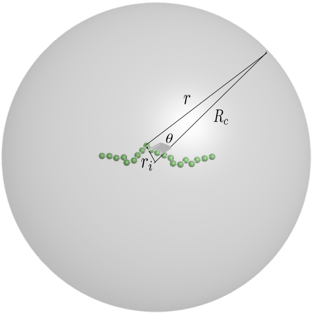
$(Z(\beta) = \sum_E g(E)\exp(-\beta E))$ is a useful signature for first-order like transitions. The Gibbs hull

$$\mathcal{H}_s(e) = s(e_{\mathrm{ads}}) + e(\partial s/\partial e)_{e=e_{\mathrm{ads}}}$$

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

$$T_{\mathrm{micro}}^{\mathrm{ads}} = \left(\frac{\partial \mathcal{H}_s}{\partial e}\right)^{-1} = \left(\frac{\partial s}{\partial e}\right)^{-1}_{e=e_{\mathrm{ads}}} = \left(\frac{\partial s}{\partial e}\right)^{-1}_{e=e_{\mathrm{des}}}$$

Curved attractive substrate – Spherical cage



Study influence of

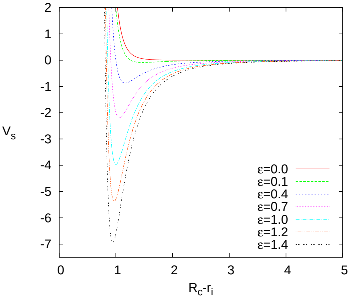
- curved vs flat substrates
- spherical confinement vs half-space

H. Arkın, WJ, Phys. Rev. E **85**, 051802 (2012); J. Phys. Chem. B **116**, 10379 (2012); Eur. Phys. J. – Special Topics (in print)

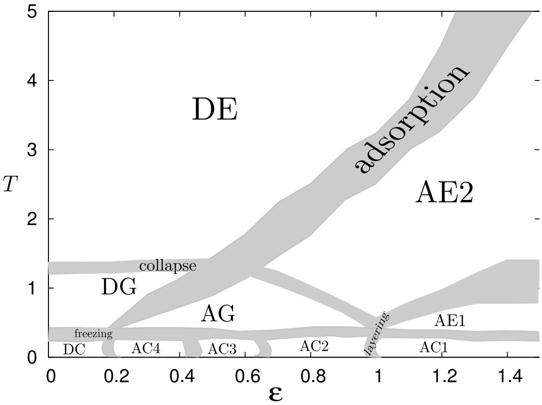
Polymer in spherical cage: Interactions

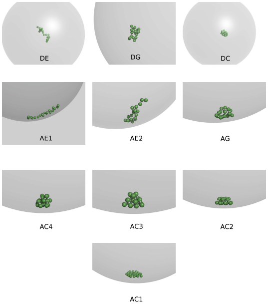
- Monomer-monomer interaction as before: $12-6$ LJ plus (very) weak bending energy
- Monomer-sphere interaction by integrating $12-6$ LJ over the surface of the sphere (radius R_c):

$$V_s = 4\frac{\pi R_c}{r_i}\left\{\frac{1}{5}\left[\left(\frac{1}{r_i - R_c}\right)^{10} - \left(\frac{1}{r_i + R_c}\right)^{10}\right] - \frac{\epsilon}{2}\left[\left(\frac{1}{r_i - R_c}\right)^{4} - \left(\frac{1}{r_i + R_c}\right)^{4}\right]\right\}$$



Polymer in spherical cage: Phase diagram





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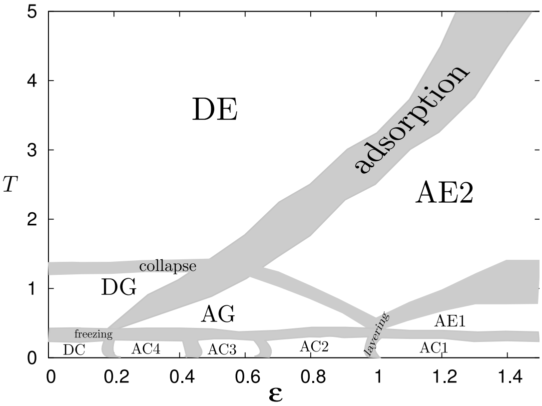
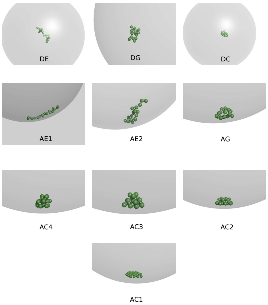
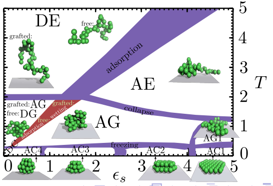




Similar to phase diagram for flat substrate:



Polymer grafted to fluctuating attractive membrane

Polymer grafted to dynamically fluctuating membrane

$$E = E^{\mathrm{mem}} + E^{\mathrm{pol}} + E^{\mathrm{int}}$$

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

$$V^{\mathrm{m}}_{\mathrm{FENE}}(r) = -\frac{K}{2} R^2_{\mathrm{m}} \ln \left\{ 1 - [(r - r_0)/R_{\mathrm{m}}]^2 \right\}$$

$$E^{\mathrm{mem}} = \sum_{k=1}^{L_x - 1} \sum_{l=1}^{L_y} V^{\mathrm{m}}_{\mathrm{FENE}}(|\mathbf{r}_{k,l} - \mathbf{r}_{k+1,l}|) + \sum_{k=1}^{L_x} \sum_{l=1}^{L_y - 1} V^{\mathrm{m}}_{\mathrm{FENE}}(|\mathbf{r}_{k,l} - \mathbf{r}_{k,l+1}|)$$

Polymer: Bead-spring model

$$E^{\mathrm{pol}} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V^{\mathrm{pp}}_{\mathrm{LJ}}(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_{i=1}^{N-1} V^{\mathrm{p}}_{\mathrm{FENE}}(|\mathbf{r}_i - \mathbf{r}_{i+1}|)$$

$$V^{\mathrm{pp}}_{\mathrm{LJ}}(r) = 4\epsilon_{\mathrm{pp}} \left[(\sigma/r)^{12} - (\sigma/r)^6 \right] ; \; V^{\mathrm{p}}_{\mathrm{FENE}}(r) = -\frac{K}{2} R^2_{\mathrm{p}} \ln \left\{ 1 - [(r - r_0)/R_{\mathrm{p}}]^2 \right\}$$

Fluctuating membrane: Parameters

Polymer-membrane attraction: Between monomers and mesh nodes

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

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

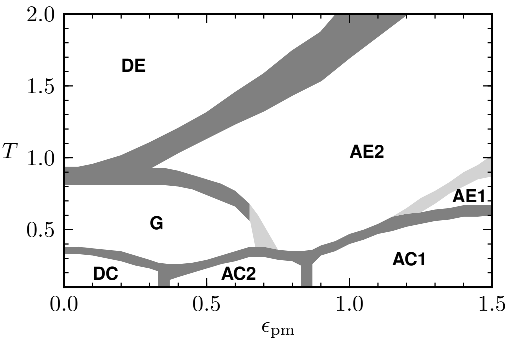
Membrane: $L_x = L_y = 27$; $K = 40$; $R_m = 0.1$
Polymer: $N = 13$, grafted at membrane center, $\epsilon_{\rm pp} = 1$; $K = 40$; $R_p = 0.3$
Membrane-polymer attraction parametrized by $\epsilon_{\rm pm} \in [0, 1.5]$

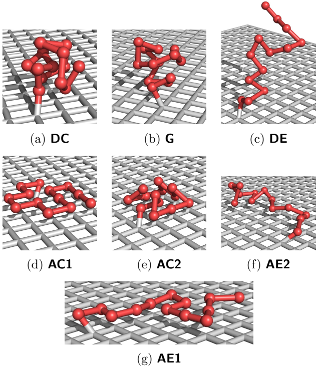
Stiff membrane (flat, static 2d mesh): Slightly different model than in our recent work on polymer adsorption to a flat substrate, so study this case first

- as reference system for fluctuating membrane
- and for comparison with flat substrate

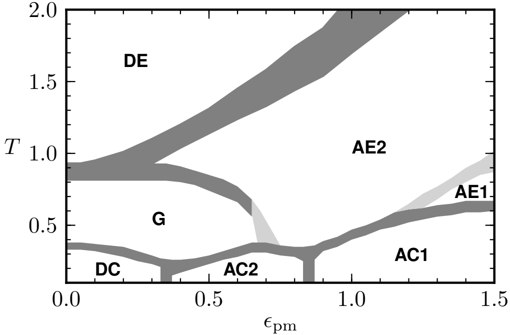
S. Karalus, WJ, M. Bachmann, Phys. Rev. E **84** (2011) 031803

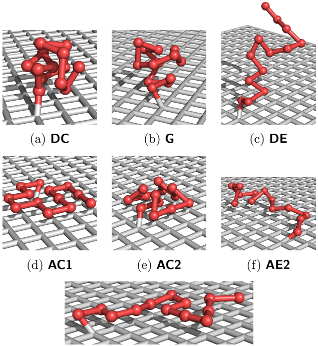
Stiff membrane: Phase diagram





Stiff membrane: Phase diagram



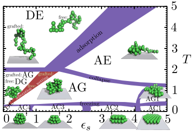


(a) **DC** (b) **G** (c) **DE**

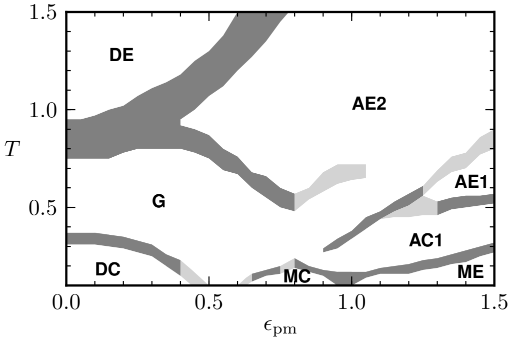
(d) **AC1** (e) **AC2** (f) **AE2**

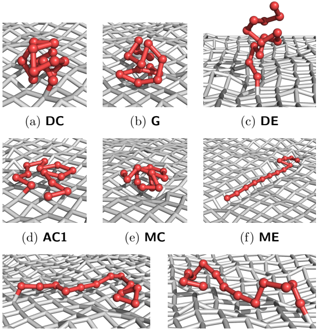
(g) **AE1**

Similar to phase diagram for flat substrate:



Fluctuating membrane: Phase diagram



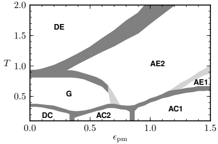


(a) **DC** (b) **G** (c) **DE**

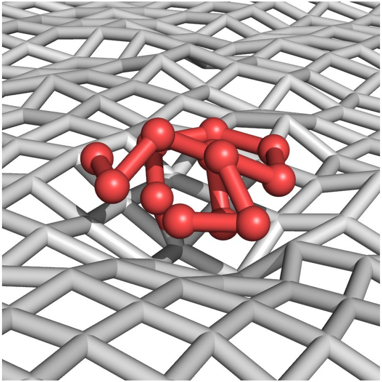
(d) **AC1** (e) **MC** (f) **ME**

(g) **AE1** (h) **AE2**

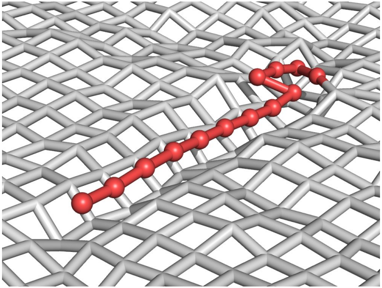
Similar to stiff membrane, but now "embedded" phases:



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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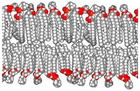
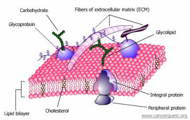
Outlook

- 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 cholesterols, membrane proteins, solvent, and . . .



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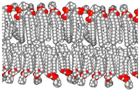

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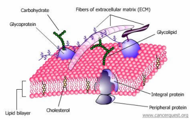

. . . something for *Wroclaw 2022* !!!

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Collaborations with

- Michael Bachmann (now Univ. of Georgia, Athens, USA)
- Monika Möddel (now Basycon Consulting, Munich, Germany)
- Handan Arkın-Olgar (on leave from Ankara University, Turkey)
- Steffen Karalus (now University of Cologne, Germany)

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13th International NTZ–Workshop on
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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 ($\epsilon = 1$, $\sigma = 2^{-1/6} r_0$, $r_0 = 0.7$):

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

Truncated at $r_c = 2.5\sigma$:

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

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

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

Total energy of a conformation $\mathcal{C} = (\mathbf{r}_1, \ldots, \mathbf{r}_N)$:

$$E(\mathcal{C}) = \sum_{i<j}^{N} E_{\rm LJ}^{\rm mod}(r_{ij}) + \sum_{i}^{N-1} E_{\rm FENE}(r_{ii+1})$$

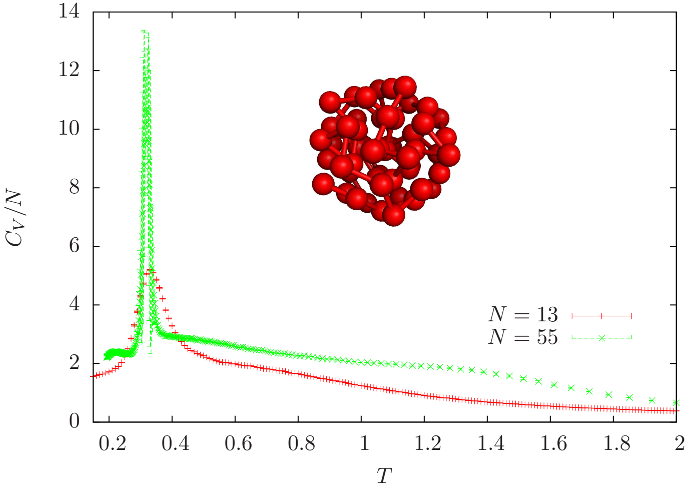
Simulation Method

Parallel tempering (replica exchange) Monte Carlo with n_r replicas:
Exchange conformations of neighboring replicas i and $i+1$ with probability

$$p = \min\left(1, \exp\left[(E_i - E_{i+1})(\beta_i - \beta_{i+1})\right]\right)$$

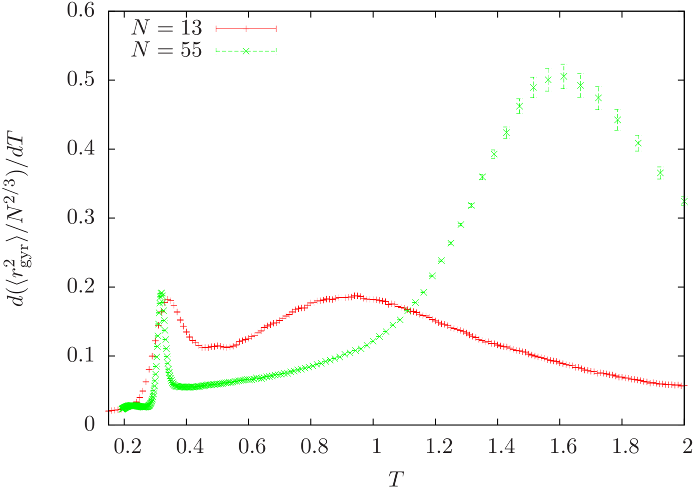
Specific Heat

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.

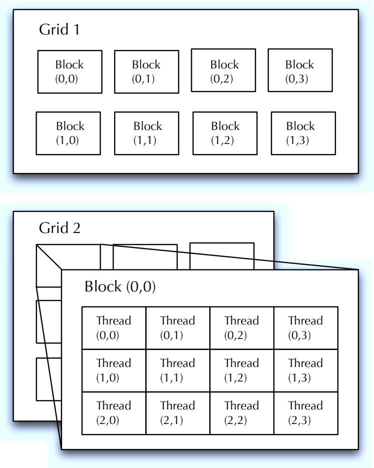


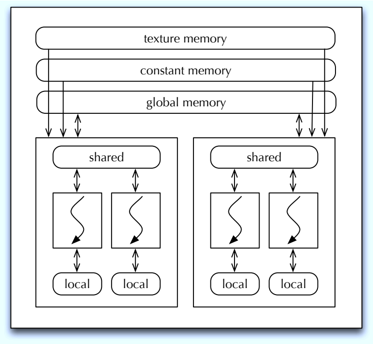
Radius of Gyration

Temperature derivative of mean squared radius of gyration.



GPU: Grid With Thread Blocks and Memory Layout



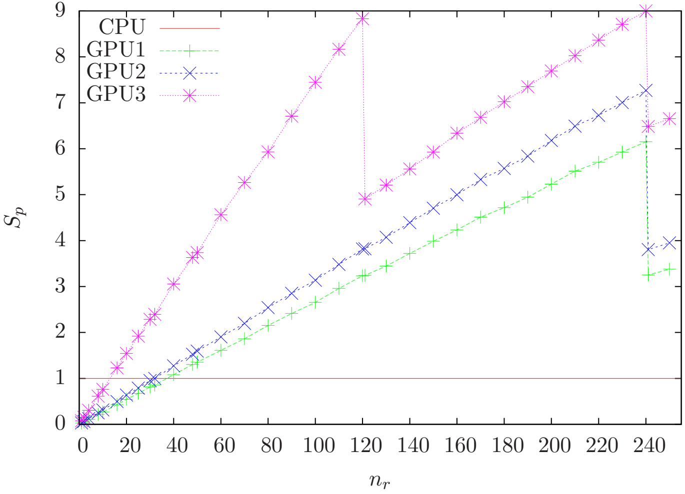


GPU: Specification of used Hardware

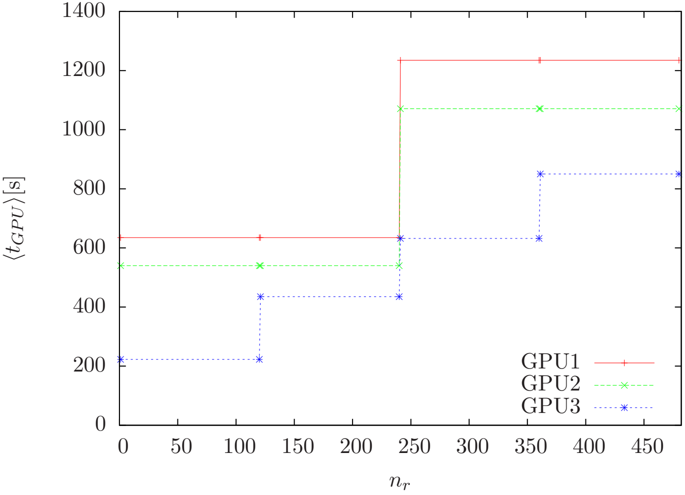
Table: Specifications of the used hardware.

	reference CPU	GPU1	GPU2	GPU3
name	Xeon E5620	Tesla C1060	GTX285	GTX480
# processors	1	30	30	15
# cores per processor	4 (1 used)	8	8	32
RAM	16384MB	4096MB	1024MB	1536MB
clock speed	2.4GHz	1.3GHz	1.48GHz	1.4GHz
max. threads per block	-	512	512	1024
shared memory size	-	16kB	16KB	48kB
registers per block	-	16384	16384	32768

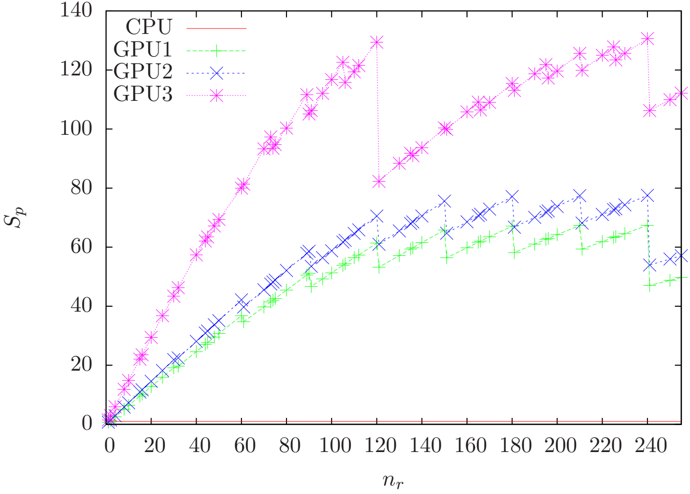
Naive Parallel Tempering Implementation



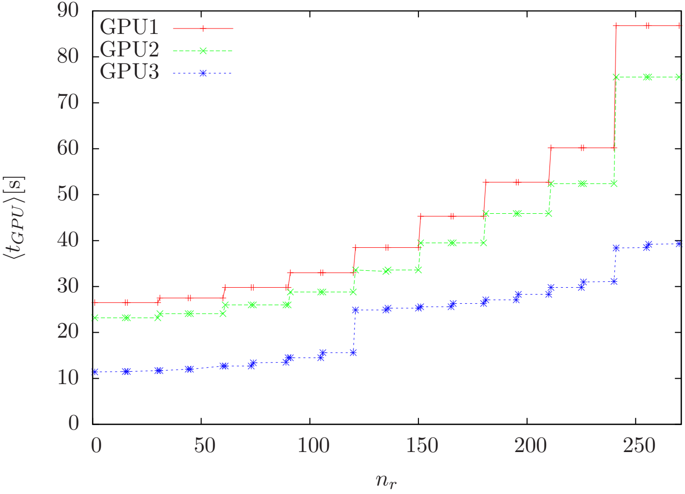
Naive Parallel Tempering Implementation



Improved Parallel Tempering Implementation



Improved Parallel Tempering Implementation



Speeup: GPU vs CPU

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.

	naive	improved
GPU1	6.1×	68×
GPU2	7.2×	78×
GPU3	9×	130×