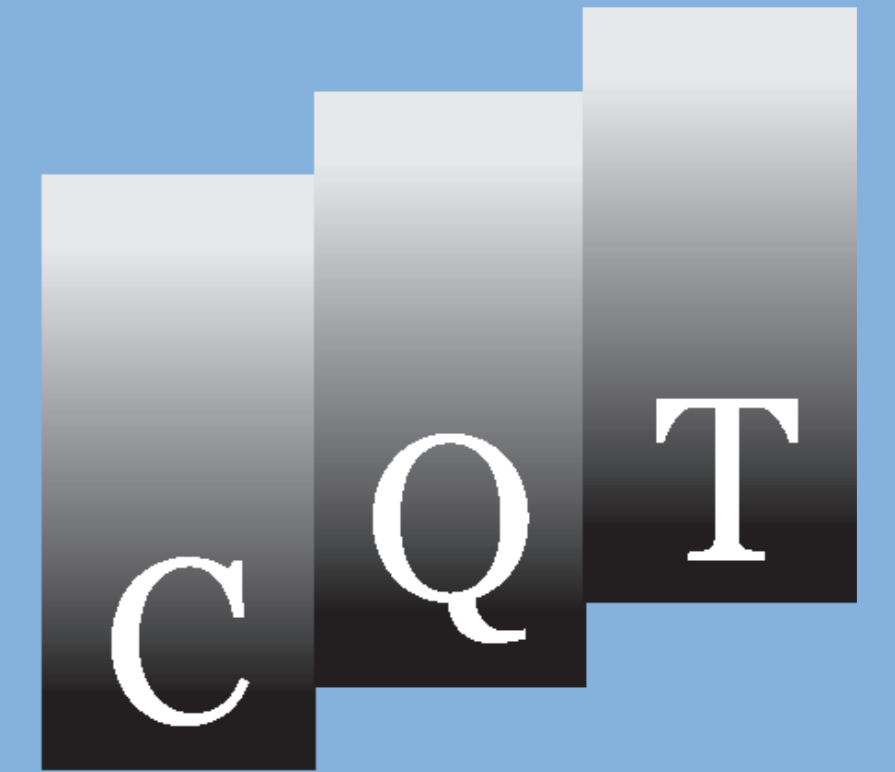




Collapse and Freezing Transitions of Polymers on Regular Lattices

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Abstract

We present simulation results for the thermodynamical behavior of flexible polymers (interacting self-avoiding walks) on simple-cubic (sc) and face-centered cubic (fcc) lattices. Besides the well-known collapse transition, we concentrate ourselves on the freezing transition occurring at lower temperatures.

We show how this transition, also called crystallization, liquid-solid [1] or globule-groundstate transition [2], is influenced by the lattice and how the transition depends on the system size.

We employ the pruned-enriched Rosenbluth method (PERM) [3] and generalized extensions of it [4,5].

- [1] F. Rampf, W. Paul, K. Binder, Europhys. Lett. 70 (2005) 628.
- [2] M. Bachmann, W. Janke, J. Chem. Phys. 120 (2004) 6779.
- [3] P. Grassberger, Phys. Rev. E 56 (1997) 3682.
- [4] M. Bachmann, W. Janke, Phys. Rev. Lett. 91 (2003) 208105.
- [5] T. Prellberg, J. Krawczyk, Phys. Rev. Lett. 92 (2004) 120602.

Method – flatPERM

The flat histogram version follows a strategy from a microcanonical view of the problem. The basic ideas are:

Use growth steps as in the normal PERM chain growth algorithm.

Consider then a microcanonical estimator for the total number of configurations of size n with energy m

$$C_{n,m}^{est} = \langle W \rangle_{n,m} = \frac{1}{S} \sum_i W_{n,m}^{(i)}$$

where $W_{n,m}^{(i)}$ is the Rosenbluth weight of the i th configuration. Now define r as the ratio of actual Rosenbluth weight and $C_{n,m}^{est}$:

$$r = \frac{W_{n,m}^{(i)}}{C_{n,m}^{est}}$$

Apply population control by pruning, when $r < 1$ and enrichment, when $r > 1$.

Peak Chaos

To investigate conformational transitions we concentrate on peaks (maxima) in the heat capacities. Figures 1 and 2 show heat capacities of short polymers on the sc lattice.

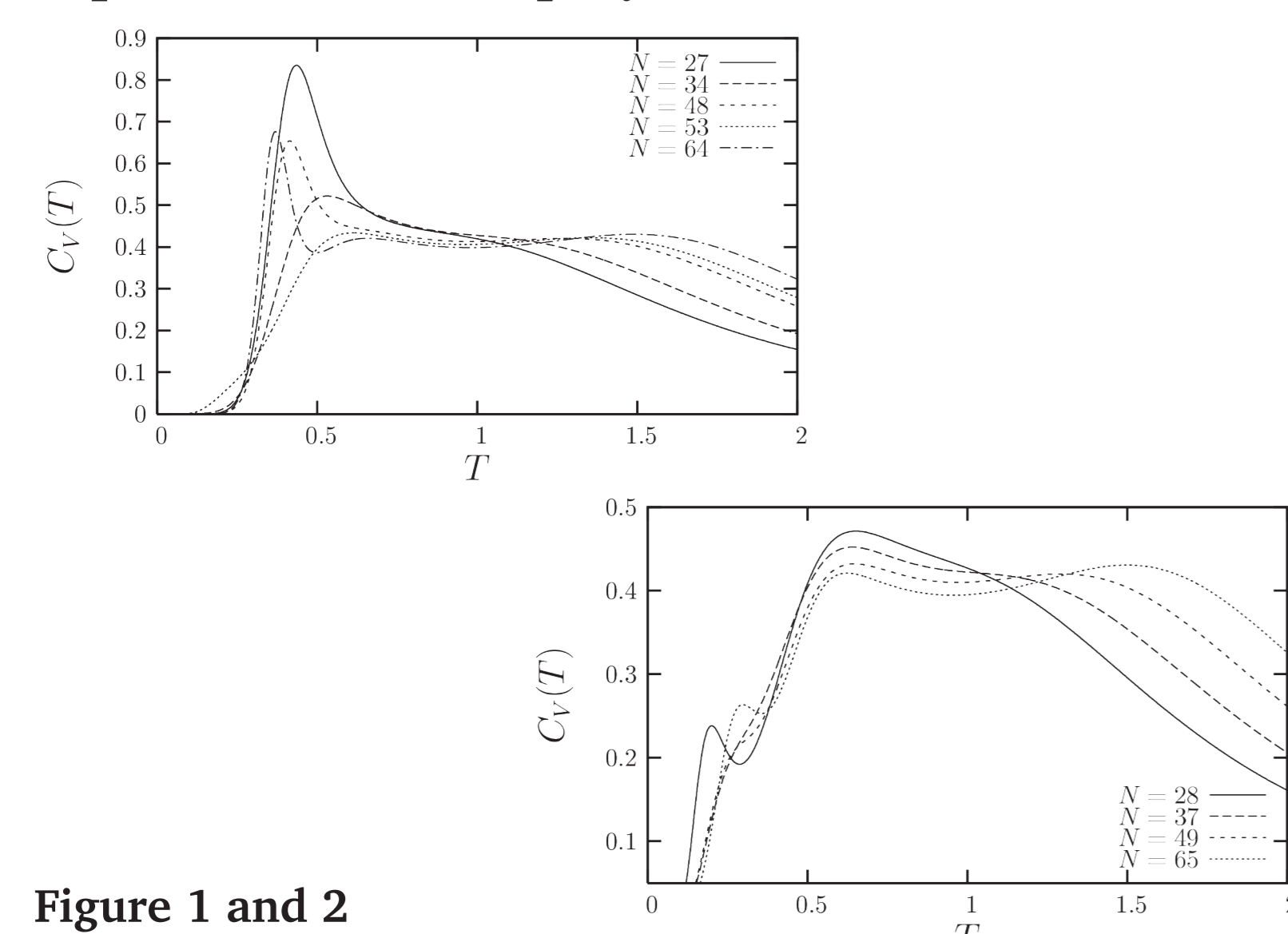


Figure 1 and 2

What we see at low temperatures ($T < 1$) are one or two maxima per chain length. There seems to be no consistent behavior depending on chain length. At high temperatures ($T > 1$) we see the well known Θ -Transition.

See Figure 5 for some visualizations of typical conformations.

The Freezing Transition

We will first concentrate on the low temperature region.

To find some regularities anyhow in that region, we plot just all peak positions (Figure 3) and rearrange them, e.g. we plot the peak temperatures depending on polymer length (Figure 4).

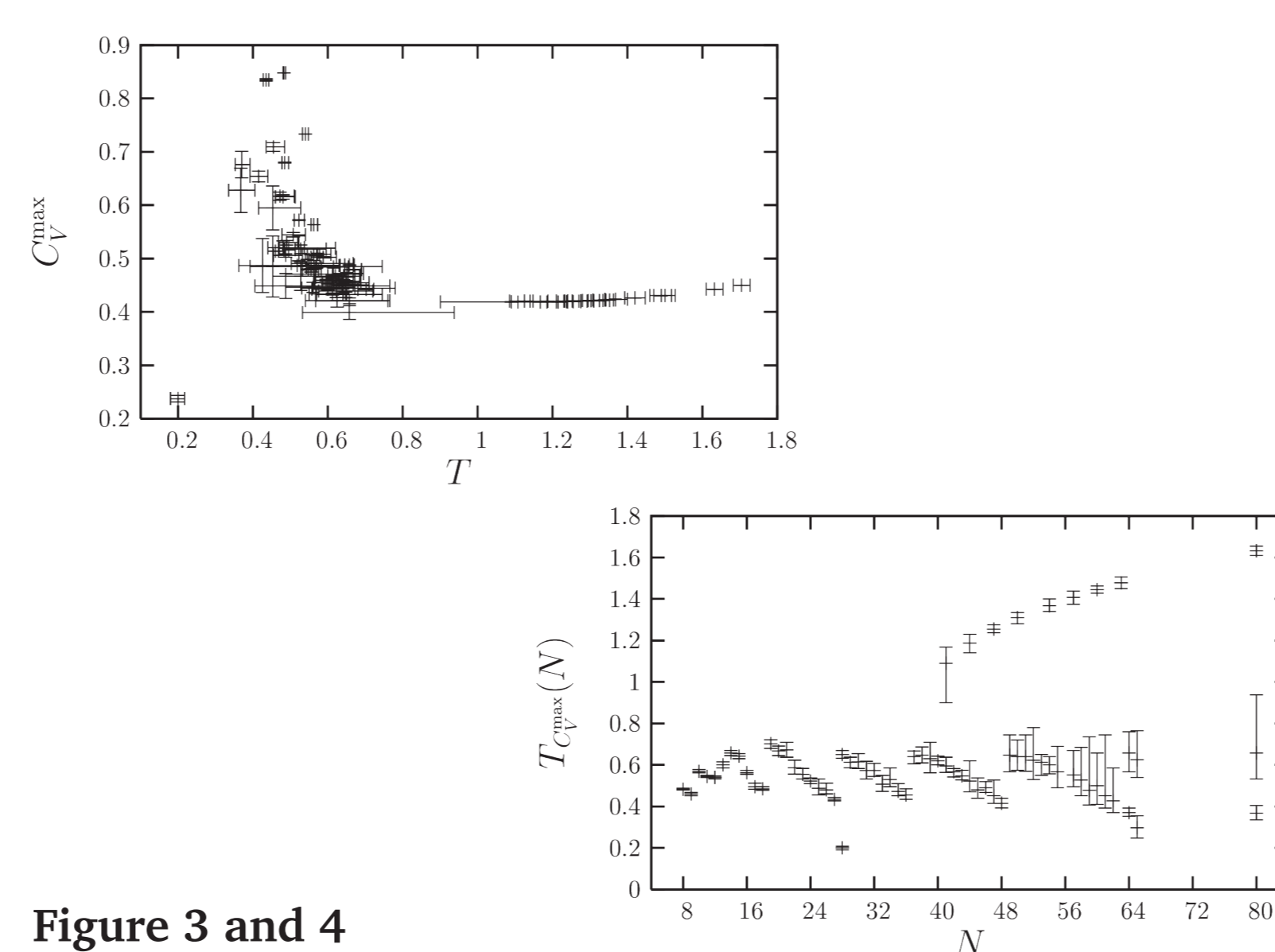


Figure 3 and 4

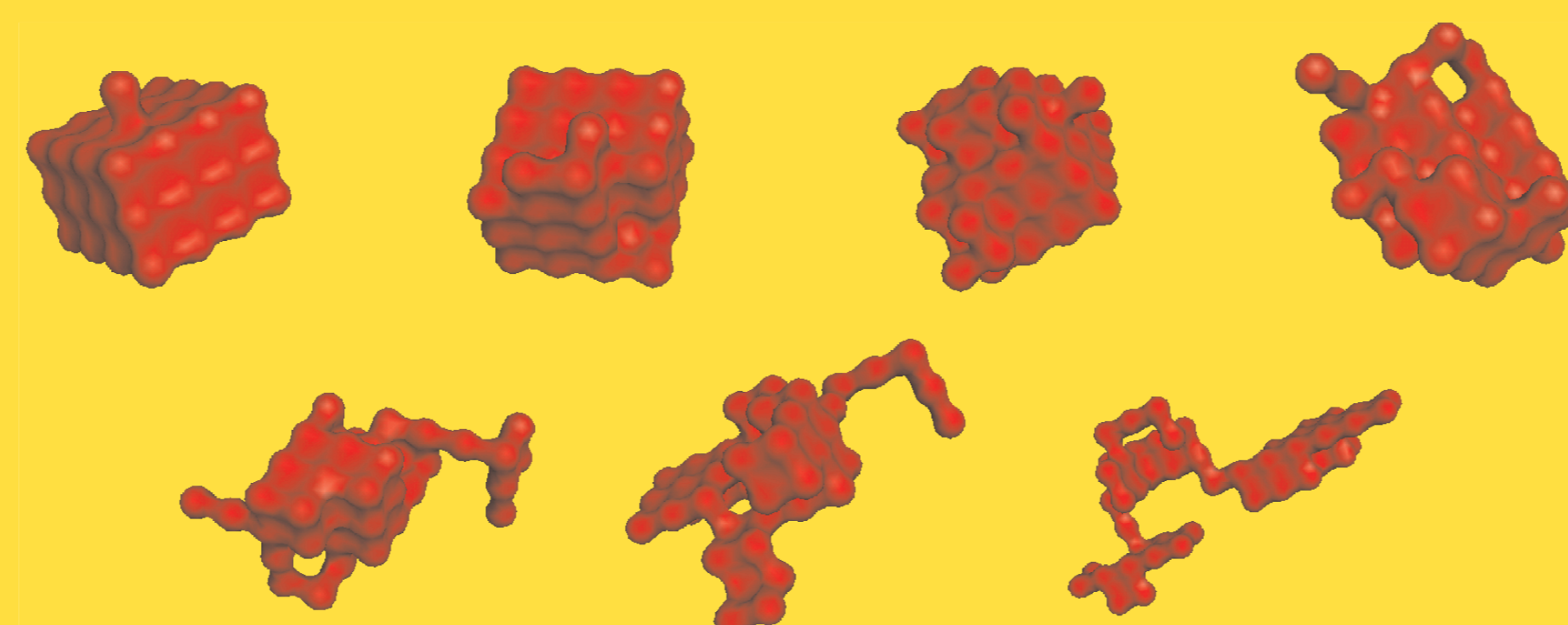


Figure 5: Typical conformations with selected energies for the $N=49$ -mer. Top: Groundstate ($E=-57$, $T \rightarrow 0$); ($E=-55$, $T \approx 0.37$); ($E=-50$, $T \approx T_{c1} = 0.6475$); ($E=-43$, $T \approx 1$). Bottom: ($E=-37$, $T \approx T_{c2} = 1.2925$); ($E=-31$, $T \approx 1.6$); ($E=-20$, $T \approx 2.4$).

Results – Interpretation

Looking at the freezing transition, we see that:

- there are periodical fluctuations of the transition temperature depending on polymer length ("saw tooth like", cp. Fig. 4)
- within these fluctuations the transition temperature remains constant

Analyzing the fluctuations, we find:

- the jumps in transition temperature occur in vicinity of polymers, whose ground-states fill a cube or a rectangle (i.e. which have compact ground-states)
- these polymers have the "magic" lengths $N_{cgs}=27, 36, 48, 64, 80$ and so on

Figure 6 shows energy distribution around the freezing transition for the polymer with $N_{cgs}=64$, Figure 7 visualizes corresponding conformations.

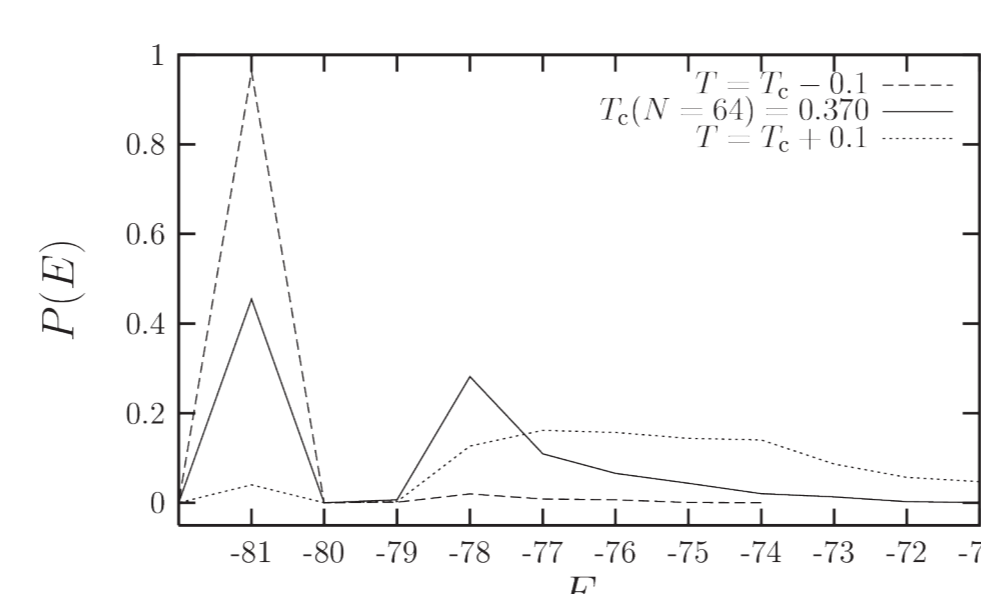


Figure 6

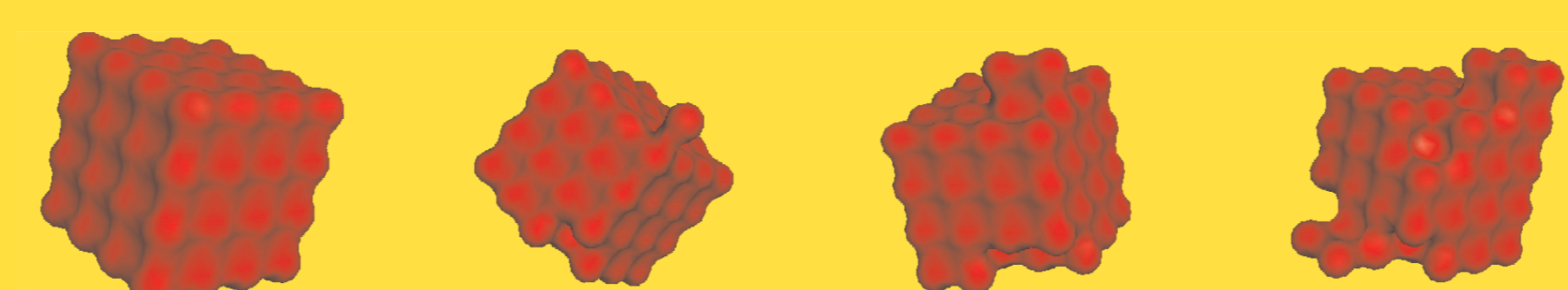


Figure 7: Typical conformations around the freezing transition for the homopolymer with $N_{cgs}=64$. From left: Groundstate ($E=-81$, $T \rightarrow 0$); ($E=-79$, $T \approx 0.36$); ($E=-78$, $T \approx 0.38$), the transition lies at $T_{c1} = 0.37$; ($E=-75$, $T \approx 0.47$).

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Freezing Transition on fcc

Of course, we also find the freezing transition on the fcc lattice.

We will show here, analogously to Figure 4, transition temperatures, but also the peak heights depending on temperature.

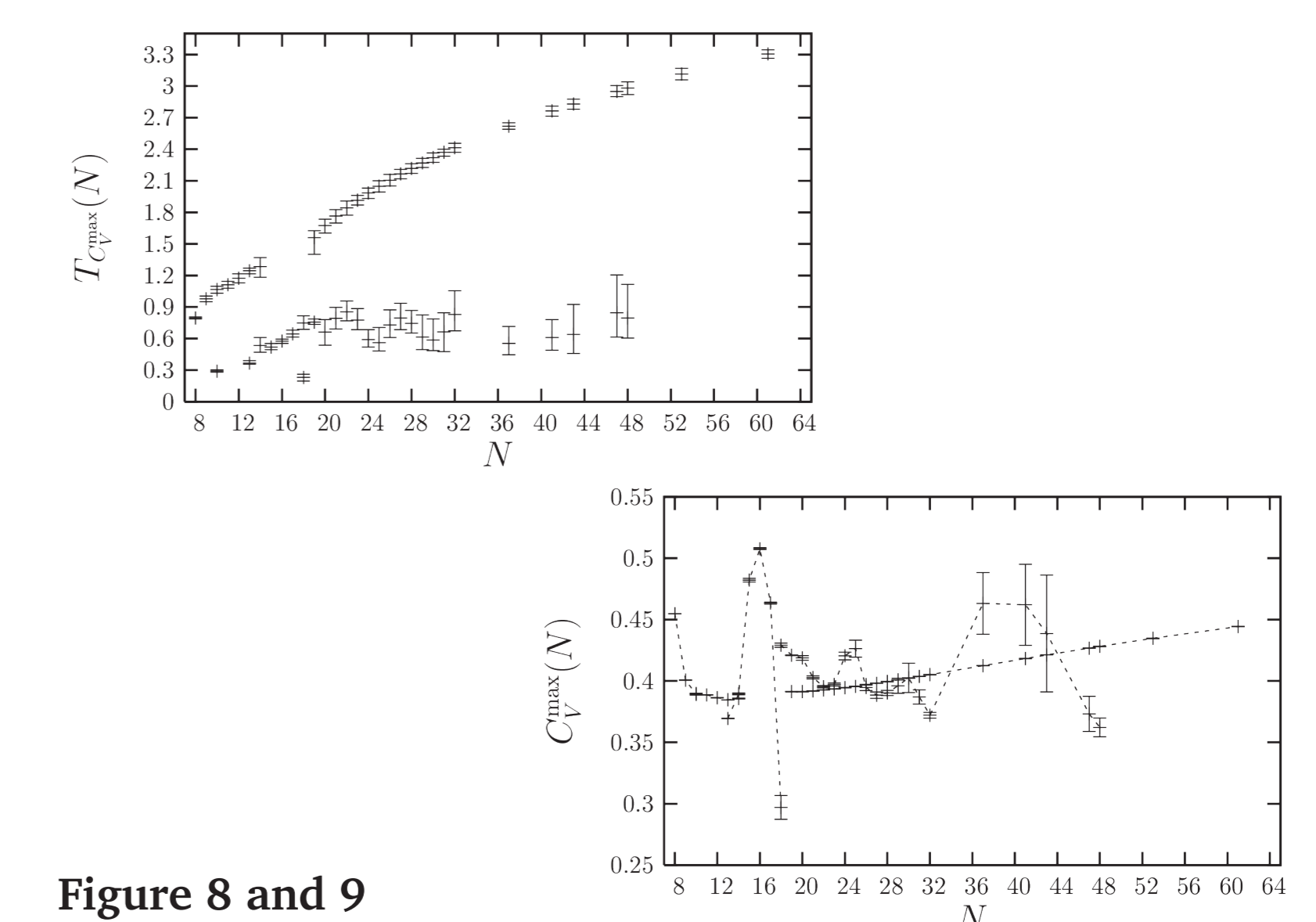


Figure 8 and 9

We see in Figure 8 a similar behavior to that in Figure 4. But the saw tooth behavior is not that clear anymore and the interpretation of the fluctuation is more complex. We found, for example, no ground-state with an energy gap, like the compact ones on the sc lattice.

From Figure 9 we see furthermore, that the height of the freezing peak is, besides some fluctuations, stable and maybe even slightly decreasing, while the height of the Θ -transition peak is monotonously increasing. The Θ -peak becomes dominating with larger polymer length.

The Θ -Transition Revisited

With presented method, it is possible to study reliably the freezing transition up to system sizes of order 10^2 . But there are no principal difficulties to study the Θ -transition at higher temperatures up to lengths of order 10^3 , and with the original PERM algorithm up to order 10^5 (at local temperatures). Results of the Θ -temperature scaling are shown in Figure 10.

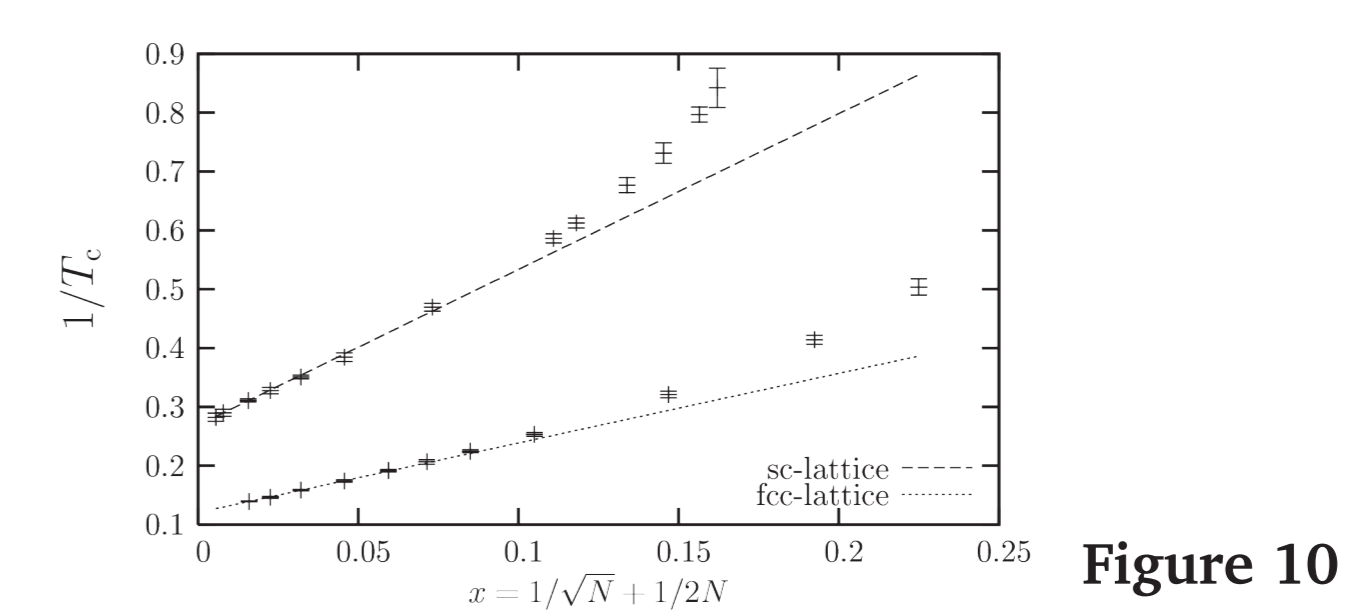


Figure 10

Fitting the finite transition temperatures to following formula (suggested by Flory-Huggins theory, similar as in [1])

$$\frac{1}{T_c(N)} - \frac{1}{T_\Theta} \sim \frac{1}{\sqrt{N}} + \frac{1}{2N}$$

we get:

- for sc: $T_\Theta = 3.72 \pm 0.02$ (in perfect agreement to, e.g. Ref. [3])
- for fcc: $T_\Theta = 8.30 \pm 0.03$

Summary

- Freezing transition exists on sc and fcc lattice
- It is strongly influenced by lattice restrictions
- Θ -transition peak becomes dominant
- Infinite Θ -temperature could be reproduced (sc) and obtained (fcc)
- Both, Θ - and freezing transition will not coincide in thermodynamic limit