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# Freezing and Collapse of Flexible Polymers

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We analyze the freezing and collapse transition of a simple model for flexible polymer chains on simple cubic and face-centered cubic lattices by means of sophisticated chain-growth methods. In contrast to bond-fluctuation polymer models in certain parameter ranges, where these two conformational transitions were found to merge in the thermodynamic limit, we conclude from our results that the two transitions remain well-separated in the limit of infinite chain lengths. The reason for this qualitatively distinct behavior is presumably due to the ultrashort attractive interaction range in the lattice models considered here.

## 1 Introduction

It is well known that single homopolymer chains undergo a structural coil-globule transition at the so-called  $\Theta$ -point. Much theoretical, experimental, and algorithmic work was, and still is, spent to localize that point for various homopolymer models. In principle, there is no longer any difficulty to investigate lattice models up to very long chain lengths. A well working technique to deal with the problem is the (n)PERM algorithm.<sup>1,2</sup>

Since a relatively short time, thanks to generalized-ensemble versions of PERM,<sup>3,4</sup> it is also possible to investigate the temperature range far below the  $\Theta$ -temperature, where another transition called ground-state-globule, liquid-solid (crystallization) or freezing transition can occur.<sup>3,5</sup> A recent study of the bond-fluctuation model with respect to these different transitions for example showed, that the crystallization and the coil-globule transitions may, but generally do not, coincide in the thermodynamic limit, depending on the interaction range.<sup>5</sup>

In this work, motivated by above mentioned studies, we will report results for the structural transitions of Interacting Self-Avoiding Walks (ISAW) on the simple cubic (sc) and face-centered cubic (fcc) lattice, the simplest model for flexible, interacting polymers.<sup>6</sup>

## 2 Model and Methods

In the ISAW model, a local attractive interaction between non-bonded nearest neighbors is assumed. The total energy of an ISAW is given by  $E = -n$ , where  $n$  is the number of such contacts. To simulate the model, we use the nPERM algorithm for the study of the  $\Theta$ -transition of very long chains and a generalized-ensemble version for the simulation of the low-temperature behavior of short polymers. The PERM method is a chain-growth algorithm based on the Rosenbluth method.<sup>7</sup> It includes population control by pruning or enriching populations during the growth, depending on threshold weights.<sup>1-4</sup>

### 3 Results and Discussion

For investigating structural transitions of the polymer model, we calculate the specific heat and analyze its peak structure. It is expected that even for polymers of finite length, peaks of fluctuating quantities signalize conformational activity.

Figure 1 (left) shows specific-heat peaks of polymers on the sc lattice with lengths  $8 \leq N \leq 125$ . We see that there is no uniform scaling behavior of the peaks as it was found for the bond-fluctuation model.<sup>8</sup> A first view does not show any regularity at all regarding the low-temperature peaks. However, the dependence of the peak temperatures on the chain length exhibits more systematics, see Fig. 1 (right).

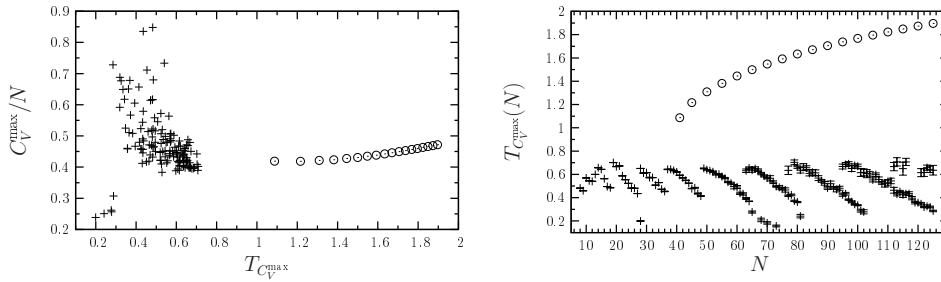


Figure 1. Left: Map of specific-heat maxima for several chain lengths. Circles ( $\odot$ ) symbolize the peaks (if any) identified as signals of the collapse ( $T_{C^{\max}} > 1$ ). The low-temperature peaks (+) belong to the excitation/freezing transitions ( $T_{C^{\max}} < 0.8$ ). Right: Collapse and excitation/freezing peak temperatures of the same specific-heat peaks.

The freezing-transition temperatures show a sawtooth-like behavior which is due to optimal monomer alignment to the underlying lattice. At the lowest peak temperatures, we find chains with very compact ground states which are arranged as cubes or compact cuboids, respectively, e.g., for  $N = 27, 36, 48$ , etc. The corresponding chains have an energy gap of  $\Delta E = 2$  between the ground state and the first excited state. For the sc lattice, this can easily be explained. The first excited state can be constructed by removing a monomer from the corner of the compact state (breaking 3 contacts) and placing it somewhere at the surface (gaining 1 contact). All these chains have a very pronounced freezing-transition peak (not shown). On the other hand, at the other side of the “teeth”, the respective chains with one more monomer reside. Here, the formerly pronounced low-temperature peak becomes very weak.

Let us briefly say some words on the  $\Theta$ -point. Despite of very precise measurements, the nature of this transition is not yet completely understood, considering for example predicted logarithmic corrections<sup>9</sup> which could not be resolved so far in numerical data. Figure 2 shows an illustrating picture of the studied objects (left) and data of transition temperatures for different chain lengths as well as fits to the data (right). There are several approaches to extrapolate  $T_{\Theta}$  by fitting  $T_c(N)$ . We used here the mean-field like fit<sup>6</sup>

$$\frac{1}{T_c(N)} - \frac{1}{T_{\Theta}} = \frac{a_1}{\sqrt{N}} + \frac{a_2}{N}, \quad (1)$$

which was found to be consistent with numerical data obtained in grandcanonical analyses of lattice homopolymers and the bond-fluctuation model.<sup>10</sup>

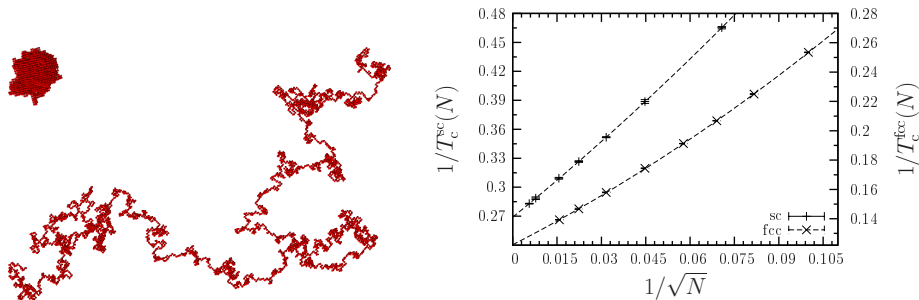


Figure 2. Left: Two typical conformations of a 4096mer on a sc lattice at different temperatures  $T \ll T_\Theta$ ;  $E = -5367$  and  $T \gg T_\Theta$ ;  $E = -1054$ . Right: Inverse collapse temperatures for several chain lengths on sc ( $N \leq 32\,000$ ) and fcc lattices ( $N \leq 4\,000$ ). Drawn lines are fits according to Eq. (1). Error bars are shown, but may not be visible.

Optimal fit parameters using the data in the intervals  $200 \leq N \leq 32\,000$  (sc) and  $100 \leq N \leq 4\,000$  (fcc) were found to be  $T_\Theta^{\text{sc}} = 3.72(1)$ ,  $a_1 \approx 2.5$ , and  $a_2 \approx 8.0$  (sc), and  $T_\Theta^{\text{fcc}} = 8.18(2)$ ,  $a_1 \approx 1.0$ , and  $a_2 \approx 5.5$  (fcc). This agrees very well with data published so far,<sup>1,11</sup> but does unfortunately not solve the problem of correction terms either. A very detailed analysis including different fit ansätze and parameter estimates can be found in Ref. 6.

To summarize, there exists a clear low-temperature freezing transition below the  $\Theta$ -point, which is strongly influenced by lattice restrictions. It is shifted with increasing chain length to lower temperatures ( $T_{C_V^{\text{max}}}(N) \approx 0.4$ ) and jumps at chains with very compact ground states back to a value of  $T_{C_V^{\text{max}}}(N) \approx 0.6$ . The temperature interval, in which the freezing peaks fluctuate, does not change when varying the chain length, whereas the finite-length  $\Theta$ -temperature does.

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## References

1. P. Grassberger, Phys. Rev. E, **56**, 3682, 1997.
2. H.-P. Hsu, V. Mehra, W. Nadler, and P. Grassberger, J. Chem. Phys., **118**, 444, 2002.
3. M. Bachmann and W. Janke, Phys. Rev. Lett., **91**, 208105, 2003; J. Chem. Phys., **120**, 6779, 2004.
4. T. Prellberg and J. Krawczyk, Phys. Rev. Lett., **109**, 7583, 2004.
5. W. Paul, T. Strauch, F. Rampf, and K. Binder, Phys. Rev. E, **75**, 060801(R), 2007.
6. T. Vogel, M. Bachmann, and W. Janke, Phys. Rev. E, **76**, 061803, 2007.
7. M.N. Rosenbluth and A.W. Rosenbluth, J. Chem. Phys., **23**, 356, 1955.

8. F. Rampf, W. Paul, and K. Binder, *Europhys. Lett.*, **70**, 628, 2005.
9. B. Duplantier, *Europhys. Lett.*, **1**, 491, 1986.
10. N.B. Wilding, M. Müller, and K. Binder, *J. Chem. Phys.*, **105**, 802, 1996.
11. K. Kremer, in: *Monte Carlo and Molecular Dynamics of Condensed Matter Systems*, K. Binder and G. Ciccotti (Eds.). Editrice Compositori, Bologna, 1996, p. 669.