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New Results on the Collapse Transition(s) of Flexible Homopolymers

Wolfgang Paul,[*1] Federica Rampf,[2] Thomas Strauch,[1] Kurt Binder[1]*

Summary: We analyze the collapse transition of flexible homopolymer chains in the bond-fluctuation model employing the Wang-Landau Monte Carlo algorithm. The coil-globule transition is followed by a first order transition into a solid state occurring in the collapsed globule. In the thermodynamic limit (chain length to infinity) the topology of the phase diagram depends on the range of the attractive interaction between the monomers. For sufficiently large interaction range a *normal* behaviour of a continuous coil-globule transition at the Θ-temperature followed by a crystallization transition at lower temperature is observed. For short interaction range the first-order transition asymptotically can pre-empt the coil-globule transition such that a first-order collapse from a random-coil into a crystalline globule occurs. This vanishing of the liquid globule state is similar to the vanishing of the vapour-liquid coexistence found for colloidal suspensions interacting by a short-ranged attraction.

Keywords: coil-globule transition; Monte Carlo simulation; phase diagram topology

Introduction

The problem of single chain collapse has a long history in polymer science.[1–4] A single polymer coil in solution can undergo a transition from an open, random coil structure to a dense compact globular state when the quality of the solvent changes from so-called good solvent conditions to poor solvent conditions. Under good solvent conditions the large scale chain structure behaves as $R_g \sim N^{\nu}$ where R_g is the radius of gyration of the chain, and the exponent ν takes the value 0.588[5,6] typical of a self-avoiding walk (SAW). In the compact state one has $\nu = 1/3$ and there exists an intermediate condition where the exponent takes the value ½, that is, the large scale chain structure behaves like that of a random walk (RW). Of course, the configurations of the chain are always self-avoiding walk configurations, only sampled with a different statistical weight. The theoretical description of the coil-globule transition starts from the existence of solvent conditions where the chain behaves as a random walk. Let us assume that this is realized by tuning the temperature of the system, like it is done in computer simulations. Then there exists a temperature where the effective interaction between monomers – that is, the second virial coefficient - is zero. At higher temperatures the effective interaction is positive, at lower temperatures it is negative. Above and at the transition the volume occupied by the chain grows faster than linear as a function of chain length such that the density within the occupied volume goes to zero. This allows for a theoretical description in terms of a virial expansion which was first performed in a mean-field theory[1] and later in a field theoretical approach.[7,8] According to the theoretical predictions the transition is continuous for flexible chains[3] and only

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[1] Institut für Physik, Johannes Gutenberg-Universität, 55099 Mainz, Germany
E-mail: wolfgang.Paul@uni-mainz.de

[2] Institut für Mikrotechnik Mainz GmbH, 55129 Mainz, Germany

becomes of first order when an additional energy scale besides the effective attraction between monomers comes into play, like, for instance, a bending stiffness of the chains.

There exists also a long tradition of computer simulations[9–17] trying to establish the coil-globule transition behaviour for different polymer models. According to these studies the continuous nature of the transition in three spatial dimensions is well established and also a first order transition for stiff enough chains has been found.[13–17] Recently, it has also become possible to study the coil-globule transition experimentally for very long chains by light scattering techniques[18] and to observe the continuous collapse of single chains.

Of course, speaking about the order of the transition requires an extrapolation to the thermodynamic limit, i.e., to infinite chain length. It is a special property of polymers that the thermodynamic limit can be reached in two ways: by considering only one chain and letting the chain length go to infinity, as for the coil-globule transition, or by keeping the chain length fixed and letting the number of chains go to infinity, like in the phase diagram of a simple substance. And indeed, there is a connection between these two thermodynamic limits. The critical point of the many chain system is the analogue of the coil-globule transition temperature of the single chain. Both converge to an infinite chain length transition temperature, the so-called Θ-temperature, which is indicated in the right part of Figure 1, where the polymer solution phase diagram is shown. For finite chain length one has $\Theta(N) = \Theta - c_1\ N^{-1/2}$ and $T_c(N) = \Theta - c_2\ N^{-1/2}$ (since a sharp transition only occurs for N infinite $\Theta(N)$ means a measure of the rounded transition temperature).

The phase diagram of a simple substance typically displays vapour, liquid and crystal as thermodynamically stable phases with first or second order phase transitions between the phases (left part of Fig. 1). In the polymer solution phase diagram we find the analogue to the vapour-liquid coexistence but we generally do not have information on the low temperature and/or high density part of the phase diagram in thermodynamic equilibrium[19] and observe kinetically arrested structures. The reason for this lies in the entropic barriers against crystallization[20] present for polymers. In

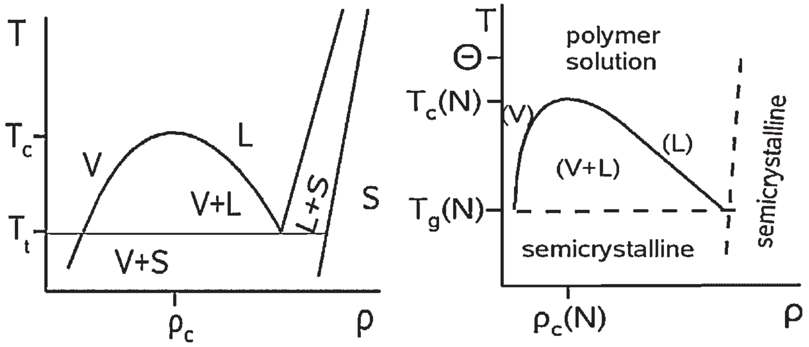

Figure 1.
Left: Projection of the phase diagram of a simple substance into the temperature density plane. Below a critical point (T_c, ρ_c) a liquid-vapour coexistence exists which turns into a vapour-solid coexistence below the triple temperature T_t. At high densities another coexistence region between liquid and solid exists. Right: Polymer solution phase diagram as the analogue to the phase diagram of a simple substance. Below a critical point ($T_c(N)$, $\rho_c(N)$) the solution phase separates into a dilute solution and a dense solution/melt. The critical point approaches the Θ-point for infinite chain length. For very low temperatures and or high densities we typically do not know the equilibrium phase diagram of the polymer solution any longer and a semi-crystalline state with frozen amorphous regions is found.

order to form a periodic, space filling structure, it is in general not sufficient for the polymer chains to undergo some local rearrangement. They have to assume a well-defined large-scale conformation (for instance extended chain crystals formed by poly-olefins) and there is a large entropy penalty against finding these states. This is akin to the protein folding problem (although the large scale structure necessary for homopolymer crystallization does not need to be unique), but the simple homopolymer chains have no "folding-funnel" helping them to overcome Levinthal's paradox.

The interesting questions one can pose now are the following: i) What would the polymer solution phase diagram look like if one could avoid the entropic barrier against crystallization normally present in polymers? ii) How would this show up in the single-chain phase diagram? From simulations of the coil-globule transition of simple polymer models there is evidence that there can be a crystallisation transition occurring in the collapsed globule[21–23] and indications for this have also been reported from experiment.[18] We intend to answer these questions in the following using two key ingredients: a polymer model able to crystallize by local rearrangements only and a simulation algorithm able to provide information on the single chain conformations at low temperature and high density in thermodynamic equilibrium.

Model and Simulation Technique

We used the Wang-Landau type Monte Carlo simulation technique to study the phase behaviour of a single polymer chain of the bond-fluctuation model on the simple cubic lattice. In this model the repeat units of the chain are represented as unit cubes on the lattice, connected by bonds that can vary in length and direction. The shortest bond length compatible with excluded volume between the monomers is $b = 2$, the largest allowed bond length of the model is $b = \sqrt{10}$. The set of allowed bond vectors is generated by the basis vectors $(2, 0, 0), (2, 1, 0), (2, 1, 1), (2, 2, 1), (3, 0, 0), (3, 1, 0)$ applying all symmetry operations of the simple cubic lattice. The chains are flexible and we employed an attractive interaction of the square-well type, also acting between bonded neighbours.

$$E = -\varepsilon \sum_{i=1}^{N-1} \sum_{j>i} H(r_{ij}^2 - d^2) = -\varepsilon N n \qquad (1)$$

Here $\varepsilon = 1$ sets the temperature (energy) scale, the Heavyside function, H, is 1 for all monomer pairs with a squared distance smaller than d^2 lattice units, the range of our attractive potential (we will set the lattice unit equal to unity), and n is the average number of neighbours per monomer. We will present results for $d^2 = 6$ and for $d^2 = 10$. The coil-globule transition for the $d^2 = 6$ model was studied in[24] for chains up to length $N = 150$ and the intersection of curves R_g^2/N for different N yielded an estimate $\Theta = 2.02 \pm 0.02$. Using the leading order prediction for the tricritical scaling, Grassberger[11] later determined $\Theta = 2.10 \pm 0.01$ from simulations of chains up to length $N = 600$. However, a renormalization group calculation of the next to leading order logarithmic correction[8] to the mean field behaviour showed that, as well as being universal, it is of the same magnitude as the leading order correction even for chain lengths $N = 10000$. Finally, extrapolating the critical temperature of the solution phase diagram of this model to infinite chain length Yan and de Pablo[25] determined $\Theta = 2.08 \pm 0.01$. For the model with $d^2 = 10$ no prior information on the collapse transition was available.

The Wang-Landau algorithm[26] was suggested as a method to determine the density of states, g(E) (up to an unknown constant scale factor), and with it the canonical partition function

$$Z(T) = \sum_E g(E) \exp(-\beta E) \qquad (2)$$

with $\beta = 1/k_B T$. Instead of using the standard Metropolis acceptance criterion for a

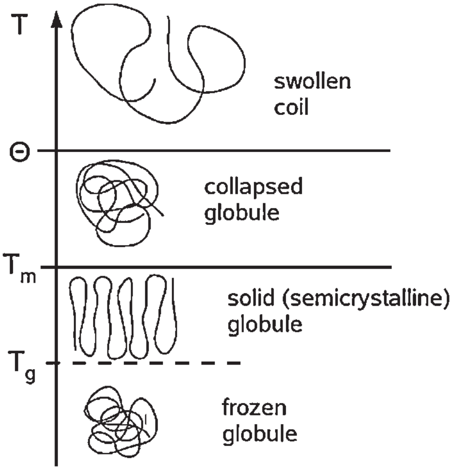

Figure 2.
Single chain phase diagram corresponding to the polymer solution phase diagram from Figure 1. The collapsed globule can undergo an equilibrium transition into a semicrystalline globule at the melting temperature T_m or at larger cooling rates a dynamic transition into an arrested glassy structure. This glass transition for polymers is already reached at normal cooling rates.

suggested new configuration this method uses

$$\text{prob}(\text{old} \rightarrow \text{new}) = \min\,(1,\; g(E(\text{old}))/g(E(\text{new}))). \qquad (3)$$

If the density of states of a model is known, this acceptance criterion generates a random walk over the available energy range if one uses a set of model specific (ergodic) Monte Carlo moves. When one then records the number of configurations visited for given energy values, H(E), one should obtain a flat histogram of visits. This idea can be turned into an iterative procedure to determine the density of states. Starting with an arbitrary choice of $g(E) = 1$ for all E, and $H(E) = 0$ for all E one modifies $g(E) = f\, g(E)$ for the energy after the MC move, where typically $f = e$ at the beginning, and increments the histogram of visits. Whenever the monitored histogram of visits H(E) is sufficiently flat (in practice we required the number of visits to any state to be at least 80% of the average number over visits for all states) one changes $f_{\text{new}} = f_{\text{old}}^{1/2}$ and resets the histogram of visits to zero. For $f \rightarrow 1$ the method fulfils detailed balance and the measured density of states converges to the exact one. In the course of the simulation, the detailed balance condition is not fulfilled because the density of states which determines the transition rates is constantly updated. The Wang-Landau method therefore does not belong to the class of Markov-chain Monte Carlo methods but is in spirit closer to an optimization method.

We also implemented a hierarchical search algorithm[27] which checks for overlaps and interactions between monomers. The algorithm has the same scaling as linked neighbour lists typically employed in Molecular Dynamics simulations.

Results

The main result of the Wang-Landau simulation algorithm is the density of states which we plot for the model with $d^2 = 6$ in Figure 3. We show there the entropy per monomer as a function of energy per monomer to bring out the convergence to the infinite chain length behaviour.

When we look at the position of the maximum entropy state ($E_{\max}$, $S(E_{\max})$) in Fig. 3 (shown in Fig. 4) we can observe an exponential convergence to the infinite

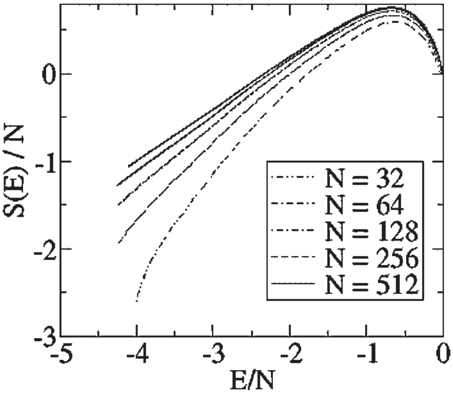

Figure 3.
Entropy per monomer [S(E) = ln(g(E))] as a function of energy per monomer for different chain lengths.

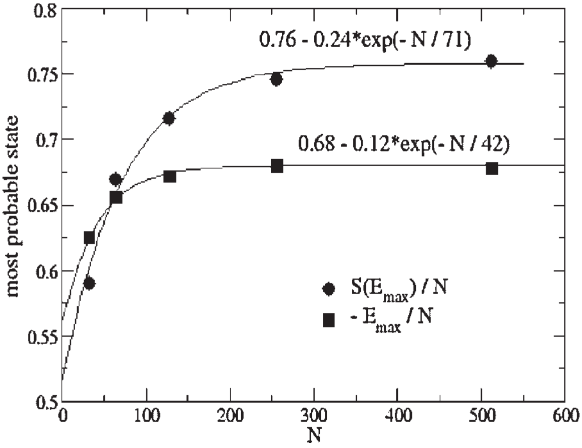

Figure 4.
Finite chain length extrapolation of the energy per monomer and the entropy per monomer of the maximum entropy state of the self-avoiding walk in the bond fluctuation model. Both values converge exponentially to their infinite chain length limit with fit laws given in the plot.

chain length limit for the energy per monomer and the entropy per monomer.

From the density of states, i.e., the microcanonical entropy we can determine the properties of our model system in the canonical ensemble by going to the partition function using eq. (2) and determine the temperature dependence of the thermodynamic potentials and response functions.

$$U(T) = \langle E \rangle = \frac{1}{Z}\sum_{E} Eg(E)\exp(-\beta E)$$
$$C(T) = \frac{\langle E^2 \rangle - \langle E \rangle^2}{k_B T^2} \tag{4}$$

The internal energy as a function of chain length shown in Fig. 5 develops a

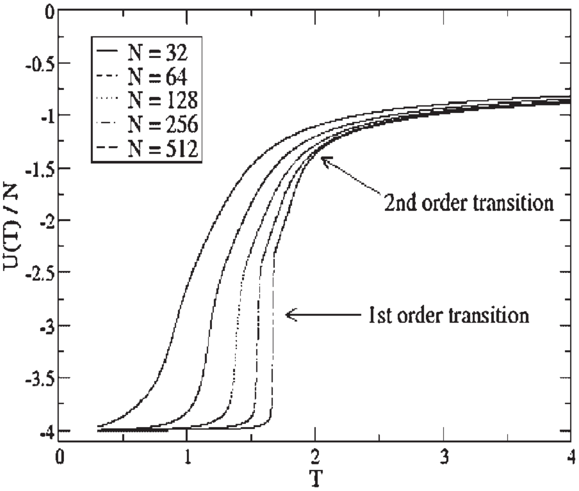

Figure 5.
Internal energy as a function of temperature for the model with $d^2 = 6$ and for different chain lengths. At low temperatures a clear first-order transition develops with increasing chain length and there is a second order transition at slightly larger temperatures.

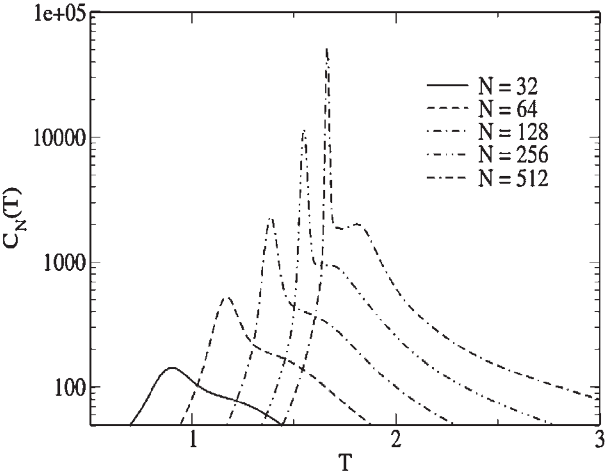

Figure 6.
Specific heat as a function of temperature for the model with $d^2 = 6$ and for different chain lengths. For the longest chains a δ-like peak develops at a first order phase transition in the collapsed globule.

clear step signature with increasing chain length showing that there is a first-order transition in the system. This transition shows up as a δ-like peak in the specific heat displayed in Fig. 6. There is a second transition which is of second order occurring at slightly higher temperature. For the longer chains this transition shows up as a separate peak in the specific heat but for the smaller chains it is buried in the high temperature flank of the first-order transition peak. One can bring this transition out more clearly[28] by determining the specific heat using the information from the density of states only for energies larger than a selected threshold value. Two observations can be made from this procedure: i) for too large threshold only the second order phase transition (the coil-globule transition) is visible and ii) the location of the transition peaks depends on the energy range over which the density of states is known. For sufficient width of the considered energy range it stabilizes and only the height of the peaks increases with further decrease of the lowest energy considered. In Fig. 7 we show 10 results for the specific heat of a chain of length $N = 32$ obtained from different, converged Wang-Landau runs. There is some observable scatter between the different results on the scale of the line thickness used in the drawing. When one determines the position of the first-order transition from these different runs one finds, however, that these agree to 3 significant digits.

The assignment of the transitions as the coil-globule transition and a first-order transition (crystallization) in the collapsed

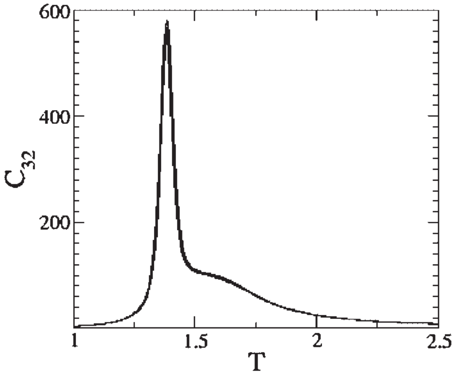

Figure 7.
Specific heat for a chain of length $N = 32$ with interaction range $d^2 = 6$. The results from ten different Wang-Landau runs are shown.

globule requires a determination of the average chain size as a function of temperature. The calculation of such a structural quantity from the Wang-Landau simulation requires the sampling of additional observables in the simulation. To determine the average radius of gyration

$$\left\langle R_g^2 \right\rangle = \frac{1}{N}\left\langle \sum_{i=1}^{N} (\vec{r}_i - \vec{R}_{cm})^2 \right\rangle \qquad (5)$$

where $\vec{R}_{cm}$ is the centre of mass of a chain one has to determine the average radius of gyration as a function of energy in the simulation and employ

$$\left\langle R_g^2 \right\rangle(T) = \frac{1}{Z}\sum_E \overline{R_g^2(E)}\, g(E)\exp(-\beta E) \qquad (6)$$

This quantity is shown in Fig. 8 in a form suggested by mean field theory which predicts a random walk behaviour of the chains at the Θ-point, i.e., a universal value for the radius of gyration squared divided by chain length. This is not what we find in our simulations. There is a clear systematic shift of the intersection point of curves for different chain lengths N, as N is increased. This shift, however, is not compatible with the logarithmic correction one would expect from the field-theoretic treatment of the coil-globule transition.[8] Still, the intersection points of curves for chain length N and 2N give us an estimate for the location of Θ(N).

Both, the specific heat and the intersection points in the radius of gyration curves provide us with estimates for the location of the coil-globule transition. The specific heat curves furthermore yield a very sharp estimate for the location of the crystallization transition in the collapsed globule. True phase transitions occur only in the thermodynamic limit, so we have to extrapolate to infinite chain lengths. For this we plot Θ(N) vs. $N^{-1/2}$,which is the finite chain length shift of the coil-globule transition predicted by mean field theory. The finite size dependence in the location of the first-order transition stems from the presence of a free surface of the collapsed globule. At the transition the free energy densities of the liquid and the crystalline globule are equal but the surface contributions disagree. The finite chain length shift in the transition temperature depends on the surface to volume ratio, i.e., it has to scale as $N^{-1/3}$. Both predictions are used in Fig. 9 where the locations of the two

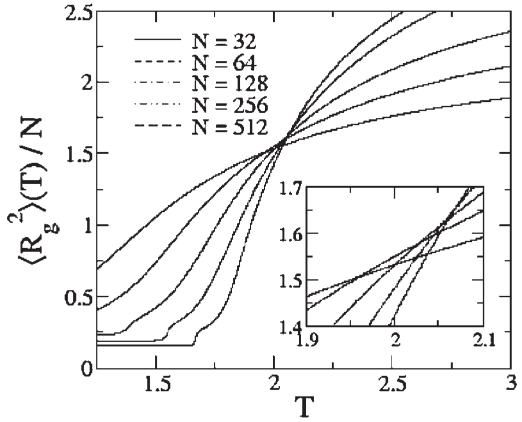

Figure 8.

Squared radius of gyration divided by chain length as a function of temperature for the model with $d^2 = 6$ and for five different chain lengths. Instead of finding a unique intersection point we find a systematic shift of the intersections points between curves for chain length N and 2N as a function of N (inset). In the main figure the first order transition in the collapsed globule shows up as a step in the temperature dependence of the size of the globule at low temperatures.

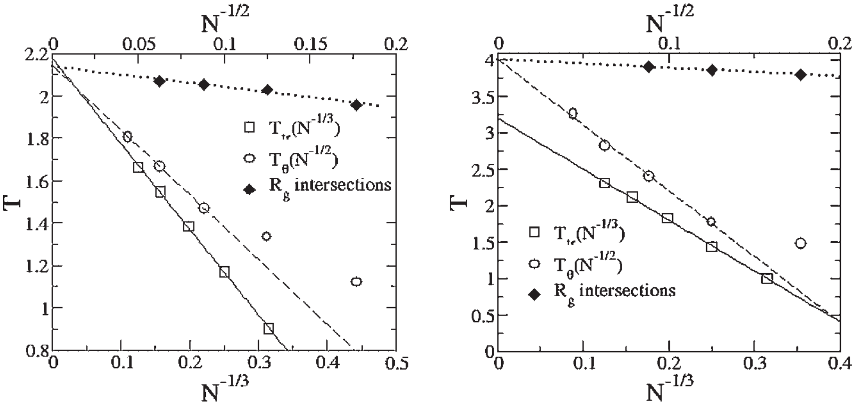

Figure 9.

Finite chain length extrapolations of the transitions found for different chain lengths in the two models studied: interaction range $d^2 = 6$ on the left and $d^2 = 10$ on the right. For a discussion see the text.

transitions as a function of chain length are plotted for both interaction ranges.

There exists a remarkable difference between the two plots in Fig. 9.[29] For the model with interaction range $d^2 = 10$ the Θ temperature is significantly higher than the infinite chain length limit of the crystallization temperature. In this model we have a continuous coil-globule transition like it is generally discussed theoretically. Then one has region of stability of a liquid globule which undergoes a first order transition into an ordered phase at a lower temperature ($\Theta = 4.01 \pm 0.02$, $T_{crys} = 3.2 \pm 0.02$). Both temperatures are obtained from linear regressions of the measured locations for the coil-globule and crystallization transition at finite N as a function of their respective scaling variables.

A very different scenario occurs for the model with interaction range $d^2 = 6$ which we analyze in a slightly different way as in.[23,28] For the coil-globule transition we now also perform a linear regression to the locations measured from the specific heat (and not a quadratic one). For the linear regression we can only use the results from the 3 longest chains. The extrapolated Θ-temperature from this analysis is 2.14 ± 0.04 agreeing with the extrapolation from the intersection points in the radius of gyration curves. The extrapolated crystallization temperature is $T_{crys} = 2.18 \pm 0.01$ meaning that the Θ temperature is identical or slightly below the crystallization temperature. This signifies that the coil-globule transition (i.e., the vapour-liquid transition of the single chain) becomes metastable. Instead, we find a direct, first-order collapse from the random coil state into the crystalline globule. This scenario of the coil-globule transition is not covered by our current theoretical understanding of this transition. As there is a coexistence between the random coil (density zero) and the crystalline globule (density one in our model) at this transition, it is not describable by the truncated virial expansion employed so far in all theoretical approaches.[3,7]

Another consequence one can derive from Fig. 9 concerns the density in the interior of the liquid globule (plateau of the radial density profile) at coexistence with the solid globule. For the model with $d^2 = 10$ this density has to approach a typical melt density of our model, which is around 0.6 ± 0.1. For the model with $d^2 = 6$ it has to go to zero. This is clearly confirmed by the data in Fig. 10.

For the model with the short interaction range we therefore find the following picture for the solution phase diagram (see Fig. 11). As the chain length is increased to infinity the critical point for the vapour-liquid coexistence approaches

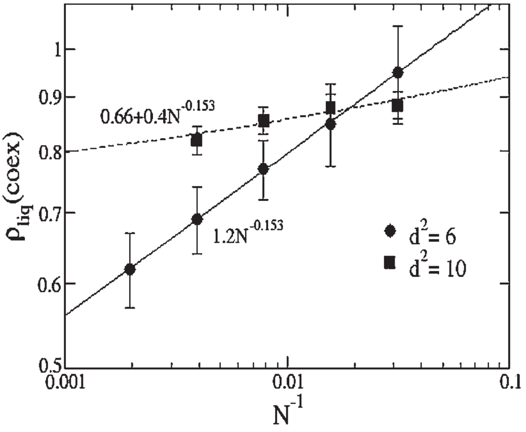

Figure 10.
Liquid density at coexistence for the model with $d^2 = 6$ (circles) and $d^2 = 10$ (squares). In the first case we can determine the exponent to be around 1/6. The second case is fitted with this exponent fixed.

the Θ-point: $(T_c, \rho_c) \rightarrow (\Theta, 0)$. Similarly, however, also the liquid-solid coexistence approaches the Θ-point: $(T_{crys}, \rho_{crys}) \rightarrow (\Theta, 0)$. As a consequence the vapour-liquid coexistence vanishes from the phase diagram.

This behaviour has been reported before for colloidal suspensions mixed with linear polymers.[30,31] The polymers have a radius of gyration much smaller than the size of the colloids and introduce a short-ranged depletion attraction between the colloids. When the ratio of the range of this attraction to the size of the colloidal particles (excluded volume) falls below a threshold,[32] the resulting phase diagram of the system was predicted to be hard sphere like, i.e., to exhibit only fluid and crystal phase. Only for sufficiently long-ranged attraction a vapour-liquid coexistence in thermodynamic equilibrium exists. When we define a scaled range of attraction as

$$\lambda = \frac{d}{\sigma} - 1 \qquad (6)$$

where d is the range of the attractive interaction and σ is the size of the particles, the threshold value separating the two

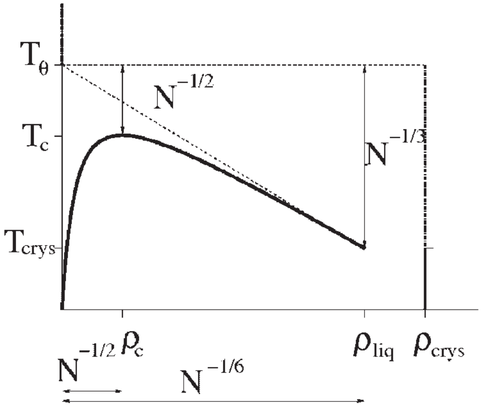

Figure 11.
Behaviour of the solution phase diagram for the model with $d^2 = 6$ with increasing chain length. For the limit $N \rightarrow \infty$ the dotted lines indicate a direct transition from a zero density gas to a high density crystal.

regimes was found to be $\lambda_c = 0.25$ from experiments.[31] We have $\lambda_1 = 0.225$ and $\lambda_2 = 0.581$ for $d^2 = 6$ and $d^2 = 10$, respectively. One might be concerned about the possibility of artefacts created by the underlying lattice structure of the model, although it is clear from the model definition and has also been confirmed by an analysis of the ordered structures formed in the crystalline state,[28] that the model does not have a simple cubic symmetry with a primitive unit cell. Nevertheless repeating our study for a continuum model would be a worthwhile task. However, although the possibility of a crystallization of the collapsed globule had been identified early on[21] for a bead-spring type model, obtaining the phase diagram with sufficient accuracy for sufficiently long chains to be able to extrapolate to the thermodynamic limit is still a challenge.[33]

Conclusion

We have presented results for the phase transitions occurring in a single, flexible homopolymer chain studying the bond fluctuation model with the Wang-Landau flat histogram Monte Carlo algorithm. Using this algorithm for a polymer model, which is able to crystallize by local conformational rearrangements alone, allows one to study also the low-temperature phase diagram in thermal equilibrium. In this way we have documented that in addition to the coil-globule transition there exists a first-order liquid to solid transition in the collapsed single chain globule. We have furthermore studied the finite size behaviour of both transitions and established the transition temperatures in the thermodynamic limit for two variants of the model. Both variants have square well attractions between the monomers. In the first variant it extends to $d = \sqrt{6}$ in the second variant it extends to $d = \sqrt{10}$. This small variation between the models, however, makes a large difference in the phase diagram topology in the thermodynamic limit. For the longer interaction range we found the expected behaviour of a continuous transition from the random coil to the liquid globule and a first order crystallization at lower temperatures. For the short interaction range, however, the coil-globule transition in the thermodynamic limit turned out to be of first order as it occurred directly into the crystalline globule. We discussed that this finding is not at all exotic but agrees with the understanding of the influence of the range of an attractive interaction on the topology of the phase diagram obtained from studies of colloidal suspensions. Further discussion of the physical consequences of these findings can be found in.[29]

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