PHYSICAL REVIEW E **75**, 060801(R) (2007)

Unexpectedly normal phase behavior of single homopolymer chains

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(Received 5 December 2006; published 1 June 2007)

Employing Monte Carlo simulations, we show that the topology of the phase diagram of a single flexible homopolymer chain changes in dependence on the range of an attractive square well interaction between the monomers. For a range of attraction larger than a critical value, the equilibrium phase diagram of the single polymer chain and the corresponding polymer solution phase diagram exhibit vapor (swollen coil, dilute solution), liquid (collapsed globule, dense solution), and solid phases. Otherwise, the liquid-vapor transition vanishes from the equilibrium phase diagram for both the single chain and the polymer solution. This change in topology of the phase diagram resembles the behavior known for colloidal dispersions. The interplay of enthalpy and conformational entropy in the polymer case thus can lead to the same topology of phase diagrams as the interplay of enthalpy and translational entropy in simple liquids.

DOI: 10.1103/PhysRevE.75.060801 PACS number(s): 61.82.Pv, 05.10.Ln, 05.70.Fh, 61.50.−f

When a simple fluid held at its critical density is cooled down from high to low temperatures, one encounters first a second-order transition at a critical temperature T_c, where the fluid separates into vapor and liquid phases, while below the triple point temperature T_t also the solid phase (crystal) comes into play. For a simple liquid it is known that a crossover to a hard-sphere-type phase diagram without a liquid-vapor coexistence region must occur as a function of the range of the attractive interaction between the particles. Decreasing the range of interaction leads to a decrease of T_c, and when T_c falls below T_t, both T_c and T_t annihilate, and the two-phase region between vapor and liquid disappears. For colloids [1–3], such a single phase separation of the colloidal dispersion between fluid and crystal phases has been discussed and realized experimentally. These phase transitions result from the competition of interaction energy and entropy, which for simple liquids is the translational entropy of the pointlike particles.

What happens to this scenario when one considers the phase diagram of a solution of flexible macromolecules [Fig. 1(a)] where the conformational entropy of the single macromolecule has to be considered in addition to its translational entropy, or the phase diagram of a single infinitely long polymer chain [Fig. 1(b)] where only conformational entropy plays a role?

Figure 1(a) sketches the many-chain phase diagram in the form of the experimentally relevant polymer solution phase diagram. In the vapor and liquid (dilute and dense solution) regime the phase diagram is similar to that of a simple liquid. On the high-density side, however, the equilibrium phase diagram of a polymer solution is generally not known. The conformational entropy of the macromolecules in most cases prevents the formation of a crystal phase [5–7] which would require not only a regular spatial arrangement of the monomers but also a definite conformational state of each molecule, able to lead to a periodic, space-filling structure. Some polymers of geometrically simple chemical repeat units are able to crystallize [6,7], but most polymers are kinetically arrested into a glassy structure at low temperatures and/or high densities [Fig. 1(a)].

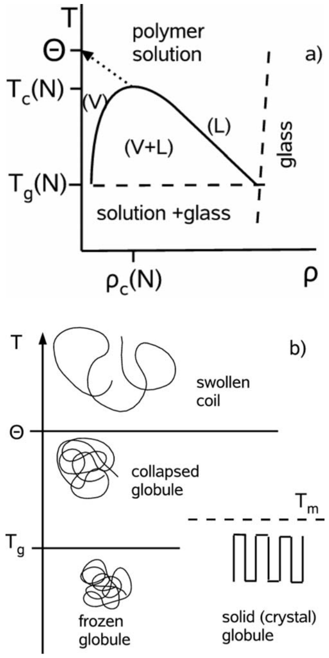

FIG. 1. Sketch of the phase diagram of a polymer solution with upper critical solution temperature (a) and a single chain in dilute solution in the limit of infinite chain length (b). In the polymer solution, phase separation occurs below $T_c(N)$ (N being the chain length of the flexible macromolecule) into a dilute solution, analogous to the vapor (V), and a concentrated solution, analogous to the liquid (L). Crystallization in most cases is kinetically hindered and the solid state reached is glasslike. In the case of single, infinitely long chains a continuous transition occurs from a swollen coil to a collapsed coil at $T=\Theta$ [4]. At lower temperatures, it is typically found in experiment and simulation that the globule freezes into a nonequilibrium glassy state. However, indications for a possible first-order transition (dashed line) into a crystal exist. The phase diagrams in (a) and (b) are related by performing the limit $N\to\infty$ in the polymer solution phase diagram, where one finds $(T_c,\rho_c,p_c)\to(\Theta,0,0)$.

For polymers, the thermodynamic limit (which is necessary for sharp, well-defined phase transitions to exist) can be reached in two ways: by letting the number of molecules go to infinity as in Fig. 1(a) or by regarding only a single molecule but letting the chain length go to infinity [Fig. 1(b)]. In the latter case, the phase behavior is determined by interaction energy and conformational entropy alone. The phase

1539-3755/2007/75(6)/060801(4)

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diagrams occurring in these two thermodynamic limits have to correspond to each other. The vapor and liquid phases of a polymer solution have their analog in the states of swollen coil, whose gyration radius scales as $R_g \propto N^{\nu}$ with $\nu \approx 0.588$, and liquidlike collapsed globule $R_g \propto N^{1/3}$ [4], which occurs below the Θ temperature. It is well known that the critical point of the solution phase diagram approaches the Θ point in the limit of infinite chain length: $T_c(N) = \Theta - c_1 N^{-1/2}$, $\rho_c(N) = c_2 N^{-1/2}$ where c_1, c_2 are positive constants. Consequently, our current theoretical understanding of the collapse transition of a single polymer chain is that it is a continuous phase transition (second order in mean-field theory [4] and tricritical in a field theoretical treatment [8]). Again, due to conformational entropy, the solid globule formed by a single chain at low temperatures typically exists in the form of a frozen, glasslike structure [9], but crystalline states have also been identified in simulations [10,11].

We show in this Rapid Communication that (i) if one is able to attain thermodynamic equilibrium also for the dense, low-temperature states of macromolecules, the phase diagram of a single macromolecule [Fig. 1(b)] as well as that of macromolecular solutions [Fig. 1(a)] are equivalent to that of a simple liquid, and (ii) that this equivalence even extends to the point that the liquid-vapor transition vanishes from the equilibrium phase diagram of the single macromolecule as well as the macromolecular solution when the range of attractive interaction between monomers falls below a critical value. We will show that, for short enough range of attractive interaction, a single first-order transition from a swollen coil to a dense solid globule occurs for single macromolecules in the limit $N \rightarrow \infty$. So far, such a first-order collapse was assumed [4] to occur only when one introduces an additional energy scale like stiffness [12,13] or directional interactions [14] into the model, where the phase diagram topology changes as a function of the ratio of the energy scales.

We are arriving at this different view of macromolecular phase behavior by studying the single-chain phase diagram. Our conclusions for the many-chain polymer solution phase diagram are then based on the correspondence between the two types of thermodynamic limit we discussed above. We are using two key ingredients: (i) we study a simple model able to crystallize by local conformational rearrangement alone, thus overcoming the kinetic limitations normally present in polymer crystallization [5], and (ii) we use a simulation method that yields the density of states of the model with complete thermodynamic information.

We are studying a single chain of the bond-fluctuation model [15], which is the lattice equivalent of a tethered-hard-spheres chain, where the spheres are replaced by unit cubes on the simple cubic lattice and the bonds between these monomer units can vary in length between 2 and $\sqrt{10}$ (all lengths are given in lattice units). Temperature is introduced into the model by an attractive square well interaction between all monomers,

$$H = -\epsilon N n, \tag{1}$$

where N is the chain length, ϵ is the depth of the square well potential setting the energy scale ($\epsilon = 1$), and n is the number of neighbors per monomer, i.e., other monomers within the interaction range. We will consider two ranges of attractive interaction: $\lambda_1 = \sqrt{6}$ and $\lambda_2 = \sqrt{10}$. The hard-core diameter of the monomers is $\sigma = 2$.

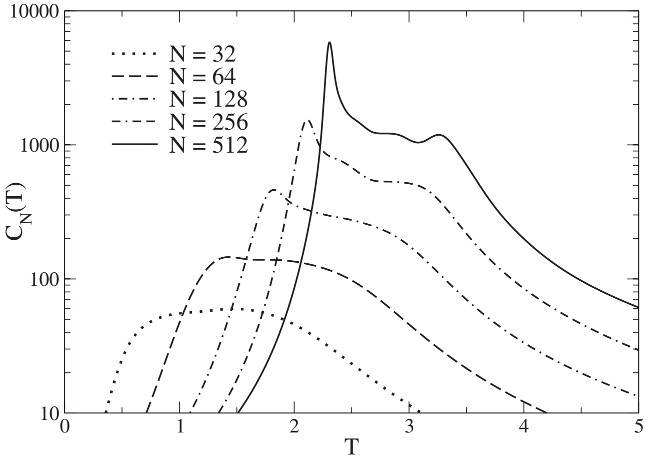

FIG. 2. Specific heat as a function of temperature obtained for different chain lengths for the interaction range λ_2. The uncertainty of the curves is below 2% as given by independent runs for the determination of $g(E)$ at fixed N.

Furthermore, we use the Wang-Landau version of flat-histogram Monte Carlo simulations [16], which iteratively determines the density of states $g(E)$ requiring a flat histogram of visits to all energy levels. The method is able to sample rare, dense low-energy configurations which are generally only accessible via advanced Monte Carlo simulation techniques [17,18]. From the density of states we can calculate the canonical partition function

$$Z(T) = \sum_E g(E) e^{-\beta E}, \tag{2}$$

where $\beta = 1/k_b T$. From the partition function thermodynamic properties like the specific heat can be determined. Determining structural properties like the radius of gyration as a function of energy during the simulation, one also gets

$$\langle R_g^2 \rangle (T) = \sum_E g(E) \overline{R_g^2(E)} e^{-\beta E}, \tag{3}$$

where the overbar indicates an arithmetic average over all configurations for a given energy.

We can locate the phase transition temperatures of our model system from the specific heat shown for the model with interaction range λ_2 in Fig. 2. With increasing chain length, two main peaks develop, indicating the transition from the coil to the globule and then from the liquid to the solid globule at lower temperature. The peak at lower temperature evolves into a δ peak [19,20]. There is an additional maximum developing between the two transition peaks for the longest chain length. The nature of this (meta)stable intermediate state is not clear and will not concern us in the following, although (meta)stable intermediate states have also been tentatively identified from experiment [9] and seen in simulations of a continuum model [21].

We take the positions of the main peaks in the specific heat as locations of the finite chain length coil-globule and

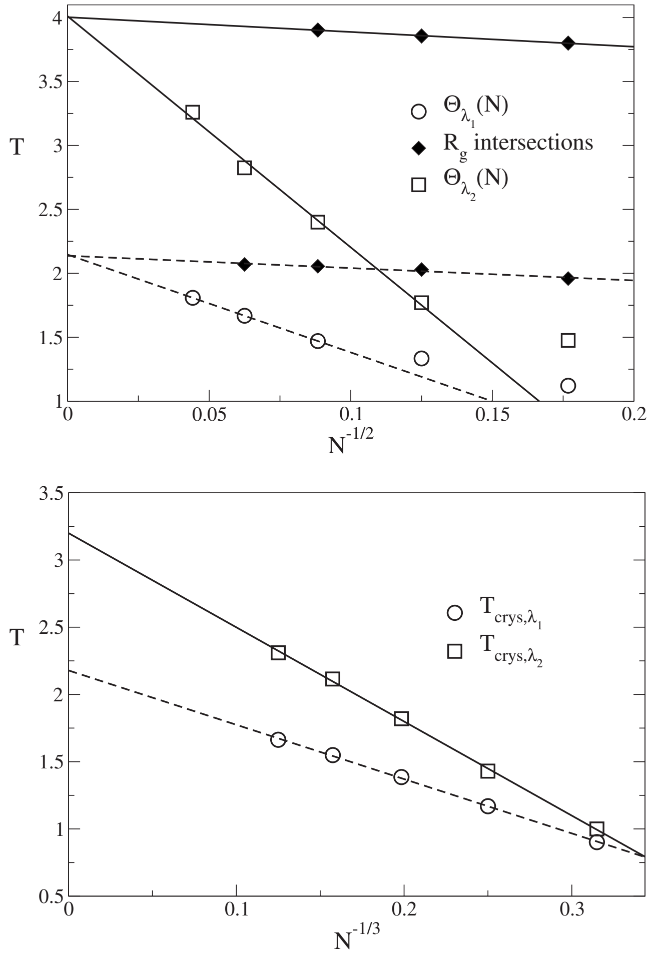

FIG. 3. Top: Finite size extrapolation of the location of the coil-globule transition located by the high-temperature peaks in the specific heat curves for a small width of the square well attraction (circles) and a larger one (squares). The diamonds indicate intersection points in plots of $\langle R_g^2(T)\rangle$ vs T for chains of length N and $2N$. Bottom: Finite size extrapolation of the location of the liquid-solid transition for the two interaction ranges. All error bars are smaller than the symbol sizes.

liquid-solid transitions (technical details are explained in [20]). The coil-globule transition can additionally be located by determining intersection points in plots of $\langle R_g^2\rangle/N$ vs T for chains of lengths N and $2N$. These intersection points are shown in the top part of Fig. 3, in addition to the locations of the specific heat peaks of the coil-globule transition for both choices of interaction range. All data are plotted vs $N^{-1/2}$ according to the prediction of mean-field theory [4]. For both choices of interaction range the different ways of locating the finite chain length coil-globule transition point extrapolate to a common Θ point, $\Theta=2.14\pm0.04$ for λ_1 and $\Theta=4.01\pm0.02$ for λ_2.

The liquid to solid transition is a first-order transition where the free energy densities in the bulk of the liquid and solid globule are identical. A shift in the location of the transition should therefore be an effect of the free surface of the globule, leading to a finite size scaling with $N^{-1/3}$. This is borne out by the data shown in the bottom part of Fig. 3 for both ranges of interaction. In the thermodynamic limit the first-order liquid to solid transition occurs at $T_{\text{crys}}=2.18\pm0.01$ for interaction range λ_1 and at $T_{\text{crys}}=3.20\pm0.02$ for λ_2.

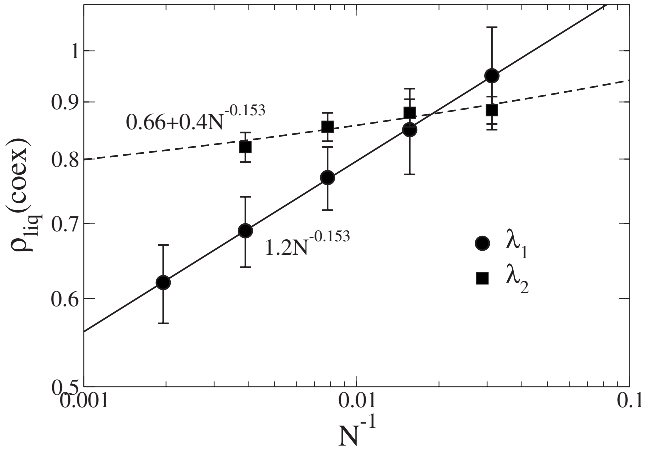

FIG. 4. Finite size extrapolation of the density in the interior of the liquid globule at coexistence with the solid globule. For the short range of attractive interaction this density extrapolates to zero whereas it extrapolates to a typical melt density of the model for the longer interaction range.

For the simple model we are using here we can therefore extend the equilibrium phase diagram of Fig. 1(a). For finite chain length and low temperatures, a crystalline ground state is attainable for a homopolymer model, for the single chain as well as for the polymer solution. There is a density jump at the liquid-solid coexistence observable as a density jump in the bulk of the collapsed single chain [20], comparable to the behavior of a simple liquid. Depending on the range of the attractive interaction, we have, however, identified two different scenarios for the collapse of a single homopolymer chain in the thermodynamic limit.

For the model with interaction range $\lambda_1=\sqrt{6}$, the liquid phase vanishes ($\Theta=T_{\text{crys}}$) and there is a first order coil-globule transition [19] from the extended coil directly into the crystalline state. Correspondingly (see Fig. 4), the liquid density at coexistence with the solid goes to zero in the infinite chain length limit [20]. For the model with interaction range $\lambda_2=\sqrt{10}$, the liquid phase remains stable in the thermodynamic limit and there are separate coil-globule (liquid-vapor) and liquid-solid transitions. Correspondingly, the liquid density at coexistence with the solid in this case stays finite in the thermodynamic limit, approaching a typical melt density value of this polymer model. For both cases, the density of the solid globule is close to the maximum possible packing on the lattice ($\rho=1$).

We have, therefore, found that the similarity of the equilibrium phase diagram of a single homopolymer chain (and the corresponding homopolymer solution phase diagram) with that of a simple liquid extends even to a comparable change in topology as a function of the range of the attractive interaction. For colloid-polymer mixtures where the polymers induce a short range square-well-type attractive depletion interaction between the colloids [1–3], a scaled width of the square well attraction was defined: $R=\lambda/\sigma-1$. It was found that $R_c=0.25$ is the critical value separating the two scenarios. For the interaction range λ_1 (R_1=0.225), we find that the coil-globule and liquid-solid transition points seem to agree in the thermodynamic limit, so the vapor-liquid coexistence has just vanished into the fluid-solid coexistence region. For the interaction range λ_2 (R_2=0.58), we have a broad range of existence of the liquid phase between the vapor and the solid, as would also be found for colloidal systems for this scaled interaction range.

To summarize, we have shown here by Wang-Landau-type Monte Carlo simulations of a simple flexible homopolymer model that the basic topological features of the equilibrium phase diagram remain unchanged upon going from a simple liquid (translational entropy only) to a single polymer chain (conformational entropy only). From the correspondence between single-chain and polymer solution phase diagrams, we predict an analogous behavior for the intermediate case of a polymer solution (both translational and conformational entropy matter). The most direct experimental and theoretical challenges arising from our results are (i) to find a theoretical description of the first-order collapse of flexible chains from an extended state to a crystalline globule and (ii) to find experimental model polymer solutions where the unmixing critical point becomes metastable, so that the crystallization from solution preempts the phase separation into a dilute and a dense solution.

The authors are grateful for helpful discussions with D. P. Landau and M. Müller. We acknowledge funding by the German Science Foundation through the collaborative research project SFB 625 and the EU network of excellence SOFT-COMP.

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