First-order scaling near a second-order phase transition: Tricritical polymer collapse

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The coil-globule transition of an isolated polymer has been well established to be a second-order phase transition described by a standard tricritical O(0) field theory. We provide compelling evidence from Monte Carlo simulations in four dimensions, where mean-field theory should apply, that the approach to this (tri)critical point is dominated by the build-up of first-order-like singularities masking the second-order nature of the coil-globule transition: the distribution of the internal energy having two clear peaks that become more distinct and sharp as the tricritical point is approached. However, the distance between the peaks slowly decays to zero. The evidence shows that the position of this (pseudo) first-order transition is shifted by an amount from the tricritical point that is asymptotically much larger than the width of the transition region. We suggest an explanation for the apparently contradictory scaling predictions in the literature.

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Mean-field theory is generally applicable to second-order phase transitions above their upper critical dimension, and so is believed to provide an adequate description of the approach to such critical points. One type of transition where mean-field theory should hold are tricritical points [1] for dimension $d > 3$. The region around a tricritical point in general dimension [1] is described by crossover scaling forms, where quantities depending on two relevant parameters can be essentially described by functions of a single scaling combination of those two parameters. However, as noted by Lawrie and Sarbach (see page 106 of [1]) there may be some breakdown of this crossover scaling for $d > 3$ due to the presence of one or more dangerous irrelevant variables. Here we provide evidence of a rather more dramatic breakdown of that simple crossover scaling for the case of the coil-globule transition of an isolated polymer, which is generally accepted to be described by tricritical theory [2–4]. We demonstrate that it is likely that the build up of the tricritical point is through the forming of singularities that have more in common with a (non-critical) first-order transition! This however can be explained by a different kind of mean-field approach (not starting with an explicitly tricritical Landau functional) and, moreover, the region around the tricritical point needs to be described by more complex scaling forms. This second issue is in fact separate from the first-order nature of the scaling approach: we speculate that this behaviour is intimately related to the general description of systems where mean-field theory is used, so may have more general applicability.

An isolated polymer in solution is usually argued to be in one of three states depending on the strength of the inter-monomer interactions which are mediated by the solvent molecules and can be controlled via the temperature T. At high temperatures and in so called "good solvents" a polymer chain is expected to be in a swollen phase (swollen coil) relative to a reference Gaussian state so that the average size R of the polymer scales with chain length faster than it would if it were behaving as a random walk. At low temperatures or in poor solvents the polymer is expected to be in a collapsed globular form with a macroscopic density inside the polymer: this implying an average size that scales slower [2] than a random walk, that is

$$R_N \sim N^{1/d} \text{ as } N \to \infty, \tag{1}$$

so the globular state has radius-of-gyration exponent $\nu_g = 1/d$. Between these two states there is expected to be a second-order phase transition (sharp in the infinite chain length limit). The standard description of the collapse transition is that of a tricritical point related to the $n \to 0$ limit of the ϕ^4–ϕ^6 O(n) field theory [2,5]. One then might expect that above the upper critical dimension ($d_u = 3$) some type of self-consistent mean-field theory based upon a suitable tricritical Landau-Ginzberg Hamiltonian [2,1] would give a full description of the transition, and hence conclude that in all dimensions $d > 3$ there is a collapse transition from a swollen state to the globular state with classical tricritical behaviour. In the correspondence [2] between a Landau-type functional for a magnetic system with a magnetisation M of n components (in the limit $n \to 0$) and the polymer problem, the coefficient of the M^4 in the Landau functional maps to the second virial coefficient B of the polymer solution and so to the temperature T of the polymer, while the temperature of the magnet τ is related to the polymer length N through $N \sim (\tau - \tau_c)^{-1}$ where $\tau_c(B)$ is the location of the phase transition line in the so-called symmetry plane [1] of the tricritical system. A finite polymer length implies the corresponding magnet is at a high temperature $\tau > \tau_c$. Hence, the finite-size scaling around the collapse transition should be described by tricritical crossover.

The application of the mean-field theory of a tricritical point to polymer collapse predicts that at the transition point the polymer actually behaves as if it were a random walk ($\nu_\theta = 1/2$), and this point has been known as the θ-point. Thermodynamically ($N = \infty$), one expects a weak transition with a jump in the specific heat $\alpha = 0$ (note that the thermodynamic polymer exponent α is related to the shift exponent in tricritical theory [1], itself not to be confused with the polymer theory finite-N scaling ψ_p shift exponent). For finite polymer length N there is no sharp transition for an isolated polymer (unless one examines a macroscopic number of such polymers) and so this mean-field transition is rounded and shifted. In three dimensions the application of various self-consistent mean-field like approaches predicts that the second-order transition is rounded and shifted on the same scale of $N^{-1/2}$, that is, the crossover exponent ϕ is 1/2, though strictly the power laws involved are modified via renormalisation group arguments by confluent logarithms. In four and higher dimensions no confluent logarithms should be present and one may expect pure mean-field behaviour with a crossover exponent of 1/2 [2] (ϕ_t is the analogous tricritical exponent [1]).

On the other hand, for $d > 3$ Sokal [6] has pointed out that the alternative method of analysing collapse which has been shown to be equivalent to the field theoretic approach, namely the continuum Edwards model, has difficulties: in fact, if one analyses the Edwards model one finds the crossover exponent is given by $\phi_E = 2 - d/2$, which for $d = 4$ gives $\phi_E = 0$! In passing we note here that the same analysis predicts the shift of the θ-point, defined say via the universal ratio of the radius of gyration to the end-to-end distance equalling its Gaussian value, should scale as $N^{-(d/2-1)}$ so $\psi_E = (d/2-1) \neq \phi_E$. This difference between the shift and the crossover exponent implies that strict crossover scaling has broken down. Of course, the theoretical fact that the swollen phase should also be Gaussian for $d > 4$ does raise the suspicion that the analysis of the Edwards model for polymer collapse may be subtle for $d > 3$.

To resolve this question of the crossover scaling one may first be tempted to try some simple scaling arguments as follows. Around the θ-point ($T \to T_\theta$ and $N \to \infty$) a crossover form [4] is generally predicted to be:

$$R_N \sim N^{1/2}\,\mathcal{F}((T_\theta - T)N^\phi). \tag{2}$$

The mathematical understanding of these forms was recently re-examined [7]. To match the behaviour of (1) consider the behaviour of (2) for $T < T_\theta$ and fixed, so we need to find the behaviour of $\mathcal{F}(z)$ for $z \to \infty$. Assuming a power law $\mathcal{F}(z) \sim z^b$, and the mean-field density exponent $\beta = 1$, one finds that $b = 1/d$ and more importantly that $\phi = (d/2 - 1)$. So we notice that the crossover exponent found from this simple scaling argument is the same as predicted from the Edwards model for the shift exponent. Hence we might conclude that for $d > 3$ the crossover scaling form might still be applicable but with shift and crossover exponents that obey $\phi = \psi_p = (d/2 - 1)$. While this implies a subtlety in the Edwards model analysis and also one in the mapping of the tricritical theory to the polymer problem, it is perhaps not completely surprising.

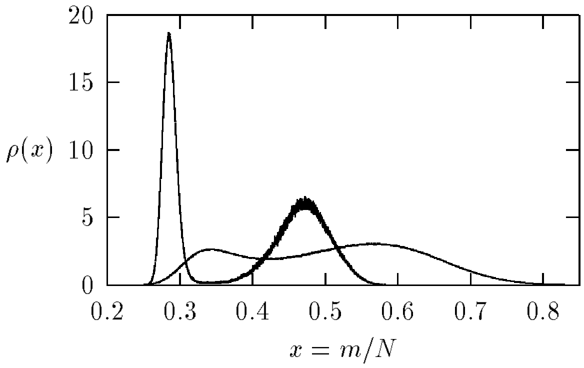

FIG. 1. *Internal energy density distributions for lengths* $N = 2048$ *and* 16384, *each at their respective transition temperatures. The more highly peaked distribution is associated with length* 16384.

To consider such issues we have simulated interacting self-avoiding walks, the canonical lattice model of polymer collapse, on the four-dimensional hyper-cubic lattice using the PERM algorithm [8] over a wide range of temperatures with surprising results. Because this algorithm is based upon kinetic growth it works well around the collapse region as well as throughout the swollen phase. As a consequence we are able to obtain reasonable data up to length $N = 16384$ (a more complete discussion of our simulations is available in [9]). Now, firstly, our results suggest that there is indeed a collapse transition in four dimensions at a finite temperature. However, the character of that transition is particularly intriguing! In $d = 4$ our scaling argument above predicts $\phi = \psi_p = 1$ while the mapping to the tricritical theory predicts $\phi = 1/2$: we find neither! In fact we find a rounded transition with a divergent specific heat, and near the transition the distribution of internal energy is clearly bimodal. This 'double-peaked' distribution becomes *more* pronounced as the chain length is increased (see figure 1). As we vary temperature through the transition region both peaks are essentially stationary and one grows as the other decreases in size: classic first-order behaviour. On the other hand we also were able to find a candidate θ-point (a critical state) where $R \sim N^{1/2}$ well above the transition region. We then considered the shift of the rounded first-order like transition to the θ-point: the best scaling produced a shift exponent of about 1/3 (see figure 2).

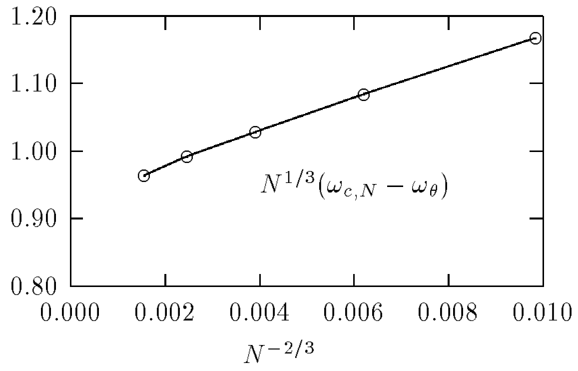

FIG. 2. *Scaling of the shift of the transition: we show the scaling combination $N^{1/3}(\omega_{c,N} - \omega_\theta)$ versus $N^{-2/3}$, where $\omega_{c,N}$ and ω_θ are the Boltzmann weights associated with the monomer-monomer interaction at $T_{c,N}$ and T_θ.*

By studying the position when the universal ratio of the mean square distance of a monomer to the end-point to the mean square end-to-end distance takes on its Gaussian value we find that the θ-point is shifted much less and may scale as $1/N$. Hence there seem to be *two* shift exponents! While these results seem at variance with standard tricritical ideas there is a mean-field type theory that describes the first-order transition region well. This framework was explained some time ago in a paper by Khokhlov [10], who applied the mean-field approach of Lifshitz, Grosberg and Khokhlov [11–13] to arbitrary dimensions. Here we argue that the conclusions of these works may be valid for $d \geq 4$. The theory is based on a phenomenological free energy in which the competition between a bulk free energy of a dense globule and its surface tension drive the transition. The consequences of this surface free energy were largely ignored in the polymer literature until recently, when its effect on the scaling form of the finite-size partition function was proposed and confirmed [14–17].

Lifshitz theory [11] is based on several phenomenological mean-field assumptions. Firstly, there exists a θ-state. Secondly, for lower temperatures there exists a globular state where the polymer behaves as a liquid drop. The results of the theory are based on a phenomenological free energy of that globular state relative to the free energy of the pure Gaussian state of the θ-point at T_θ. The starting point of this analysis is a bulk free energy with a quadratic dependence on the distance to the θ-point and so an exponent $\alpha = 0$, implying a second-order phase transition occurs in the thermodynamic limit. From the theory one finds a rounded transition for finite N occurring at temperature $T_{c,N} < T_\theta$ with *shift* exponent

$$\psi_p = 1/(d-1) \tag{3}$$

so that the collapse occurs at finite length at a temperature that scales towards the θ-point quite slowly and is below the θ-point. This then concurs with our finding that $\psi_p \approx 1/3$ in $d = 4$. The width of this transition ΔT at finite N can be found and has *crossover* exponent

$$\phi = (d-2)/(d-1). \tag{4}$$

All the exponents are derived from the assumptions of mean field thermodynamic behaviour and of eq. (1). Hence all the exponents quoted here are related to each other (only one independent exponent). Our simulations show just such a narrow crossover region with a crossover exponent that is certainly larger than the shift exponent (the data is compatible with exponent 2/3 in $d = 4$).

By considering the difference of the density ρ_s of the swollen state to the globular state ρ_g relative to the density of the swollen state at $T_{c,N}$, Khokhlov [10] concluded from its divergence that ‘the coil-globule transition is first-order’, though we now interpret this to mean that the finite-size corrections to the thermodynamic second-order transition are first-order like. We point out that the terminology of Khokhlov was presumably that explained in Section I.C.2 of [13] but may be misleading to the modern reader. However, both $\rho_g(T_{c,N})$ and $\rho_s(T_{c,N})$ tend to zero as $N \to \infty$ and it is simply that $\rho_g(T_{c,N})$ tends to zero asymptotically slower than $\rho_s(T_{c,N})$ that makes the relative difference diverge. The analysis can be used to deduce the scaling of R_N at $T_{c,N}$ with an exponent $\nu_c = 1/(d-1)$. Note that $\nu_\theta > \nu_c > \nu_g$, so that this scaling is in-between the scaling fixed at the θ-point and at any temperature fixed in the collapsed phase. Following the work of Lifshitz, Grosberg and Khokhlov [13] one can also calculate the change in the internal energy over the crossover width of the transition ΔT as the latent heat ΔU from the free energy expression. The latent heat decays as N increases with exponent $1/(1-d)$. The corresponding height of the peak in the specific heat diverges with exponent $(d-3)/(d-1)$. From our simulational data we were unfortunately unable to extract reasonable estimates for ν_c or the exponents of the latent and specific heats.

To interpret our results we can take the understanding of this mean-field theory further. Let us consider the distribution of internal energy, which we measured in our simulations, as a function of temperature and length. For any temperature above the θ-point and well below $T_{c,N}$ one expects the distribution of internal energy to look like a single peaked distribution centred close to the thermodynamic limit value: a Gaussian distribution is expected around the peak with variance $O(N^{-1/2})$. In fact this picture should be valid for all temperatures outside a range of order $O(N^{-(d-2)/(d-1)})$ centred on $T_{c,N}$. When we enter this region we will expect to see a double peaked distribution as in a first-order transition region. For any temperature in this transition region there should be two peaks in the internal energy distribution separated at the order of $O(N^{-1/(d-1)})$ (the value of the gap being the latent heat). Each of these peaks should be of Gaussian type with individual variances again of the order $O(N^{-1/2})$. Hence as N increases the peaks will become more and more distinct and relatively sharper but the peak positions will be getting closer together. Hence we refer to this scenario as a *pseudo*-first-order transition or, more correctly, as first-order-like finite-size corrections to a second-order phase transition. If there were a real first-order transition then the distance between the peaks should converge to a non-zero constant. A comprehensive interpretation of our computer simulations in $d = 4$ [9] is most consistent with just such a scenario and leads us to conjecture that this theoretical picture is indeed correct for the coil-globule transition for $d \geq 4$.

Let us return to the question of crossover scaling forms and our finding of two shift exponents from our computer simulations. While we cannot ascertain either with great accuracy let us assume that we have a region around the θ-point that is approximated well by a form like (2) with crossover exponent $\phi_\theta = (d/2 - 1)$. Now, despite the fact that this does not describe the collapse transition region, we notice that substituting $t \sim N^{1/(d-1)}$, and using the asymptotics derived from our matching argument above, leads to $R \sim N^{1/(d-1)}$, which is precisely the correct scaling for the real transition region! Hence we conjecture a phenomenological *product* scaling form (for $T < T_\theta$)

$$R_N \sim N^{1/2}\,\mathcal{F}((T_\theta - T)N^{\phi_\theta})\mathcal{G}((T_{c,N} - T)N^{\phi}) \qquad (5)$$

with $T_{c,N} \sim T_\theta - aN^{-\psi_p}$ and where $\mathcal{G}(y) \sim 1$ for $y \to \pm\infty$. This form will then correctly describe both the region around the θ-point and the rounded transition around $T_{c,N}$ and will match with the behaviour of the collapsed phase for fixed $T < T_\theta$. Such a form is not dependent on the finding of pseudo-first-order behaviour and may be useful for analysing data whenever two shift exponents are found. Two shift exponents may appear in systems that are described by mean-field theories.

Finally let us re-examine the crossover exponent derived from the Edwards model. This is essentially only valid for $T > T_\theta$. For $d \geq 5$ the swollen phase is Gaussian itself and the polymer temperature is an irrelevant variable ($\phi_E < 0$), and in $d = 4$ it is marginal, so one might suspect that the scaling theory for $T > T_\theta$ is very different from that for $T < T_\theta$. Hence while the scaling form (2) from the Edwards model with $\phi = \phi_E$ correctly predicts that $R \sim N^{1/2} f(T)$ for $d \geq 5$ it does not describe the collapse.

In conclusion, Monte Carlo simulations of lattice polymers in four dimensions show that for finite length the rounded coil-globule transition appears first order but we argue that the tricritical predictions may well reappear in the infinite length limit as our results fit best the predictions of Lifshitz-Grosberg-Khokhlov (LGK) theory applied to high dimensions. We suggest that the crossover scaling forms are more complicated than at low dimensions and suggest a generalisation that may be heuristically useful. The Edwards model is valid above the θ-point while the coil-globule transition is described by LGK theory.

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