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Four-dimensional polymer collapse: Pseudo-first-order transition in interacting self-avoiding walks

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In an earlier work we provided the first evidence that the collapse, or coil-globule transition of an isolated polymer in solution can be seen in a four-dimensional model. Here we investigate, via Monte Carlo simulations, the canonical lattice model of polymer collapse, namely, interacting self-avoiding walks, to show that it not only has a distinct collapse transition at finite temperature but that for any finite polymer length this collapse has many characteristics of a rounded first-order phase transition. However, we also show that there exists a ‘‘θ point’’ where the polymer behaves in a simple Gaussian manner (which is a critical state), to which these finite-size transition temperatures approach as the polymer length is increased. The resolution of these seemingly incompatible conclusions involves the argument that the first-order-like rounded transition is scaled away in the thermodynamic limit to leave a mean-field second-order transition. Essentially this happens because the finite-size *shift* of the transition is asymptotically much larger than the *width* of the pseudotransition and the latent heat decays to zero (algebraically) with polymer length. This scenario can be inferred from the application of the theory of Lifshitz, Grosberg, and Khokhlov (based upon the framework of Lifshitz) to four dimensions: the conclusions of which were written down some time ago by Khokhlov. In fact it is precisely above the upper critical dimension, which is 3 for this problem, that the theory of Lifshitz may be quantitatively applicable to polymer collapse.

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I. INTRODUCTION

The collapse or coil-globule transition of an isolated polymer in solution has been studied by a variety of different theoretical approaches over the past 50 years ranging from phenomenological arguments, field theoretic renormalization-group approaches, continuum path integrals, and the analysis of discrete lattice walks [1]. Application and testing of these theories has mainly been confined to the ‘‘physical’’ dimensions of two and three. However, the phase transition of polymer collapse has been long believed to have an upper critical dimension of three ($d_u=3$) and so the differences between the predictions of many of the theories in that dimension lie in subtle logarithmic factors that are difficult to ascertain numerically [2]. In two dimensions the field theoretic (excluding conformal field theories) and continuum models have not given exact answers and cannot be compared to the conjectured [3] and numerically resolved [4] values of universal quantities. Until recently [5] four dimensions has largely been ignored but here we argue that not only may four-dimensional studies be important to delineate which theoretical descriptions are valid, but that the collapse transition in four dimensions has some intriguing features of general interest in the field of phase transition and critical phenomena in statistical mechanics.

An isolated polymer in solution is usually considered to be in one of three states depending on the strength of the intermonomer interactions that 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 of the polymer scales with chain length algebraically 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 implies an average size that scales slower than a random walk. 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 a tricritical point related to the $n\to 0$ limit of the $(\phi^2)^2-(\phi^2)^3$ O(n) field theory [6–8]. One might then 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 [9] 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 behavior. There have been various other mean-field type approaches to this problem though their conclusions in three dimensions are similar [6,10] to each other.

The application of the mean-field theory of a tricritical point to polymer collapse predicts that at the transition point the polymer behaves as a random walk ($\nu=1/2$), and this point has been known as the θ point (the θ point was originally defined as the point where the second virial coefficient of a dilute solution of polymers is zero, though it is expected that these definitions are equivalent). Thermodynamically, one expects a weak transition with a jump in the specific heat

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$\alpha=0$ (note that the thermodynamic polymer exponent α is related to the shift exponent $\psi=2-\alpha$ in tricritical theory [9], itself not to be confused with the polymer theory finite-size scaling 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. In three dimensions the application of various self-consistent mean-field-like approaches leads to the prediction 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 renormalization-group arguments [11,12] by confluent logarithms. (In particular note that it is predicted that in three dimensions the specific heat should be divergent logarithmically.) In four and higher dimensions no confluent logarithms should be present and one may expect pure mean-field behavior with a crossover exponent of 1/2 (ϕ_t is the relevant tricritical exponent here [9]).

On the other hand, Domb [13] suggested some time ago that polymer collapse may be a first-order transition in three dimensions and the analysis by de Gennes [6] of the three-dimensional case of a suitably extended (Flory type) self-consistent mean-field approach predicted in some parameter regions a first-order transition: this was superseded by his renormalization-group approach [6,14]. In contrast some time ago there was the conjecture that the collapse transition disappears altogether above three dimensions, at least at finite temperature [15]. For $d>3$, Sokal [16] has also pointed out that the field theoretic/Edwards model approaches have difficulties: in fact, if one analyzes the Edwards model one finds the crossover exponent is given by $\phi=2-d/2$, which for $d=4$ gives $\phi=0$! 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 $N^{-(d/2-1)}$ which has (polymer) shift exponent 1 in dimension $d=4$. 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 $d>3$.

As a first attempt to explore the issues raised above, we recently [5] considered the problem of interacting self-avoiding trails on the four-dimensional hyper-cubic lattice with a special set of Boltzmann weights as generated by a kinetic growth algorithm. Interacting self-avoiding trails are a candidate lattice model for polymer collapse. They are defined to be lattice paths such that each bond of the lattice may either be unoccupied or occupied by a single bond of the path, though sites can be multiply occupied. Attractive interactions are associated with those multiply visited sites so that the strength of this interaction drives a collapse. This paper had several virtues. First, since trails are allowed to intersect, but still possess excluded volume, we were able to grow configurations without the normal attrition that appears in growing self-avoiding walks through the ‘‘trapping’’ of the growth in dense sections of the polymer. Second, in lower dimensions it had been seen that whenever a kinetic growth algorithm was unhindered by trapping it mapped precisely onto the collapse transition point of the model [17,18,4,19]. In Ref. [5] we indeed found a set of Boltzmann weights where the model appears to have the Gaussian characteristics of a θ point. The two drawbacks of this approach are, first, that the simulations cannot effectively be extended away from the special temperature and, second, that the canonical lattice model of polymer collapse is rather self-avoiding walks (SAW) interacting via nearest-neighbor site (monomer) attraction. This canonical model is known as interacting self-avoiding walks, hence ISAW. A new algorithm, known as pruned-enriched Rosenbluth method (PERM), for the Monte Carlo simulation of ISAW (among other things) has been recently developed by Grassberger and collaborators [20–22]. This is essentially a kinetic growth strategy that adds clever enhancements to simultaneously allow a wide range of temperatures to be accessed and for the attrition of samples through trapping to be lessened (see Sec. IV for a fuller description). In this paper we have simulated ISAW on the four-dimensional hyper-cubic lattice using the PERM algorithm over a wide range of temperatures.

The reason for choosing the PERM algorithm for this particular simulation was the claim that PERM was particularly well suited for the simulation of a collapse transition in polymers [20–22]. Moreover, while the basic algorithmic idea of PERM was quite straightforward, there seemed to be quite a flexibility in the choice of the actual implementation. Due to the authors' previous experience with kinetic growth type algorithms [4,19,5], PERM was therefore a natural choice over other established algorithms, such as Markov Chain Monte Carlo methods [23,24], which may perform equally well. Moreover, this paper presents the first implementation of PERM independent of Grassberger and collaborators.

Now, to begin, 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! We find a distinct double peak distribution for the internal energy far below a point that we clearly identify as a candidate θ point. This double peak distribution becomes *more* pronounced as the chain length is increased. This would seem to suggest a first-order transition. If this was the case there would be a delta function peak forming in the specific heat but we find that while a peak is indeed forming it seems not to be growing linearly with the size of the polymer. More importantly, the location of a distinct θ point is incompatible with a first-order transition if there is only one collapse! However there is a theoretical framework (whose conclusions are suitably extended here) that is consistent with the evidence we present. This framework was explained in a paper by Khokhlov [25] who applied the mean-field approach of Lifshitz, Grosberg, and Khokhlov (LGK) [10,26,27] to arbitrary dimensions.[1] The LGK 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. Until recently [28] the

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[1] We warn the reader that the abstract (and parts of the conclusions) of the paper [25] may be misleading as it reads that ‘‘for $d>3$ the coil-globule transition is of first-order.’’ Moreover the application of this mean-field theory to $d<3$ is inappropriate and its conclusions have now been superseded.

consequences of this surface free energy were largely ignored in the polymer literature. Its effect on the scaling form of the finite-size partition function was argued and confirmed [28,29,2,30]. We shall refer to the LGK theory as applied to dimensions four and above as KLG to distinguish it from the original three-dimensional work of Lifshitz, Grosberg, and Khokhlov [26,27].

Hence the major conclusions of our paper are that the finite-size character of the coil-globule transition in four dimensions is first-order despite the thermodynamic limit being probably adequately described by mean-field tricritical behavior. The only alternative conclusion from our data is that the transition is truly first order and our finding of a θ state is fortuitous. The whole theory of crossover scaling for this transition needs to be reworked. This curious state of affairs where a second-order transition looks distinctly first order may be of interest in other physical situations where mean-field theory is used to describe thermodynamics.

The layout of the paper is as follows. In the next section we define the model we consider and review the generally expected behavior of the quantities we have calculated in four dimensions. Then in Sec. III we explain the results of KLG theory as applied to four dimensions. In Sec. IV we explain our Monte Carlo approach, PERM, and finally in Sec. V we carefully describe the numerical results of our simulations and how well they conform to the theory of KLG.

II. THE ISAW MODEL AND A REVIEW OF BASIC SCALING RESULTS

The interacting self-avoiding walk model is the canonical lattice model of the coil-globule transition and has been long studied in two and three dimensions. Here we shall consider the four-dimensional hyper-cubic lattice (coordination number 8). The monomers are imagined to be sitting on the sites of the lattice and a self-avoiding path of such sites form the polymer. The self-avoidance means that no two monomers can sit at the same site of the lattice.

The partition function of the self-interacting self-avoiding walk model (ISAW) is given by

$$Z_N(\omega)=\sum_{\varphi\in\Omega_N}\omega^{m(\varphi)}, \tag{2.1}$$

where the sum is over the set of all self-avoiding walks Ω_N of length N steps ($N+1$ monomers) with one end at some fixed origin and $m(\varphi)$ is the number of nonconsecutive nearest-neighbor monomers for a given walk φ. The Boltzmann weight $\omega=e^{\beta\epsilon}$ is associated with a nearest-neighbor contact of energy $-\epsilon$ so that $\omega>1.0$ for attractive interactions. We define a reduced finite-size free energy per step $\kappa_N(\omega)$ as

$$\kappa_N(\omega)=\frac{1}{N}\log Z_N(\omega). \tag{2.2}$$

The usual free energy is related to this by $-\beta F_N\equiv N\kappa_N(\omega)$.

The average of any quantity Q over the ensemble set of allowed paths Ω_N of length N is given generically by

$$\langle Q\rangle_N(\omega)=\frac{\sum_{\varphi\in\Omega_N}Q(\varphi)\omega^{m(\varphi)}}{\sum_{\varphi\in\Omega_N}\omega^{m(\varphi)}}. \tag{2.3}$$

We define a normalized finite-size internal energy per step by

$$U_N(\omega)=\frac{\langle m\rangle}{N}, \tag{2.4}$$

and a normalized finite-size specific heat per step by

$$C_N(\omega)=\frac{\langle m^2\rangle-\langle m\rangle^2}{N}. \tag{2.5}$$

These quantities are related in the usual way to the reduced free energy via $U_N=\partial\kappa_N/\partial\log\omega$ and $C_N=\partial U_N/\partial\log\omega$.

The thermodynamic limit in this problem is given by the limit $N\to\infty$ so that the thermodynamic free energy per step $f_\infty(\omega)$ is given by

$$-\beta f_\infty(\omega)=\kappa_\infty(\omega)=\lim_{N\to\infty}\kappa_N(\omega). \tag{2.6}$$

This quantity determines the partition function asymptotics, i.e., $Z_N(\omega)$ grows to leading order exponentially as $\mu(\omega)^N$ with $\mu(\omega)=e^{\kappa_\infty(\omega)}$.

In our simulations we calculated two measures of the polymer's average size. First, specifying a walk by the sequence of position vectors $\mathbf{r}_0,\mathbf{r}_1,\ldots,\mathbf{r}_N$ the average mean-square end-to-end distance is

$$\langle R_e^2\rangle_N=\langle(\mathbf{r}_N-\mathbf{r}_0)\cdot(\mathbf{r}_N-\mathbf{r}_0)\rangle. \tag{2.7}$$

We shall use the symbol $R_{e,N}^2$ to be equivalent to

$$R_{e,N}^2(\omega)\equiv\langle R_e^2\rangle_N. \tag{2.8}$$

The mean-square distance of a monomer from the endpoint $\mathbf{r}_0$ is given by

$$\langle R_m^2\rangle_N=\frac{1}{N+1}\sum_{i=0}^{N}\langle(\mathbf{r}_i-\mathbf{r}_0)\cdot(\mathbf{r}_i-\mathbf{r}_0)\rangle. \tag{2.9}$$

Again we define

$$R_{m,N}^2(\omega)\equiv\langle R_m^2\rangle_N. \tag{2.10}$$

We also define the ratio

$$B_N(\omega)=\frac{R_{m,N}^2}{R_{e,N}^2}, \tag{2.11}$$

which should have a universal limit in each critical phase of the model.

Now let us *assume* for a moment that there is a single collapse transition at some value of ω and let us explore the (four-dimensional) behavior we might expect from the above-defined quantities in each of the phases. As discussed above, the basic physics of the coil-globule (collapse) transition can be understood by the consideration of the average size of the polymer R_N, either $R_{e,N}$ or $R_{m,N}$, as a function of length N in each of the phases, so let us consider this first. Generally one always expects that

$$R_N^2 \sim a(\omega) N^{2\nu} \quad \text{as} \quad N \to \infty \tag{2.12}$$

for any fixed temperature. In four dimensions at infinite temperature, $\omega = 1$, it has been predicted [31] that

$$R_N^2 \sim a^+ N[\log(N)]^{1/4}. \tag{2.13}$$

If there does exist a collapse transition then one would expect that this scaling extends (with a constant a^+ that depends on temperature) down to the transition point. In the collapsed phase the polymer is expected to assume a dense configuration on average and hence the globular value of the radius-of-gyration exponent is $\nu_g = 1/d = 1/4$ [6] with

$$R_N^2 \sim a^-(\omega) N^{1/2}. \tag{2.14}$$

Finally at some finite transition temperature $1.0 < \omega_t < \infty$ a Gaussian scaling of the radius of gyration should occur, that is

$$R_N^2 \sim a^\theta N, \tag{2.15}$$

so that $\nu_t = 1/2$. This Gaussian scaling is often used (theoretically at least) to define the θ point $\omega = \omega_\theta$ of an isolated polymer so that $\omega_t = \omega_\theta$. The universal ratio B_N is expected to converge to the value $B_\infty = 1/2$ both in the swollen phase and at ω_θ. However, one would expect slow logarithmic corrections for $\omega < \omega_\theta$ and algebraic corrections at ω_θ. For $\omega > \omega_\theta$ the phase is no longer expected to be critical and so B_∞ is no longer universal and may be a nonconstant function of ω.

One can also consider the scaling of the partition function in each of the regimes, given that there is a transition. For high temperatures $1.0 < \omega < \omega_\theta$, one expects the infinite temperature behavior, which is [31]

$$Z_N \sim b^+(\omega) \mu(\omega)^N (\log N)^{1/4}, \tag{2.16}$$

while at low temperatures [28] one expects asymptotics of the form

$$Z_N \sim b^-(\omega) \mu(\omega)^N \mu_s(\omega)^{N^{3/4}} N^g, \tag{2.17}$$

where μ_s is related to the surface free energy of the polymer globule and the exponent g need not be universal (we only write it for completeness of the asymptotic form). For $\omega = \omega_\theta$ one expects

$$Z_N \sim b^\theta \mu(\omega_\theta)^N \tag{2.18}$$

as a reflection of Gaussian behavior.

In the thermodynamic limit the thermodynamic functions $f_\infty(\omega)$, $U_\infty(\omega)$, and $C_\infty(\omega)$ are all expected to be analytic functions of ω except at ω_θ. By using the correspondence to the tricritical model [6] the mean-field theory would imply that the specific heat had a jump discontinuity at ω_θ since $\alpha = 2 - \psi = 0$. Of course, for finite N there is no sharp transition for an isolated polymer (unless one examines a macroscopic number of such polymers). Around the collapse temperature in *three* dimensions the finite-size corrections are expected to take on a crossover scaling form [6] so that

$$R_N^2 \sim a^\theta N \, \mathcal{R}((T - T_\theta) N^\phi) \tag{2.19}$$

with $\phi = 1/2$ but this form implies that the transition is rounded and shifted on the *same* scale of $N^{-\phi}$ and so its applicability to four dimensions needs careful thought.

III. THE THEORY OF KHOKHLOV, LIFSHITZ, AND GROSBERG (KLG)

We now review the results of Khokhlov [25] paying special attention to the predicted behavior of the quantities we have calculated. The theory originally proposed by Lifshitz for the general mean-field description of the globular state, extended by Lifshitz, Grosberg, and Khokhlov to fully describe the transition, and finally applied to four dimensions by Khokhlov [25], is based on several phenomenological mean-field assumptions. First, there exists a state where the excluded volume property of long chain molecules is exactly cancelled by the attractive interactions between parts of the polymer as mediated by the solvent. This is the θ state. Second, when the attraction becomes even stronger, there eventuates 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. Hence the condition applied to find the finite-size position of the transition is to equate the relative free energy to zero. The relative free energy is given as

$$F_N = F_{bulk} + F_{surface}, \tag{3.1}$$

where the F_{bulk} and $F_{surface}$ are given in terms of the second and third virial coefficients, the length of the chains, and the linear size of the polymer found from the globular density. In particular both the bulk and surface free energies are proportional to the square of the second virial coefficient. It is assumed that on approaching the θ point the second virial coefficient goes to zero linearly with temperature while the third virial coefficient remains nonzero. Note that this implies a quadratic dependence of the bulk free energy on the distance to the θ point. Since the free energy has exponent $2 - \alpha$ this implies an exponent $\alpha = 0$ (assuming that this part of the free energy is singular). Therefore a second-order phase transition occurs in the thermodynamic limit.

It is further assumed that the density in the globule is proportional to the second virial coefficient and hence also goes to zero linearly with temperature on approaching the θ point ($\beta = 1$). By applying the condition $F_N = 0$, Khokhlov [25] finds a finite-size transition temperature $T_{c,N}$ that approaches the θ temperature from below as $N^{-1/3}$. Applying this result to the ISAW model gives

$$\omega_{c,N} - \omega_\theta \sim \frac{s}{N^{1/3}} \tag{3.2}$$

for some constant s. That is, the polymer collapse *shift* exponent is 1/3.

Now Khokhlov [25] found that the free energy (for $T < T_\theta$) can be rewritten in terms of $T_{c,N}$ as

$$F_N \sim -NT(T_\theta - T)^2 \left(1 - \left| \frac{T_\theta - T_{c,N}}{T_\theta - T} \right|^{3/4} \right). \tag{3.3}$$

Actually KLG's unwritten assumption is that F_N is the minimum of zero and the right-hand side of Eq. (3.3) so it is zero for $T_\theta < T < T_{c,N}$. Khokhlov [25] deduces that the width of the transition ΔT at finite N can be found from this and scales as $N^{-2/3}$. Hence the ISAW model should have a transition width $\Delta\omega$ that scales as

$$\Delta\omega \sim \frac{w}{N^{2/3}} \tag{3.4}$$

for some constant w. That is, the polymer collapse *crossover* exponent is 2/3. Hence note that the size of the crossover region is asymptotically small relative to the shift of the transition, and that crossover forms such as Eq. (2.19) may not be useful.

Even though there can be no sharp transition for a single polymer of finite length N, the theory can describe the nature of the rounded transition by considering the difference between the density of the globular state ρ_g at $T_{c,N}$ and that of the coil state ρ_c at the same temperature. This is

$$\frac{\rho_g(T_{c,N}) - \rho_c(T_{c,N})}{\rho_c(T_{c,N})} \propto N^{2/3}, \tag{3.5}$$

which diverges as N becomes large. Hence Khokhlov [25] concluded 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.[2] However, both $\rho_g(T_{c,N})$ and $\rho_c(T_{c,N})$ tend to zero as $N \to \infty$ and it is simply that $\rho_g(T_{c,N})$ tends to zero asymptotically slower than $\rho_c(T_{c,N})$ that makes the relative difference quoted above diverge. Noting that $\rho = N/R^4$ and $R_c \sim N^{1/2}$, the above equation can be used to deduce the scaling of R_N at $T_{c,N}$ as

$$R_N(T_{c,N}) \sim a^c N^{1/3}. \tag{3.6}$$

Hence we define an effective radius-of-gyration exponent $\nu_c = 1/3$ for the scaling of the size of the polymer when following the finite-size transition temperatures. Note that this exponent value obeys $\nu_\theta = 1/2 > \nu_c > \nu_g = 1/4$.

Following the work of Lifshitz, Grosberg, and Khokhlov [27] one can also calculate the change in the internal energy over the crossover width of the transition ΔT as the latent heat (or ''heat of the transition'') by using expression (3.3):

$$\Delta U \sim \frac{u^c}{N^{1/3}}. \tag{3.7}$$

The corresponding height of the peak in the specific heat is

$$C_N(T_{c,N}) \sim h^c N^{1/3}. \tag{3.8}$$

So to summarize the picture so far, the theory predicts a thermodynamic second-order transition at a θ point with a jump in the specific heat. For finite polymer length this transition is shifted below the θ point by a temperature of the order of $O(N^{-1/3})$ with the width of the transition of the order of $O(N^{-2/3})$. Over this width there is a rapid change in the internal energy that scales as $O(N^{-1/3})$: the important point here of course is that this tends to zero for infinite length so the effect of the peak in the specific heat is scaled away for N large, leaving a finite jump in the thermodynamic limit. To understand this further let us consider the distribution of internal energy 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 centered 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 the range $[T_{c,N} - O(N^{-2/3}), T_{c,N} + O(N^{-2/3})]$. When we enter this region we expect to see a double peaked distribution as in a first-order transition region. For any temperature in this region there should be two peaks in the internal energy distribution separated by a gap δU of the order of $\delta U \approx \Delta U \propto O(N^{-1/3})$. Each peak is of Gaussian type with individual variances again of the order of $O(N^{-1/2})$. Hence as N increases, the peaks will become more and more distinct and relatively sharper but the peak positions will be getting closer together. 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 nonzero constant.

IV. PERM

We have simulated ISAW using PERM, a recently proposed generalization of a simple kinetic growth algorithm [20,21]. PERM builds upon the Rosenbluth-Rosenbluth method [32], in which walks are generated by simply growing an existing walk kinetically, i.e., by choosing the next step with equal probability from all possible accessible lattice sites. Eventually, a walk generated thus gets trapped in a configuration in which it cannot be continued, leading generally to an exponential ''attrition.'' Moreover, in order to simulate ISAW at a particular temperature, one needs to reweight the kinetically grown samples in such a way that the generated sample is usually dominated by a few configurations that carry large weight after the reweighting.

In order to overcome these obstacles, PERM uses a combination of enrichment and pruning strategies to generate walks whose weights are largely distributed around the expected peak of the distribution. On the one hand, if the weight of a configuration becomes too small, the configuration gets pruned probabilistically and the weight adjusted correspondingly. Alternatively, if the weight of a configuration becomes too large, copies of the walk are made and the respective weights reduced accordingly. While this does not eliminate trapping, it is generally sufficient to compensate for it: trapping occurs when the end of the walk is in an area

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[2] We point out that the terminology of Khokhlov was presumably that explained in Sec. I C 2 of [27] but may be misleading to the modern reader.

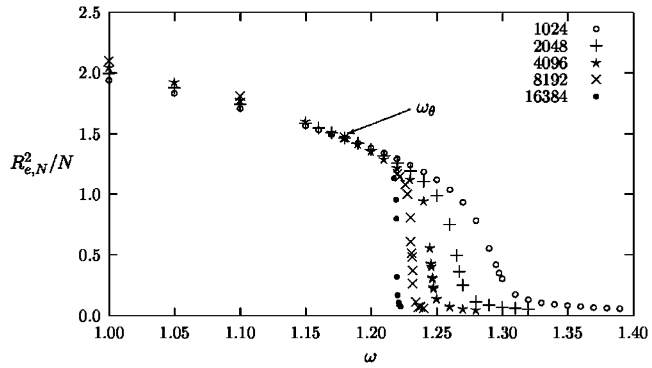

FIG. 1. $R^2_{e,N}/N$ versus ω for lengths $N=1024$, 2048, 4096, 8192, and 16 384. The error is less than the size of the symbols.

of high density, which in turn increases the likelihood of enrichment. The algorithm can be implemented in a self-tuning way by choosing dynamically adjusted upper- and lower-threshold values to control pruning and enrichment rates.

It is plausible that the algorithm works best at temperatures in which the thermal distribution is close to the distribution of walks generated by kinetic growth. In sufficiently large dimensions, this temperature should be quite close to the θ temperature, so that the algorithm is expected to be well suited to the study of polymer collapse. As mentioned in the introduction, there are lattice models of interacting polymers for which there is an exact mapping of the corresponding kinetic growth models to their respective θ points, in which case a PERM simulation at the θ temperature reduces to simple kinetic growth. In fact, it turns out that the algorithm performs well over a whole range of temperatures covering all of the swollen phase and the scaling regions around the collapse transition. However, we find that the performance of PERM in the collapsed phase is far less satisfactory.

The guiding principle for any choice of implementation should be the observation [20] that the algorithm essentially produces a random walk in chain length with reflecting boundaries at 0 and N_{max}. Considered in such a way, the algorithm performs best if this random walk is unbiased and if the associated diffusion coefficient is large. To eliminate bias, pruning, trapping, and enrichment rates have to compensate each other. To maximize the diffusion coefficient, the pruning and trapping rates have to be as small as possible. The choice of pruning and enrichment thresholds needs to take both into account. (In contrast with the original work on PERM, where trapping was viewed as a special case of pruning, we find it instructive to distinguish between these two effects: trapping is unavoidable due to the geometry of the lattice, whereas pruning is done optionally to adjust weights.)

In our implementation, we chose upper and lower thresholds W^u and W^l proportional to the current estimate of the average weight of a walk at length N, $\langle Z_N\rangle/s_N$, where s_N is the number of generated samples at length N, and $\langle Z_N\rangle$ is the current estimate of the partition function at length N. That is to say,

$$W^u_N=c^u_N\langle Z_N\rangle/s_N, \quad W^l_N=c^l_N\langle Z_N\rangle/s_N. \tag{4.1}$$

In order to enforce an even sample size distribution we allow for dynamic adjustment of c^u_N and c^l_N. Thus, if for example, at any particular length, we have an excess of pruning, the algorithm ‘‘relents’’ and increases both c^u_N and c^l_N in order to reduce pruning and enhance enrichment, keeping the quotient of the thresholds $Q=c^u_N/c^l_N$ constant. To stabilize the dynamic adjustment, we enforce $c^u_N>c^u_{min}$ and $c^l_N<c^l_{max}$. After some initial experimentation, we chose $c^u_{min}=2$ and $c^l_{max}=1/2$, which leaves us with the threshold quotient Q as the sole adjustable parameter. (We also experimented with a dynamic length-dependent Q_N, but the dynamic adjustment seemed to be too unstable to pursue this avenue further.) For each run, we attempted to choose the smallest threshold quotient Q for which we could obtain an even sample size distribution.

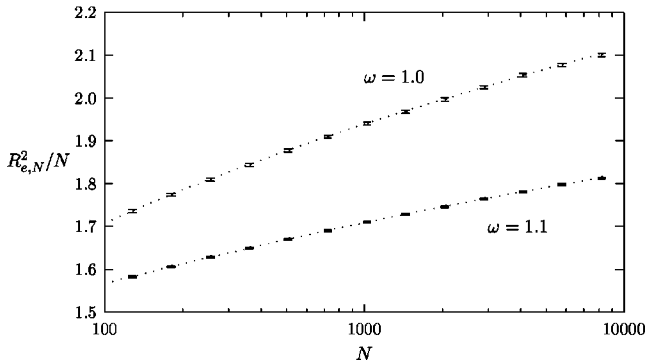

FIG. 2. $R^2_{e,N}/N$ versus N at $\omega=1.0$ and $\omega=1.1$. The curves are fits to $R^2_{e,N}/N=a\log(N+b)^c$ over the shown range.

The disadvantage of PERM is that due to the enrichment the generated data is not independent. All the data generated during one ‘‘tour,’’ i.e., between two successive returns of the algorithm to length 0, is correlated. Therefore, we keep track of the statistics of tour sizes t to get a rough idea of the quality of the data. In our statistical evaluation we use (somewhat arbitrarily) the quotient of s_N and $\sqrt{\langle t^2\rangle}$ as a measure of an effective independent sample size. This is correct as long as the tour sizes don’t fluctuate too strongly, and, more importantly, as long as individual tours explore the sample space evenly. When simulating in the collapsed phase, both of these assumptions break down, and the sample is dominated by few huge tours. Moreover, the pruning and enrichment rates become so large that the efficiency of the algorithm is significantly decreased.

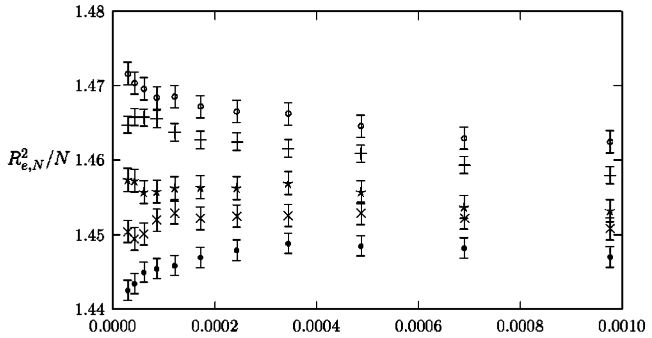

FIG. 3. $R^2_{e,N}/N$ versus $1/N$ in the θ region: $\omega=1.180$, 1.181, 1.182, 1.183, and 1.184 from top to bottom.

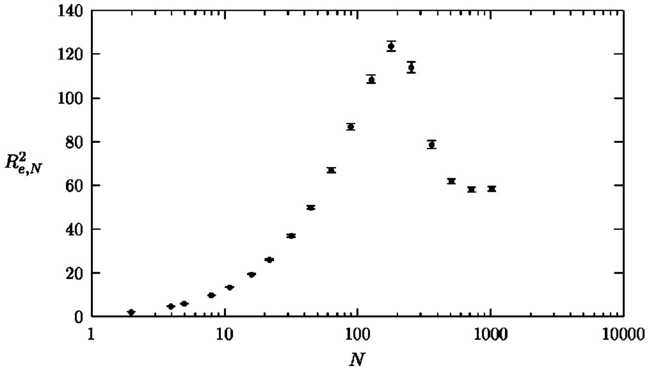

FIG. 4. $R^2_{e,N}$ versus N for $\omega = 1.4$.

For further details of the algorithm and suggestions of various other improvements such as Markovian anticipation, we refer to Refs. [21] and [22].

V. RESULTS

We simulated ISAW on a four-dimensional hyper-cubic lattice using PERM with N_{max} set to 1024, 2048, 4096, 8192, and 16 384 at values of ω ranging from 1.0 to 1.4 ($N_{max} = 1024$) to 1.2175 to 1.2225 ($N_{max} = 16\,384$) and the threshold quotient Q ranging from 10 to 160. At each fixed ω, we generated 10^7 walks. To illustrate the computational effort, the generation of a sample of size 10^7 at length $N_{max} = 16\,384$ took about 2 weeks CPU time on a 600 MHz DEC Alpha.

We computed statistics for $R^2_{e,N}$ and $R^2_{m,N}$, the partition function Z_N, the internal energy U_N, and specific heat C_N. Moreover, we generated the distribution of the number of interactions at N_{max}. The distributions obtained at various temperatures were then combined using the multiple histogram method [33].

Error bars, when given, are based on our method of error estimation as described in the previous section. This method gives reasonable error estimates in the swollen regime up to the θ point. On the other hand, in the collapsed regime only highly subjective error estimates are possible. Therefore no error bars are given in e.g., Figs. 11 and 14, even though the data has converged sufficiently.

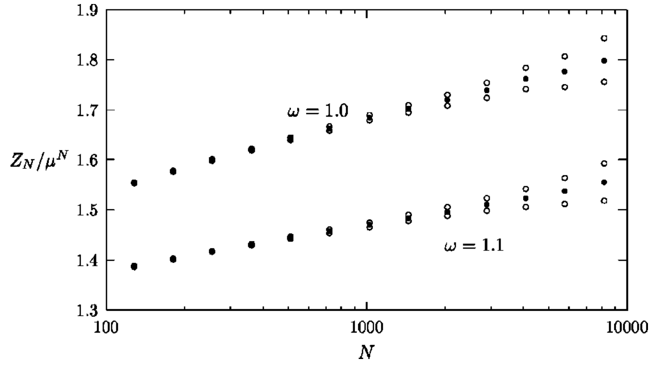

FIG. 5. Z_N/μ^N versus N at $\omega = 1.0$ and $\omega = 1.1$. At each value of ω, three different values of μ are shown. We estimate $\mu(1.0) = 6.774\,04(2)$ and $\mu(1.1) = 6.896\,99(2)$. The filled circles correspond to the central estimates of μ while open circles correspond to shifting μ by the error estimate quoted.

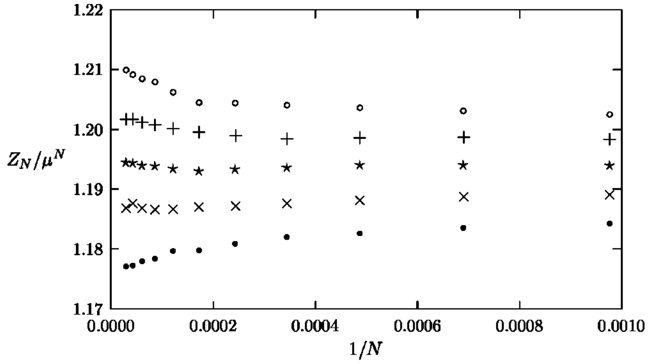

FIG. 6. Z_N/μ^N versus $1/N$ using our best estimates of μ in the θ region: $\omega = 1.180$, 1.181, 1.182, 1.183, and 1.184 from top to bottom.

In discussing our findings on the nature of this polymer collapse transition, it is natural to first present the change of size of the polymer as the interaction strength changes. In Fig. 1, we display the mean-squared end-to-end distance normalized by walk length, $R^2_{e,N}/N$ for lengths 1024 up to 16 384 (we have analogous data for the quantity $R^2_{m,N}/N$). As discussed, one expects this quantity to increase logarithmically in N in the swollen regime, approach a constant at a random-walk-like θ point, and decrease in N as a power law in the collapsed regime. As can be seen clearly from Fig. 1, there is indeed a transition from a swollen region, where this parameter increases with N to a collapsed region, where the value has dropped sharply. In the transition region, however, two phenomena can be noticed. On the one hand, around $\omega = 1.18$, the quantity $R^2_{e,N}/N$ approaches a constant, which is indicative of θ point behavior. On the other hand, the collapse occurs in a region that is well separated from this θ point. With increasing polymer length, the region where the collapse occurs approaches the θ point, but simultaneously sharpens so strongly that it remains well separated from it.

In the swollen phase, our results are in correspondence with the logarithmic corrections seen by Grassberger *et al.* [34], see Fig. 2. As in that paper, we observe that $R^2_{e,N}$ grows as $N(\log N)^c$, albeit not with the exponent predicted by field theory. At $\omega = 1.0$ we find $c = 0.30$. This value shifts to $c = 0.22$ at $\omega = 1.1$, indicating the presence of strong temperature-dependent correction terms.

Near the suspected θ point, we extended our simulations to walks of length 32 768. Figure 3 shows a plot of $R^2_{e,N}/N$

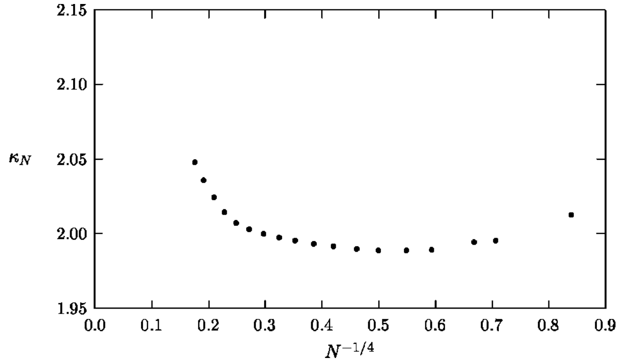

FIG. 7. Finite-size free energy κ_N versus $N^{-1/4}$ for $\omega = 1.4$. The error is less than the size of the symbols.

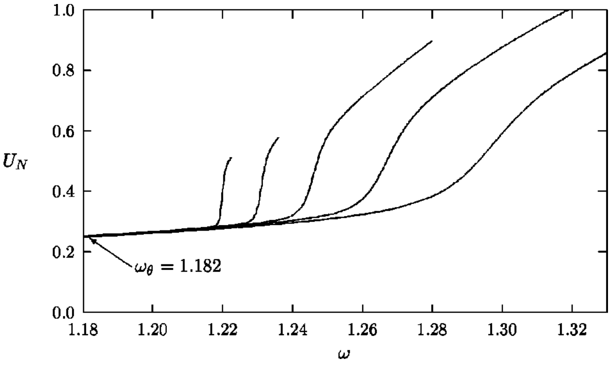

FIG. 8. Internal energy U_N versus ω for lengths $N=1024$, 2048, 4096, 8192, and 16 384 from right to left, respectively, using the multihistogram method.

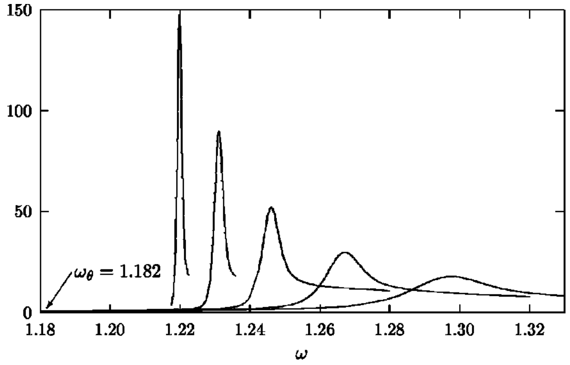

FIG. 9. Specific-heat C_N versus ω for lengths $N=1024$, 2048, 4096, 8192, and 16 384 from right to left, respectively, using the multihistogram method.

versus $1/N$ for values of ω between 1.180 and 1.184. At $\omega = 1.182(1)$ we have indeed an asymptotically linear dependence of $R_{e,N}^2$ on N. Moreover, at $\omega = 1.182$ we estimate from our data $B_N = R_{m,N}^2 / R_{e,N}^2 = 0.500(1)$, which is also indicative of Gaussian behavior.

As was already seen from Fig. 1, the collapse happens very rapidly as ω increases. An alternative way of visualizing this is to consider how the size of the polymer changes at fixed ω in the collapsed phase as the length N increases. As shown in Fig. 4 for $\omega = 1.4$, $R_{e,N}^2$ changes nonmonotonically in N! After an initial increase, the size of the polymer actually shrinks around $N = 250$ as it undergoes collapse[3] corresponding to a rapid increase of the density. For large enough N, we expect to see the true collapsed behavior, i.e., $R_{e,N}^2$ growing again as $N^{1/2}$, but this regime is beyond the reach of our PERM simulations on current computer hardware.

The swollen phase and the θ-point behavior can also be clearly identified from the free-energy scaling. In the swollen phase we find again the same behavior as Ref. [34]. Figure 5 shows Z_N / μ^N for $\omega = 1.0$ and $\omega = 1.1$. For each ω, this quantity is plotted with three values of μ, which differ in the sixth digit, showing both the accuracy in the estimation of the free energy and the presence of logarithmic corrections. At $\omega = 1$, we estimate $\mu(1) = \mu_{SAW} = 6.77\,404(2)$. Our estimate is based on Fig. 5, where the central estimate is commensurate with a power-law dependence of Z_N / μ^N on $\log N$, while the estimate obtained by shifting μ by the error quoted is not. This can be compared to earlier estimates of 6.7720(5) [35], 6.774(5) [36], and 6.774 04(3) [34].

In the θ region, a similar analysis shows that here Z_N scales as μ^N with weak $1/N$ corrections. Figure 6 shows Z_N / μ^N plotted versus $1/N$, with respective values of μ obtained in a similar fashion to the one shown in Fig. 5. We estimate the θ point to be $\omega_\theta = 1.182(1)$ and $\mu_\theta = 7.011(2)$. [At fixed ω, the accuracy is of course higher: for $\omega = 1.182$, we estimate $\mu = 7.011\,767\,5(5)$.]

In the collapsed region, one expects the finite-size free energy to have a strong correction term of the order $N^{-1/4}$ due to surface effects. Figure 7 shows this for $\omega = 1.4$. As argued above, the globule collapses when the length is above $N = 250$, and we notice here the onset of a corresponding strong change in the behavior of the finite-size free energy around this length ($N^{-1/4} \approx 0.25$). Even though we cannot simulate long enough chain lengths to clearly determine the precise nature of the correction term, our data is certainly compatible with a $N^{-1/4}$ correction for $N^{-1/4} < 0.2$.

In order to study the collapse transition more closely, we now focus our attention on the internal energy and specific heat. As can be seen from Figs. 8 and 9, the internal energy increases rapidly over a small temperature interval with a corresponding diverging specific heat. As N increases, the transition becomes sharper and stays well separated from the θ point, even though the location of the transition approaches the θ point slowly.

The scaling of the shift of the transition towards the θ point $\omega_{c,N} - \omega_\theta$ and the sharpening of the transition width $\Delta\omega$ are both shown in Fig. 10. Here, we defined the location of the collapse transition by the location of the specific-heat peak, and the width of the transition is given by the interval in which the specific heat is greater or equal to half the value of the peak height. Expecting from the KLG theory that $\omega_{c,N} - \omega_\theta$ scales as $N^{-1/3}$ and that $\Delta\omega$ scales as $N^{-2/3}$, we plot both $N^{1/3}(\omega_{c,N} - \omega_\theta)$ and $\Delta\omega N^{2/3}$ versus $N^{-2/3}$ which was chosen empirically. Both quantities can be seen to be asymptotic to constants: on the graph extrapolations give nonzero intercepts. Hence, Fig. 10 shows that the KLG pre-

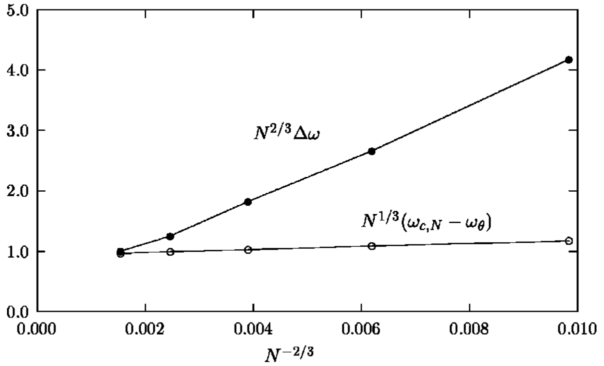

FIG. 10. Scaling of the transition: shift and width of the collapse region. Shown are the scaling combinations $N^{1/3}(\omega_{c,N} - \omega_\theta)$ and $N^{2/3}\Delta\omega$ versus $N^{-2/3}$.

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[3] Note that this lack of monotonicity is *not* an indication of a first-order transition. A similar nonmonotonous behavior can be observed for ISAW in three dimensions, where the collapse transition is second-order [2].

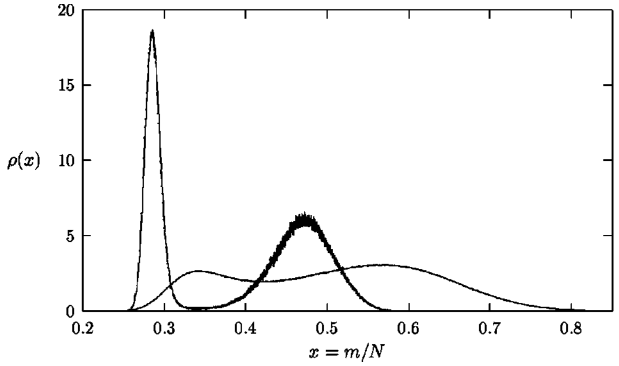

FIG. 11. Internal energy density distributions at $\omega_{c,N}$ for 2048 and 16 384. The more highly peaked distribution is associated with length 16 384.

dictions are compatible with our simulations. We do note that the corrections to scaling for $\Delta\omega$ are much larger than for $\omega_{c,N}-\omega_{\theta}$.

The character of the transition becomes apparent if one plots the internal energy density distribution (rescaled density of interactions) at the finite-size collapse transition $\omega_{c,N}$. Figure 11 shows the emergence of a bimodal distribution. At length 2048 one sees a slight nonconvexity, which at length 16 384 has evolved into a distribution dominated by two sharp and well-separated peaks. The values of the minima and maxima of the distribution are different by two orders of magnitude.

It is instructive to study the transition by how this distribution changes over a large range of ω. Figure 12 shows this for $N=4096$. One sees that there is not much of a change in the shape and location of the distribution between the noninteracting case $\omega=1$ and the θ point $\omega=1.182$. However, in a very small interval around the collapse transition, the density distribution changes dramatically as ω increases. The density distribution switches from a peak located around 0.3 to a peak located around 0.55, corresponding to a sudden change in the internal energy. In the collapsed phase, the width of the peak is much wider than in the swollen phase, implying a larger specific heat. It is this difference between the swollen and collapsed phases' specific heats that will eventually become the thermodynamic second-order jump.

The rapid first-order-like switch between two peaks in the distribution becomes more pronounced at larger polymer lengths. At $N=16\,384$, this ''switching'' is shown in Fig. 13: over a range of ω of the order of 10^{-3}, a peak near $x=0.3$ disappears while another peak near $x=0.5$ emerges.

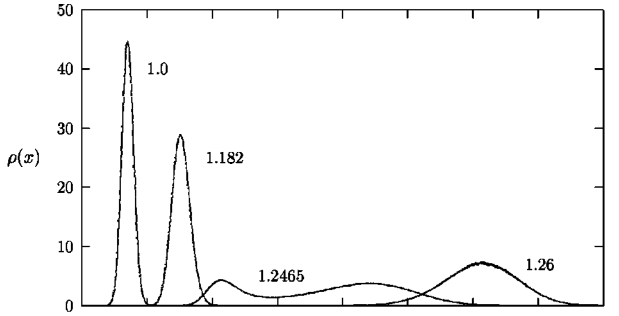

FIG. 12. Internal energy density distributions at $\omega=1.0$, 1.182, 1.2465, and 1.26 for $N=4096$.

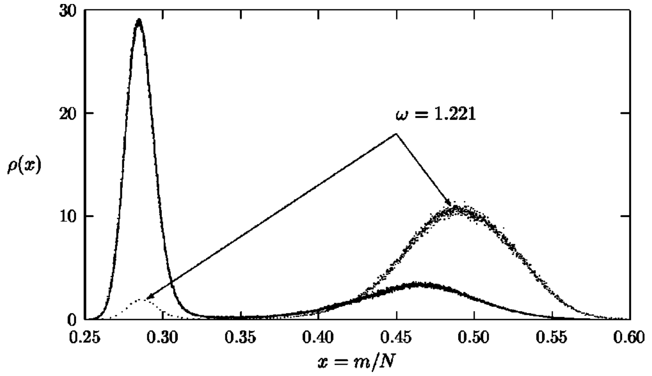

FIG. 13. Internal energy density distributions at $\omega=1.2195$ and 1.2210 for $N=16\,384$.

Returning to the scaling predictions from KLG theory, a suitably defined finite-size latent heat, ΔQ, should tend to zero as $N^{-1/3}$ in the thermodynamic limit. One possible measure of this latent heat is given by the product of specific-heat peak $C_N(\omega_{c,N})$ and specific-heat width $\Delta\omega$, and another is given by the distance δU of the peaks in the bimodal internal energy distribution. Figure 14 shows the behavior of both of these quantities. One notices two things from this figure. First, we are unable to confirm or deny the predicted scaling behavior for ΔU and, second, even at length $N=2048$ $(N^{-1/3}\approx 0.08)$ there is considerable discrepancy between the two quantities, so that it is not surprising that one cannot discern a clear scaling behavior. The explanation for the discrepancy between the two quantities as well as of the difficulty of observing the predicted scaling behavior is of course that in order to observe the asymptotic behavior the two peaks in the histogram have to be well separated and distinct, and we see from Fig. 11 that this is only the case when N is of the order of 10^4. This explains why we are unable to find a value for the exponent related to the divergence of the specific heat consistent with the rest of our theoretical picture. We do concede that Fig. 14 alone could be used to argue for the existence of a real first-order transition in the thermodynamic limit, but we believe the rest of our data and other theoretical facts provide a more consistent picture.

In conclusion, our ISAW simulations elucidate the structure of the polymer collapse transition in four dimensions.

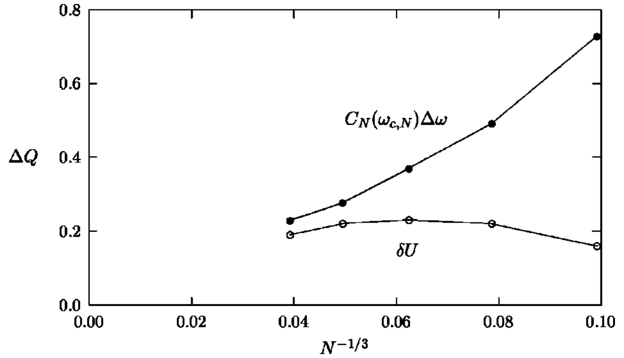

FIG. 14. Scaling of the latent heat ΔU: our two measures of ΔU, $C_N(\omega_{c,N})\Delta\omega$ and peak distance δU are plotted versus $N^{-1/3}$.

We show conclusively that there is indeed a collapse transition at a finite temperature. Secondly, we find evidence for a θ temperature at which the polymer is well approximated by Gaussian behavior as well as for a collapse transition that is well separated from the θ point. The collapse transition shows many first-order-like features, such as a bimodal distribution in the internal energy. An analysis of the scaling behavior of this transition in the context of the theory of Lifshitz, Grosberg, and Khokhlov [27,25] shows that a consistent interpretation of these findings is that of first-order-like finite-size corrections to a thermodynamic second-order transition. We note that these findings are reminiscent of results for interacting self-avoiding trails on the diamond lattice, where a θ point was found in [19] and subsequent simulations revealed a bimodal distribution in the internal energy density [37]. In Ref. [19] it was concluded that the transition is second order, whereas in Ref. [37] the conclusion was that the transition is first order. In the context of the findings presented here, it is tempting to expect a similar resolution of this apparent contradiction in terms of a pseudo-first-order transition.

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