Brief Reports

Scaling analysis of the collapse of branched polymers

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The specific heat of branched polymers having an attractive monomer-monomer interaction is calculated using Monte Carlo methods in the lattice-animal model on the simple-cubic lattice, for animals of various sizes N, up to $N=80$. The data confirm a scaling function for the specific heat derived from a scaling analysis in analogy with linear polymers. This gives better estimates for the collapse transition temperature T_c and the crossover exponent ϕ.

Branched polymers in dilute solvents in the high-temperature limit are well modeled by lattice animals,[1,2] which are connected clusters of occupied sites on a lattice. Introducing attractive monomer-monomer interaction can lead to a collapse of the branched polymers at low temperatures. Such a transition can in fact be realized experimentally at low temperatures or in good solvent when monomer-monomer affinity can become the dominant effect.[3-6] In linear polymers, the collapse temperature is known as the θ point and it coincides with the point where the second virial coefficient vanishes. The θ point in linear polymers has been much studied both theoretically and experimentally (see references cited in Ref. 7). Much less is known in the case of branched polymers. Derrida and Herrmann[7] did a theoretical study of the collapse of branched polymers in two dimensions using transfer matrix methods on strips. They obtained the transition temperature T_c and certain critical exponents, including the crossover exponent ϕ. However, their method cannot be easily extended to three dimensions in which most experiments are usually performed. Later, Dickman and Schieve[8] studied this problem using a Monte Carlo method for some two- and three-dimensional lattices. In two dimensions, they obtained a transition temperature in close agreement with that of Ref. 7. However, they did not determine any exponent. In three dimensions, their data were insufficient to determine either the transition temperature or the exponent.

Using the same method as in Ref. 8 we had performed Monte Carlo studies of this problem on the simple-cubic lattice.[9] We were able to estimate both the collapse point T_c and the crossover exponent ϕ. In this paper we perform a scaling analysis of our data reported in Ref. 9 for the specific heat using a scaling function derived in analogy with linear polymers. This results in better estimates of the collapse temperature T_c and the crossover exponent ϕ.
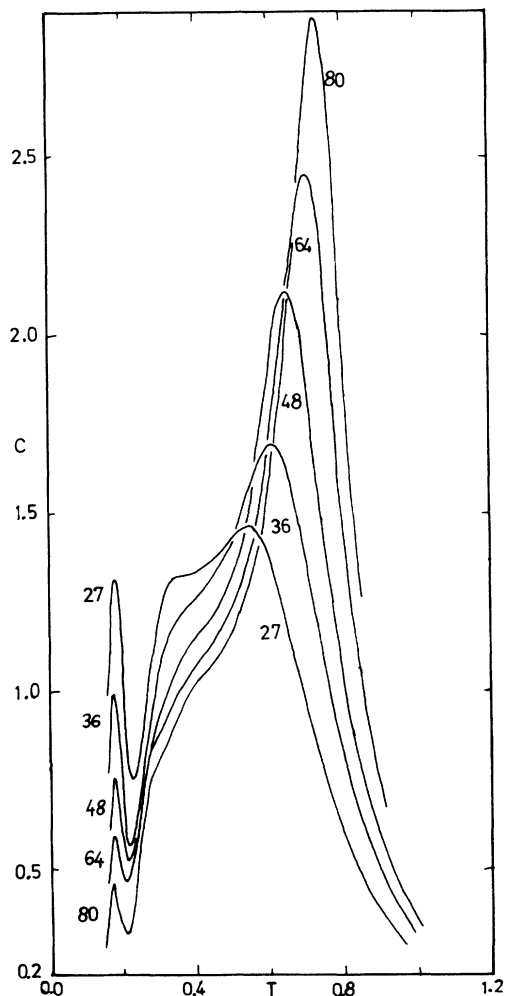

FIG. 1. Specific heat vs temperature T for various animal size N.

In Fig. 1 we reproduce the result of the specific heat reported in Ref. 9. The specific heat as a function of the temperature exhibits a peak at $T_m(N)$ depending on the size of the animal N. As N increases both $T_m(N)$ and the height of the peak $C_m(N)$ increase monotonically. We have $T_m(27) = 0.5433$, $T_m(36) = 0.6090$, $T_m(48) = 0.6482$, $T_m(64) = 0.7037$, $T_m(80) = 0.7279$, and $C_m(27) = 1.4668$, $C_m(36) = 1.6929$, $C_m(48) = 2.1179$, $C_m(64) = 2.4565$, $C_m(80) = 2.8871$. In Ref. 9 we obtained a first estimate of T_c and ϕ by using the finite-size scaling relation

$$T_m(N) = T_c + aN^{-\phi} , \qquad (1)$$

and least-squares fitting the data for $T_m(N)$ to determine the three unknowns T_c, a, and ϕ. We obtain the rough estimate $T_c \approx 0.97$, $\phi \approx 0.52$.

These estimates can be improved using a scaling analysis for the specific heat. For linear polymers, it is known that the partition function has the scaling form[10] for $N \to \infty$ and $t \equiv (T - T_c)/T_c \to 0$,

$$Z_N = N^{\gamma - 1}\psi(tN^\phi) , \qquad (2)$$

where T_c is the collapse temperature, ϕ is the crossover exponent, and ψ is a universal scaling function. From (2) and the relation $a = 2 - 1/\phi$ for the specific-heat exponent a one obtains the scaling form for the specific heat for $N \to \infty$ and $t \to 0$,

$$C \sim N^{2\phi - 1}g(tN^\phi) . \qquad (3)$$

Although the scaling form (3) was derived only for linear polymers, we feel that the scaling structure carries over straightforwardly into the case of branched polymers. Only the critical exponents, upper critical dimension, scaling functions such as ψ and g change.
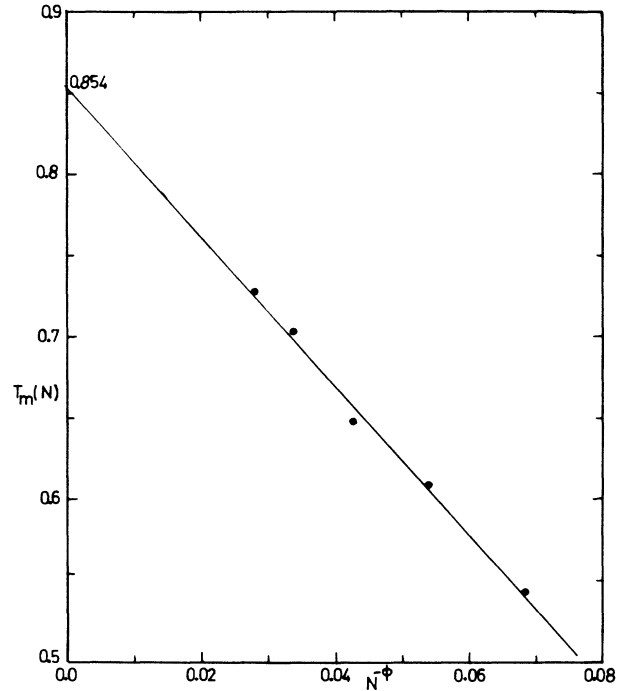

FIG. 2. Positions of the specific-heat peaks $T_m(N)$ vs $N^{-\phi}$, with $\phi = 0.814$.

The crossover exponent ϕ is obtained by fitting the values $C_m(N)$ to the form $C_m(N) \sim N^{2\phi - 1}$. This procedure relies on the tentative assumption that the data in Fig. 1 are already close enough to the asymptotic region where Eq. (3) holds. We obtain $\phi \approx 0.814$. Using this value of ϕ in the finite size scaling relation (1) and fitting
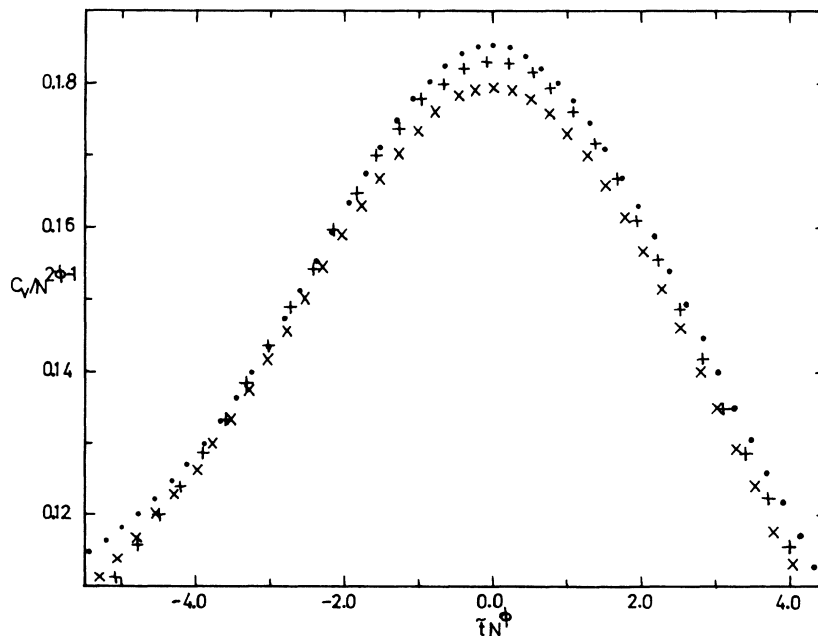

FIG. 3. Scaled specific heat $C/N^{2\phi - 1}$ vs scaling variable tN^ϕ, with $t \equiv [T - T_m(N)]/T_m(N)$ and $\phi = 0.814$, for various N: ●, $N = 48$; ×, $N = 64$; +, $N = 80$.

the values of $T_m(N)$ we find $T_c \approx 0.854$. We consider these to be better estimates of T_c and ϕ, since an independent relation (3) was used to determine ϕ. In Fig. 2 we plot $T_m(N)$ vs $N^{-\phi}$ with $\phi = 0.814$. The points lie more or less on a straight line with intercept at T_c and thus are consistent with finite-size scaling.

To test the scaling form (3), we plot in Fig. 3 the quantity $C/N^{2\phi-1}$ vs the scaling variable $\tilde{t}N^\phi$, where here we have taken $\tilde{t} \equiv [T - T_m(N)]/T_m(N)$. Since $T_m(N)$ approaches T_c for large N, $\tilde{t}$, and t are equivalent for large N. From Fig. 3 we see that except for values near the peak, the data for various N fall more or less on the same curve, which is the scaling function g. This confirms the

scaling form (3). The deviations near the peak may be due to the inaccuracy with which the height of the peak is determined or to the possibility that the asymptotic region where (3) holds is not yet reached. The increasing deviations in the wing of the scaling function are interpreted as corrections to scaling. However, our data do not cover a wide enough range of N to allow a systematic analysis of these corrections.

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