Specific heat and collapse transition of branched polymers

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We computed the specific heat of site lattice animals with nearest-neighbor attractive interaction for various animal sizes N, with N up to 80, on the simple-cubic lattice. For fixed N, the specific heat as a function of the temperature exhibits a peak at a temperature $T_m(N)$ depending on N. As N increases, this peak gets higher and sharper and $T_m(N)$ seems to approach a collapse transition temperature T_c from below. A least-squares fit together with finite-size scaling then gives both the transition temperature T_c and the specific-heat exponent α. The cycle-number distribution for the number of animals with fixed size N is also calculated. They seem to obey a scaling law for large N.

I. INTRODUCTION

Connected clusters of occupied site or lattice animals are good models for branched polymers in dilute solvents, for they take into account the excluded-volume effect,[1,2] which is important there. They are also intimately related to the percolation problem.[2] Normal animals describe the high-temperature limit of branched polymers when the excluded-volume effect dominates over the monomer-monomer affinity. At low-temperatures, or in a good solvent, the monomer-monomer affinity can become the dominant effect, leading to a collapse of the polymer. Such collapse had actually been studied experimentally.[3-6] The related collapse transition in linear polymers at the Θ point, at which the collapse temperature coincides with the point where the second virial coefficient vanishes, had long been studied both experimentally and theoretically (see the references quoted in Ref. 7). Derrida and Herrmann[7] did a theoretical study of the collapse transition of branched polymers in two dimensions using the transfer matrix method. They obtained the transition temperature T_c and certain critical exponents, including the specific-heat exponent α. However, their method cannot be easily extended to three dimensions, at which experiments can be most conveniently performed. Later, Dickman and Schieve[8] studied the same problem using a Monte Carlo method for some two- and three-dimensional lattices. In two dimensions, they obtained a transition temperature in closed agreement with that of Derrida and Herrmann. However, they were not able to determine any exponent. In three dimensions their numerical data were insufficient to determine either the transition temperature or the exponent. Recently Lam and Duarte[9] applied the method of Dickman and Schieve to study the collapse problem of directed lattice animals in two and three dimensions. Using a least-squares fit, together with finite-size scaling, we were able to estimate both the transition temperatures and specific-heat exponents for both the square and simple-cubic lattices. Encouraged by the success with the directed animal problem, we perform now a similar calculation of the undirected animal problem on the simple-cubic lattice, which may be of relevance to experimental studies. Thermal properties of lattice animals may be derived from the partition function

$$Z_N=\sum_B A'_N(B)e^{B/T}\ , \tag{1}$$

in which $A'_N(B)$ is the number of animals of size N with B nearest-neighbor bonds, and T is the absolute temperature. We have expressed the energy in units such that $\varepsilon/k_B=1$, with ε the nearest-neighbor attractive potential, and k_B is Boltzmann's constant. Using the Euler relation $B=N+C-1$, with C the number of cycles in the animal, (1) can be rewritten as

$$Z_N=e^{(N-1)/T}\sum_{C=0}^{M(N)} A_N(C)e^{C/T}\ , \tag{2}$$

where $A_N(C)$ is the number of animals with exactly C cycles and $M(N)$ is the maximum number of cycles in animals of size N. For the simple-cubic lattice,

$$M(N)=[\![3(N-N^{2/3})]\!] -N+[\delta(N,L^3)+\delta(N,L^2(L+1)) +\delta(N,(L+1)^2L)]\ ,$$

where the open square brackets denote the largest integer value of their argument, δ is the Kronecker δ function, and L is an integer. Using the Monte Carlo method of Dickman and Schieve, the ratios

$$r_N(C)\equiv A_N(C)/A_N(C+1)$$

for successive, nonzero values of $A_N(C)$ are estimated for fixed animal size N. In this way we have simultaneously calculated estimates for the cycle-number distribution for animals of size N defined by

$$P_N(C)\equiv A_N(C)\Big/\sum_{C=0}^{M(N)} A_N(C)\ . \tag{3}$$

Our data for $P_N(C)$ suggest that $P_N(C)$ satisfies the scaling law for large N. For fixed C, $A_N(C)$ behaves

asymptotically for large N as

$$A_N(C)=\sigma_C\lambda_0^N N^{C-\Theta}\ , \tag{4}$$

where λ_0 is a lattice-dependent growth parameter for lattice trees or zero-cycle animals, Θ is a universal exponent, and σ_C is an amplitude factor depending on C. Our estimate for $r_N(C)$ also allows an investigation of the amplitude factors σ_C. The result strongly suggests that the amplitude factors for different cycles are simply related.

II. MONTE CARLO METHOD FOR ESTIMATING THE NUMBER OF LATTICE ANIMALS

We review briefly the method of Dickman and Schieve. One starts initially with a connected cluster of fixed size N connected to the site at the origin. One then generates different configurations of connected clusters of the same size N by removing randomly any of the $N-1$ sites with the exception of the site at the origin, and attaching it at a randomly chosen unoccupied perimeter site. During this process one checks every time that the cluster does not break up into two or more disconnected clusters. This connectivity constraint can be most easily checked by using the "burning" algorithm.[10] Let $\mathbf{x}$ be the position of the site to be removed and $\mathbf{x}^*$ be the position of the site to be occupied. We denote the new configuration to be the one in which $\mathbf{x}^*$ is occupied and $\mathbf{x}$ is empty, and the old configuration as the reversed situation. In the new configuration, we start the "burning" from an arbitrarily chosen neighbor site of $\mathbf{x}$. During the process of "burning" we check if all the neighboring sites of $\mathbf{x}$ have been "burned." If so, the new configuration is a connected cluster. Otherwise, the new configuration is disconnected and is rejected. After this new configuration has passed the connectivity test, it is accepted with a probability p determined in the following way. One determines in the new configuration the number of neighboring sites n_p' of $\mathbf{x}$ and the number of bonds n_b' of $\mathbf{x}^*$, and similarly in the old configuration, the number of neighboring sites n_p of $\mathbf{x}^*$ and the number of bonds n_b of $\mathbf{x}$. If n_b' is greater than or equal to n_b, the new configuration is accepted with probability $p=n_p'/n_p$. Otherwise it is accepted with probability

$$p=\exp[(n_b'-n_b)/T]\ ,$$

where T is the temperature. An unbiased estimate of the ratios $A_N(C)/A_N(C+1)$ is then given by

$$\exp[(C'-C)/T]Y_c/Y_{c'}\ ,$$

where Y_C is the number of realizations of C-cycle animals. For large N, animals with small C are generated only with sufficiently large T, and those with very large C are only generated with sufficiently small T. Therefore, for large N, one has to use several different temperature (four or five) in order to generate animals with cycle numbers ranging all the way from $C=0$ to $C=M(N)$. For each temperature we make about 100 million trials at generating new configurations starting from an initial connected cluster. An accepted configuration is called an event. At $T\sim 1.0$, the number of events is about one-fourth the total number of trials. For lower T, this fraction can be considerably smaller. At the start of each run 10 or 20 million trials are allowed for relaxation. For $N\le 12$ we have checked that our Monte Carlo data are in excellent agreement with exact results.[11]

III. LATTICE ANIMAL SPECIFIC HEAT

The specific heat per particle in an N-particle animal is

$$C_v=(\langle B^2\rangle-\langle B\rangle^2)/(NT^2)\sim(T-T_c)^{-\alpha}\ , \tag{5}$$

where

$$\langle B^n\rangle=Z_N^{-1}\sum_B B^n A_N'(B)e^{B/T}\ ,$$

and $A_N'(B)$ is the number of animals of size N with B bonds. Since $A_N(M(N)-1)=0$ for $N=L^3$, $L^2(L+1)$, or $(L+1)^2L$, with L an integer, we can define

$$r_N(C)\equiv A_N(C)/A_N(C+1),\quad C\le M(N)-3 \tag{6}$$

and

$$r_N'\equiv A_N(M(N)-2)/A_N(M(N))\ . \tag{7}$$

Then Z_N can be written as

$$Z_N=e^{(N-1)/T}A_N(0)\left[1+\sum_{C=0}^{M(N)-3}\prod_{j=0}^{c}[e^{1/T}/r_N(j)]+(e^{2/T}/r_N')\prod_{C=0}^{M(N)-3}[e^{1/T}/r_N(C)]\right]\ , \tag{8}$$

and $Z_N\langle B^n\rangle$ as

$$Z_N\langle B^n\rangle=(N-1)^n+\sum_{C=0}^{M(N)-3}(N+C)^n\prod_{j=0}^{c}[e^{1/T}/r_N(j)]+[N+M(N)-1]^n(e^{2/T}/r_N')\prod_{C=0}^{M(N)-3}[e^{1/T}/r_N(C)]\ . \tag{9}$$

We have calculated $r_N(C)$ on the simple-cubic lattice using the Monte Carlo method of the preceding section, for $N=27$, 36, 48, 64, and 80. The specific heat obtained using (5)–(9) is plotted as a function of T in Fig. 1 for various sizes N. From Fig. 1, we see that besides the subsidiary peak at low temperatures, the specific heat exhibits also a strong, fairly broad peak at a higher temperature. We identify this as the collapse point $T_m(N)$

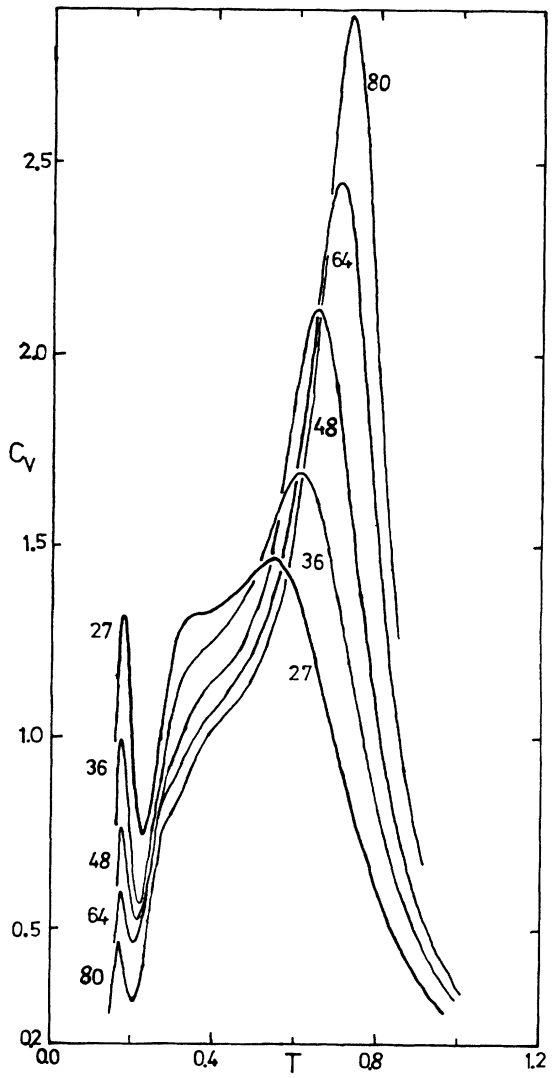

FIG. 1. Specific heat C_v vs temperature T for various animal sizes N on the simple-cubic lattice.

for animals of size N. As the size of the animals increases, the temperature $T_m(N)$ at which the specific heat attains its maximum, shifts toward higher temperatures and the peak grows higher and sharper. From finite-size scaling[12] we know that $T_m(N)$ scales as

$$T_m(N)=T_c-aN^{-\Phi}\ , \tag{10}$$

with a crossover exponent Φ. We have used our data $T_m(27)=0.5433$, $T_m(36)=0.6090$, $T_m(48)=0.6482$, $T_m(64)=0.7037$, and $T_m(80)=0.7279$ in a least-squares fit to determine the three parameters T_c, Φ, and a in (10). We find $T_c=0.972$ and $\Phi=0.521$. In Fig. 2 we plot $T_m(N)$ versus $N^{-\Phi}$, using the crossover exponent value $\Phi=0.521$. We see that the data fall fairly well on a straight line, confirming finite-size scaling theory. The specific-heat exponent α can be related to the crossover exponent Φ as follows.[7] If the thermal correlation length ξ_T of lattice animals near the collapse point goes as

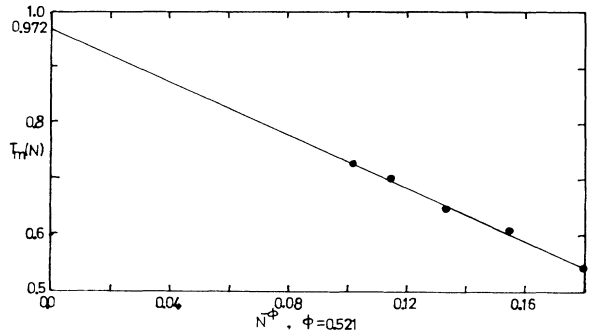

FIG. 2. Variation of $T_m(N)$ with size for simple-cubic lattice animals. The straight line is obtained by a least-squares fit.

$$\xi_T\sim|T-T_c|^{-\nu_2} \tag{11}$$

with an exponent ν_2, then the free energy per particle f is given by

$$f\sim\xi_T^{-\bar{d}}\sim|T-T_c|^{\bar{d}\nu_2}\ , \tag{12}$$

where $\bar{d}$ is the fractal dimension of the lattice animal at the collapse point. From (12), it follows that the free energy f also has the exponent $2-\alpha$. Therefore, we have

$$\bar{d}\nu_2=2-\alpha\ . \tag{13}$$

If, at the collapse point, the radius of gyration exponent of lattice animals is ν_1, we have $\bar{d}=1/\nu_1$ and

$$\alpha=2-\nu_2/\nu_1=2-1/\Phi\ , \tag{14}$$

with $\Phi=\nu_1/\nu_2$, the same crossover exponent as in (10). Using $\Phi=0.521$ in (14), we obtain $\alpha=0.18$.

IV. CYCLE-NUMBER DISTRIBUTION

The cycle-number distribution defined in (3) can be written in terms of the $r_N(C)$ and r'_N as

$$P_N(C)=\left[1+\sum_{C'=0}^{C-1}\prod_{j=C'}^{C-1}r_N(j)+\sum_{C'=C}^{M(N)-2}\prod_{j=C}^{C'-1}r_N(j)^{-1}+r_N'^{-1}\prod_{j=C}^{M(N)-3}r_N(j)^{-1}\right]^{-1}\ ,$$

$$0<C<M(N)\ . \tag{15}$$

We have calculated $P_N(C)$ on the simple-cubic lattice using (15). The result is most conveniently presented in terms of the quantity

$$Q_N(X)\equiv\log P_N(C)/\log P_N(M(N))$$

as a function of the variable $X\equiv C/M(N)$.

In Fig. 3 we show the quantity $Q_N(X)$ as a function of X. From this figure, we notice that there is evidence of scaling behavior as observed by Dickman and Schieve for two-dimensional lattice animals[13] and also by Lam and Duarte[9] for directed lattice animals in two and three dimensions.

From (3), since $A_N(C)$ can be written as

$$A_N(C) \sim A_N(0) \prod_{j=0}^{C-1} r_N(j)^{-1}, \quad C < M(N)-2 \tag{16}$$

we see that the errors in $P_N(C)$ increase with C; let Δr_j be the statistical error in $r_N(j)$, then

$$\prod_{j=0}^{C-1} [r_N(j)+\Delta r_j]^{-1} \approx \left[1-\sum_{j=0}^{C-1} \Delta r_j / r_N(j)\right] \prod_{j=0}^{C-1} r_N(j)^{-1} . \tag{17}$$

We have in our calculation $\Delta r_j / r_N(j) \approx 0.01$. At $X=1$, $Q_N(X)$ is normalized to 1 for all N. For small X, we see from Fig. 3 that there is excellent scaling behavior for large N. For X between 0.5 and 0.8, the scaling behavior deteriorates somewhat. But, however, according to (17), the error bars in this region are also larger. We see that the data are not inconsistent even with the conjecture of an exact scaling behavior for all X at large N.

For fixed cycle-number C it is known[11,14,15] that $A_N(C)$ has the following asymptotic behavior for large N:

$$A_N(C) = \sigma_C \lambda_0^N N^{C-\Theta}, \quad N \gg 1 \tag{18}$$

where σ_c is a cycle-dependent amplitude factor, λ_0 is the growth parameter for lattice trees, i.e., $C=0$ lattice animals, and Θ is a universal exponent. From (18) we see that the ratio of successive amplitude factors σ_C/σ_{C+1} can be obtained from

$$\sigma_C/\sigma_{C+1} = N A_N(C)/A_N(C+1) = N r_N(C) . \tag{19}$$

In Fig. 4, we have plotted the successive ratios $N r_N(C)$ as a function of C. This figure strongly suggests the following relation between the successive amplitude factors σ_C/σ_{C+1}:

$$-\sigma_C/\sigma_{C+1} + \sigma_{C+1}/\sigma_{C+2} = K , \tag{20}$$

where K is a constant. From Fig. 4 we find $K \approx 14.5$. From (20) it follows that

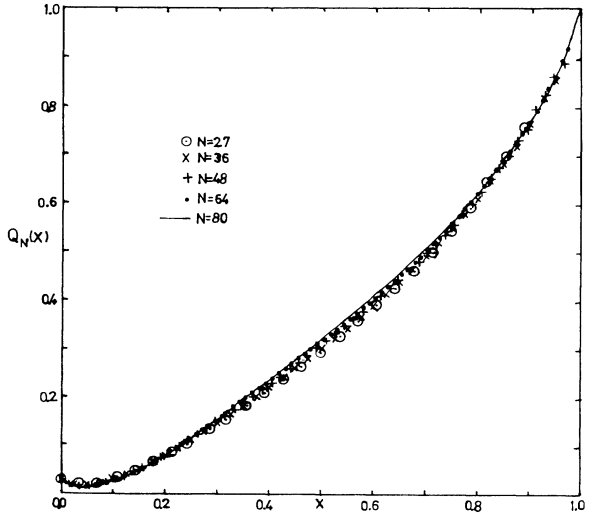

FIG. 3. Quantity $Q_N(X)$ vs X for lattice animals on the simple-cubic lattice.

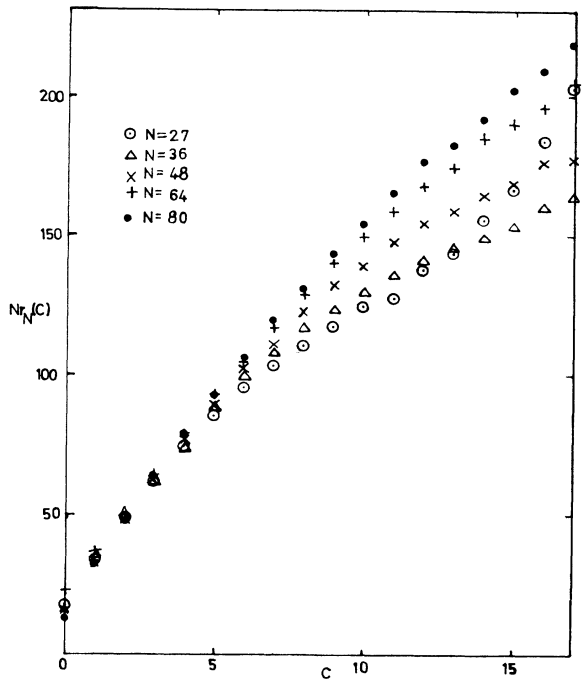

FIG. 4. Ratio $N r_N(C)$ of the number of animals with fixed size N but successive cycle numbers C and $C+1$ as a function of C for the simple-cubic lattice.

$$\sigma_C = \sigma_0 (\sigma_1/\sigma_0)^C \Big/ \prod_{j=1}^{C-1} (1+jK\sigma_1/\sigma_0) . \tag{21}$$

If we sum (18) over all cycles C, we obtain the total number of animals of size N, A_N, which has the asymptotic behavior at large N,

$$A_N = \sigma \lambda^N N^{-\Theta} , \tag{22}$$

where λ is the growth parameter for the total number of lattice animals and Θ is the same universal exponent as in (18). We have, therefore, the equation

$$(\sigma_c/\sigma)(1+N\sigma_1/\sigma_0+N^2\sigma_2/\sigma_0+\cdots+N^{M(N)}\sigma_{M(N)}/\sigma_0) = (\lambda/\lambda_0)^N . \tag{23}$$

In the limit $N \to \infty$, the left-hand side of (22) must tend towards an exponential function $\exp(aN)$, with $a=\log(\lambda/\lambda_0)$ and $\sigma_0=\sigma$. If we substitute (21) into (23), we have

$$(\lambda/\lambda_0)^N = \sum_{C=0}^{M(N)} (N\sigma_1/\sigma_0)^C C! \times \prod_{n=1}^{C} n[1+(n-1)K\sigma_1/\sigma_0]^{-1} . \tag{24}$$

Now since $K\sigma_1/\sigma_0 \approx 1$, we have for large n

$$n[1+(n-1)K\sigma_1/\sigma_0]^{-1} \approx \sigma_0/(K\sigma_1) .$$

Therefore, (24) becomes

$$(\lambda/\lambda_0)^N \approx \sum_{C=0}^{M(N)} (N/K)^C/C! \approx \exp(N/K) , \tag{25}$$

with $K^{-1}=\ln(\lambda/\lambda_0)$. Using the values $\lambda=8.368$ (Ref. 16) and $\lambda_0=7.8$ (Ref. 11) determined elsewhere, we obtain $\ln(\lambda/\lambda_0)=0.0703=K^{-1}$, in reasonable agreement with our graphically determined value $K\approx 14.5$. A particular solution of (20) is the Poisson distribution $\sigma_C=\sigma_0/(K^C C!)$. Substituting this into (18) and summing over all C up to $C=M(N)$, we obtain in the limit $N\to\infty$, again $K^{-1}=\ln(\lambda/\lambda_0)$. Our Eq. (21) reduces to the above Poisson distribution if $\sigma_0=K\sigma_1$. But in general, (20) alone does not give such a relation between σ_1 and σ_0.

V. CONCLUSION

We have calculated the collapse transition temperature and specific-heat exponent for lattice animals on the simple-cubic lattice. In addition, the cycle-number distributions are also calculated. They seem to obey the scaling law for large N. We have also found numerical support for a relation between the amplitude factors σ_C for different C in the asymptotic formula

$$A_N(C)=\sigma_C\lambda_0^N N^{C-\Theta}\ .$$

Besides the main peak corresponding to the collapse transition, there is also a subsidiary peak at a lower temperature. As discussed elsewhere[8,9] this subsidiary peak presumably describes the roughening transition. This peak seems to approach a finite temperature as $N\to\infty$, as appropriate for the roughening transition in three dimensions.

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[1]P. G. de Gennes, *Scaling Properties in Polymer Physics* (Cornell University Press, Ithaca, 1979).
[2]D. Stauffer, *Introduction to Percolation Theory* (Taylor and Francis, London, 1985).
[3]T. Tanaka, G. Swislow, and I. Ohmine, Phys. Rev. Lett. **42**, 1556 (1979).
[4]A. Hochberg, T. Tanaka, and D. Nicoli, Phys. Rev. Lett. **43**, 217 (1979).
[5]T. Tanaka, D. Filmore, S. T. Sun, I. Nishio, G. Swislow, and A. Shah, Phys. Rev. Lett. **45**, 1636 (1980).
[6]K. Tanaka, Sci. Am. **244**, 124 (1981).
[7]B. Derrida and H. J. Herrmann, J. Phys. (Paris) **44**, 1365 (1983).
[8]R. Dickman and W. C. Schieve, J. Phys. (Paris) **45**, 1727 (1984).
[9]P. M. Lam and J.A.M.S. Duarte (unpublished).
[10]H. J. Herrmann, D. C. Hong, and H. E. Stanley, J. Phys. A **17**, L261 (1984).
[11]P. M. Lam, Phys. Rev. A **35**, 349 (1987).
[12]R. R. dos Santos and R. B. Stinchcombe, J. Phys. A **14**, 2741 (1981).
[13]R. Dickman and W. C. Schieve, J. Stat. Phys. **44**, 465 (1986).
[14]D. S. Gaunt, M. F. Sykes, G. M. Torrie, and S. G. Whittington, J. Phys. A **15**, 3209 (1982).
[15]J.A.M.S. Duarte, J. Phys. Lett. **46**, L523 (1985).
[16]P. M. Lam, Phys. Rev. A **34**, 2339 (1987).