Concentrated, Semiflexible Lattice Chain Systems and Criticism of the Scanning Technique

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ABSTRACT: The thermodynamics of concentrated, semiflexible lattice chain systems are determined by computer simulation. An order–disorder transition is observed in both two and three dimensions. In two dimensions the transition is second-order and critical. In three dimensions it is first-order. The entropy is obtained as a function of temperature with sufficient accuracy to test the scanning technique, a procedure devised to simulate the entropy of lattice chains. The scanning procedure cannot approximate the entropy of the systems considered here. Scanning is unreliable whenever interactions occur between parts of the system constructed at widely different times. Unfortunately, this includes all systems to which it is now being routinely applied. The problem is most severe in concentrated multiple chain systems and less so in isolated self-avoiding walks.

1. Introduction

This paper examines by computer simulation the problem of a dense (i.e., all sites occupied) simple square or simple cubic lattice polymer system with inherent chain stiffness. Mean-field models of such systems have been examined by Flory[1] and by Starkweather and Boyd,[2] who observed a first-order transition to a highly ordered state and concluded that the model provided a thermodynamic description of polymer freezing. Furthermore, by neglecting the low-temperature frozen phase in the Flory formulation, one obtains a model of a supercooled polymer liquid with unusual entropy behavior.[3] In this form the model has been influential in stimulating entropy models of the glass transition.[3–8]

More recently, the existence of a first-order transition has been challenged.[9,10] Obviously, the fact that real polymers freeze is not in question, but it has been asserted that a first-order transition should not be expected in these simple lattice polymer systems. Several Monte Carlo simulations of diamond, simple square, and simple cubic lattice systems then appeared, all of which produced evidence for a first-order transition.[11–14]

The initial intention of this study was to estimate the entropy of the supercooled lattice polymer melt in order to test the claims of the Gibbs–DiMarzio theory[3–8] of the glass transition. I planned first to simulate the equilibrium properties of the system on both sides of the transition with sufficient accuracy to estimate the entropy as a function of temperature. Then the entropy of the supercooled liquid would be estimated using Meirovitch's "hypothetical scanning" method,[15–24] employing the assumption that the disordered liquid at two different temperatures, one above and one below the freezing point, has nearly the same structure. Since the equilibrium entropy would be known above the transition, this assumption could be independently tested at two different higher temperatures. However, as the study progressed, it became obvious that the hypothetical scanning technique cannot adequately estimate the entropy.

Therefore, this paper reports careful, thorough Monte Carlo calculations on both the simple square and simple cubic lattice. The chains are quite long (ca. 1000 lattice sites) and the simulations have been done with sufficient precision that the entropy and other thermodynamic functions can be determined with reasonable accuracy. It also includes a criticism of both the scanning and hypothetical scanning techniques for simulating polymer systems. It appears that the range of problems which can be successfully treated by scanning is rather limited.

In three dimensions, there is indeed a first-order transition to an ordered state. However, in two dimensions, the transition is second-order and critical. Finite chain effects probably account for the absence of criticality in other two-dimensional systems.[11] A minor technicality arises in connection with the ordered state: Chain lengths in these simulations exceed the box size, and therefore the chains can never become completely elongated. Therefore we expect minor differences between the results of these simulations and the thermodynamics of systems in very large boxes. However, this is not expected to affect any of the results obtained for the disordered phase.

2. Computational Techniques

I employed a previously reported Monte Carlo method,[25–30] so specific details of the technique are omitted here. The method is an efficient technique for studying dense (all sites occupied), long polymers on either the simple square or simple cubic lattice. The efficiency of the technique comes at some cost, namely the resulting chain length distribution is polydisperse. In the original study,[27] chain length polydispersity was controlled to some degree by introducing a lower molecular weight cutoff. It has proven possible to exercise much greater control by applying both upper and lower cutoffs without adversely compromising the efficiency of the technique.[30] For example, the chain ensembles reported here all have polydispersities of about 1.003.

In three dimensions, the system consists of a box of dimensions $40 \times 40 \times 40$ containing 64 chains, while in two dimensions the box has dimensions 250×250 and contains 62 chains. Periodic boundary conditions are enforced. Chain lengths below 900 and above 1100 are forbidden.

Chain stiffness is controlled by assuming that a bond parallel to its predecessor contributes 0 to the total energy of the system, while a perpendicular bond contributes +1. The total energy of the system, therefore, is just the total number of bent bonds. Temperature units are set such that Boltzmann's constant is 1. T represents the absolute temperature and β its reciprocal.

Equilibrium biasing was achieved by the standard Metropolis method. Except in the vicinity of the phase

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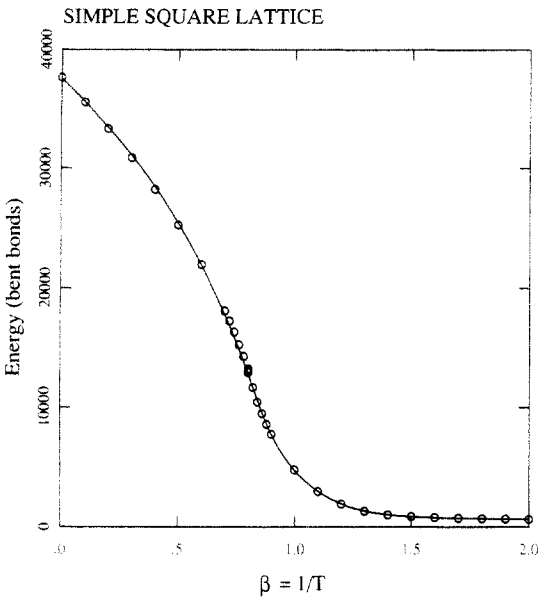

Figure 1. Total energy as a function of reciprocal temperature for the simple square system. Symbols are the simulation results, the solid curve is given by eq 2.

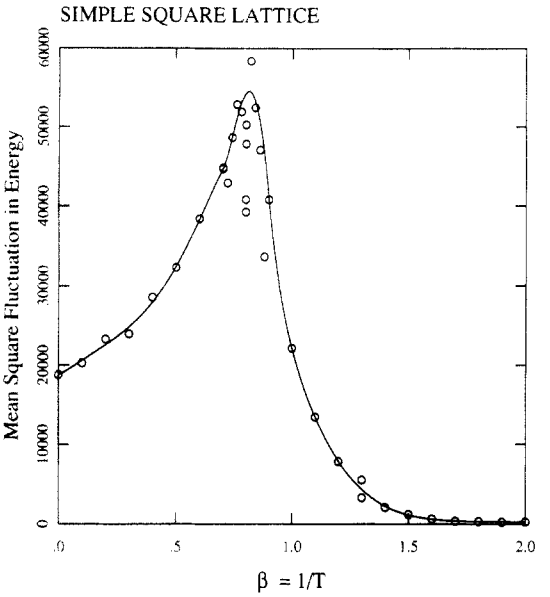

Figure 2. Mean-square fluctuation in the energy of the simple square system as a function of reciprocal temperature. Symbols are the simulation results, the solid curve is obtained from the derivative of eq 2.

transitions, it was always possible to confirm relaxation to equilibrium by monitoring the drift in total energy. Near the phase transitions the relaxation was obviously much slower and subject to hysteresis effects, etc., making it difficult to confirm relaxation. A technique that worked well in such cases was to initiate the calculation from a two-phase structure, one phase being highly ordered and the other having the structure of the disordered melt at infinite temperature. (Such structures can be obtained by performing the Monte Carlo procedure at infinite temperature on a system that is originally highly ordered but in which rearrangements are only permitted in one half of the box.) Relaxation could be verified by waiting for one phase to completely consume the other. The system was assumed to be at equilibrium when it became homogeneous and when the total energy had stabilized. Relaxation requires anywhere from several million to several billion Monte Carlo iterations, depending on temperature, initial conditions, and on the proximity of a phase transition. A million iterations consume about 10 min of CPU time on an IBM RS-6000.

3. Results in Two Dimensions

Figures 1 and 2 display results for the total energy (i.e., average number of bent bonds) and the mean-square fluctuation in the total energy, respectively, for the simple square lattice. Note that the total energy can be determined much more accurately than can the fluctuation magnitude. One is proportional to the derivative of the other, since

$$\sigma(\beta) = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial E}{\partial \beta} \tag{1}$$

where we let σ represent the mean-square fluctuation in the energy.

Purely for purposes of numerical approximation, the following three functions have been developed. The first is the sixth-order polynomial in β that best fits both the energy and the fluctuation data in the domain $0 \le \beta \le 0.7$, obtained by simultaneous least-squares fitting of the polynomial to the energy data and of its derivative to the fluctuation data. The third function was determined in like manner in the domain $0.9 \le \beta \le 2$, in powers of $1/\beta$.

The second curve is the fifth-order polynomial that interpolates between the other two with continuity through second derivatives. The coefficients appearing in eq 2 are

$$E(\beta) = \begin{cases} \sum_{j=0}^{6} A_j \beta^j & (0 \le \beta \le 0.7) \\ \sum_{j=0}^{5} B_j \beta^j & (0.7 \le \beta \le 0.9) \\ \sum_{j=0}^{6} C_j \beta^{-j} & (0.9 \le \beta \le 2.0) \end{cases} \tag{2}$$

tabulated in Table 1. The solid curves in Figures 1 and 2 were drawn with eq 2 and its derivative, respectively. These expressions give the total energy of the system. The energy per site is obtained from these expressions by dividing by 62500.

Figure 3 displays an anisotropy index, defined as $|f_x - f_y|$ where f_x and f_y are, respectively, the fraction of steps in the x and y directions.

The data in Figures 1 through 3 all indicate the existence of a critical point at about $\beta = 0.8$. Additional evidence of criticality includes a critical slowing-down of the Monte Carlo process near $\beta = 0.8$, as well as direct observation of model structure, as in Figure 4.

Equation 2, in combination with the following thermodynamic relationship

$$S(\beta) = S(0) - \int_0^\beta \beta' \sigma(\beta') d\beta' \tag{3}$$

yields the following relationship for the entropy:

$$S(\beta) = \begin{cases} \sum_{j=0}^{7} a_j \beta^j & (0 \le \beta \le 0.7) \\ \sum_{j=0}^{6} b_j \beta^j & (0.7 \le \beta \le 0.9) \\ c_l \ln\left(\frac{\beta}{0.9}\right) + \sum_{j=0}^{5} c_j \beta^{-j} & (0.9 \le \beta \le 2) \end{cases} \tag{4}$$

The value S_0 in eq 3 represents the entropy at zero β

Table 1. Coefficients in the Energy and Entropy Expansions, Eqs 2 and 4, for the Simple Square Lattice System

j	A_j	B_j	C_j	a_j	b_j	c_j
0	37558.022	1748327.5	60285.700	24200.000	253267.10	-1497671.9
1	-18755.870	-10561620	-538467.17	0.0000000	0.0000000	3932252.0
2	-8269.8557	25681880	1966126.0	-9377.9350	-5280810.0	-5568750.6
3	-11587.773	-30871469	-3712500.4	-5513.2371	17121253	5088015.6
4	50654.406	18227599	3816011.7	-8690.8298	-23153602	-2527692.6
5	-107441.70	-4219041.1	-2022154.1	40523.525	14582079	522514.87
6	61593.373	N/A	435429.06	-89534.750	-3515867.6	N/A
7	N/A	N/A	N/A	52794.320	N/A	N/A
l	N/A	N/A	N/A	N/A	N/A	538467.17

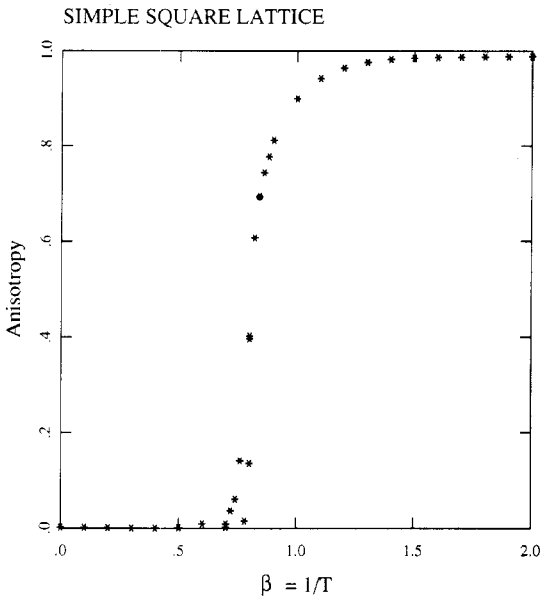

Figure 3. Anisotropy index as a function of reciprocal temperature.

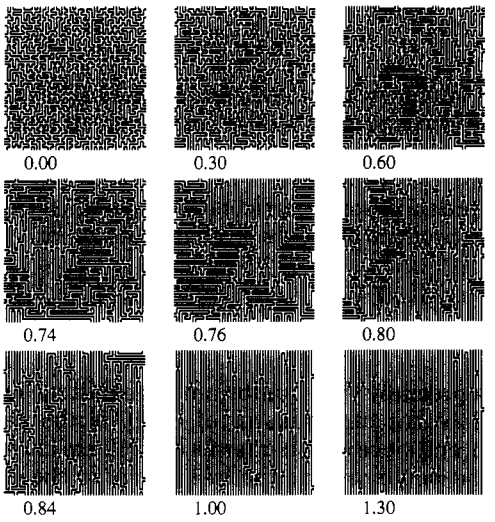

Figure 4. Snapshots of a portion of the simple square system at various values of $1/T$.

(infinite temperature), which cannot be determined directly from the simulation. Good numerical estimates for the entropy of this model at infinite temperature are available. The site entropy at infinite temperature is about ln(1.742),[31] so we can set S_0 = 62500 ln(1.742) = 24200. The coefficients appearing in eq 4 are listed in Table 1.

4. Results in Three Dimensions

Figure 5 displays the results for total energy as a function of reciprocal temperature. Energy fluctuations were not determined in three dimensions. Obviously a first-order transition appears between $\beta = 1.22$ and $\beta = 1.23$. For the sake of numerical approximation, we assume a value of

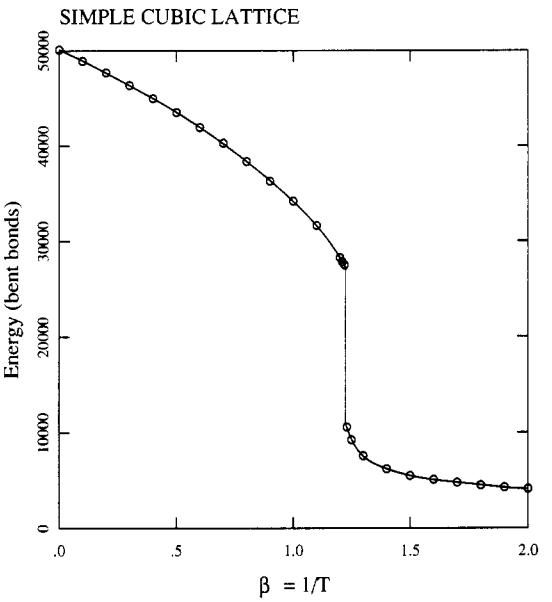

Figure 5. Total energy of the simple cubic model as a function of reciprocal temperature. Symbols are simulation data, the solid curve represents eq 5.

1.225 for the transition point. The data points can be well fit by the following function

$$E(\beta) = \begin{cases} \sum_{j=0}^{6} A_j \beta^j & 0 \le \beta \le 1.225 \\ \sum_{j=0}^{6} B_j \beta^{-j} & 1.225 \le \beta \le 2 \end{cases} \quad (5)$$

which was obtained by least-squaring fitting. The site energy can be determined from eq 5 by dividing by 64000. The values of the coefficients appearing in eq 5 are given in Table 2. We can obtain the entropy from eqs 3 and 5:

$$S(\beta) = \begin{cases} \sum_{j=0}^{7} a_j \beta^j & (0 \le \beta \le 1.225) \\ b_l \ln\left(\frac{\beta}{1.225}\right) + \sum_{j=0}^{5} b_j \beta^{-j} & (1.225 \le \beta \le 2) \end{cases} \quad (6)$$

with coefficients appearing in Table 2. I am unaware of any previous estimates of the three-dimensional site entropy at $\beta = 0$, so that an appropriate value of S_0 remains to be determined, and our only guide in fixing S_0 is that the low-temperature entropy must be small and positive. In writing the particular coefficients given in Table 2, we are assuming that the entropy at $\beta = 2$ is 500. However, any value between 0 and about 1000 is probably reasonable, so that the entropy is determined absolutely to perhaps about ±500. Assuming that the energy function is well-fit by eq 5 and that the entropy at $\beta = 2$ is between 0 and 1000 provides 0.720 and 0.735 as lower and upper bounds,

Table 2. Coefficients in the Energy and Entropy Expansions, Eqs 5 and 6, for the Simple Cubic Lattice System

j	A_j	B_j	a_j	b_j
0	50108.377	8014261.7	46569.823	-197000310
1	-10325.050	-77198328	0.0000000	617064360
2	-16107.381	308532180	-5162.5250	-982064700
3	54112.926	-654709800	-10738.254	1037583300
4	-102903.33	778187440	40584.694	-614169400
5	87239.904	-491335520	-82322.664	154539940
6	-27952.437	-128783280	72699.920	N/A
7	N/A	N/A	-23959.232	N/A
l	N/A	N/A	N/A	77198328

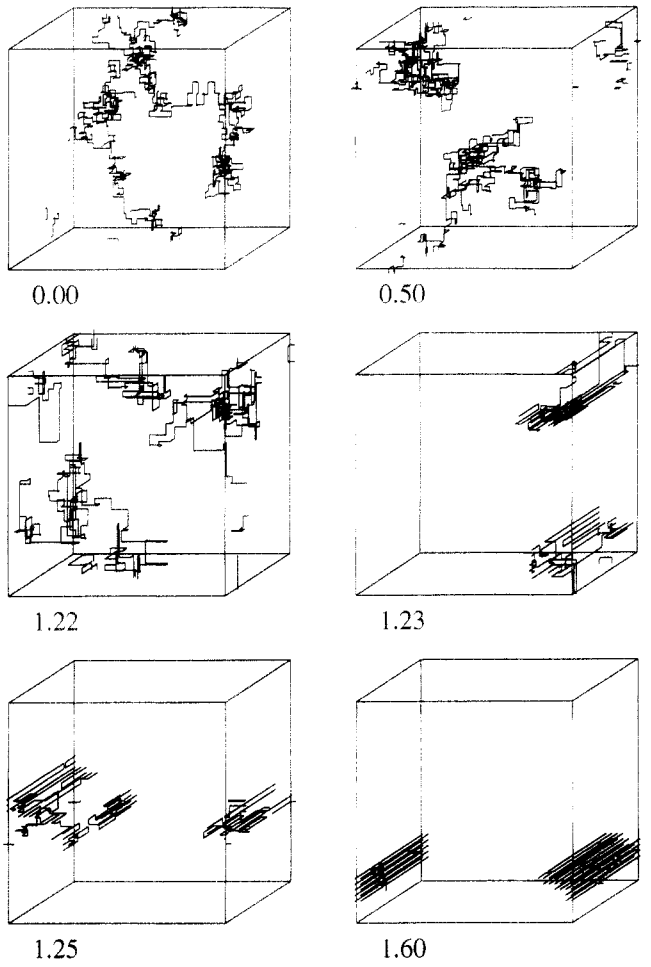

Figure 6. Projections of an arbitrarily selected chain at various values of $1/T$.

respectively, for the site entropy at infinite temperature in three dimensions.

Figure 6 displays projections of several different chains obtained at different temperatures. These diagrams demonstrate the change in order brought about by the transition.

5. A Critical Analysis of the Scanning and the Hypothetical Scanning Techniques

The scanning technique has been applied both to generate ensembles of polymer lattice systems and to estimate their entropy.[15-24] The algorithm can be summarized as follows. Chains are grown in step-wise fashion. Before the addition of each successive step, one "scans" ahead, enumerating all possible paths for m steps "into the future". Each such path has an associated weight; the combined weights of all those paths whose first steps are in a given direction on the lattice define a probability for taking a single step in that direction. A new step is then taken, selected according to these single-step probabilities. When the chain (or system of chains) is grown to completion, it may be sampled for any properties of interest. Furthermore, the net probability of obtaining that particular configuration is the product of the individual step probabilities, each of which were determined during the growth of the chain. Therefore, the entropy can be computed from the expression $S = -k \ln P$. Obviously, we should take m as large as possible, but it is also obvious that very large values are impractical.

It is not hard to show that the scanning method would be rigorous if we were to scan ahead, not just m steps, but completely through the system.[21] For example, assume that we have a system completely specified by a set of variables x_1, x_2, x_3, ..., $x3n$. These might be atomic positions, lattice spin states, or directions on a lattice. Each configuration of the system has Boltzmann weight

$$W(x_1, x_2, x_3, ..., x_n) = \exp[-\beta H(x_1, x_2, x_3, ..., x_n)] \quad (7)$$

where H is the Hamiltonian. We now imagine that we construct a particular configuration of the system in piecewise fashion, assigning values for each of the variables in sequence as follows. The value of the first variable is assigned with the following probability:

$$p_1(x_1) = \frac{\sum_{x_2}\sum_{x_3}\sum_{x_4}\cdots\sum_{x_n} W}{\sum_{x_1}\sum_{x_2}\sum_{x_3}\cdots\sum_{x_n} W} \quad (8)$$

Each succeeding variable is assigned according to the probability

$$p_j(x_j) = \frac{\sum_{x_{j+1}}\sum_{x_{j+2}}\cdots\sum_{x_n} W}{\sum_{x_j}\sum_{x_{j+1}}\cdots\sum_{x_n} W} \quad (9)$$

In other words, each successive variable is determined by scanning through all possible values of all succeeding variables, while keeping all previous variables fixed at the values previously assigned. Then the probability that this process produces some particular configuration (x_1, x_2, x_3, ...) is the product of all the probabilities p_j, or

$$P = \prod_j p_j = \frac{W}{\sum_{x_1}\sum_{x_2}\cdots\sum_{x_n} W} \quad (10)$$

which is precisely the equilibrium probability. Furthermore, since the denominator of eq 10 is the partition function, and since all other terms in eq 10 are known, this technique would provide the free energy or the entropy. Therefore, if it were possible to scan completely to the end in each step, this procedure would be rigorous. (Of course, if we could scan to the end, then the procedure would be unnecessary.) Practical applications of the technique only allow limited scanning, and the obvious question is whether or not the technique then continues to be valid.

A second technique, known as hypothetical scanning, has been applied to those cases for which the scanning method routinely converges on states of zero probability. For example, it is difficult to construct concentrated polymer systems by scanning, since one invariably isolates regions of space too small to contain a full chain. First, one uses any other valid simulation technique to generate an equilibrium configuration. Then one applies the original scanning procedure except that each successive step is taken, not in a randomly determined direction, but

in the direction specified by the configuration already in hand. Obviously, this approach would be rigorous if the configuration were at equilibrium and if scanning continued through the end of the system.

We can identify one case in which limited-range scanning is valid. Suppose we have a system for which transfer matrix methods are applicable. Formally, this means that the total Boltzmann weight can be factored into pairwise contributions:

$$W = L(x_1)\, G(x_1, x_2)\, G(x_2, x_3) \cdots G(x_{n-1}, x_n)\, R(x_n) \quad (11)$$

where the variable x_j denotes the state of the jth layer of the system. Furthermore, we let the system be homogeneous, i.e., each G function appearing above is identical. (This assumption is not necessary for validity of limited-range scanning, but it simplifies the demonstration.) Substition of eq 11 into eq 9 yields:

$$p_j = \frac{G(x_{j-1}, x_j)\, V(x_j)}{\alpha V(x_{j-1})} \quad (12)$$

where α is the dominant eigenvalue of the transfer matrix G and where V is its corresponding eigenvector, i.e.,

$$\sum_{x_j} G(x_{j-1}, x_j)\, V(x_j) = \alpha V(x_{j-1}) \quad (13)$$

On the other hand, we obtain the same expression for p_j if we scan over a limited range m, as long as m is so large that

$$\alpha^m \gg (\alpha')^m \quad (14)$$

and where α' is any other eigenvalue of G. Limited-range scanning is valid for such systems as long as m is selected large enough to satisfy eq 14.

The validity of limited-range scanning in this transfer matrix example is a direct result of the short-range nature of the interactions between successive variables. In principle, limited-range scanning is not valid if interactions exist between variables assigned at widely different times during the procedure. A few examples will make this obvious.

A. The 2 × *N* Ising Model. We consider an Ising model constructed on a narrow strip of the simple square lattice, the dimensions of the strip being $2 \times N$. Obviously, this model can be easily studied by transfer matrix techniques, but for the sake of argument, we will also estimate its entropy by several scanning procedures. The Hamiltonian of the system includes only nearest-neighbor interactions, and spins assume only two values, ±1. We let all nearest-neighbor parallel spin pairs contribute −1 to the Hamiltonian, and antiparallel spin pairs contribute +1. Figure 7 displays results for the entropy, assuming $N = 1000$, obtained in four different ways: (1) naive scanning, in which we scan first down one row and then back along the other; (2) naive hypothetical scanning, in which we scan along the same path as before, but we use an independently generated equilibrium configuration to dictate the spin state at each lattice site; (3) proper scanning, in which we build up the system by scanning both rows simultaneously and in which one step of the procedure assigns the spin states of two spins simultaneously; (4) rigorous transfer matrix results. In each case, scans are done over the states of ten "future" spins. It is obvious from Figure 7 that the two naive scanning calculations fail to predict the entropy.

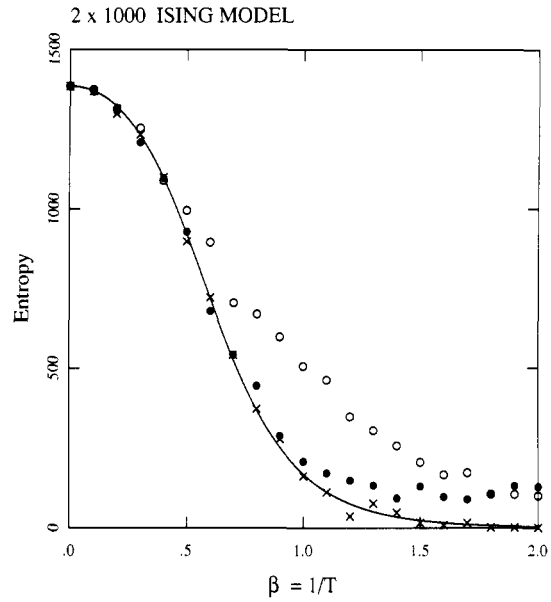

Figure 7. Entropy vs reciprocal temperature for a 2 × 1000 Ising model. The solid curve is exact. The symbols ○, ●, and × represent results obtained by naive scanning, naive hypothetical scanning, and proper scanning, respectively. See text for details.

With naive scanning, the first row develops with the structure of the simple one-dimensional Ising chain and accumulates entropy at that rate. The procedure simply does not "know" that we plan to come back and add a second row. The second row develops with the structure of a one-dimensional Ising chain interacting with another Ising chain having frozen-in structure and accumulates entropy at that rate. The final entropy and structure are melanges of two different models, neither of which has the entropy nor the structure of the model we intended to study. With hypothetical scanning, we are forcing the procedure to converge on the proper structure, but it still "thinks" it is trying to construct a different model, and it still converges on an invalid entropy. Only with proper scanning, by including in the scan all relevant interactions, can we get valid entropies.

B. Concentrated polymer systems. Figures 8 and 9 compare the results of the entropy given by eqs 4 and 6, respectively, with the results of a hypothetical scanning calculation. Obviously, the procedure has been unable to converge on the proper entropy. In fact, it becomes obvious that this example has much in common with the naive scanning of the above Ising model example. When the scanning procedure lays down the first chain, it "thinks" it is being asked to construct an isolated self-avoiding walk. So, for example, in the first chain, entropy is accumulated at the rate of $\ln(4.68) = 1.54$, where 4.68 is the "connectivity constant" of this lattice,[32-34] significantly greater than the correct value of about 0.73 (see above). When it lays down the last chain, it "thinks" it is being asked to construct a chain in a confined environment of other chains having frozen-in structure, which is not the same problem as a chain in the melt. Never does it "know" what sort of system we want it to produce.

C. Isolated Self-Avoiding Walks. The scanning method was first applied to isolated self-avoiding walks, and a number of successful simulations have been reported. However, it is obvious that even this application cannot be entirely valid. Near the outset of chain growth, the procedure "thinks" it is being asked to grow a short chain, and it will converge on such a structure. Furthermore, it never "knows" exactly how long the resultant chain is going to be. Obviously, the resulting chain cannot have end-

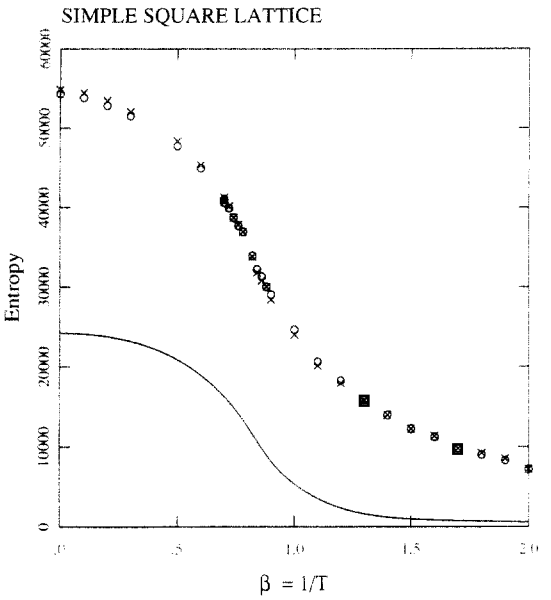

Figure 8. Entropy vs reciprocal temperature for the simple-square chain system. The solid curve represents eq 4. Symbols represent the results of hypothetical scanning. Displayed values are the results of extrapolations in $1/m$ to $m = \infty$, using m values of 1 through 6 (×) or 3 through 6 (○).

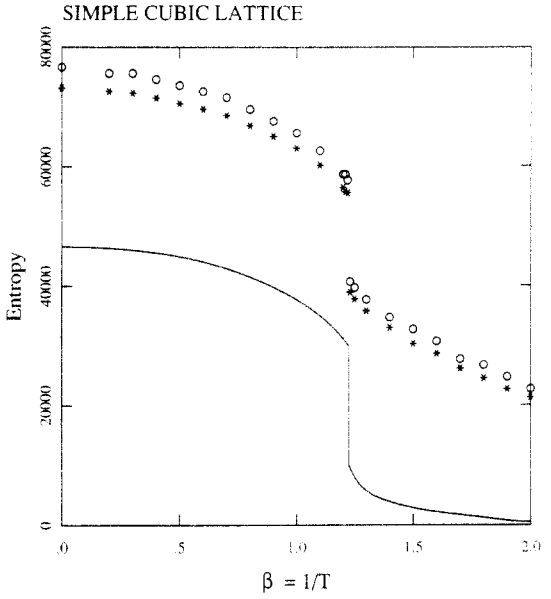

Figure 9. Entropy vs reciprocal temperature for the simple-cubic chain system. The solid curve represents eq 6. Symbols represent the results of hypothetical scanning: (*) scanning at $m = 5$; (○) extrapolations in $1/m$ to $m = \infty$ using entropy values scanned at $m = 3$, 4, and 5.

to-end symmetry, the terminal half will be more extended than the initial half. The resultant entropy should also contain systematic errors. The effect may in fact be weak, requiring extensive computation to detect, since the complicating interactions are at their weakest with self-avoiding walks. Undoubtedly, this accounts for the reported successes of the technique when applied to the problem of self-avoiding walks.

Obviously, the only scanning procedures which can be completely trusted are those in which later parts of the simulation do not interact with earlier ones, as in the transfer matrix example producing eq 12. This does not include any of the applications to which it is currently being made.

6. Conclusions

The thermodynamic properties of condensed, semiflexible lattice polymers on both the simple cubic and simple square lattices have been determined by computer simulation. In three dimensions, the system exhibits a first-order order–disorder transition similar to the freezing transition of real polymers. In two dimensions, the order–disorder transition is second-order and critical. There must certainly also be a relationship between the order–disorder transition considered here and the isotropic-nematic liquid crystal transition. In that regard, it is interesting to note an old prediction[35,36] that the two-dimensional isotropic–nematic transition is also second order.

These results permit a critical analysis of the scanning procedure for simulating the entropy of lattice polymer systems. We find that the scanning procedure is not trustworthy if interactions exist between parts of the system constructed at widely different times. Most significantly, the approach is not expected to be valid for any of the systems to which it is routinely applied. However, results for isolated, self-avoiding walks may still be at least approximately correct.

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