

Assumption of separability of the excluded-volume interaction in polymer physics: Flory-Huggins theory reviewed

Somendra M. Bhattacharjee

Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

(Received 13 December 1985)

Rotational isomerism and the excluded-volume interaction are generally considered to be the two major factors in polymer crystallization, glass transition, etc. The calculations supporting this belief are based on the assumption that the contribution to the free energy from the excluded-volume interaction is separable from the rest of the interactions. This separability assumption is studied here by mapping a single-polymer-chain problem to a spin problem with a cluster interaction. Using a variational principle, which provides an upper bound to the free energy, it is shown that the separability assumption gives a qualitatively incorrect description of the system in the low-temperature region. The consequences of this result for general models are also discussed.

I. INTRODUCTION

The Flory-Huggins theory is the starting point¹ for many calculations involving polymers if the excluded-volume interaction plays a crucial role in determining the behavior of the system. This theory is generally considered to be the mean-field theory¹ for polymers. In this paper, we study the basic assumption of this theory as applied to semiflexible chains.

The configuration of a large, completely flexible polymer chain of N monomers can be described¹ by a self-avoiding walk (SAW) on a lattice where the walker takes steps to the nearest neighbors with equal probability, with the restriction that a site once visited cannot be visited again. (Stepping to any nearest neighbor with equal probability models the free rotation of a bond in the chain; the self-avoiding restriction models the excluded-volume (EV) interaction.) However, for a real polymer chain, because of steric hindrances, equal probabilities are not expected. As shown in Fig. 1, the potential energy² of a bond for a polyethylene ($-\text{CH}_2-\text{CH}_2-$) chain has three minima.

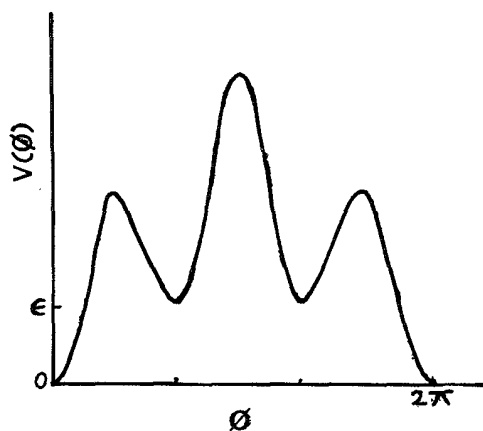


FIG. 1. Schematic representation of the potential energy of a C—C bond in a polyethylene chain as a function of the rotation angle ϕ . The energy difference ϵ between the two minima is generally of the order of 0.5 kcal per mole (Ref. 2).

For simplicity, one replaces the potential by a three-state model, one with zero energy (the trans state) and two high-energy gauche states [the number (> 1) of which is not crucial]. Such a model of a polymer chain where different directions have different energies is called the rotational isomeric model.

On a lattice, the lack of flexibility (and hence the name semiflexibility) in the rotational isomeric model can be introduced by taking the forward step as the trans state and all other steps as the gauche states. The ground state of this model consists of a rodlike configuration where the chain is in the all-trans state. At any nonzero temperature, if the excluded volume interaction is ignored, the size of such a semiflexible chain as measured, say, by the mean end-to-end distance, in the limit of $N \rightarrow \infty$, is similar to that of a free random walk on the lattice.³ However, nontrivial temperature effects occur^{1,4} when the excluded volume interaction is taken into account.

Using the Flory-Huggins approximation^{4,5} for semiflexible chains with the EV interaction, one finds a first-order transition (see Sec. II). For a many-chain system, the high-temperature phase is an isotropic phase where the chains are in a coiled state, but in the low-temperature phase they are rodlike in the all-trans state. For a single chain covering the whole lattice, the low-temperature phase is an inactive phase where the chain is in its ground state at all temperatures below the transition temperature T_c . The chain is in a disordered state only at temperatures above T_c . This low-temperature phase is identified^{4,5} as the crystalline phase of polymers.

The crucial assumption in the Flory-Huggins approximation, clearly stated by Flory,⁵ is the *separability* of the excluded-volume contribution to the partition function from the rotational isomeric contribution (see Sec. II). This separability assumption was also used by Gibbs and DiMarzio⁶ to show the existence of a glass transition in a polymeric system. Thanks to these early successes (and to the intuitive understanding⁷ of how rotational isomerism and the EV interaction can lead to crystallization and/or a glassy state), a wide variety of problems, including liquid-crystalline transitions in polymers,⁸ have been stud-

ied by using this assumption.

The validity of the Flory-Huggins theory has been questioned⁹⁻¹² in the past. Nagle's criticism⁹ was based on the results of a few exactly solvable models of statistical mechanics. Although some of these models do exhibit a frozen low-temperature behavior, the one which is the best analog of polymers, the F model, shows a completely different type of phase transition (an "infinite-order" transition; the free energy has a natural boundary at the critical point, and there is no frozen behavior¹³). A more direct way of questioning the validity of this theory was the construction of an upper bound^{10,11} for the free energy of the polymer chain. On a finite lattice, in the close-packed limit, certain configurations with a known density of gauche states are constructed. Since these states do not include all the allowed configurations, one gets a lower bound for the entropy and an upper bound for the free energy. For a frozen state, the free energy is zero and lies above this bound. Such an analysis argues against a low-temperature frozen phase but cannot rule out the possibility of a phase transition. This is yet to be done.¹⁴

The Flory-Huggins theory, as already mentioned, is considered^{1,4-7} to be the mean-field theory for polymeric systems. The mean-field theory in critical phenomena is well understood in the sense that there are models for which it is exact.¹⁵ In contrast, no polymeric model is known for which the Flory-Huggins theory can be considered to be exact. In such a situation, we would like to know why this theory can be wrong. We wish to study a problem that can be handled rigorously, even in the thermodynamic limit,¹⁶ and that is also easy enough for intuitive understanding. We emphasize that we are proposing neither a model nor a method for studying the ordering transition of polymer chains.

In this paper, the simplest problem of a single semiflexible polymer chain on an infinite lattice is considered and it is shown that the separability assumption leads to *inconsistencies*. This is done by mapping the polymer problem into a spin problem in Sec. III. In Sec. IV, we study the spin Hamiltonian by using the separability assumption. A variational principle¹⁷ is used in Sec. V to obtain an upper bound for the free energy. The results are summarized and discussed in Sec. VI. For completeness, the Flory-Huggins approximation is discussed in Sec. II, where the separability assumption is also explained.

II. CLASSICAL FLORY-HUGGINS APPROXIMATION

The classical Flory-Huggins approximation⁴ can be used to study the many-chain problem on a lattice. For simplicity, we consider the case of a single chain covering the whole lattice. The chain visits every site of the lattice and no site is visited more than once. This is the Hamilton walk problem of graph theory.¹⁸

The partition function one wants to calculate is given by

$$Z = \sum \exp(-n\beta\epsilon), \quad (2.1)$$

where $\beta = (k_B T)^{-1}$, k_B is Boltzmann's constant, ϵ is the energy of a gauche state, and n is the number of gauche

states in a particular configuration. The sum in (2.1) is over all Hamilton walks. The *separability assumption* can be stated as⁵

$$Z = Z_{EV} Z_{rot} \quad (2.2)$$

or, equivalently

$$F = F_{EV} + F_{rot}, \quad (2.3)$$

where the free energy F is related to the partition function via the relation $F = -k_B T \ln Z$. In (2.2) and (2.3), Z_{EV} and F_{EV} refer to the EV interaction, and Z_{rot} and F_{rot} refer to rotational isomerism. This is not a simple-minded factorization of the partition function; such a factorization would involve a double counting of states. As explained below, Z_{EV} contains only the part responsible for the changes in the behavior of the system when the excluded-volume interaction is turned on.

For a chain of N steps, the partition function for the rotational isomeric part is given by

$$Z_{rot} = (1 + pe^{-\beta\epsilon})^N, \quad (2.4)$$

because the steps, in the absence of the EV interaction, are independent of each other. Here, p is the number of gauche states available to the chain at each step.

To obtain Z_{EV} or F_{EV} in (2.2) or (2.3), note that on a lattice the EV interaction involves no energy; rather its inclusion reduces the number of configurations available to the chain. In other words, F_{EV} is purely entropic in character. If F_{RW} is the free energy of an N -step random walk and F_{HW} is that of the corresponding Hamilton walk, then F_{EV} is taken as

$$F_{EV} = F_{HW} - F_{RW}. \quad (2.5)$$

The subtraction in (2.5) is necessary because F_{rot} in (2.4) already contains the random-walk part as the $T \rightarrow \infty$ limit. Since the entropy of a Hamilton walk is necessarily less than that of a random walk,

$$F_{EV} > 0. \quad (2.6)$$

Unfortunately, F_{EV} cannot be calculated exactly. Since F_{EV} is purely entropic in nature, we can write it as

$$F_{EV} = Nk_B T c, \quad (2.7)$$

with c as a positive constant. Various approximate values of c are known.^{5,9,11,19} The simple-minded Flory approximation gives $c = 1$ for any lattice whereas the improved Huggins approximation gives

$$c = \frac{1}{2}(q-2)\ln[q/(q-2)]$$

for a lattice of coordination number q . For a square lattice, rigorous bounds for the entropy of a Hamilton walk are known,¹¹ and the improved Huggins approximation lies within those bounds. This just shows that the approximations made to obtain the above values are not the root of the problems mentioned in the Introduction.

Using (2.4) and (2.7) in (2.3), the free energy per monomer is obtained as

$$f \equiv \frac{F}{N} = k_B T [c - \ln(1 + pe^{-\beta\epsilon})]. \quad (2.8)$$

That there exists at least one ground state with zero energy implies

$$f \leq 0. \quad (2.9)$$

However, since $c > 0$ [see Eq. (2.7)], the free energy in (2.8) becomes positive for $T < T_c$, where T_c is determined by

$$c = \ln \left[1 + p \exp \left[-\frac{\epsilon}{k_B T_c} \right] \right]. \quad (2.10)$$

In other words, below T_c the ground state is thermodynamically the stable phase. The polymer chain is in a disordered, coiled state at high temperatures but is frozen in the ground state at all temperatures below the transition temperature T_c .

This result has been interpreted^{5,7} as a consequence of the packing problem. Below a certain density of gauche states (the density at $T = T_c$), the number of ways of packing the chain is not large enough to contribute significantly to the thermodynamics of the system (i.e., the number grows less rapidly than exponentially as $N \rightarrow \infty$).

III. THE MODEL

Let us consider a long polymer chain represented by a random walk on a simple-cubic lattice. The steps of the walker correspond to the bonds of the polymer chain. If the bonds of the chain are represented by the vectors \mathbf{S}_i , as in Fig. 2(a), then the rotational isomeric energy can be represented by

$$\epsilon - \epsilon \mathbf{S}_i \cdot \mathbf{S}_{i+1}, \quad (3.1)$$

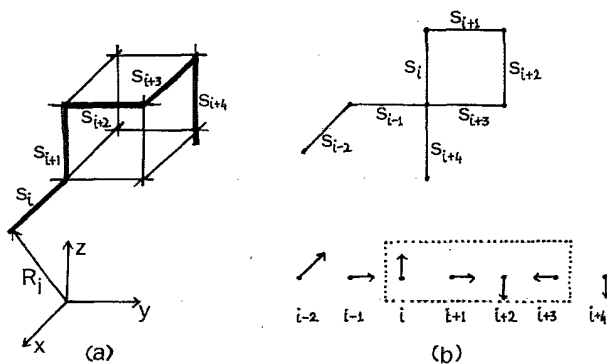


FIG. 2. (a) Model of the polymer chain. The bonds are of unit length and can point in six possible directions on a simple-cubic lattice. Rotational isomerism is considered by taking a potential energy of the form $\epsilon - \epsilon \mathbf{S}_i \cdot \mathbf{S}_{i+1}$ for two successive bonds \mathbf{S}_i and \mathbf{S}_{i+1} . This interaction favors a rodlike configuration over a random one, the latter being the favorable arrangement from the entropic point of view. The position of the i th monomer is represented by \mathbf{R}_i from an arbitrarily chosen origin. (b) Spin representation of the model in (a). The spins are the bond vectors \mathbf{S}_i . The excluded-volume interaction, in the strict sense, would forbid a configuration shown here because of the overlap of the i and $i+4$ monomers. For the spin model, the magnetization of the cluster, set off by the dotted line, is zero. The strict excluded-volume interaction is replaced by a softer one which penalizes such configurations over the ordered ones but still does not exclude them.

where each \mathbf{S}_i can have six possible orientations ($\pm x, \pm y, \pm z$). For simplicity, we shall take $|\mathbf{S}_i| = 1$. For a trans configuration, two successive bonds (\mathbf{S}_i and \mathbf{S}_{i+1}) have to be in the same direction and, by (3.1), the energy will be zero. For a gauche state, \mathbf{S}_i and \mathbf{S}_{i+1} are mutually perpendicular to each other and so the energy is ϵ , as defined in the Introduction. One should note here that the form of energy in (3.1) allows immediate reversal of a bond when \mathbf{S}_i is antiparallel to \mathbf{S}_{i+1} . As will be seen below, this minor change of the model of Sec. II is of no significance.²⁰ The total energy for $N+1$ bonds is obtained by summing over all bonds as

$$H_{\text{rot}} = N\epsilon - \epsilon \sum_{i=1}^N \mathbf{S}_i \cdot \mathbf{S}_{i+1}. \quad (3.2)$$

Note that the energy of the ground state is zero.

The form of the Hamiltonian in (3.2) permits a random configuration of the chain in which a lattice site can be visited more than once by the walker. The excluded volume interaction can be incorporated by excluding those configurations which involve multiple occupancy. However, to make the analysis tractable, we choose a softer form²¹ of the EV interaction for which the configurations with multiple occupancy are penalized but not excluded. This is done by adding to (3.2) an energy term of the type $+mw$ where m is the number of contacts for a particular configuration and w is the energy per contact ($w > 0$). If \mathbf{R}_i and \mathbf{R}_j are the absolute positions of the walker at the i th and j th steps, respectively, then an overlap occurs when

$$\mathbf{R}_i - \mathbf{R}_j = 0, \quad (3.3)$$

or, in terms of the bond vectors \mathbf{S}_p ,

$$\sum_{p=i}^{j-1} \mathbf{S}_p = 0. \quad (3.4)$$

To obtain (3.4) from (3.3) one should note that $\mathbf{R}_j = \mathbf{R}_i + \sum_{p=i}^{j-1} \mathbf{S}_p$ because of the connectivity of the chain. Using (3.4), the "excluded-volume" part of the energy can be written as

$$H_{\text{ex}} = w \sum_{\substack{i,j \\ (i < j)}} \delta \left[\sum_{p=i}^{j-1} \mathbf{S}_p, 0 \right], \quad (3.5)$$

where $\delta(a, b)$ is the Kronecker δ , defined as

$$\delta(a, b) = \begin{cases} 1 & \text{if } a = b, \\ 0 & \text{if } a \neq b. \end{cases} \quad (3.6)$$

The total Hamiltonian is given by

$$\begin{aligned} H &= H_{\text{rot}} + H_{\text{ex}} \\ &= N\epsilon - \epsilon \sum_{i=1}^N \mathbf{S}_i \cdot \mathbf{S}_{i+1} + w \sum_{\substack{i,j \\ (i < j)}} \delta \left[\sum_{p=i}^{j-1} \mathbf{S}_p, 0 \right]. \end{aligned} \quad (3.7)$$

For $w = 0$, (3.7) reduces to H_{rot} which corresponds to a weighted random walk. For $w \rightarrow \infty$, the partition function has contributions only from those configurations for which there is no overlap; this is the SAW limit.

The Hamiltonian in (3.7) can be interpreted as the

Hamiltonian for a one-dimensional spin system as shown in Fig. 2(b). This means that the thermodynamics of the polymer chain on a hypercubic lattice in d dimensions is formally equivalent to that of a d -component spin system arranged in a one-dimensional array. Each spin, because of the choice of the cubic lattice, can only point in $2d$ allowed directions (i.e., along the Cartesian axes). These spins \mathbf{S}_i interact via the usual¹⁵ nearest-neighbor ferromagnetic interaction (H_{rot} , apart from a constant term). In addition, there is a cluster interaction which contributes only if the cluster is disordered ($\sum \mathbf{S}_p = 0$, i.e., no magnetization). Summing over all the clusters in (3.5) means penalizing the states which are disordered at all length scales. For H_{rot} , the ground state consists of well-ordered spins and has zero energy. Since for this state there is no overlap, the ground state of the total Hamiltonian in (3.7) also has zero energy. One can also see that an ordering transition for the polymer chain implies a magnetic transition in the spin system. This equivalence is shown below.

For a polymer, one generally calculates¹ the end-to-end distance

$$\mathbf{R} = \sum_{p=1}^{N+1} \mathbf{S}_p. \quad (3.8)$$

If, for large N , the exponent ν describes the mean end-to-end distance as

$$\langle R^2 \rangle^{1/2} \sim N^\nu \quad (3.9)$$

then, it is known¹ that

$$\nu = \frac{1}{2}, \quad (3.10a)$$

for a random walk, but

$$\nu \approx \frac{3}{d+2}, \quad (3.10b)$$

for a SAW or for H_{ex} of (3.5) in d dimensions ($d < 4$).²² In the spin language, $\langle R^2 \rangle^{1/2}$ is the total magnetization so that, in the limit of $N \rightarrow \infty$, the magnetization per spin is

$$m = \lim_{N \rightarrow \infty} \left[\frac{\langle R^2 \rangle^{1/2}}{N} \right] = 0, \quad (3.11)$$

because, from (3.10), $\nu < 1$. However, if the polymer is rodlike, as in the low-temperature phase in the Flory-Huggins approximation, then $\langle R^2 \rangle^{1/2} \sim N^2$, and $\nu = 1$. In such a case, there will be a net magnetization in the system with a nonzero average of each spin \mathbf{S}_i .

It is well known¹⁵ that with just H_{rot} , there cannot be a phase transition in the spin system because the interaction is short ranged. This is just a restatement of the already mentioned fact³ that the size of a semiflexible chain has the same scaling behavior [e.g., Eq. (3.9)] as a completely flexible chain. The question one then asks is this: When H_{ex} is added to H_{rot} as in (3.7), can there be a transition to a well-ordered state in the low-temperature region?

IV. SEPARABILITY APPROXIMATION

To study the Hamiltonian in (3.7) using the separability assumption of Sec. II, we need to evaluate (1) F_{rot} from H_{rot} in (3.2), and (2) F_{EV} from H_{ex} . These are done separately below.

A. Evaluation of F_{rot}

The partition function for H_{rot} can be obtained by the transfer matrix¹⁵ method. The free energy in the limit of large N is given by

$$f_{\text{rot}} \equiv \lim_{N \rightarrow \infty} \frac{F_{\text{rot}}}{N} = -k_B T \ln [1 + (q-2)e^{-\beta\epsilon} + e^{-2\beta\epsilon}]. \quad (4.1)$$

Equations (4.1) and (2.4) differ by the term $e^{-2\beta\epsilon}$. This term arises from the backward steps which are allowed in (3.2). These steps cost an energy 2ϵ .

B. Evaluation of F_{EV}

The free energy due to H_{ex} in (3.6) is not known in a closed form. As will be seen below, an explicit form of F_{EV} is not necessary for the conclusion we will draw. We therefore do not attempt to get a closed form for F_{EV} .

For any finite chain with N bonds, the partition function for H_{ex} is given by

$$Z_N(x) = \sum_m C_{Nm} x^m, \quad (4.2)$$

where $x = e^{-\beta w}$ and C_{Nm} is the number of N -step random walks with m contacts. Since we are interested in the range $0 < w < \infty$, x lies between

$$0 \leq x \leq 1. \quad (4.3)$$

One recovers the random-walk result for $x = 1$ and the SAW result for $x = 0$. For a random walk on a lattice of coordination number q ,

$$Z_N(1) = q^N, \quad (4.4)$$

for any N . In the SAW limit, for $N \rightarrow \infty$, it is known^{1,22} that

$$Z_N(0) \approx C \mu_0^N N^\gamma, \quad (4.5)$$

where C is a constant independent of N , μ_0 is the effective coordination number ($\mu_0 < q$), and γ is a universal exponent depending only on the dimensionality of the lattice.

Using (4.3) and the positivity of the summand in (4.2), one has the basic inequality

$$\frac{1}{N} \ln Z_N(0) \leq \frac{1}{N} \ln Z_N(x) \leq \frac{1}{N} \ln Z_N(1) = \ln q. \quad (4.6)$$

In the limit of $N \rightarrow \infty$, we have, from (4.5),

$$\ln \mu_0 \leq \lim_{N \rightarrow \infty} \frac{1}{N} \ln Z_N(x) \leq \ln q. \quad (4.7)$$

Assuming that the limit exists, we define $\mu(x)$ by

$$\ln \mu(x) = \lim_{N \rightarrow \infty} \frac{1}{N} \ln Z_N(x), \quad (4.8)$$

where $\mu(x)=\mu_0$ for $x=0$ and $\mu(x)=q$ for $x=1$. In terms of this function, the free energy is given by

$$f_{\text{ex}} = -k_B T \ln \mu(x). \quad (4.9)$$

Therefore, the excluded volume part of the free energy per monomer, as explained in Sec. II, is given by

$$f_{\text{EV}} = k_B T \ln \frac{q}{\mu(x)}. \quad (4.10)$$

C. Total free energy

The free energy per monomer for the Hamiltonian of (3.7) under the separability assumption is obtained by adding (4.10) and (4.11) as

$$f = k_B T \left[\ln \frac{q}{\mu(x)} - \ln [1 + (q-2)e^{-\beta\epsilon} + e^{-2\beta\epsilon}] \right]. \quad (4.11)$$

In the SAW limit with $w \rightarrow \infty$, we see that the free energy becomes positive at a temperature T_c , which is given by

$$\frac{q}{\mu_0} = 1 + (q-2)e^{-\beta_c\epsilon} + e^{-2\beta_c\epsilon}. \quad (4.12)$$

For a simple-cubic lattice,¹ for example, $q=6$ and $\mu_0=4.68$. The corresponding free energy is shown in Fig. 3. For a finite w , $q/\mu(x) > 1$, and $\mu(x)$ is a monotonically decreasing function of temperature. In such a case, f becomes positive at a temperature $T_c(w)$ given by

$$\frac{q}{\mu(x_c)} = 1 + (q-2)e^{-\beta_c\epsilon} + e^{-2\beta_c\epsilon}. \quad (4.13)$$

We therefore find that there exists a w -dependent critical temperature $T_c(w)$ below which the ground state is thermodynamically the stable phase, just as we found for the Hamilton walk problem in Sec. II.

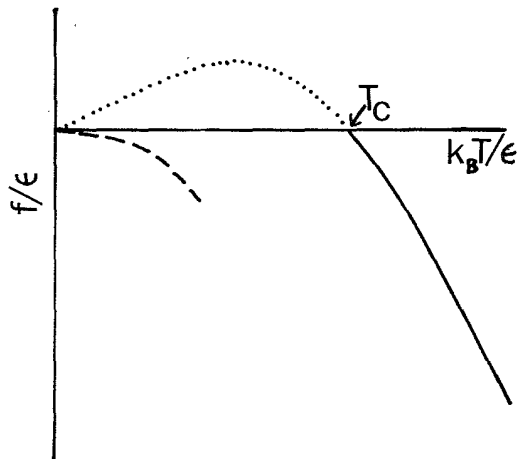


FIG. 3. Free energy for a simple-cubic lattice, obtained by using the separability assumption, is shown as a function of temperature ($k_B T/\epsilon$), by the thick line. The dotted line is the extension of the high-temperature phase to $T < T_c = 0.375\epsilon/k_B$. This part is unstable because of the existence of the ground state with lower free energy. The dashed line is a schematic drawing of the upper bound obtained in Sec. V.

V. UPPER BOUND FOR THE FREE ENERGY USING A VARIATIONAL PRINCIPLE

The variational principle¹⁷ in statistical mechanics states that for any trial Hamiltonian \hat{H} , one has

$$F \leq \hat{F} + \langle H - \hat{H} \rangle_{\hat{H}}, \quad (5.1)$$

where \hat{F} is the free energy for \hat{H} and $\langle \dots \rangle_{\hat{H}}$ is the average taken with the Hamiltonian \hat{H} . An upper bound for F can then be obtained by minimizing the right-hand side of (5.1) with respect to a parameter in the trial Hamiltonian.

We choose an independent spin Hamiltonian of the form

$$\hat{H} = \mathbf{h} \cdot \sum_{i=1}^{N+1} \mathbf{S}_i, \quad (5.2)$$

with \mathbf{h} in the z direction. For this \hat{H} , we have, in d dimensions,

$$\hat{F} = -(N+1)k_B T \ln \left[2(d-1) + 2 \cosh \left[\frac{h}{k_B T} \right] \right] \quad (5.3)$$

and

$$\langle \hat{H} \rangle_{\hat{H}} = -(N+1)h\mathcal{M}, \quad (5.4)$$

where $\mathcal{M} = \langle S_{iz} \rangle_{\hat{H}}$ is the net magnetization per spin in the z direction; it is given by

$$\mathcal{M} = \frac{\sinh(h/k_B T)}{(d-1) + \cosh(h/k_B T)}. \quad (5.5)$$

A. Evaluation of $\langle H \rangle_{\hat{H}}$

To evaluate the average of H with respect to \hat{H} , we consider H_{rot} and H_{ex} separately. Since the spins in the trial Hamiltonian are independent, we have

$$\langle H_{\text{rot}} \rangle_{\hat{H}} = N\epsilon - N\epsilon\mathcal{M}^2. \quad (5.6)$$

For $\langle H_{\text{ex}} \rangle_{\hat{H}}$, let us consider one particular cluster of size r and find the average of $\delta(\sum \mathbf{S}_p, 0)$. By definition,

$$\left\langle \delta \left[\sum \mathbf{S}_p, 0 \right] \right\rangle_{\hat{H}} = \frac{\sum \delta \left[\sum \mathbf{S}_p, 0 \right] e^{-\beta \hat{H}}}{\hat{Z}^{N+1}}, \quad (5.7)$$

where

$$\hat{Z} = 2(d-1) + 2 \cosh(h/k_B T), \quad (5.8)$$

is the single-spin partition function for the trial Hamiltonian. When summed over different configurations, there is a contribution to the sum in (5.7) only when the magnetization of the cluster is zero. If P_r denotes the number of ways a random walker, which starts from an arbitrarily chosen point on the underlying lattice of the polymer chain, comes back to that point in r steps, then

$$\left\langle \delta \left[\sum S_p, 0 \right] \right\rangle_{\hat{H}} = \frac{P_r}{\hat{Z}^r} \quad (5.9)$$

Using (5.9) and also taking advantage of the translational invariance, we have

$$\lim_{N \rightarrow \infty} \frac{1}{N} \langle H_{\text{ex}} \rangle_{\hat{H}} = w \sum_{r=2}^{\infty} \frac{P_r}{\hat{Z}^r} \quad (5.10)$$

If we define the generating function for P_r by

$$P(x) = \sum P_r x^r, \quad (5.11)$$

we have

$$\lim_{N \rightarrow \infty} \frac{1}{N} \langle H_{\text{ex}} \rangle_{\hat{H}} = wP(\hat{Z}^{-1}). \quad (5.12)$$

For a simple-cubic lattice, the generating function $P(x)$ is given by^{23,24}

$$P(x) = \int d^3k [1 - x\lambda(\mathbf{k})]^{-1}, \quad (5.13)$$

with $\lambda(\mathbf{k}) = 2(\cos k_x + \cos k_y + \cos k_z)$. Combining (5.3), (5.4), (5.5), and (5.10), we obtain

$$\begin{aligned} f^* &\equiv \lim_{N \rightarrow \infty} \frac{1}{N} (\hat{F} + \langle H - \hat{H} \rangle_{\hat{H}}) \\ &= \hat{f} - \varepsilon \mathcal{M}^2 + wP(\hat{Z}^{-1}) + h\mathcal{M} + \varepsilon. \end{aligned} \quad (5.14)$$

Minimizing f^* with respect to h , one obtains

$$h = g(\beta h) \equiv 2\varepsilon \mathcal{M} + w\mathcal{M} \left[\frac{\partial \mathcal{M}}{\partial (\beta h)} \right]^{-1} \sum \frac{rP_r}{\hat{Z}^r}. \quad (5.15)$$

The last term on the right-hand side of (5.15) is an extra term to the usual mean-field solution¹⁵ of the nearest-neighbor spin model (H_{rot}) from the excluded-volume part of the Hamiltonian in (3.7).

The solution of (5.15), when substituted in (5.14), gives the upper bound for the free energy for the Hamiltonian in (3.7). The solution is given by the intersection of $y = k_B T x$ with $y = g(x)$, where $x = \beta h$. One can very easily see that $g(x) \rightarrow 2\varepsilon$ as $x \rightarrow \infty$. For $T \rightarrow 0$, the intersection is obviously at large values of x (ignoring the trivial solution at $x = 0$) so that a first-order iterative solution is

$$h = 2\varepsilon + (2wP_2 - 4\varepsilon)e^{-2\varepsilon/k_B T}, \quad (5.16)$$

for a simple-cubic lattice. Substituting this h in (5.14), one has, asymptotically close to $T = 0$,

$$f^* \approx -4k_B T e^{-2\varepsilon/k_B T}. \quad (5.17)$$

Equation (5.15) can, in fact, be solved numerically to obtain the bound for all temperatures. However, Eq. (5.17) is good for our conclusion. It shows that, sufficiently close to $T = 0$, the free energy is *negative and nonzero*. This rules out the possibility of a frozen state in the low-temperature region.

VI. DISCUSSION

We have shown that the result based on the assumption of the separability of the rotational isomeric part and the excluded-volume interaction, as explained in Sec. II, is incorrect in the low-temperature region. Although the limit $w \rightarrow \infty$ in Eqs. (5.14) or (5.15) is not a sensible one, the bound in Eq. (5.17) is independent of w . This means that for any w , however large it may be, one can always find a range around $T = 0$ where (5.17) will be valid, thereby ruling out the possibility of a frozen phase. One way of seeing this is to start from the ground state where the chain is in the all-trans state. Local fluctuations, such as kinks, do not involve any overlap of the chain in this single-chain system and are, therefore, important for the low-temperature behavior of the chain. In other words, low-lying excitations of H_{rot} are also the low-lying excitations of the total Hamiltonian H in (3.7), and these states will always be excited at low temperatures. This is true even for the SAW limit ($w \rightarrow \infty$), because the self-avoiding constraint is not violated. This gives a justification for taking (5.17) as valid for the SAW limit. The variational principle alleviates the problem of taking the thermodynamic limit¹⁶ of $N \rightarrow \infty$ because the bound for the free energy is found to be proportional to the number of monomers—as it should be if a thermodynamic limit of the free energy exists.

We have not studied the possibility of a phase transition for Hamiltonian (3.7); it is not apparent that the mean-field solution of Sec. V can be trusted to address this question. Even if there is a phase transition, it is more gradual than that predicted by the separability assumption and the underlying mechanism has to be of different type than the instability of the high-temperature phase. Since the free energy in (4.11) has the same form as the Flory-Huggins result of Sec. II, which has been derived under the same assumption, any interpretation given to Eq. (2.8), for the Hamilton walk problem, should be applicable to Eq. (4.11). This questions the credibility of the usual interpretation^{5,7} of (2.8) as a packing problem. Our result suggests that the problem lies in the construction of the free energy. In fact, one may expect to see a first-order transition in almost all cases, even if it is not there, because of the two competing terms one obtains by using the separability assumption. The conclusion, therefore, is that the separability assumption cannot be given the status of a mean-field theory and that any prediction based on such a theory is likely to be incorrect.

ACKNOWLEDGMENTS

I am indebted to Sudha Murthy for helpful discussions which initiated this research. Thanks are also due to J-S. Ho, Julie Johnson, M. Muthukumar, J. F. Nagle, and Scott K. Starry for discussions and/or comments on the manuscript. This research is supported by the National Science Foundation (NSF) Grant No. DMR-8420962.

- ¹P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).
- ²M. V. Volkenstein, *Configurational Statistics of Polymer Chains* (Interscience, New York, 1963).
- ³M. N. Barber and B. W. Ninham, *Random and Restricted Walks: Theory and Applications* (Gordon and Breach, New York, 1970).
- ⁴P. J. Flory, Proc. R. Soc. London, Ser. A 234, 60 (1956); M. L. Huggins, Ann. N. Y. Acad. Sci. 43, 1 (1942).
- ⁵P. J. Flory, Proc. Natl. Acad. Sci. U.S.A. 79, 4510 (1982).
- ⁶J. H. Gibbs and E. A. DiMarzio, J. Chem. Phys. 28, 373 (1958).
- ⁷E. A. DiMarzio, Ann. N.Y. Acad. Sci. 371, 1 (1981).
- ⁸A. R. Khokholov and A. N. Semenov, J. Stat. Phys. 38, 161 (1985); G. Ronca and D. Y. Yoon, J. Chem. Phys. 76, 3295 (1982); P. J. Flory, Adv. Poly. Sci. 59, 1 (1984).
- ⁹J. F. Nagle, Proc. R. Soc. London, Ser. A 337, 569 (1974).
- ¹⁰P. D. Gujrati, J. Phys. A 13, L437 (1980).
- ¹¹P. D. Gujrati and M. Goldstein, J. Chem. Phys. 74, 2596 (1981).
- ¹²J. F. Nagle, P. D. Gujrati, and M. Goldstein, J. Phys. Chem. 88, 4599 (1984).
- ¹³For a review, see E. H. Lieb and F. Y. Wu, in *Phase Transition and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London, 1972), Vol. 1. The correspondence between the F model and the polymer chain requires the existence of a few short loops (see Fig. 6 of Ref. 9) which have been assumed to be unimportant. However, because of the similarity between the F -model phase transition and the Kosterlitz-Thouless transition (see, e.g., H. J. F. Knops, in *Fundamental Problems in Statistical Mechanics V*, edited by E. G. D. Cohen (North-Holland, Amsterdam, 1980), it remains to be seen whether the closed loops are really unimportant.
- ¹⁴The series expansion method has been attempted [R. G. Petschek, Phys. Rev. B 32, 474 (1985)], but the series is too small for any prediction. Computer simulations also failed to come up with a definite answer. See, e.g., A. Baumgartner and D. Y. Yoon, J. Chem. Phys. 79, 521 (1983); R. G. Petschek, *ibid.* 81, 5210 (1984).
- ¹⁵H. E. Stanley, *Phase Transition and Critical Phenomena* (Oxford University Press, New York, 1971).
- ¹⁶Reference 5, for example, questions the applicability of the methods of Refs. 10 and 11 in the thermodynamic limit of $N \rightarrow \infty$.
- ¹⁷R. P. Feynman, *Statistical Mechanics* (Cummings, Reading, MA, 1982).
- ¹⁸J. A. Bondy and U. S. R. Murty, *Graph Theory with Applications* (North-Holland, New York, 1976).
- ¹⁹H. Orland, C. Itzykson, and C. de Dominicis, J. Phys. Lett. (Paris) 46, 353 (1985). The field theoretical technique used in this paper gives $c = \ln[e(q-1)/q]$.
- ²⁰The strict EV interaction automatically forbids such a configuration. However, the softer form chosen in this paper [Eq. (3.5)] does not exclude it.
- ²¹C. Domb and G. S. Joyce, J. Phys. C 5, 956 (1972).
- ²²C. Domb, J. Stat. Phys. 30, 425 (1983).
- ²³E. W. Montroll and G. Weiss, J. Math. Phys. 6, 167 (1965).
- ²⁴This is the place where the infinite extent of the underlying lattice is explicitly used. For finite lattices, one would have to do a sum over the reciprocal vectors instead of the integral.