*Journal of Statistical Physics, Vol. 28, No. 3, 1982*

# Lower Bounds on Entropy for Polymer Chains on a Square and a Cubic Lattice

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*Received June 5, 1981*

Rigorous lower bounds on the entropy per particle as a function of the fraction $g$ of the *gauche* bonds of a system of semiflexible polymer chains is obtained in the thermodynamic limit. Only square and cubic lattices are considered. For the case of a single chain having $l$ monomers, the bound is obtained for all $g \leqslant \tilde{g} = 2/3$. For the case of $p > 1$ chains, each having $l$ monomers, where $l$ is a multiple of 4, the bound is obtained for all $g \leqslant \tilde{g}' = 13/90$. In both cases, it is shown that the entropy is always *nonzero* for all $0 < g < g_m(l)$, where $g_m(l) = (l-2)/l$. This *contradicts* the prediction from the Flory–Huggins approximations that the entropy is zero for all $g \leqslant g_0$, where $g_0$ is some finite nonzero number. It is also pointed out that it is *not* impossible to pack a lattice with "disordered" configurations of rodlike chains with finite entropy, again contradicting an assertion by Flory that it is impossible to do so. Finally, it is concluded that one *cannot* trust the Flory–Huggins approximations at least at low temperatures. The study also casts doubts on the validity of the Gibbs–DiMarzio theory of glass transitions in polymeric systems.

**KEY WORDS:** Polymer chains; gauche bonds; Flory–Huggins approximations; Hamilton walks; glass transition.

## 1. INTRODUCTION

The quasilattice model of Meyer,[1] Flory,[2] and Huggins[3] has been a standard and useful model in the understanding of the statistical mechanical properties of polymer systems. A polymer chain is assumed to be made up of $l$ monomer units (also called segments), all equal in size and also equal in size to that of a solvent molecule. A site of the lattice is either

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0022-4715/82/0700-0441$03.00/0 

occupied by a solvent molecule or by a segment. The segments of a polymer chain *must* occupy a continuous sequence of $l$ occupied sites connected by nearest-neighbor bonds. Excluded volume effects are taken into account by the requirement that a site can be occupied *only once*, either by a solvent molecule or by a segment. The central problem in the study of the statistical mechanics of polymers on a lattice is the calculation of the number $W_{p,l}$ where $W_{p,l}$ is the number of ways of putting $p$ polymer chains, each having $l$ segments on a lattice with $n = p \cdot l + n_0$ sites, $n_0$ being the number of solvent molecules. In the absence of an exact method to calculate $W_{p,l}$ for cases of interest, Flory[2,4,5] introduced an approximation to estimate this number. Huggins[3] introduced a refinement of this approximation that in some cases provides a better estimate of $W_{p,l}$. Common usage denotes both approximations collectively as Flory–Huggins approximations. These (F–H) approximations have been used extensively in the literature for various types of calculations and have been regarded as well established in that they provide qualitatively "correct" predictions.

It has been known for some time that the F–H approximations are inaccurate to varying degrees.[6] However, it has been pointed out only recently[7,8] that these approximations could not be trusted without serious reservations and could even be misleading in some cases. When the F–H approximations are applied[4,7,8] to the Flory Model[4] of semiflexible polymer chains, it is found that the model exhibits a first-order phase transition (curve $f_{FH}$, Fig. 1) from a completely ordered state, i.e., a crystal phase to a disordered phase at a finite temperature $T_c$. A special case of this model was considered in Refs. 7 and 8: a single polymer chain ($p = 1$) in the absence of any solvent molecules ($n_0 = 0$) on a square lattice. Since there are no solvent molecules, the polymer chain covers all the sites of the lattice. This limit of covering a lattice with a polymer chain, i.e., a

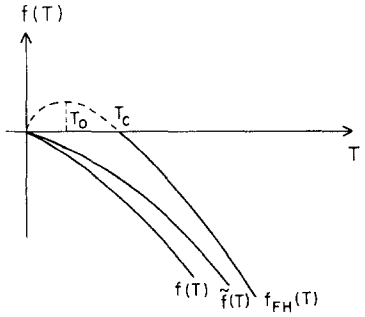


Fig. 1. Schematic representation of $f_{FH}(T)$, $\tilde{f}(T)$, and $f(T)$. The behavior of the actual free energy $f(T)$ is different from that of $f_{FH}(T)$.

self-avoiding walk, is known in the literature as the Hamilton walk limit.[9] A Hamilton circuit is a closed Hamilton walk. As usual, we relate self-avoiding walks on the lattice to possible configurations of the polymer chain, using the term *trans* to refer to two consecutive steps of such a walk in the same direction, and *gauche* to refer to two consecutive steps at right angles to each other, recognizing however, that our use of these terms does not correspond to their meanings in the actual geometry of a real polymer molecule. Since our objective is to test the validity of the F–H approximations, it is sufficient to apply these approximations to a square (or a cubic) lattice and compare their predictions with some rigorous results valid for this lattice. Let $g$ denote the fraction of the gauche bonds and $s(g)$ [this quantity was denoted by $s_H(g)$ in Refs. 7 and 8] the actual entropy per segment of the system in the thermodynamic limit. The quantity $s_{FH}(g)$ is the F–H estimate of $s(g)$ and $g_0$ is some positive nonzero number. It was established rigorously by direct analysis in Ref. 7 (for the sake of brevity, we will refer hereafter to Refs. 7 and 8 as I and II) that

$$\text{(i)} \qquad 0 < g < 1, \qquad s(g) > 0 \tag{1a}$$

$$\text{(ii)} \qquad s(g) \geqslant \tilde{s}(g) = (g/8)\ln(4/g - 3) \tag{1b}$$

where

$$g = 4/(m+3) \tag{1c}$$

Here $m$ is some nonzero positive integer. The above results (1a) and (1b) are contrary to the prediction from the F–H approximations that

$$s_{FH}(g) = 0 \qquad \text{for} \quad g \leqslant g_0 \tag{2}$$

with the value of $g_0$ depending on whether one uses the Flory or the Huggins approximation. The inequality (1) was demonstrated by explicit construction of the number of ways of putting the polymer chain on a square or a cubic lattice: the *trans* conformation was identified with two consecutive bonds being collinear and the *gauche* conformation was identified with two consecutive bonds at right angles. It was shown in II that the inequality (1b) can be improved, i.e., the lower bound for $s(g)$ can be raised to an even higher value [see (4), Section 2]. However, the lower bounds for $s(g)$ obtained in I and II were established for only certain values of $g$, given by (1c) for some integer $m$.

Our aim in the present paper is threefold. First, we wish to show that (1b) is a strict inequality for *all* continuous values of $g \leqslant \tilde{g} = 2/3$:

$$s(g) \geqslant \tilde{s}(g) \qquad \text{for} \quad g \leqslant \tilde{g} = 2/3 \tag{1d}$$

Our second aim is to extend the previous constructions of I and II to the case of many chains ($p > 1$), each $l$ segment long. (In the following, we will

call a polymer chain to be of length $l$ for short, even though the chain has only $l$ monomers and, therefore, is of length $l-1$.) We will again consider the case $n_0 = 0$. The thermodynamic limit on a square lattice is obtained by considering $n = \nu'^2 l^2$, $p = \nu'^2 l, \nu'$ an integer and taking $\nu' \to \infty$. On a cubic lattice, the limit is obtained by considering $n = \nu'^3 l^3$, $p = \nu'^3 l^2$, $\nu'$ an integer and taking $\nu' \to \infty$. We will establish rigorously that for $l = 4q$, where $q$ is some integer:

$$\text{(i)} \qquad 0 < g \leqslant g_m(l), \qquad s_l(g) \geqslant \tilde{s}_l(0) = (1/l^2)\ln 2 \tag{3a}$$

$$\text{(ii)} \qquad \forall g \leqslant \tilde{g}', \qquad s_l(g) \geqslant \tilde{s}_l(g) = \tilde{s}_l(0) + \tilde{s}(g) \tag{3b}$$

where $\tilde{s}(g)$ is given in (1b) and

$$\begin{aligned} g_m(l) &= (l-2)/l \\ \tilde{g}' &= 13/90 \end{aligned} \tag{3c}$$

Here $g_m(l)$ is the maximum possible value of $g$ that can be obtained as will be explained below (see Section 4), and $s_l(g)$ is the actual entropy per segment in the thermodynamic limit for a given value of $g$. For very small values of $g$ so that 3 can be neglected compared with $4/g$, (3b) reduces to (11) of I which was quoted there without any proof. Our final aim is to show that it is *possible* to pack a lattice with rigid rodlike polymers of finite lengths in a disordered manner. This is again in contradiction with the claim of Flory[4] that implies that it is impossible to pack a lattice with rodlike polymers in disordered configurations. Apart from the important consequences of (1) and (3) that have been discussed in detail previously,[7,8] such lower bounds on the entropy are of interest in themselves in the absence of exact enumeration methods to calculate $W_{p,l}$. The analysis again starts with the explicit construction and enumeration of a subset of $W_{p,l}$. The construction involves the following four main steps:

i. The lattice is divided into square cells of size $l \times l$.

ii. Each cell is covered by loops of some given sizes. The sizes of these loops determine the value of $g$. By a suitable choice of the sizes of these loops, one covers a *continuous* range for $g$.

iii. The loops are connected together to generate circuits, each one covering $l$ sites of the cell, in such a way that the total number of the corners can be counted exactly.

iv. Each circuit is then broken by deleting a bond without changing the number of the corners. The broken circuit is then identified as a possible configuration of a single polymer chain with $l$ monomers.

The construction obviously produces a lower bound for $W_{p,l}(G)$, where $W_{p,l}(G)$ is the number of ways of putting $p$ chains, each with $l$ segments so that the number of the *gauche* bonds is $G$. Using these lower

bounds, we show that both (3a) and (3b) are satisfied rigorously. The validity of (3) for $l \neq 4q$ will be reported elsewhere because of the complexity of the construction.

The layout of the paper is as follows. We revisit the case of a single polymer chain in Sections 2 and 3 and show that (1a) is valid for all *continuous* values of $g$. We also show that (1d) is valid for all $g \leqslant \tilde{g}$. In contrast, the constructions in I and II showed (1a) and (1b) to be valid only for certain discrete values of $g$. We also present in Section 2 a new construction for a single chain that is used to prove (1d). This construction is valid even when the length of the chain is finite. (In contrast, the construction in II is valid in the case when the chain length goes to infinity.) This construction will be used later on when we consider the case of many chains, each of finite length (Section 4). Before considering the case of many chains, we digress for a moment and consider in Section 3 the case of a single chain on a cubic lattice, and describe a construction that yields extra entropy per segment. The case of many chains is considered in Section 4 and contains the proof of (3). We start with a square lattice and then extend the result to a cubic lattice. Throughout the paper, we consider the case of pure polymer, i.e., we set $n_0 = 0$. We briefly discuss the effect of solvent molecules on our bounds in the final section. This section also summarizes our results.

## 2. SINGLE POLYMER CHAIN—SQUARE LATTICE

The central idea in the explicit construction of allowed ways of putting a polymer chain in I and II is to cover the lattice by identical loops of size $2 \times (m + 3)$ (Fig. 2) and then to connect the adjacent loops at various allowed places. The lower bound obtained in I is given by

$$s(g) \geqslant (g/8)\ln(4/g - 3)$$

in the thermodynamic limit, while the lower bound in II in the same limit is given by

$$s(g) \geqslant (g/4)\left[\ln(4/g - 3) - 0.2841 \ldots\right] \tag{4}$$

[Here we have denoted the quantity $s_H(g)$ of I and II by $s(g)$ by suppressing $H$.] The extra entropy contained in (4) comes from moving the top–bottom pairs, to be called T–B in the following, of two adjacent loops one on top of another to any of the allowed possible positions once the two loops have been connected to their neighboring loops in their respective rows (see II for details). However, the calculation of the lower bound (4) presented in II is valid only for polymer chains that are infinitely long ($l \to \infty$) since it is based on probability arguments. As we will finally be

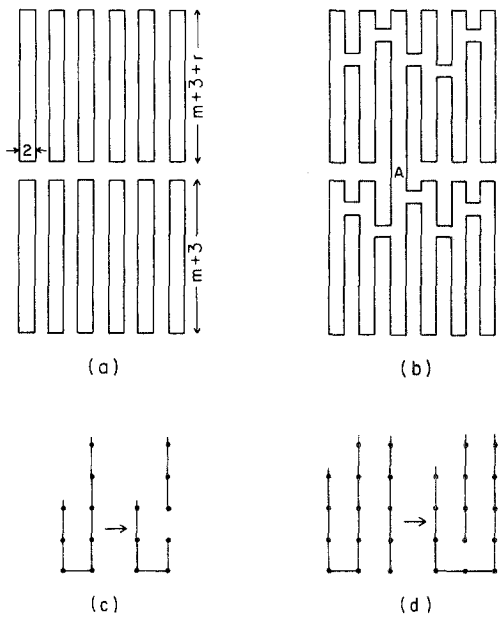


Fig. 2. (a) Covering the lattice with rectangular loops λ's. (b) Constructing a Hamilton circuit. (c)–(d) Constructing a Hamilton walk from a Hamilton circuit.

interested in obtaining a lower bound for the case of polymer chains of finite length ($l < \infty$), we will present here a calculation similar in spirit to the one given in II but valid for chains of finite length.

As usual, we start by covering the square lattice ($\nu \times \nu$) by rectangular loops (denoted by λ) of size $2 \times (m + 3)$ as described in I and II and is shown in Fig. 2. We will set $n_0 = 0$, so that we are dealing with a pure polymer system. Define $l = n = \nu^2$. Let $I(x)$ denote the largest integer less than or equal to $x$. It was assumed in I and II that $\nu$ was an integral multiple of $m + 3$. However, in the present work, we wish to consider the general case by relaxing this restriction. Let $R$ stand for $I(\nu/(m + 3))$:

$$\nu = R(m + 3) + r \qquad (m \geqslant 1) \tag{5a}$$

where the remainder $r$ is such that $0 \leqslant r < m + 3$. Also, let $C = I(\nu/2)$:

$$\nu = 2C + c \qquad (C \geqslant 2) \tag{5b}$$

where $c$ is either zero or one. The case of $c = 0$ is shown in Fig. 2. We have $C$ identical columns of the λ loops, and there are $(R - 1)$ λ loops of size $2 \times (m + 3)$ and one λ loop of size $2 \times (m + r + 3)$ at the top of the column in each column. Because of the particular choice of the height of the top loop, each column has $R$ λ loops covering $2\nu$ sites. For the case $c = 1$, we

have an additional vertical line with $v$ sites along with $C$ columns of the $\lambda$ loops. This vertical line should be placed, either to the extreme left or to the extreme right of the assembly of the $\lambda$ loops. The whole lattice is covered by these $\lambda$ loops and the single vertical line. For $c = 0$ the vertical line is not required. The number of the $\lambda$ loops is given by

$$L = RC = \frac{n - (r + c)v + rc}{2(m + 3)} \tag{5c}$$

Our construction implies that there are $R$ rows of the loops. We make sure that each row has loops of identical heights, as shown in Fig. 2a.

Consider a row of the $\lambda$ loops. Each loop can be joined to the neighboring $\lambda$ loop on the right by using two consecutive sites on vertical sides, as shown in Fig. 2b. If one excludes connections that involve the top or the bottom sites, then there are $m$ ways ($m + r$ ways) to join a $\lambda$ of height $(m + 3)$[height $(m + r + 3)$] to the neighboring $\lambda$, and there are $C - 1$ places to make this connection in each row. This construction produces a circuit, to be called $\Lambda_r$ in the following, in each row. It is evident that the number of ways of producing distinct configurations of $R$ $\Lambda_r$'s is given by

$$m^{(R-1)(C-1)}(m + r)^{C-1} \geqslant m^{R(C-1)}$$

Each $\Lambda_r$ contributes

$$G_r = 8(C - 2) + 12 = 8C - 4$$

number of corners: each interior $\lambda$ contributes eight corners and the two exterior $\lambda$'s contribute six each. Thus, the total number of corners is

$$G_t = RG_r = 8L - 4R$$

In order to generate Hamilton walks, we must connect various $\Lambda_r$'s in the following manner: we connect a $\Lambda_r$ to the $\Lambda_r$ just below it at any of the $C$ columns (see point A in Fig. 2b), and there are $R - 1$ pairs of $\Lambda_r$'s to be connected. Thus, we generate at least

$$\tilde{W}(G) = C^{(R-1)}m^{R(C-1)}$$

distinct Hamilton circuits $\Lambda_H$ (see Fig. 2b). Each time two neighboring $\Lambda_r$'s are joined, we lose four corners. Thus, the total number of corners is reduced to

$$G = G_t - 4(R - 1) = 8L - 8R + 4$$

and the fraction of corners is given by

$$g(n) = G/n = \frac{4}{m + 3} - \frac{4(r + c + 2)}{v(m + 3)} + \frac{4}{n}\left[1 + \frac{r(c + 2)}{m + 3}\right]$$

In order to produce Hamilton walks, we treat the two cases $c = 0$ and $c = 1$ separately. For $c = 0$, we delete a vertical bond, for example, the second one from the bottom on the right side of each $\Lambda_H$ (see Fig. 2c). For $c = 1$, we connect each $\Lambda_H$ with the single vertical line by deleting, for example, the bottom vertical bond of $\Lambda_H$ which is right next to the line (see Fig. 2d). In both cases, the value of $G$ remains unaltered. Now, each Hamilton walk is identified with a possible configuration of the polymer chain with $n$ segments and having the number the *gauche* bonds given by $G$. If $W(G)$ is the actual number of polymer configurations with a given $G$, then it should be evident that $\tilde{W}(G)$ obtained above is a strict lower bound for it:

$$W(G) \geqslant \tilde{W}(G)$$

Let us introduce the following quantities:

$$\begin{aligned} s(g) &= \lim_{\nu\to\infty} \frac{1}{n} \ln W(g) \\ \tilde{s}(g) &= \lim_{\nu\to\infty} \frac{1}{n} \ln \tilde{W}(g) \\ g &= \lim_{\nu\to\infty} g(n) \end{aligned} \tag{6}$$

We find that $g$ is given by (1c) and that $s(g) \geqslant \tilde{s}(g)$, where $\tilde{s}(g)$ is defined in (1b). However, it should be evident from the construction that (1b) is shown to be valid only for certain discrete values of $g$ given by setting $m = 1, 2, 3, \ldots$ in (1c). We now wish to prove (1d) for all continuous values of $g \leqslant \tilde{g}$. Our construction cannot be used to prove (1d) for $g > \tilde{g}$. However, this does not mean that it is impossible to show (1d) to be valid for all $g$. We will only prove (1d) here.

The procedure to be followed below involves a slight modification of the one given above. The new construction is closer in spirit to that given in II. However, this construction can be used even when the chains are of finite lengths, as will be seen in Section 4. On the other hand, the construction used in II is valid only for chains with $l \to \infty$.

In order to obtain a value of $g$ between $g_1 = 4/(m + 3)$ and $g_2 = 4/(m + 4)$, we must cover each column with a mixture of $\lambda$ loops of sizes $2 \times (m + 3)$ and $2 \times (m + 4)$ in the following manner. Let $R'$ be the total number of the $\lambda$ loops in a given column. The value of $R'$ will be determined below and will, in general, be different from $R$ given in (5a). Let there be $\alpha R'$ $\lambda$ loops of the height $m + 3$, $\beta R' - 1$ $\lambda$ loops of the height $m + 4$, and the top $\lambda$ loop of the height $m + r' + 4$. Here and in the following, $\beta = 1 - \alpha$. If these loops cover the whole column, we must have

$$\begin{aligned} \nu &= \alpha R'(m + 3) + (\beta R' - 1)(m + 4) + (m + r' + 4) \\ &= R'(m + 3 + \beta) + r' \end{aligned}$$

We choose $R' = I(\nu/(m+3+\beta))$. Evidently $R'$ and $R$ are different except for $\alpha = 1$. Moreover, $R'$ lies between $I(\nu/(m+3))$ and $I(\nu/(m+4))$. Let us consider two consecutive values of $\alpha$ defined by

$$\alpha_1 R_1' = I \qquad (I \leqslant R_1')$$

$$\alpha_2 R_2' = I - 1$$

where $I$ is some integer, and $R_1' = I(\nu/(m+4-\alpha_1))$ and $R_2' = I(\nu/(m+4-\alpha_2))$. It is easily seen that $R_2' = R_1'$ or $R_2' = R_1' - 1$. If $R_2' = R_1'$, then $\Delta\alpha = \alpha_1 - \alpha_2 = 1/R_1'$. For $R_2' = R_1' - 1$, $\Delta\alpha = (R_1' - I)/R_1'(R_1' - 1)$. In either case, we note that in the thermodynamic limit $n \to \infty$ (i.e., $\nu \to \infty$)

$$\Delta\alpha \to 0 \qquad \text{as} \quad \nu \to \infty \tag{7a}$$

provided

$$\frac{\nu}{m+3+\beta} \to \infty \qquad \text{as} \quad \nu \to \infty \tag{7b}$$

Thus, provided (7b) is satisfied, the variable $\alpha$ can be treated as a *continuous variable* between zero and one. As will be seen below, this implies that by a suitable choice of $\alpha$, the value of $g$ can take any continuous value between $g_1$ and $g_2$.

We arrange the above mixture of the $\lambda$ loops on the lattice so that there are $\alpha R'$ rows of $\lambda$ loops of the height $m+3$, $\beta R' - 1$ rows of $\lambda$ loops of the height $m+4$, and the top row of $\lambda$ loops of the height $m + r' + 4$. There are $C$ $\lambda$ loops in each row. If $c = 1$, there will also be a vertical line of $\nu$ sites along with these $\lambda$ loops, as explained before. Let us introduce $m' = I(m/2)$:

$$m = 2m' + m'', \qquad m'' = 0 \text{ or } 1$$

Consider two neighboring loops of the height, for example, $m+3$. Instead of joining them at $m$ places as before, we join them at only the top $m' + m''$ places (again excluding the top corners) as shown in Fig. 3a. For the $\lambda$ loops of the height $m+4$, we connect them at only the top $m' + 1 + m''$ places. We now note that there are $m' + 1$ sites near the bottom of each $\lambda$ loop that have not been used in obtaining the above Hamilton walks (see Fig. 3a). The next step in the construction is to note that the top–bottom pair T–B of any two neighboring loops, one on top of another, can be moved together such that the bottom B of the top loop may occupy any of the unused $m' + 1$ sites near its bottom (see Fig. 3b). There are altogether

$$(R' - 1)(C - 1)$$

such T–B pairs to be moved. Each one can be moved in $m' + 1$ ways as explained above. Thus, the total number of Hamilton circuits $\Lambda_H$ generated by the above construction is at least ($G$ is the total number of corners)

$$\tilde{W}'(G) = \left[(m' + m'')^{\alpha R'}(m' + 1 + m'')^{\beta R'}\right]^C (m' + 1)^{(R'-1)(C-1)} \leqslant W(G)$$

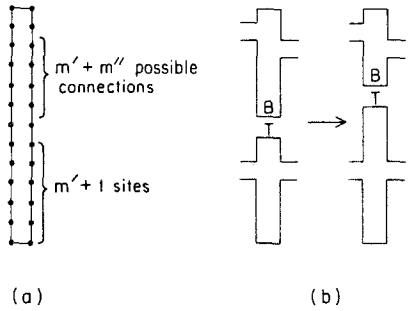


Fig. 3. (a) A rectangular loop $\lambda$ with $2m' + m'' + 3$ vertical sites. (b) Moving a B–T pair to one of the possible $m' + 1$ positions.

Each of these $\Lambda_H$ can now be converted into a Hamilton walk in at least one way. Thus, there are at least these many Hamilton walks. It is easily seen that in the thermodynamic limit, the fraction $g$ of the *gauche* bonds is given by

$$g = \frac{4}{m + 3 + \beta} = \frac{4}{m + 4 - \alpha} \tag{8}$$

In the same limit, the lower bound $\tilde{s}'(g)$ on the entropy $s(g)$ is given by

$$\tilde{s}'(g) = \lim_{\nu \to \infty} \frac{1}{n} \ln \tilde{W}'(g)$$

$$= \frac{1}{2(m + 3 + \beta)} \left[ \alpha \ln(m' + m'') + \beta \ln(m' + 1 + m'') + \ln(m' + 1) \right]$$

Since $m' + m'' \geqslant m/2$, and $m' \geqslant (m - 1)/2$, we find that

$$\tilde{s}'(g) \geqslant \frac{1}{2(m + 3 + \beta)} \left[ \alpha \ln m + \beta \ln(m + 2) + \ln(m + 1) - 2 \ln 2 \right]$$

$$= \frac{1}{2(m + 3 + \beta)} \left[ \ln m(m + 1) + \beta \ln(m + 2/m) - 2 \ln 2 \right].$$

We will now establish that $\Delta = \tilde{s}'(g) - \tilde{s}(g) \geqslant 0$ for some $g \leqslant \tilde{g}$. Here, $g$ is given by (8) and $\tilde{s}(g)$ is given in (1b). We find that

$$\Delta \geqslant \frac{1}{2(m + 3 + \beta)} \left[ \ln \frac{m(m + 1)}{4(m + \beta)} + \beta \ln \frac{m + 2}{m} \right]$$

Consider the function $\sigma(\beta)$ within the square brackets. The extremum of $\sigma(\beta)$ is given by

$$m + \beta_m = 1 \Big/ \ln \frac{m + 2}{m}$$

For $m \geqslant 1$, the extremum value $\beta_m$ is always negative, and, therefore, does not lie within the range of interest, i.e., between zero and one. Moreover, $\sigma(0) < \sigma(1)$. Thus, if $\sigma(0) \geqslant 0$, this will imply that $\Delta \geqslant 0$. This, in turn, will ensure that $\tilde{s}(g)$ is a strict lower bound for all $g \leqslant \tilde{g}$, where $\tilde{g}$ is to be determined below. Now,

$$\sigma(0) = \ln \frac{m+1}{4} \geqslant 0$$

if

$$m \geqslant 3.$$

Thus, we establish that $\tilde{s}(g)$ is a strict lower bound for $s(g)$ for all $g \leqslant \tilde{g}$ where $\tilde{g} = 2/3$ obtained by setting $m = 3$ and $\alpha = 1$ (i.e., $\beta = 0$) in (8). It should be remarked that (1d) is shown to be valid only if (7b) is obeyed. Otherwise, one cannot cover a continuous range for $g$.

If, instead of using the above construction to prove (1d) for all continuous $g \leqslant \tilde{g} = 2/3$, we connect the two neighboring $\lambda$ loops of the heights $m + 3$ (or $m + 4$) at $m$ (or $m + 1$) places as was used previously to prove (1b) for $g$ given by (1c), we find that the lower bound for the entropy in the thermodynamic limit is given by

$$\frac{1}{2(m+3+\beta)} \left[\alpha \ln m + \beta \ln(m+1)\right] \tag{9}$$

and lies below the straight line between $\tilde{s}(g_1)$ and $\tilde{s}(g_2)$. On the other hand, $\tilde{s}(g)$ is a convex function of $g$ and lies above this straight line:

$$\tilde{s}(g) > \alpha \tilde{s}(g_1) + \beta \tilde{s}(g_2), \qquad \alpha \neq 0 \text{ or } 1$$

Thus, the simple construction is not enough to prove that $\tilde{s}(g)$ is a strict lower bound for all $g$. It is for this reason that the new construction has been introduced. However, (9) is enough to show that (1a) is valid for all continuous values of $g$ between zero and one.

## 3. SINGLE POLYMER CHAIN—SIMPLE CUBIC LATTICE

Let us now imagine constructing Hamilton walks covering the whole simple cubic lattice ($\nu \times \nu \times \nu$). As was pointed out in I and II, this is readily done if one imagines dividing the cubic lattice into $\nu$ different layers of $\nu \times \nu$ square lattices. We draw Hamilton circuits on each of the $\nu$ layers as described in the previous section, and join these Hamilton circuits in each layer to give Hamilton circuits covering all the sites of the cubic lattice. Finally, one deletes any one bond to obtain Hamilton walks. It is evident that (1a) and (1d) still remain valid for $s(g)$ for the simple cubic lattice. However, our attempt in this section is to obtain an even better

bound for $s(g)$ for the cubic lattice. Let $l = n = \nu^3$. The thermodynamic limit is obtained by taking $\nu \to \infty$. We will assume this limit in the following.

We divide the cubic lattice into $\nu$ different vertical square planes ($\nu \times \nu$). We now cover each of the $\nu$ vertical square lattices by *identical* arrangements of $\lambda$ loops so that there are $R'$ $\lambda$ loops in each column in any given square lattice [see the construction described after (6) in Section 2]. Here the value of $R'$ is given by $I(\nu/(m + 3 + \beta))$. Thus, we have essentially $\nu$ identical replicas of any vertical plane. Since there are $R'$ loops in each vertical column, we can divide the cubic lattice into $N_H = R'$ horizontal layers of rectangular loops, so that each layer contains only one rectangular loop from each vertical column (see Fig. 4a). In each layer there are $N_L = \nu C$ loops, where $C = I(\nu/2)$. There are altogether $L = N_H N_L = \nu R' C$ rectangular loops covering the cubic lattice. For the moment, we assume $c$ in (5b) to be zero.

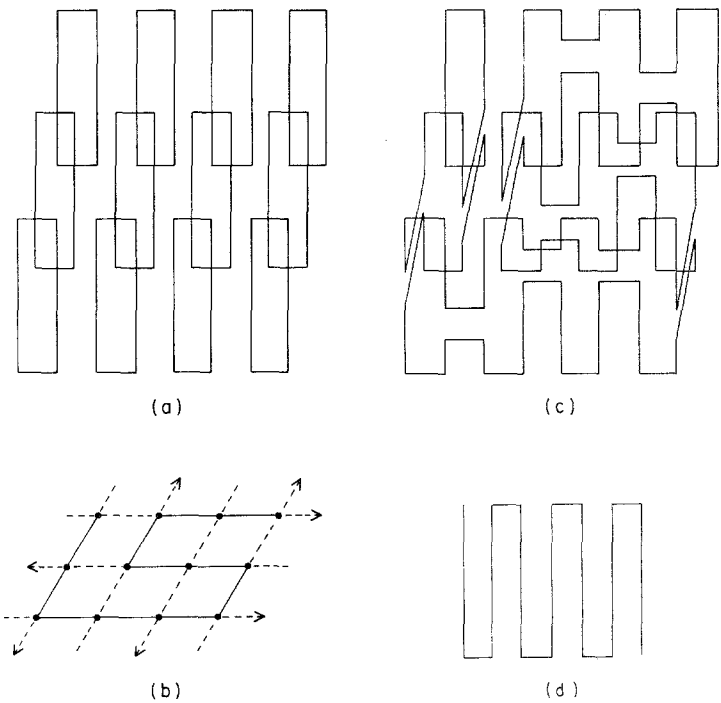


Fig. 4. (a) A horizontal layer $P$ of $N_H$ $\lambda$'s. (b) Oriented square lattice $S'$ according to the Manhattan traffic rule and a possible Hamilton walk on $S'$. (c) Connecting $\lambda$'s in $P$ according to the Hamilton walk in (b).

Let us now focus our attention on any one of the $N_H$ horizontal layers of the loops. We will denote this layer by $P$. Let us replace each loop by a point. This gives us a simple square lattice with $N_L$ sites. We will denote this square lattice by $S$. We now orient this square lattice $S$ according to the Manhattan traffic rules[9,10]: alternate rows and columns of the lattice are oriented in opposite directions (see I for detail). The number of Hamilton walks on this oriented lattice $S'$ obtained from $S$ has been calculated exactly by Kastelyen[9,10] and is given by

$$W_H^M = (1.338\ldots)^{N_L} \qquad (N_L \to \infty)$$

These walks are oriented walks since the underlying lattice $S'$ is an oriented lattice. Consider one of these oriented Hamilton walks (Fig. 4b). The orientation of this walk uniquely determines the way of connecting the $N_L$ rectangular loops of the above horizontal layer $P$ underlying the oriented square lattice $S'$ (Fig. 4c). The observation to be made at this point is that one is not required to orient $S$ according to the Manhattan traffic rule. Any Hamilton walk on $S$ describes a unique connection of loops on $P$ and yields a Hamilton walk on $P$. The reason for orienting $S$ into $S'$ is that $W_H^M$ is known exactly. Since we are interested in obtaining a lower bound for entropy, orienting $S$ into $S'$ will be sufficient for our purpose. The adjacent loops on $P$ are connected as described in the previous section. Thus, the number of Hamilton circuits thus obtained is given by

$$\tilde{W}'(G) W_H^M \qquad (\nu \to \infty)$$

where $\tilde{W}'(G)$ is given in the previous section [just before (8)]. It should be evident that the value of $g$ is still given by (8). Thus, the entropy per segment is bounded below by

$$\begin{aligned} \forall g \leqslant \tilde{g}, \qquad s(g) &\geqslant (g/8)\left[\ln(4/g - 3) + \ln(1.338\ldots)\right] \\ &= (g/8)\left[\ln(4/g - 3) + 0.292\ldots\right] \end{aligned} \tag{10}$$

and yields a better bound than (1d) for the cubic lattice. This completes our discussion of a single-chain case. For $c = 1$, we have an extra line covering a vertical plane $(\nu \times \nu)$ (see Fig. 4d) which can be connected to the Hamilton circuits generated above (see Fig. 2d) without changing any of the above conclusions. Finally it should be evident that (1a) is still valid.

## 4. MANY POLYMER CHAINS—SQUARE LATTICE

This is the most important section of the paper and contains the proof of (3). The proof again proceeds with explicit construction of some of the possible ways of covering the lattice by $p$ polymer chains, each with $l$

monomers or segments. We will treat the special case of pure polymer system: $n_0 = 0$. Thus, we require a lattice with $n = p \cdot l$ sites that will be completely covered by these chains. We start with a square lattice of size $\nu \times \nu$, $n = \nu^2$. We will assume in the following that $\nu$ is a multiple of $l$:

$$\nu = \nu' l \tag{11a}$$

This implies that

$$p = \nu'^2 l \tag{11b}$$

so that the lattice can be covered by the $p$ chains. The thermodynamic limit $p \to \infty$ is obtained by considering a sequence $[p]$ defined by (11b) for $\nu' = 1, 2, \ldots$ and taking the limit $\nu' \to \infty$. Thus, not all values of $p$ are allowed when we take the thermodynamic limit: only those values of $p$ are allowed that are square multiples of $l$. In what follows, we will always assume $p$ to be given by (11b). With this remark about the thermodynamic limit, we return to the pure polymer system.

One might be tempted to treat this $p > 1$ case by breaking Hamilton walks covering the whole lattice into $p$ equal pieces, each covering $l$ sites. This certainly provides us with configurations of $p$ chains. But there are two problems with this:

i. It is easily checked that not all configurations obtained by breaking Hamilton walks are distinct. An example of this is shown in Fig. 5 where a portion of three Hamilton walks (a), (b), and (c) are shown and all give rise to the same configuration (d) of chains. The bonds to be removed are shown by broken bonds in (a), (b), and (c).

ii. When we break a Hamilton walk into pieces, we have to delete bonds. Each deleted bond may change the value of $G$, the total number of

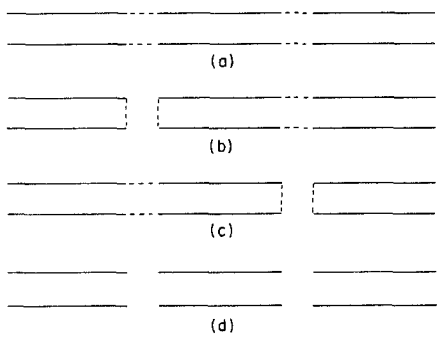


Fig. 5. Breaking three different Hamilton walks (a), (b), and (c) that give the same configuration (d).

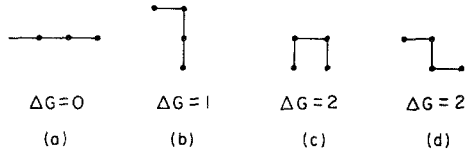


Fig. 6. Possible changes $\Delta G$.

*gauche* bonds by 0, 1, or 2. This is exhibited in Fig. 6, where the middle bond has to be deleted. Thus, after the Hamilton walk is broken into $p$ equal pieces, the total change $\Delta G$ in $G$ is bounded by

$$2p \geqslant \Delta G \geqslant 0.$$

This implies that the total change in the fraction of gauche bonds is bounded by

$$2/l \geqslant \Delta g \geqslant 0$$

where we have replaced $n/p$ by $l$. Therefore, unless $l \to \infty$, the process of breaking Hamilton walks into $p$ pieces changes the value of $g$ by an amount that is finite and must be calculated for each configuration of the chains. This is not a trivial problem.

These two problems together imply that another construction has to be developed for the case of finite $l$. This will be done below. For the case $l \to \infty$, we observe from above that $\Delta g \to 0$ and therefore the value of $g$ does not change in breaking the walks into $p$ pieces. Moreover, one can also check that the indistinctness of various configurations in this case is also of no physical consequence. This is easily done by comparing the number of configurations obtained by breaking the Hamilton walks with the number of distinct configurations obtained by dividing the lattice into $p$ equal cells, each with $l$ sites, and covering each cell by Hamilton walks. The special case of $l = p = v$ was considered in I.

We now proceed to describe the explicit construction to obtain a lower bound on entropy and prove (3) for the general case of $p$ chains of finite lengths ($l < \infty$). We first observe that for $g = 0$, all chains must be straight. On a square lattice, they can either lie vertically or horizontally. Let us divide the square lattice ($v \times v$) into square cells of size $l \times l$. We will denote these cells by the symbol $C$. (This should not be confused with the symbol $C$ introduced in Section 2.) Because of the size of these cells, we can put $l$ different chains into each. For $g = 0$, there are two ways of putting $l$ chains in a $C$ cell: either all lie vertically or horizontally. Thus, there are at least

$$2^{N_C} = 2^{n/l^2} = 2^{v'^2}$$

different ways of putting chains into configuration with $g = 0$. Here $N_C$ is the number of the $C$ cells:

$$N_C = n/l^2 = \nu'^2 \tag{12}$$

Let $W_{p,l}(0)$ stand for the actual number of ways of putting $p$ chains, each $l$ segments long, with $g = 0$. We must have

$$W_{p,l}(0) \geqslant 2^{N_C}$$

Define

$$s_l(0) = \lim_{\nu' \to \infty} \frac{1}{n} \ln W_{p,l}(0)$$

This is the actual entropy of the system for $g = 0$, and is bounded from below,

$$s_l(0) \geqslant \tilde{s}_l(0) \tag{13}$$

where

$$\tilde{s}_l(0) = \lim_{\nu' \to \infty} \frac{1}{n} \ln 2^{N_C} = \frac{1}{l^2} \ln 2 \tag{14}$$

The bound (13) shows that there is a finite nonzero entropy even in the ground state, i.e., $g = 0$ of the Flory model.[4] This is also the lower bound on the entropy at $T = 0$ in the Flory model for chains of finite length (see I and below). As $l \to \infty$, this lower bound $s_l(0)$ approaches zero. This was the case of a single polymer chain that was discussed in detail in I and II.

The nonzero value of $\tilde{s}_l(0)$ for any finite $l$ has a very important consequence. Since the orientations of the chains in various cells are completely uncorrelated, the configurations generated above have nonzero orientational correlations *only* between two chains that are closer than or equal to $l$ lattice spacing. In other words, the orientation correlations are finite ranged for any finite value of $l$. From this point of view, the above configurations of chains are *disordered*. The nonzero value of $\tilde{s}_l(0)$ implies that it is *possible* to fill up the lattice with disordered configurations of straight chains, i.e., rodlike polymer molecules with *finite nonzero entropy*. In contrast, Flory[4] has claimed that it is *impossible* to cover the lattice with rodlike molecules in a disordered manner.

In the following, we will restrict ourselves to the special case of $l$ being a multiple of four:

$$l = 4q \tag{15}$$

where $q$ is some integer. We have restricted ourselves to this special case because the proof involved in the establishment of the rigorous lower bound (3b) for $g \leqslant \tilde{g}$ is considerably simpler here than for the general

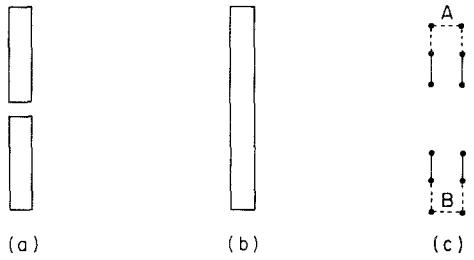


Fig. 7. (a)–(b) Construction for the case $0 \leqslant g \leqslant 4/l$. (c) The broken bonds should not be deleted.

values of $l$. The case of the most general form of $l$ will be the subject matter of a future publication. However, it is hoped that the simple case considered here will give an idea of how one produces a lower bound on the entropy. Moreover, and importantly, it will also show that the configurations generated here are *disordered* in the sense described above: the orientational correlations are of finite range. We divide each $C$ into $l/2$ groups so that there are two loops one on top of another in each group (Fig. 7a). There are $M = 2qN_C$ such groups. Now choose $\alpha M$, $0 \leqslant \alpha \leqslant 1$, such groups. There are

$$N_\alpha(M) = \binom{M}{\alpha M} \tag{16}$$

different ways of making such a selection from $M$ groups. We convert each of the $\alpha M$ groups into two chains by deleting a bond from each loop (Fig. 7a), so that each chain contributes four *gauche* bonds. Evidently, each chain has $l$ monomers. Each group of the remainder $\beta M$, $\beta = 1 - \alpha$, groups is first joined into a single loop of size $2 \times l$ (Fig. 7b) and then converted into two chains of length $l$ by deleting the top and the bottom horizontal bonds. These produce chains that contribute zero *gauche* bond each. In the thermodynamic limit, as $\nu' \to \infty$ we find that $\alpha$ becomes a continuous variable between zero and one. In the same limit, the fraction of the *gauche* bonds in each configuration is given by

$$g = \lim_{\nu' \to \infty} (G/n) = (4/l)\alpha$$

where $G$ is the total number of the *gauche* bonds. By varying $\alpha$, we cover the range from zero to $1/q$ for $g$. Let us now compute the number of configurations that are generated. The value of $g$ is just the fraction of corners in loops of Fig. 7a. From our construction, it must be obvious that the corners always appear in pairs as at A or B in Fig. 7c. When we delete a bond from the circuit to obtain a polymer configuration, we must ensure that the deleted bond does not change the number of corners in the circuit.

This can be achieved if we make sure that we do not delete any of the three bonds shown by broken bonds in Fig. 7c that determine the corners. Let $b$ denote the number of corners in the circuit. The *maximum* number of bonds that could not be chosen as the ones to be deleted is $(3/2)b$. Thus the *minimum* number of bonds that can be deleted to turn the circuit into a polymer is

$$N_D = l - 3b/2 \tag{17}$$

This ensures that the value of $g$ remains unchanged. In the following, we will make sure that $N_D$ remains positive, nonzero integer. Now, the number of bonds that can be deleted to produce polymer configurations containing four *gauche* bonds in each loop in Fig. 7a is $l-6$. Thus, we require $q \geqslant 2$ ($l \geqslant 8$) so that this number remains positive. There is, however, only one way to turn Fig. 7b into two straight chains. Moreover, in each cell, we can put the loops either horizontally or vertically. Thus, the number $W_{p,l}(G)$ of configurations for a given number $G$ of the *gauche* bonds is bounded by

$$W_{p,l}(G) \geqslant 2^{N_C} N_\alpha(M)(l-6)^{2\alpha M}$$

Let us introduce the following quantity:

$$s_l(g) = \lim_{\nu' \to \infty} \frac{1}{n} \ln W_{p,l}(G) \tag{18}$$

This is the actual entropy per segment for a given value of $g$ in the thermodynamic limit. Using Stirling's approximations in $N_\alpha(M)$, we find that $s_l(g)$ is bounded by

$$s_l(g) \geqslant \tilde{s}_l(0) + \frac{\alpha}{l} \ln(l-6) + \frac{\alpha}{2l} \ln \frac{1}{\alpha} + \frac{\beta}{2l} \ln \frac{1}{\beta} \tag{19}$$

Consider the difference $\Delta = s_l(g) - \tilde{s}_l(g)$, where $\tilde{s}_l(g)$ is given in (3b). We find that

$$\begin{aligned} 2l\Delta &\geqslant \alpha \ln\left[(l-6)^2/(l-3\alpha)\right] + \beta \ln(1/\beta) \\ &\geqslant \alpha \ln\left[(l-6)^2/l\right] \end{aligned}$$

If

$$(l-6)^2 \geqslant l, \quad \text{i.e.} \quad l \geqslant 12$$

(remember that $l$ is a multiple of 4), then $\Delta \geqslant 0$. This means that for $l \geqslant 12$, (3b) is a strict lower bound for $0 \leqslant g \leqslant 4/l$.

We will now consider the cases $l = 8$ and $l = 4$ separately. First consider $l = 8$. We break the two loops of Fig. 7a by deleting a bond so that each one has three *gauche* bonds. The loop in Fig. 7b is broken as before. The value of $g$ is now given by $3\alpha/8$. Following above, we find that $s_l(g)$ is

now bounded by the same expression as (19) except that $\ln(l-6)$ is replaced by $\ln 4$ as there are four ways to break a loop in Fig. 7a to yield three corners. We find that

$$2l\Delta \geqslant \alpha \ln\left[(4)^2/\alpha(4l/3-3\alpha)^{3/4}\right] + \beta \ln(1/\beta) > 0$$

for $l = 8$. Thus, (3b) is still valid for $g \leqslant 3/l = 3/8$. We now consider $l = 4$. We can delete any of the four bonds in each loop in Fig. 7a to yield two *gauche* bonds each. The loop in Fig. 7b is broken as before. Evidently, $g \leqslant 2\alpha/l = \alpha/2$. Proceeding as before, and calculating $\Delta$, we find that

$$2l\Delta \geqslant \alpha \ln\left[(4)^2/\alpha(2l-3\alpha)^{1/2}\right] + \beta \ln(1/\beta) > 0$$

for $l = 4$. Thus, (3b) is valid for $g \leqslant 2/l = 1/2$. Putting all these results together, we conclude that (3b) is a strict inequality for all $g \leqslant \tilde{g}' = 13/90$ [see (3c)] for $q \leqslant 6$, i.e., $l = 4q \leqslant 24$.

As $l$ increases, $g$ decreases and eventually becomes smaller than $\tilde{g}'$, with $\tilde{g}'$ given in (3c). Thus for $q > 6$, we must produce configurations with more and more *gauche* bonds in order to cover all values of $g \leqslant \tilde{g}'$. This is what will be done below. We will accomplish this in stages so that we can appreciate the pattern common to all these configurations.

We divide each $C$ into $l/2$ groups so that there are two rows of two $\lambda$ loops of size $2 \times q$ in each group as shown in Fig. 8a. Again, there are $M = 2qN_C$ groups. We choose $\alpha M$ out of these $M$ groups and connect them (Fig. 8a) to give rise to two separate chains with 12 *gauche* bonds each. The two loops in a given row are connected at $q-3$ places to give rise to a circuit that can be broken at at least $l-18$ places [set $b = 12$ in (17)] to produce a possible configuration of a chain with 12 *gauche* bonds. There are $\beta M$ groups that are left and each of these is turned into two loops of size $2 \times (2q)$ as shown in Fig. 8b. This configuration is identical with the one shown in Fig. 7a. We now turn these loops into two chains with four *gauche* bonds each. As said above, there are $l-6$ ways of turning a loop in Fig. 8b into a configuration of a chain with four *gauche* bonds. Thus, we

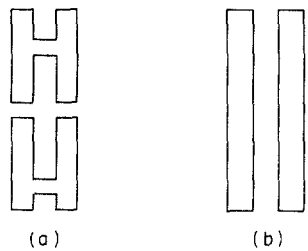


Fig. 8. Construction for the case $4/l \leqslant g \leqslant 12/l$.

finally find that $W_{p,l}(G)$ is bounded by

$$W_{p,l}(G) \geqslant 2^{N_C} N_\alpha(M)\left(\frac{l}{4}-3\right)^{2\alpha M}(l-18)^{2\alpha M}(l-6)^{2\beta M}$$

with $G$ given by

$$G = 12\alpha M + 4\beta M$$

The factor of $2^{N_C}$ is due to the fact that we can choose the $\lambda$ loops to be either vertical or horizontal. In the thermodynamic limit, we find that the fraction $g$ of the *gauche* bonds is given by

$$g = \lim_{p'\to\infty}(G/n) = 4(3\alpha+\beta)/l$$

where $\alpha$ is now a continuous variable between zero and one. We also find that the entropy is bounded by

$$s_l(g) \geqslant \tilde{s}_l(0) + \frac{\alpha}{l}\ln\left(\frac{l}{4}-3\right)(l-18) + \frac{\beta}{l}\ln(l-6) + \frac{\alpha}{2l}\ln\frac{1}{\alpha} + \frac{\beta}{2l}\ln\frac{1}{\beta}$$

Let us calculate $\Delta = s_l(g) - \tilde{s}_l(g)$, where $\tilde{s}_l(g)$ is given in (3b). We find that

$$2l\Delta \geqslant \alpha\ln\frac{(l/4-3)^2(l-18)^2}{\alpha(l/(1+2\alpha)-3)^3} + \beta\ln\frac{(l-6)^2}{\beta(l/(3-2\beta)-3)} \geqslant 0$$

if

$$(l/4-3)^2(l-18)^2 \geqslant \max_\alpha \alpha\left(\frac{l}{1+2\alpha}-3\right)^3$$

and

$$(l-6)^2 \geqslant \max_\beta \beta\left(\frac{l}{3-2\beta}-3\right) = l-3$$

We find from the Appendix that the first condition implies that

$$\left(\frac{l}{4}-3\right)^2(l-18)^2 \geqslant \frac{l(2-\xi)}{l(1+\xi)}\left[\frac{l}{3}(1+\xi)-3\right]^3$$

where $\xi = [(1+9/l)]^{1/2}$, and is satisfied for $q \geqslant 5$. The second condition is also satisfied for $q \geqslant 5$. Therefore, we conclude that (3b) is a strict lower bound for $q \leqslant I(3/\tilde{g}') = 20$, i.e., $l = 4q \leqslant 80$ for $g \leqslant \tilde{g}'$.

We now proceed to describe how to generate configurations that produce more and more *gauche* bonds as $l$ increases. This construction will also establish that (3b) is a strict lower bound for all $g \leqslant \tilde{g}'$ no matter how large $l$ is.

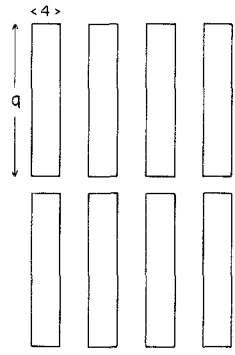


Fig. 9. A part of the cell $C$ covered by vertical rectangles $R$'s of size $4 \times q$. We have shown only two out of four rows of $R$'s.

Let us now focus our attention on any one of the square cells $C$. We divide $C$ into $l$ rectangles, each of size $4 \times q$. We will denote these rectangles by the symbol $R$ (this should not be confused with the symbol $R$ in Section 2): any given $R$ has four sites along the horizontal direction and $q$ sites along the vertical direction. We will call these $R$'s as vertical rectangles. There are four rows of these $R$'s, and there are $q$ $R$'s in each row in any given $C$ (see Fig. 9). Choose one of these $R$'s. The rectangle $R$ has $l$ sites and can be covered, therefore, by a single chain. This is what we intend to do in the following in order to obtain a lower bound $\tilde{s}_l(g)$ for the actual entropy $s_l(g)$ for any $g$. The idea is again to cover $R$ by rectangular loops $\lambda$ as usual. Let $s = I(q/r)$:

$$q = r \cdot s + t \qquad (0 \leqslant t < r) \tag{20}$$

We now cover $R$ by two identical vertical arrangements of loops such that there are $r - 1$ loops of size $2 \times s$ and one loop of size $2 \times (s + t)$ in each of the two vertical columns. We have shown one such arrangement in Fig. 10a where the top loop is of the size $2 \times (s + t)$. Notice that along any given row the loops are of equal heights. For $r = 1$, the construction is identical with that of Fig. 8a, and has been considered above. In the following we will assume $r \geqslant 2$. We now connect the two rectangles in the same row at any two consecutive points (excluding the two corner points) as usual. There are

$$(s-3)^{r-1}(s+t-3) \geqslant (s-3)^r$$

ways of doing that. We have assumed here that $s - 3 \geqslant 1$. This implies that $q \geqslant 4$, i.e., $l \geqslant 16$. Thus, our construction is *valid* only when $l \geqslant 16$. This construction gives $r$ circuits, one in each row in $R$. Each of the top $r - 1$

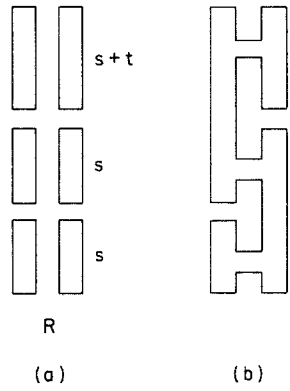


Fig. 10. (a) Covering $R$ by rectangular loops $\lambda$'s such that there are $r-1$ $\lambda$'s of size $2 \times s$ and one $\lambda'$ of size $2 \times (s+t)$. (b) A possible connection giving a circuit covering $R$. A bond on the outer sides must be deleted to convert this circuit into a polymer chain covering $R$.

circuits is now joined with the one just below it at any of the two columns, either the left one or the right one, as shown in Fig. 10b. This yields an extra factor of $2^{r-1}$. Thus, we have constructed

$$2^{r-1}(s-3)^{r-1}(s+t-3) \geqslant 2^{r-1}(s-3)^r \tag{21}$$

different circuits covering all the $l$ sites of $R$. Let $G_R$ be the number of the *gauche* bonds in any one of these circuits. This is just the number of corners, i.e., bends in the circuit covering $R$ that is, for example, shown in Fig. 10b. It should be evident that all the above circuits have the same number $G_R$ of the *gauche* bonds. In order to generate a configuration that can be identified with a configuration of a polymer chain, we must delete a bond from each circuit, so that $G_R$ remains unchanged. There are $2r$ $\lambda$ loops in Fig. 10a, and in each of them we can delete any of the $s-3$ bonds on the outer side (i.e., the side not used in the connection in Fig. 10b). Thus, there are at least $2r(s-3)$ ways of deleting a bond without changing $G_R$. Therefore, the total number $w_l(G_R)$ of configurations of a single polymer with the number of the *gauche* bonds $G_R$ is evidently bounded by

$$w_l(G_R) \geqslant \tilde{w}_l(G_R) = 2^r(s-3)^{r+1}r \tag{22}$$

Let us now compute $G_R$. We note that the two $\lambda$'s at the top in Fig. 10b contribute ten *gauche* bonds, i.e., corners. The same is true for the two $\lambda$'s at the bottom in Fig. 10b. The remaining rows contribute eight *gauche* bonds each. Thus, the value of $G_R$ is given:

$$G_R = 8(r-2) + 2 \times 10 = 8r + 4 \tag{23}$$

In order that two loops can be connected, we must have $s \geqslant 4$. This implies

that

$$r \leqslant \bar{r} = l/16 \tag{24a}$$

$$G_R \leqslant \bar{G}_R = l/2 + 4 \tag{24b}$$

Here, $\bar{r}$ and $\bar{G}_R$ denote the maximum possible values of $r$ and $G_R$, respectively.

It has been remarked above that we are considering $r \geqslant 2$. Then, an even better bound than (22) can be obtained by following the improvement suggested in Section 2. We connect two loops in the same row at only "half" of the $s-3$ places and then move the top–bottom pairs without changing $G_R$. Let us assume

$$s = 2(u+1) + v$$

where $u$ is some nonzero integer, and $v$ is either zero or one. Then it is easily seen that the total number of configurations thus generated for a polymer chain in $R$ is given by [compare with (22)]

$$\tilde{w}_l'(G_R) = 2^r u^{r-1}(u+t)(u+v)^{r-1} ru \qquad (r \geqslant 2)$$

The factor $(s-3)^{r-1}(s+t-3)$ in (21) has been replaced by $u^{r-1}(u+t)$ while the remaining $(u+v)^{r-1}$ comes from moving the top–bottom pairs in adjacent rows. There are at least $2ru$ different ways of breaking the circuits: There are at least $u$ different bonds that can be deleted on the outer side of each of the $2r$ loops. Thus, we finally have

$$w_l(G_R) \geqslant (2u^2)^r r \qquad (r \geqslant 2) \tag{25}$$

where $G_R$ is given in (23) since the new construction does not alter the value of $G_R$. Using the following inequality

$$2u = s - 2 - v \geqslant s - 3 \tag{26}$$

we find another bound:

$$w_l(G_R) \geqslant \left[(s-3)/\sqrt{2}\,\right]^{2r} r \tag{27}$$

Because of the size of $R$'s, we know that there are $lN_C$ different $R$'s. Let us choose $\alpha lN_C$ out of $lN_C$ $R$'s ($0 \leqslant \alpha \leqslant 1$) that are turned into polymer configurations, as described above, with $s = I(q/r)$, where $r$ is some given value ($r \geqslant 2$). The remainder of $\beta lN_c$, $\beta = 1-\alpha$, of the $R$'s are turned into polymer configurations with $s' = I(q/(r-1))$. Let $u'$ be given in terms of $s'$ by $s' = 2(u'+1) + v'$, $v' = 0$ or 1. Then, using (25), we find that the total number $W_{p,l}(G)$ of configurations is bounded by

$$W_{p,l}(G) \geqslant 2^{N_C}\binom{lN_C}{\alpha lN_C}\left[(2u^2)^r r\right]^{\alpha lN_C}\left[(2u'^2)^{r'} r'\right]^{\beta lN_C}$$

where $r' = r - 1$. The factor $2^{N_C}$ is due to the fact that we can divide each $C$ into either vertical rectangles $R$ of size $4 \times q$, as assumed above, or into horizontal rectangles of size $q \times 4$. The value of $G$ is given by

$$G = \alpha l N_C(8r + 4) + \beta l N_C(8r' + 4).$$

Using $N_C$ given in (12) and taking the thermodynamic limit $\nu' \to \infty$, we find that

$$g = \lim_{\nu' \to \infty} (G/n) = \frac{\alpha}{l}(8r + 4) + \frac{\beta}{l}(8r' + 4) \tag{28}$$

The actual entropy $s_l(g)$ is bounded by

$$s_l(g) \geqslant \tilde{s}_l(0) + \frac{\alpha}{l} \ln \frac{(2u^2)^r r}{\alpha} + \frac{\beta}{l} \ln \frac{(2u'^2)^{r'} r'}{\beta}$$

Let us compute the difference $\Delta = s_l(g) - \tilde{s}_l(g)$, where $\tilde{s}_l(g)$ is defined in (3b). We find that

$$\Delta \geqslant \frac{\alpha}{l} \ln \left[ \frac{(2u^2)^r r}{\alpha} (\mu - 3)^{-(r+1/2)} \right] + \frac{\beta}{l} \ln \left[ \frac{(2u'^2)^{r'} r'}{\beta} (\mu - 3)^{-(r'+1/2)} \right]$$

where we have used the Striling's approximations in $N_\alpha(lN_C)$ and where

$$\mu = \frac{l}{\alpha(1 + 2r) + \beta(1 + 2r')} \tag{29}$$

We now establish the conditions under which $\Delta \geqslant 0$. If $\Delta$ is nonnegative, this would imply that $\tilde{s}_l(g)$ is a strict lower bound of $s_l(g)$. It is evident that for $\Delta \geqslant 0$, it is sufficient to have

$$(2u^2)^r r \geqslant \max_\alpha \left[ \alpha(\mu - 3)^{r+1/2} \right] \tag{30a}$$

and

$$(2u'^2)^{r'} r' \geqslant \max_\beta \left[ \beta(\mu - 3)^{r'+1/2} \right] \tag{30b}$$

Here $\max_\alpha \phi(\alpha)$ means the maximum value of the functions $\phi(\alpha)$ for $0 \leqslant \alpha \leqslant 1$, and a similar meaning for $\max_\beta \psi(\beta)$. Rewriting $\mu$ as $\mu = l/[1 + 2r - 2\beta(r - r')] = l/(1 + 2r - 2\beta)$, we conclude that

$$\max_\beta \left[ \beta(\mu - 3)^{r'+1/2} \right] = \left[ \beta(\mu - 3)^{r'+1/2} \right]_{\beta=1}$$

$$= \left( \frac{l}{2r - 1} - 3 \right)^{r-1/2}$$

Thus, (30b) reduces to the condition

$$(2u'^2)^{r-1}(r - 1) \geqslant \left( \frac{l}{2r - 1} - 3 \right)^{r-1/2} \tag{30c}$$

From the Appendix A, we find that

$$\psi = \max_{\alpha}\left[\alpha(\mu - 3)^{r+1/2}\right]$$

$$= \frac{2r-1}{2}\,\frac{(2r+3)/(2r-1) - \sigma_l(r)}{1+\sigma_l(r)}\left\{\frac{l\left[1+\sigma_l(r)\right]}{2(2r+1)} - 3\right\}^{r+1/2}$$

$$< \frac{2r+3}{2}\left[\frac{l\xi_l(r)}{2(2r+1)} - 3\right]^{r+1/2}$$

where

$$\sigma_l(r) = \left[1 + \frac{24(2r+1)}{l(2r-1)}\right]^{1/2}$$

and

$$\xi_l(r) = 1 + \sigma_l(r)$$

Evidently, (30a) will be automatically satisfied if we can satisfy the following inequality

$$(2u^2)^r \geqslant \frac{2r+3}{2r}\left[\frac{l\xi_l(r)}{4r+2} - 3\right]^{r+1/2} \qquad (r \geqslant 2). \tag{30d}$$

It is easily seen from (30c) and (30d) that there always exist some number $l_c(r)$, which is a function of $r$, such that for all $l \geqslant l_c(r)$, the inequalities (30c) and (30d) are jointly satisfied. Here, $l_c(r)$ is some number, not necessarily an integer, for which at least one of the two inequalities turns into an equality. The function $l_c(r)$ is an increasing function of $r$. We will now demonstrate that $\tilde{s}_l(g)$ is a strict lower bound for $s_l(g)$ for all $g \leqslant \tilde{g}'$, where $\tilde{g}'$ is given in (3c), no matter how large $l$ is. It is convenient for this purpose to go back to (30a) and (30c). The maximum value of $\mu$ is obtained by setting $\alpha = 0$ in (29). Thus, (30a) is certainly satisfied if

$$(2u^2)^r \geqslant \left(\frac{l}{2r-1} - 3\right)^{r+1/2} \tag{30e}$$

Since $u' > u$, we note that (30c) is certainly obeyed if

$$(2u^2)^{r-1} \geqslant \left(\frac{l}{2r-1} - 3\right)^{r-1/2} \tag{30f}$$

If (30f) is obeyed then the inequality

$$2u^2 \geqslant \frac{l}{2r-1} - 3 \tag{30g}$$

is automatically satisfied. Using (30f) and (30g), we find that (30e) is also

obeyed. Therefore, our aim is to obtain the condition on how large $l$ should be as a function of $r$, so that (30f) is satisfied. Let $\tilde{l}_c(r)$ be the solution of

$$(2u^2)^{r-1} = \left(\frac{l}{2r-1} - 3\right)^{r-1/2}$$

which is nothing but (30f) as an equality. It is evident that (30f) is always obeyed for $l \geqslant \tilde{l}_c(r)$. Let us introduce

$$\tilde{l}(r) = 4m(2r+1) \tag{31a}$$

where $m$ is some integer, to be determined below, so that $\tilde{l}(r) \geqslant \tilde{l}_c(r)$. If $\tilde{q}(r) = \tilde{l}(r)/4$, then

$$\tilde{s}(r) = I\left[\frac{\tilde{q}(r)}{r}\right] \geqslant 2m$$

We will see below that $r$ and $m$ are chosen in such a way that $r \geqslant m$. This means that

$$\tilde{s}(r) \leqslant 2m+1$$

Now, $\tilde{u}(r) = I(\tilde{s}(r)/2) - 1 \geqslant m-1$ and the largest value of $l$ consistent with $u = \tilde{u}(r)$ is given by

$$\tilde{l}_m = 8rm + 8r - 4$$

If (30f) can be satisfied for the above value of $l = \tilde{l}_m$ and $u = \tilde{u}(r)$, then it will certainly be satisfied for $\tilde{l} = \tilde{l}(r)$ and $u = \tilde{u}(r)[\tilde{l}_m > \tilde{l}(r)]$. Thus, in order to satisfy (30f), we demand that

$$\left[2(m-1)^2\right]^{r-1} \geqslant \left[4m\left(1 + \frac{1}{2r-1}\right) + 1\right]^{r-1/2} \tag{30h}$$

If (30h) is satisfied for some $r = \tilde{r}$, then, using (30g) and noting that $(2r+1)/(2r-1)$ is a decreasing function of $r$, we find that (30h) is satisfied for all $r \geqslant \tilde{r}$; note that $m$ is treated as a constant in (30h). However, the value of $m$ depends upon the particular choice of $r = \tilde{r}$. For the sake of definiteness, we will assume in the following that $\tilde{r} = 6$. Then, the value of $m$ is determined by the following inequality:

$$\left[2(m-1)^2\right]^5 \geqslant \left(\frac{48m}{11} + 1\right)^{11/2}$$

and is satisfied for $m \geqslant 6$. We will choose $m = 6$ so that we can obtain the maximum value for $\tilde{g}'$, as explained below.

For $m = 6$, $\tilde{l}(r)$ is given by

$$\tilde{l} = 24(2r+1), \qquad r \geqslant 6 \tag{31b}$$

Let us take some $l$ lying between $\tilde{l}(r+1)$ and $\tilde{l}(r)$:

$$\tilde{l}(r) \leqslant l < \tilde{l}(r+1) \tag{32}$$

We divide $q = l/4$ into $r$ parts as usual: $q = rs + t$. The maximum value of $g$ is obtained by setting $\alpha = 0$ in (28):

$$g = \frac{8r+4}{l} > \frac{8r+4}{24(2r+3)}$$

where we have used the fact $l < \tilde{l}(r+1)$. We rewrite $g$ as follows:

$$\begin{aligned} g &= \frac{1}{6}\left(1 - \frac{2}{2r+3}\right) \\ &> \frac{1}{6}\left(1 - \frac{2}{2\tilde{r}+3}\right) \qquad (r \geqslant \tilde{r} = 6) \\ &= \frac{1}{6}\left(1 - \frac{2}{15}\right) = \frac{13}{90} = \tilde{g}' \end{aligned}$$

Thus, we see that as long as $r \geqslant \tilde{r} = 6$, (3b) is valid for all $g \leqslant \tilde{g}' = 13/90$. For $r = 6$, $\tilde{l}(r) = 312$. It is easily seen that for $2 \leqslant r \leqslant 5$, and $l$ satisfying (32), the inequalities (30c) and (30d) are simultaneously satisfied. Therefore, we finally conclude that for any $l$, (3b) is always satisfied.

We now wish to show that (3a) is also satisfied for all $l = 4q$. We first notice that the maximum possible value of $g$ is obtained when every chain is in a configuration which has $l-2$ corners. Two examples of such a configuration are shown in Fig. 11. Therefore, the maximum value of $g$ is given by

$$g_m(l) = (l-2)/l.$$

As $l \to \infty$, $g_m(l) \to 1$ and was the case considered in I and II. However, for any finite $l$, $g_m(l) < 1$. For $l = 4$, i.e., $q = 1$, $g_m(4) = 1/2$ and can be achieved by the construction described above for $l = 4$ [see the paragraph

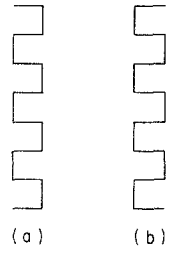


Fig. 11. Construction for $g = g_m(l)$.

after (19)]. For any other $l$, the maximum value $\bar{g}(l)$ of $g$ obtained in the constructions described above is always smaller than $g_m(l)$. It is evident from above, however, that $s_l(g) > \tilde{s}_l(0)$ for $0 < g \leqslant \bar{g}(l)$. For $l \geqslant 16$, we find from (24b) that $\bar{g}(l) = 1/2 + 4/l$, while for $l = 12$ and 8, we can produce $\bar{g}(l) = 4/l$. Therefore, in order to cover the range between $\bar{g}(l)$ and $g_m(l)$, we again use the following familiar trick: We use a fraction $\alpha$ of the $C$ cells that are covered with configurations that were produced to yield $g = \bar{g}(l)$. The remainder fraction $\beta$ of the $C$ cells are covered with configurations shown in Fig. 11. For the later, we cover the $C$ cell by rectangles of the size $2 \times (2q)$ or the size $(2q) \times 2$. In each rectangle, we draw either of the two configurations shown in Fig. 11. It is evident that for all values of $\alpha$ between zero and one, $s_l(g) > \tilde{s}_l(0)$. This proves (3a).

Our final remark regarding the proof of (3a) and (3b) is that the configurations generated here have orientational order that are of finite range: Since we can cover each cell by either vertical or horizontal loops (or rectangles), there is no orientational order between chains that belong to two different cells. From this point of view, the configurations generated above are disordered, and, from what has been said above, have nonzero entropy associated with these configurations, no matter how small $g$ is. Even for $g = 0$ the configurations have only short-range order as has been explained above [see the paragraph after (14)], and have nonzero entropy for any finite $l$. This constitutes a contradiction with the statement of Flory[4] that it is impossible to pack a lattice with disordered configurations of rodlike molecules ($g = 0$ in our terminology).

The above analysis can easily be extended to the case of a cubic lattice. We divide the lattice into layers of square lattices. Since the construction described above can be carried out for each square lattice, we conclude that (3) must remain valid even on a cubic lattice. (However, because $l$ is finite, one cannot follow the construction of Section 3 to get extra entropy [see (10)].) We consider a $\nu \times \nu \times \nu$ cubic lattice ($n = \nu^3$) where $\nu$ is again an integral multiple of $l$, i.e., $\nu$ is given by (11a). Since $p = n/l$, $p$ must be of the form $p = \nu'^3 l^2$. The thermodynamic limit is obtained by taking $\nu' \to \infty$.

## 5. DISCUSSION AND CONCLUSIONS

We have extended the analysis of I and II to establish *rigorously* that for the case of a single polymer chain in the absence of solvent molecules, (1a) and (1d) are valid for all continuous values of $g$ in the proper range. We have also considered the case of a single chain on a cubic lattice and showed (10) to be valid for all $g \leqslant \tilde{g}$, where $\tilde{g} = 2/3$. However, our main objective was to consider an assembly of $p$ polymer chains, each with $l$

segments. We have established by explicit construction that (3a) and (3b) are *rigorously* satisfied. The proof was carried out for the case $l = 4q$, $q$ an integer and the thermodynamic limit was obtained by considering $\nu = \nu' l$ with $\nu'$ an integer and taking the limit $\nu \to \infty$. The general case $l \neq 4q$ is much more complicated and will be reported elsewhere. However, the simple case ($l = 4q$) is enough to show that (3a) and (3b) are in contradiction with (2), the prediction from the F–H approximations. We have also shown that it is *not* impossible to cover the lattice with *disordered* configurations of polymer chains with $g = 0$, i.e., rodlike molecules. This is also in contradiction with the claim of Flory[4] that it is impossible to cover a lattice with rodlike molecules in a disordered configuration. The above results are also valid on a cubic lattice.

As has been pointed out in I, the case of nonzero $n_0$, i.e., the case when there are *solvent* molecules present can easily be treated by dividing the lattice with $n + n_0$ sites into two pieces $L_1$ and $L_2$ such that $L_1$ contains $n$ sites and $L_2$ contains $n_0$ sites. We then cover $L_1$ by polymer chains as described above. It should be evident that the lower bounds obtained here remain valid even for $n_0 \neq 0$. The meaning of $g$ is again the same: it is the number of the *gauche* bonds per segment in the thermodynamic limit.

As was observed in II, our lower bounds are useful only for small values of $g$, especially for $g \leqslant g_0$ [see (2)], for which the F–H approximations $s_{\mathrm{FH}}(g)$ must be regarded as identically zero. It was also noted there that there is a value $\bar{g}$ of $g$, such that

$$\bar{g} > g_0 \tag{33}$$

and [the lower bound $\tilde{s}_{\mathrm{H}}(g)$ in I and II is denoted by $\tilde{s}(g)$ here]

$$\begin{aligned} &\tilde{s}(g) \geqslant s_{\mathrm{FH}}(g) \qquad \text{for } g \leqslant \bar{g} \\ &\tilde{s}(g) < s_{\mathrm{FH}}(g) \qquad \text{for } g > \bar{g} \end{aligned} \tag{34}$$

(see Fig. 6 in II). For the case of many chains, we note that $\tilde{s}_l(g) > \tilde{s}(g)$ [see (1) and (3)]. Moreover, we find that even in this case there exist two numbers $g_0$ and $\bar{g}$ such that (2) and (33) are satisfied and that $\tilde{s}_l(g)$ satisfies (34) [replace $\tilde{s}(g)$ by $\tilde{s}_l(g)$].

Let us now consider the thermodynamics of the Flory model[4] for many chains. According to the model described in Ref. 4, the energy $E(g)$ in the configuration with $g$ as the fraction of the *gauche* bonds is given by (we will assume $n_0 = 0$)

$$E(g) = \epsilon \cdot g \cdot n \tag{35}$$

where $\epsilon > 0$: $\epsilon$ is the energy required to create a *gauche* bond. Since $\tilde{W}_{p,l}(g)$ is a lower bound on $W_{p,l}(g)$, we find that the partition function $Z$ satisfies

the following inequality:

$$Z = \sum_g W_{p,l}(g) e^{-\epsilon \cdot g \cdot n/T} \qquad (k_B = 1)$$
$$\geqslant \sum_g \tilde{W}_{p,l}(g) e^{-\epsilon \cdot g \cdot n/T}$$
$$= \tilde{Z} \tag{36}$$

Let $f(T) = -T \ln Z/n$ be the actual free energy per particle and $\tilde{f}(T) = -T \ln \tilde{Z}/n$ in the thermodynamic limit $\nu' \to \infty$. We find from (36) that

$$f(T) \leqslant \tilde{f}(T) \tag{37}$$

At very low temperatures, we expect the sum in $Z$ to be dominated by small values of $g$. Thus, one can use (3b) for $\tilde{s}_l(g)$ to obtain

$$\tilde{f}(T) = -T\tilde{s}_l(0) - \frac{T}{2e} e^{-8\epsilon/T} \tag{38}$$

at very low temperatures. Here we have neglected 3 compared with $4/g$ in (3b). Using (37) and (38), we find that the curve for $f(T)$ must lie *below* the curve for $\tilde{f}(T)$. Moreover, at $T = 0$, both curves must meet. We have shown this schematically in Fig. 1. The function $f_{\mathrm{FH}}(T)$ is the free-energy estimate obtained by using $W_{\mathrm{FH}}(g)$ in place of $W_{p,l}(g)$ in $Z$. The actual free energy $f(T)$ has a qualitatively *different* behavior than that of $f_{\mathrm{FH}}(T)$ at low temperatures. Thus, the actual free energy $f(T)$ does not produce a first-order transition to a *completely* ordered state as $f_{\mathrm{FH}}(T)$ shows at $T = T_c$ (see I and II for details). Moreover, since $f(T)$ lies below $\tilde{f}(T)$, it should be evident that the actual entropy

$$s_l(T) = -\partial f(T)/\partial T$$

per segment must reach a constant value at $T = 0$ which is bounded by $\tilde{s}_l(0)$:

$$s_l(T = 0) \geqslant \tilde{s}_l(0) = \frac{1}{l^2} \ln 2 > 0 \tag{39}$$

Thus, for finite $l$, the system approaches $T = 0$ with finite entropy. For $l \to \infty$, the case discussed in I and II, we find that $\tilde{s}_l(0) \to 0$ and that (39) reduces to

$$s_l(T = 0) \geqslant 0$$

We had assumed in I and II that the entropy of the system at $T = 0$ was zero ($l \to \infty$). It can be argued that this in fact is the case by considering an upper bound of the entropy and noting that this bound vanishes as $g \to 0$. For $l < \infty$, (39) shows clearly that there is a finite entropy in the system at $T = 0$.

We finally remark that our conclusion in I and II regarding the validity of the Gibbs–DiMarzio explanation of the glass transition remains unchanged: It is not obvious that the actual free energy $f(T)$ has a metastable extension like that produced by $f_{FH}(T)$ and shown by the broken part of it in Fig. 1, and therefore their explanation of an ideal glass transition at a finite temperature $T_0$, where the metastable extension of $f_{FH}(T)$ has zero entropy, can at best be a conjecture.

## ACKNOWLEDGMENTS

I wish to thank R. B. Griffiths and J. F. Nagle for various helpful comments. The work was supported by the NSF Grant No. DMR 78-26630 at Carnegie–Mellon University and the NSF Grant No. DMR 78-26630 (Polymer Program) and MRL (NSF) facilities at The University of Chicago.

## APPENDIX

Consider the function

$$\phi(\alpha) = \alpha^{1/p}\left(\frac{\lambda}{a + b\alpha} - 3\right) \tag{A1}$$

where $\lambda$, $a$, $b$, and $p$ are some constants. We wish to find the maximum of $\phi(\alpha)$ for $0 \leqslant \alpha \leqslant 1$. The condition for the extremum of $\phi(\alpha)$ is given by

$$x - 3 = p(\lambda - ax)x/\lambda \tag{A2}$$

where

$$x = \lambda/(a + b\alpha) \tag{A3}$$

The solution of (A2) so that the corresponding $\alpha$ lies within zero and one is given by

$$x_m = \frac{(p-1)\lambda}{2ap}\left\{1 + \left[1 + \frac{12ap}{(p-1)^2\lambda}\right]^{1/2}\right\} \tag{A4}$$

It is easily seen that the above extremum point (A4) is actually a point of maximum for $\phi(\alpha)$. Let $\alpha_m$ denote the point of maximum. Then,

$$\left[\phi(\alpha)\right]^p \leqslant \left[\phi(\alpha_m)\right]^p = \frac{a}{b}\,\frac{(p+1)/(p-1) - \sigma}{1+\sigma}\left[\frac{p-1}{2ap}\lambda(1+\sigma) - 3\right]^p$$

where

$$\sigma = \left[1 + 12ap/(p-1)^2\lambda\right]^{1/2}$$

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