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LETTER TO THE EDITOR

On the absence of the completely ordered phase in the Flory model of semi-flexible linear polymers

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Abstract. It is shown that in the Flory model of semi-flexible polymer chains, an assumption of random occupation of sites is not valid for estimating the excluded volume effects when the fraction of gauche bonds is small. Thus the model is *never* completely ordered except presumably at $T=0$, and the free energy is such that it cannot give rise to a melting transition from a state of zero configurational entropy at some finite temperature. This study also casts doubts on the conclusion of Gibbs and DiMarzio that the above model exhibits a second-order phase transition, i.e. a glass transition at a finite temperature in the super-cooled phase.

The quasi-lattice model of Meyer (1939), Flory (1942) and Huggins (1942) is a standard and reasonable model in the study of the statistical mechanical properties of linear polymer systems. A polymer chain is assumed to consist of n equal segments, each equal in size to that of the solvent molecule. A site of the lattice may be occupied by a solvent molecule or by a segment. The segments of a polymer chain must occupy a continuous sequence of sites connected by nearest-neighbour bonds. A bond which is not collinear with the preceding bond is termed 'gauche'. In the semi-flexible polymer chains considered here, there is an energy $\epsilon > 0$ for each gauche bond. Excluded volume effects are taken into account by the requirement that a site can be occupied once, either by a solvent molecule or by a polymer segment. Flory (1942, 1956) introduced an approximation to estimate the number of configurations $W(g)$ for a given fraction g of gauche bonds. The nature of the approximation is such that it predicts that the estimate $W_F(g) \rightarrow 0$ in the thermodynamic limit for all $g \leq g_0$, where g_0 is some finite value (see (3) below). This is taken to imply that the entropy $s(g) = 0$ for $g \leq g_0$. However, in this Letter we will establish rigorously that $s(g) > 0$ for all $g > 0$, and that the form of the free energy (curve (c), figure 1) is very different from the one proposed by Flory (curve OCB, figure 1).

In this Letter we consider in detail a limiting case of the situation, namely a *single* polymer chain of n segments in the absence of any solvent molecules, so that the chain covers the whole lattice. This limit is the appropriate one for the physical case of pure polymer melting. We will also give the result for the case of many polymer chains. The extension to the case with solvent molecules is easy and will also be discussed later in this Letter.

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For simplicity, take a square lattice ($\sqrt{n} \times \sqrt{n}$) of n sites that will be covered by the single polymer chain. The problem is better known as the *Hamilton walk problem* (Kasteleyn 1963a, 1967). Let $W_H(g)$ be the number of Hamilton walks with fraction g of gauche bonds. The Flory approximation (Flory 1942, 1956) applied to this problem yields the following estimate $W_F(g)$ for $W_H(g)$:

$$W_F(g) = \left(\frac{2^g}{e g^g (1-g)^{(1-g)}} \right)^n, \quad n \gg 1, \tag{1}$$

for the square lattice. In the Flory model, the internal energy is $E(g) = \epsilon g n$, where $\epsilon > 0$ is the energy required to bend a segment. Thus, according to (1), the free energy per site is given by

$$\begin{aligned} f_F(T) &= -\frac{T}{n} \ln \left(\sum_g W_F(g) e^{-\epsilon g n / T} \right) \\ &= T [1 - \ln(1 + 2e^{-\epsilon/T})]. \end{aligned} \tag{2}$$

The function $f_F(T)$ is shown in figure 1 by the curve OACB. The segment BC represents the liquid phase above T_c , and the stable phase below T_c corresponding to a perfectly ordered crystal ($\bar{g} = 0, E = 0, s = 0$) is described by the zero free-energy line OC (Flory 1956). The phase transition at T_c is a first-order transition. It is easily seen that

$$W_F(g) \xrightarrow[n \rightarrow \infty]{} 0 \quad \text{for } g \leq g_0 \approx 0.45. \tag{3}$$

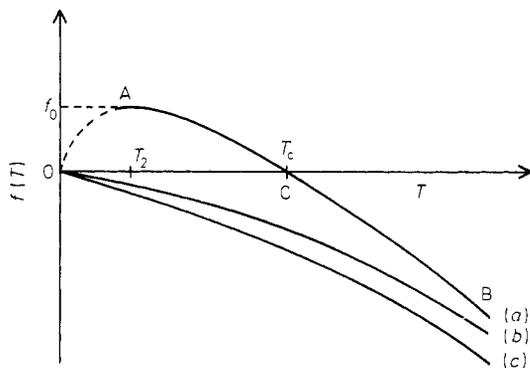


Figure 1. Various free energies: (a) $f_F(T)$, (b) $\tilde{f}_H(T)$, (c) $f_H(T)$.

The vanishing of $W_F(g)$ for small values of $g (\leq g_0)$ gives rise to the first-order transition at T_c . It should be noted that if we use the Huggins approximation instead of the Flory approximation, a similar result to (3) is obtained except that $g_0 = 0.227$ (Gujrati and Goldstein 1980 to be published).

There are some previous exact results which show that the Flory approximation is qualitatively inaccurate. One result concerns W_H , which is defined to be the total number of Hamilton walks summed over all values of g . On the square lattice, one has the rigorous bounds

$$(1.338 \dots)^n \leq W_H \leq (1.539 \dots)^n. \tag{4}$$

The lower bound is the exact result of Kasteleyn (1963a) for the number of Hamilton walks, W_H^M , with the Manhattan rule for traffic. (A square lattice with the Manhattan traffic rule is an oriented square lattice such that the orientations along various rows or columns alternate.) This Manhattan constraint disallows some walks that appear in W_H , but does not introduce any new ones and is, therefore, a lower bound to W_H as noted by Gordon *et al* (1976). The upper bound comes from the total number of configurations of 'square' ice as noted by Domb (1974). Now if one sums (1) over all g to obtain the Flory approximation, W_F , for W_H , one finds

$$W_F = (3/e)^n = (1.1036 \dots)^n \quad (5)$$

which is well outside the rigorous bounds. (However, if one adopts the Huggins approximation, then W_H is estimated by $(3/2)^n$ which is inside the bounds (Gujrati and Goldstein 1980, to be published).) Another test of the Flory approximation is to apply it directly to the Manhattan lattice result, as noted by Nagle (1974), with the result that $W_H^M = (1.338 \dots)^n$ is estimated by

$$W_F^M = (2/e)^n \xrightarrow{n \rightarrow \infty} 0. \quad (6)$$

(Using the Huggins approximation, we estimate W_H^M to be unity (Gujrati and Goldstein 1980, to be published).) Similar tests for various exactly solvable chain models which are not Hamilton walks have also been made by Nagle (1974). All of these exact results establish that the Flory–Huggins approximations are inaccurate to varying degrees, but none of them diagnoses the fundamental, qualitative discrepancy found in this paper.

Comparisons of (4) and (5) and of (6) with W_H^M show that, at least for some g , (1) is an underestimate. However, we shall now demonstrate that (1) is even more misleading, in that the entropy per segment

$$s_H(g) = n^{-1} \ln W_H(g)$$

is finite for any $g > 0$, i.e. there is not a $g_0 > 0$, where $s_H(g)$ goes to zero. Presumably this entropy $s_H(g)$ approaches zero as $g \rightarrow 0$. The proof proceeds by explicit construction of some of the possible Hamilton walks, and yields a rigorous lower bound for $s_H(g)$. Consider a set of $n/2(m+3)$, $m > 0$, identical rectangles, each having $(m+3)$ sites along the vertical sides and the two sites along the horizontal sides. Arrange them into $\sqrt{n}/2$ columns, each having $\sqrt{n}/(m+3)$ rectangles, one on top of another. This arrangement covers all the n sites of the lattice. Take any row of rectangles and join them at any two consecutive points, excluding the corner points (see figure 2), giving rise to a long horizontal circuit. Now join these $\sqrt{n}/(m+3)$ circuits at any of the columns (for

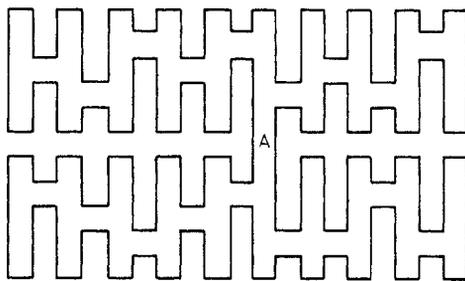


Figure 2. A Hamilton circuit.

example, at the point A in figure 2) to get a Hamilton circuit. The Hamilton walks are obtained by deleting any one of the n bonds of this circuit. It is easily seen that the total number of Hamilton walks thus generated is given by (we will neglect terms that do not contribute to the entropy per segment in the thermodynamic limit)

$$\tilde{W}_H(g) = m^{[n/2(m+3)]}, \quad n \gg 1. \quad (7)$$

Since each rectangle contributes eight gauche bonds, we have

$$g = \frac{8}{2(m+3)} = \frac{4}{m+3}$$

for the fraction of the gauche bonds. If $\tilde{s}_H(g) = (1/n) \ln \tilde{W}_H(g)$, we have

$$\tilde{s}_H(g) = \frac{1}{8}g \ln(4/g - 3), \quad (8)$$

which is positive for any $g > 0$. It is obvious that what we have obtained is a lower bound $\tilde{W}_H(g)$ for $W_H(g)$. Thus, the actual entropy $s_H(g)$ per segment must be such that

$$s_H(g) \geq \tilde{s}_H(g), \quad (9)$$

and hence $s_H(g)$ is positive for any $g > 0$, in contrast with (3).

Let us now consider the thermodynamics of this model. Let $f_H(T)$ be the actual free energy per site ($W_F(g)$ replaced by $W_H(g)$ in (2)) for the Flory model, and $\tilde{f}_H(T)$ the free energy per site obtained by using the lower bound $\tilde{W}_H(g)$ in place of $W_H(g)$. Since $W_H(g) \geq \tilde{W}_H(g)$, we find that

$$f_H(T) \leq \tilde{f}_H(T). \quad (10)$$

At $T = 0$, the system must be in its ground state, i.e. $E(g) = 0$. Thus, $f_H(T = 0) = 0$. We also find that, at low temperatures,

$$\tilde{f}_H(T) = -(T/2e) e^{-8\epsilon/T}$$

so that $\tilde{f}_H(T = 0) = 0$. Since the curve $f_H(T)$ lies below $\tilde{f}_H(T)$ (according to (10)) and meets it at $T = 0$ (see figure 1), and is a concave function of T , it is obvious that the actual entropy $s_H = -\partial f_H / \partial T$ per site must be finite at any temperature. It presumably approaches zero as $T \rightarrow 0$. Thus, the system is *never completely ordered*, except (presumably) at $T = 0$. It is evident that the behaviour of $f_F(T)$, curve (a) in figure 1, is quantitatively incorrect at low temperatures. The above conclusions remain unchanged even when the refinement due to Huggins (1942) is taken into account to obtain a better estimate of $W_H(g)$ (Gujrati and Goldstein 1980, to be published).

Until now we have considered the special case of a single polymer chain. It is not hard to extend the above analysis to a system of p polymer chains, each having l monomers ($n = p \times l$). For simplicity, consider the case $p = l = \sqrt{n}$. We can divide the square lattice into square cells, each with \sqrt{n} sites, and cover each cell with a single polymer chain, as described above. Another way of obtaining the lower bound is to cut the Hamilton walks obtained in the case of a single polymer chain into \sqrt{n} pieces, each covering \sqrt{n} sites. It must be obvious that (8) is a lower bound even for this case. The case of finite but large l is involved, but the idea is again the same: divide the lattice into cells and cover each cell by a certain number of polymers by the kind of construction described here. The detailed analysis will be presented elsewhere (Gujrati 1980, to be published) but we will quote the result here and make some observations. The entropy

per segment is bounded from below by

$$s(g) \geq \ln 2/l^2 + \frac{1}{8}g \ln(4/g) \quad (11)$$

for small values of g . For $g = 0$, $s(g)$ is bounded by $\ln 2/l^2$, obtained by covering cells of size $l \times l$ by l different polymer chains all lying either vertically or horizontally. For small g , we can neglect 3 compared to $4/g$ in (8), and we note from (11) that $s(g) \geq \tilde{s}_H(g)$. In the case where there are n_0 solvent molecules, we treat them as lattice sites not covered by polymer chains. There are $n + n_0$ sites on the lattice and we divide the lattice into two pieces L_1 and L_2 , L_1 containing n sites and L_2 containing n_0 sites. We now cover L_1 by polymer chains, and it is obvious that (8) again is a lower bound for the entropy. The calculation for the three-dimensional cubic lattice is done by treating the lattice as an assembly of square lattices and covering each square lattice as above. Thus (8) again forms the lower bound (see also Gujrati 1980, to be published). It should be clear, therefore, that the conclusions given in the paragraph immediately after (9) remain valid for all these cases.

We have shown above that the Flory model of flexible linear chains is *never* completely ordered except at $T = 0$. This behaviour is *drastically* different from the one originally proposed by Flory and implied by the free energy curve OCB (see figure 1). Thus, it should be obvious that the assumption of random occupation of sites to account for excluded volume effects is *not valid*, at least for small g . It should be mentioned that there are other models, namely the KDP model of Slater (1941) (see also Nagle 1969, Lieb 1967a, Sutherland 1967), the F -model of Rys (1963) (see also Lieb 1967b) and the Kasteleyn dimer model (1963b) that has been applied to polymer systems by Nagle (1974). The KDP model and the dimer model have free energies which are similar to the one originally proposed by Flory for his model, namely OCB (figure 1). However, both these models have an artificial anisotropic constraint which is necessary for this behaviour. On the other hand, the F -model which does not have this constraint has an infinite-order phase transition, that is, the free energy and all its derivatives are continuous at T_c , but the free energy is not analytically continuable through T_c . The entropy of the system in this model at any finite temperature is non-zero, just like it is in the Flory model as shown in this paper. It is obvious that the F -model cannot describe polymer crystallisation, but when kinetics are taken into account it is conceivable that this model will have a glass transition at low temperatures (Nagle 1974), because the low-lying excitations in the model are best described as chain folding, which would be kinetically very slow (see below). Both the KDP and F -models suffer from the drawback that they allow closed polymer rings which, however, are probably not very serious at low temperatures.

Finally, we wish to point out the relevance of our result to the theory of the glass transition as given by Gibbs and DiMarzio (1958). The fact that the actual free energy $f_H(T)$ does not have the form proposed by Flory (figure 1) also casts doubt (see also Gujrati and Goldstein 1980, to be published) on the use of his calculations (more precisely, the Flory-Huggins approximation) by Gibbs and DiMarzio. They have proposed that the curve AC in figure 1 is the free energy of a supercooled liquid phase which undergoes a second-order phase transition at a temperature T_2 where the entropy $s_F(T_2)$ goes to zero, but $g_F(T_2) > 0$ (point A on the curve AC in figure 1). They suggest that the vanishing of $s_F(T_2)$ is indirectly related to the slowing down of the kinetic phenomena observed experimentally at some higher temperature T_g . According to Gibbs and DiMarzio, the free energy remains constant at f_0 (see figure 1) below T_2 , in the 'ideal' glassy state, with zero slope, i.e. zero entropy, but finite and constant

$g_F = f_0/\epsilon$. However, it is implicitly assumed in their calculation that $W_F(g)$ is a good estimate of $W(g)$, even at small g , contrary to what has been established here. And we have also shown that the curve OAC is qualitatively incorrect, at low temperatures. Thus, there are serious doubts about the validity of the conclusions arrived at by Gibbs and DiMarzio (1958). To be sure, it is possible that the correct $f_H(T)$ could have a first-order phase transition at a finite temperature, but there is no reason to suppose that a metastable extension of the liquid free energy would behave similarly to the curve AC in figure 1.

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