Three statistical mechanical arguments that favour chain folding in polymer systems of lamellar morphology

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(Received 22 January 1980)

Three arguments are given that imply substantial chain folding in crystalline–amorphous polymer systems of lamellar morphology. These arguments assume random coil behaviour in the amorphous region. (1) The random walk character of the polymer chain portions comprizing the amorphous regions topologically constrains the number of crystalline stems that connect covalently with the amorphous regions to be small. Quantitative estimates are made and lower bounds on the amount of chain folding are given. Estimates of (2) the tightness of loops and (3) the average spatial separation between consecutive crystal stems (along a given chain) are made. The results favour substantial amounts of adjacent and near-adjacent re-entry. Existing experimental measurements on diblock copolymers consisting of crystallizable and non-crystallizable blocks provide a measure of the random walk character of the chains in the amorphous region. It is argued that such systems form lamellar structures with large amounts of chain folding in the crystalline regions as a condition of *thermodynamic equilibrium.*

INTRODUCTION

There are two rival views of the microstructure of polycrystalline polymers of lamellar morphology: the *switchboard model* and the *adjacent re-entry model.*

Figures 1a, 1b, and *6* illustrate various aspects of the switchboard model. The common feature in these figures is that the chains in the amorphous region are random. They leave the crystal at some point and re-enter at a point which is determined by random walk statistics). The point of re-entry is generally thought to occur some distance from the exit point.

Figures 4a, 5a, 5b and *7* illustrate various aspects of adjacent re-entry. The common feature in these figures are the tight loops which force adjacent re-entry.

If we grant the existence of these two rival views, it is also necessary for us to allow intermediate situations. Both theory and experiment can be used in an attempt to decide which situation prevails in real systems. The experimental situation probably corresponds to some mix of the two extreme models. However, we think that the experimental situation approximates the adjacent re-entry model *more closely* than the switchboard model.

In this work, we shall devote ourselves exclusively to the *theory* of the crystalline–amorphous lamellar complex. We shall find that the switchboard model, which is a hypothesis on how polymers behave at an interface, is incompatible with the statistics of polymers near interfaces.

This paper presents three statistical mechanical observations on the nature of the crystal–amorphous interface.

Observation I uses a simple density argument to show that the chain folding at an interface is substantial. Quantitative estimates and bounds are given. The meaning of random behaviour of polymers near a surface is explored and in the process the lattice model in the presence of a surface is solved. Also, the Gamblers Ruin problem is shown to describe polymer behaviour in homopolymer systems of lamellar morphology.

Observation II shows that loops are generally tight, provided there is a surface in the vicinity of the loop. The crystalline lamella provides this surface.

Observation III is an actual quantitative estimate of the amount of adjacency.

The above observations are based on the assumption of random coil behaviour in amorphous regions close to interfaces. If extensive orientation is imagined to occur in the amorphous regions, then uncertainties are introduced. For this reason, it is useful to have experimental support for the assumption of unoriented amorphous regions. We shall see that amphiphilic diblock copolymers provide such evidence. Finally, it is pointed out that these amphiphilic diblock copolymers show chain folding as a condition of thermodynamic equilibrium.

THREE STATISTICAL MECHANICAL OBSERVATIONS WHICH FAVOUR CHAIN FOLDING

Observation I. Some chain folding is a topological necessity in every lamellar structure

Consider the crystalline–amorphous complexes displayed in *Figures 1a* and *1b.* In both, there is a region of crystal which changes abruptly to an amorphous region. In these models, each crystal stem leaves the crystal and goes into the amorphous region. In the crystalline region, the chains are all oriented in the same direction; in the amorphous region, each chain consists of N_a elements which form a random walk. Because of the random coil nature of the amorphous segments, we shall assume that the thickness of the amorphous layer is of the order of $N_a^{1/2}$. In *Figure 1a*, the random coil portions form tie-chains (bridges) between

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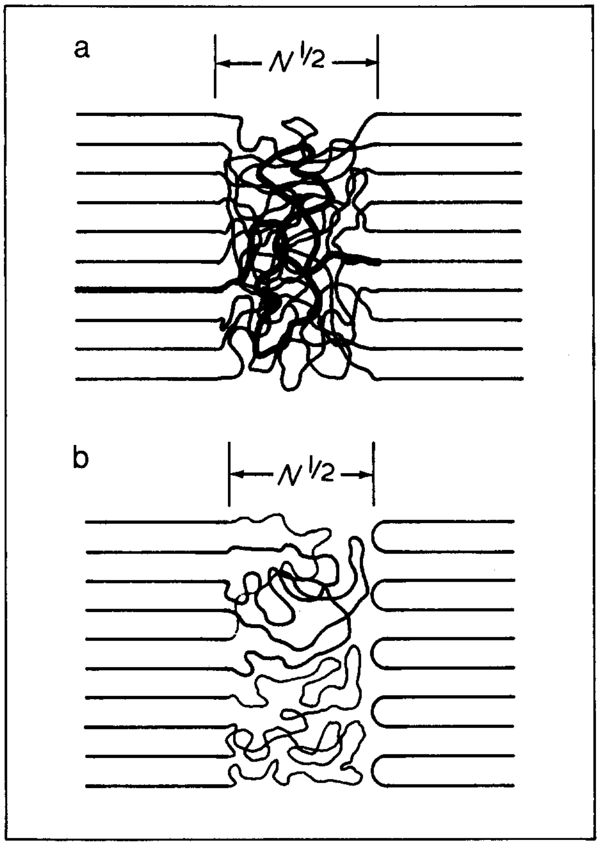

Figure 1 *Figure 1a* displays an amorphous layer consisting of tie-chains (bridges). Because the prolongation of the straight crystalline portion through the interlamellar region would result in a interlamellar density equal to the crystal density, we can see that the turning of the chains in the amorphous region results in a density which is much higher than the crystalline density. See text for quantitative estimates. *Figure 1b* Ditto, but for loops rather than bridges

adjacent crystal lamellae. In *Figure 1b*, the random coil portions form loops.

The existence of such structures as depicted in Figures 1a and 1b is impossible[1]. To see this clearly, we write the volume of the amorphous region as:

$$V = M^2 N_a^{1/2} \tag{1}$$

where M is the number of stems in each of the two directions parallel to the lamella and V is expressed in units of the volume of a segment. The number of segments, n, in this volume is given by:

$$n = M^2 N_a \tag{2}$$

so that the density ρ of the amorphous region is given by:

$$\rho = \frac{n}{V} = N_a^{1/2} \tag{3}$$

which is much greater than 1. This startling result deserves further discussion.

The first point is that such high density cannot be sustained by the crystal. The amorphous region would simply expand laterally and pull the crystalline regions apart. Thus, the models depicted in *Figure 1* can have no reality and cannot be used as models of a semicrystalline polymer.

The second point is that one can alleviate the packing difficulty by postulating that only a fraction, f, of polymer chain stems continue into the amorphous region. The remainder, $1-f$, of the stems do not enter into the amorphous region. The amorphous density in this case becomes:

$$\rho = f N_a^{1/2} \tag{4}$$

An estimate of the fraction of folded chains is obtained by choosing $f = 1/N_a^{1/2}$. Then the fraction of chain folding for the case that $l \ll L$ (where l is the lamellar thickness and L the length of the molecule) is given by:

$$1 - f = (N_a^{1/2} - 1)/N_a^{1/2} \tag{5}$$

Thus, in contradistinction to *Figure 1*, the model of *Figure 2* represents an *a priori* possibility since it allows the amorphous density to be of a proper magnitude.

The packing problem is not alleviated by postulating adsorbed polymers (polymers not covalently attached to the crystal stems) since, for a given degree of crystallinity, one must have more chain folding–not less–when adsorbed molecules are present (if all the amorphous region consisted of adsorbed molecules, the amount of chain folding would be 100%).

The above arguments are forceful because of their extreme simplicity and because of the strong belief in the random walk character of polymer in an amorphous region. Nonetheless, legitimate questions can be raised which require further discussion.

The assumption that the amorphous lamellar thickness M is proportional to $N_a^{1/2}$ needs to be examined. One would expect that M depends on whether kinetic or equilibrium factors are dominant during the crystallization process. Indeed each of the three equilibrium calculations we shall use below give different dependences of M on N_a. In the first treatment (for a system consisting of bridges only) $M \propto N_a^{1/2}$, in the second treatment (applicable to diblock copolymers) $M \propto N_a^{2/3}$, while in the third treatment (applicable to homopolymers with lamellar morphology) $M \propto N_a$. However, each of these treatments results in extensive chain folding and adjacent reentry, as we shall see.

The use of an average N_a needs to be examined. Experiments span a spectrum of possibilities. For diblock copolymer, with one part crystalline and the other amorphous (amphiphilic copolymers), N_a is the actual molecular weight of the amorphous portion. Also, we know that the incom-

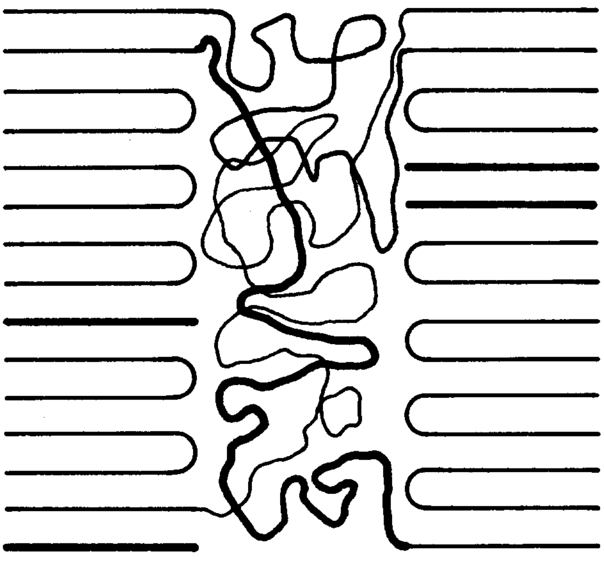

Figure 2 By allowing a substantial number of tight folds, the density of the amorphous region can be lowered to a reasonable value

patibility of the two halves forces (for proper molecular weight) a lamellar morphology. Thus, the requirements of the model are satisfied exactly for block copolymers. The molecular weight N_a is known and the lamellar thickness M exists. See below for a discussion of this system. However, one may also have a homopolymer of lamellar morphology. In this case, N_a is not the molecular weight of the homopolymer but a smaller number. Also, it is an average value. The amorphous portions of the chains have a wide distribution of length. The question of how the amorphous regions are filled by these chain portions is asked and partially answered below also.

The presence of a surface modifies the concept of a 'random walk polymer'. Fortunately, the problem of the isolated polymer near a surface has received a recent and extensive examination so that we now have much information to draw on. The dimensions of the molecules and, therefore, the characteristics of the random walk, are influenced by the presence of the surface. Also the surface forces us to classify the chains according to whether they are (1) cilia, (2) bridges, (3) loops or (4) free chains. Each of these kinds of chains has different statistics[2]. The amount of chain folding will depend on their relative abundance.

The effect of the chemical structure of the chains must be considered also. Chemical structure determines the statistical length of the random walk in free space. We shall assume that the presence of the surface does not alter the statistical length. We know that this is only an approximation. The problem of a semiflexible chain near a surface is solved[3] and the chain dimensions involve both surface energetics and stiffness in a complicated way.

We are not dealing with isolated chains, but with chains competing with each other for space at the same time as they are influenced by the surface. What we need is an analogue of the Flory–Huggins lattice model but near a surface, which can accommodate various amounts of cilia, bridges, loops and free chains.

Thus, the problem of determining the extent of chain folding is both complex and difficult. Therefore, we proceed by establishing an exact result relating the amount of chain folding to the properties of the amorphous region. Next we establish some exact lower bounds on the amount of chain folding.

We then proceed to three models of the amorphous lamellae: a simple entropy argument that the amorphous lamellar thickness varies as $N_a^{1/2}$; a treatment of amphiphilic diblock copolymers which gives lamellar thickness varying as $N^{2/3}$; and a demonstration that the amorphous portions of a homopolymer of lamellar morphology can be understood in terms of the Classical Gambler's Ruin Problem.

Simple space filling arguments show that a substantial amount of chain folding exists. The degree of crystallinity, χ_c, of a polycrystalline polyethylene of lamellar morphology can be written in two ways:

$$\chi_c = \frac{\rho_c l_c}{\rho_c l_c + \rho_a l_a} \tag{6}$$

$$\chi_c = \frac{r_c}{r_a + r_c} \tag{7}$$

where r_a is the average number of CH_2 units in a run of amorphous segments, r_c is the average number of CH_2 units in a run of crystalline segments, and l_a and l_c are lamellar thicknesses in Å. Equation 6 simply defines a mole fraction crystallinity. *Equation (7)* is a consequence for large molecular weight; we simply follow each molecule along its contour as it traverses through crystalline and amorphous portions. *Equations (6)* and *(7)* give:

$$\frac{r_c}{l_c}\,\frac{l_a}{r_a} = \frac{\rho_c}{\rho_a} \tag{8}$$

which is a unique relation between the properties of the crystalline and amorphous regions. $1.27\, r_c/l_c$ is the ratio of the number of CH_2 units in a crystalline run of segments to the number of CH_2 units in a stem. It is also the same as the number of stems comprising a run which we call cluster size. The relation between cluster size and the fraction f of stems leaving and entering the amorphous region is given by:

$$f = \frac{l_c}{1.27\, r_c} = \left(\frac{l_a}{1.27\, r_a}\right)\frac{\rho_a}{\rho_c} \tag{9}$$

Equations (8) and (9) show that the amount of chain folding within the crystalline lamella is related uniquely to the average length of a run in the amorphous region. If intuitively, the ratio $l_a/1.27\, r_a$ is thought to be small, then of logical necessity, f is also, intuitively, small (see Eq. 9).

A computer simulation by Yoon and Flory[4] throws interesting light on the discussion. For polyethylene crystals of lamellar morphology, a polymer chain is allowed to walk randomly across a lamellar spacing of 90 Å, and it is found that it takes, on average, 130 ± 20 CH_2 units to find a first contact with the amorphous–crystal interface. A perfect *trans–trans* crossing of the lamella would consume 71 CH_2 units. It is plain that if every crystal stem were connected to an amorphous section of an average length of 130 CH_2 units, the density of the amorphous region would be $130/71 = 1.83$. If we wish the amorphous density to be 0.85, then only a fraction of the crystal stems can be connected to the amorphous segments, otherwise there would be an overfilling of the amorphous region. Using $\rho_a/\rho = 0.85$, we obtain $f = 0.463$ from equation (9), i.e. less than 1/2 of the time a stem continues into the amorphous region. The other 0.537 of the time, it must fold back into the crystal. There is a suggestion that the value of f calculated here is an upper bound because, as soon as the random walk touches a surface, it is forced by the rules of Yoon and Flory to become a stem. However, in reality, we must allow the random walk to reflect sometimes off the surface. If it always reflects off, the value of f would be zero. If it never reflects off, the value of f is 0.463. The Yoon–Flory model will be discussed further below.

The model of this section is a two-phase model with the folds being tight adjacent re-entry folds and part of the crystal phase. It is to be emphasized that the amorphous region consists of both bridges and loops. These loops which are far more numerous than bridges (see equation (34)) are not counted as adjacent re-entry folds.

Free chains, cilia and solvent in the amorphous region all have the effect of reducing f in equation (9). To determine the effect due to free chains and solvent, we simply use for ρ_a the density due to loops and bridges only. For cilia, we imagine that only half of the segments in the cilia contribute to the amorphous density.

Tilt in the crystal stems is accounted for easily by dividing the right-hand side of equation (9) by cos ϕ, where ϕ is the angle of tilt.

Rigorous bounds on the amount of folding. In a previous paper, Flory used general arguments to recognize that 1/2 was a *lower bound* to the amount of chain folding in systems of lamellar morphologies[5]. We wish to show that this lower bound must be raised whenever loops, cilia and free chains are considered and that the 1/2 lower bound applies only to lamellar systems in which the amorphous region consists entirely of bridges (tie chains). Consider a bond with equal *a priori* probability, p_0, of lying in any direction (*Figure 3a*):

$$p_0 = \frac{1}{4\pi}, \quad 0 \leqslant \theta \leqslant \pi, \quad 0 \leqslant \phi \leqslant 2\pi \tag{10}$$

where θ is the co-latitude, ϕ the longitude.

If we now consider only the right half of this distribution (*Figure 3b*), we have the probability of always stepping to the right:

$$\begin{aligned} p_1 &= \frac{1}{2\pi} \quad 0 \leqslant \theta \leqslant \frac{\pi}{2} \\ & \qquad\qquad\qquad\qquad 0 \leqslant \phi \leqslant 2\pi \\ p_1 &= 0 \quad \frac{\pi}{2} < \theta \leqslant \pi \end{aligned} \tag{11}$$

Optically, both the distribution in equations (10) and (11) are isotropic so that one cannot distinguish between them on the basis of optical measurements. Flory used this latter distribution (equation (11)) to estimate the number of chain folds[5]. The average length of a step to the right, d, is the projection of the bond of length l onto the unique direction:

$$d = l \int_0^{\pi/2} p_1 \cos\theta \, \mathrm{d}\Omega \Bigg/ \int_0^{\pi/2} p_1 \, \mathrm{d}\Omega = l/2 \tag{12}$$

This result would lead to a density of 2 if every chain were to continue from one crystal to the other. To keep the density normal, 1/2 of the chains are imagined to fold back before they enter the amorphous region. 1/2 is a lower bound because, in reality, chains do not always press forward, but double back, due to their random walk character. In fact, if the chains were allowed to double back freely, we would expect the distribution of equation (10). A bridge with the distribution of equation (10) would consist of more segments than a bridge with the distribution of equation (11). Therefore, we conclude that, for an amorphous region consisting of bridges only, $f < 1/2$.

If we have a volume fraction, ν_f, of free chains (chains unattached to any crystal), a fraction, ν_b, of chains that are bridges, and a fraction, ν_c, of cilia, all of the same contour length, then the fraction of crystal stems that continue from the crystal into the amorphous interface region, f, is:

$$f = \nu_c/4 + \nu_b/2 + 0\,\nu_f \quad (\textit{continuum, no reversals}) \tag{13}$$

where $\nu_c + \nu_b + \nu_f = 1$. All the chains are imagined to start at one interface and end at the other. The density is uniform throughout the amorphous region and is taken to be the same as the crystal density. To allow for different densities, the right-hand side of equation (12) is multiplied by ρ_a/ρ_c. The result does not depend on how the cilia are apportioned into the two crystalline boundaries.

One could define an isotropic distribution which is some linear combination of equations (10) and (11). The f of equation (13) is an upper bound to any such isotropic distribution. If all the chains are free we have 100% chain folding. If all the chains (n the amorphous region) are cilia, then we have a minimum of 75% chain folding.

If one imagines that the chains lie on a simple cubic lattice such that 1/3 of the bonds are in each of the the three possible orientations and that in the unique orientation (perpendicular to the lamella) the steps are in one direction, then the methods leading to equation (13) give:

$$f < \nu_c/6 + \nu_b/3 + 0\,\nu_f (\textit{simple cubic lattice, no reversals}) \tag{14}$$

The above results are predicted by an isotropic distribution of bonds. One can avoid these conclusions by assuming that the distribution is anisotropic (i.e. the bonds orient preferentially normal to the lamella).

Equilibrium calculations. Improved evaluation of f. We imagine a simple cubic lattice between two plates of

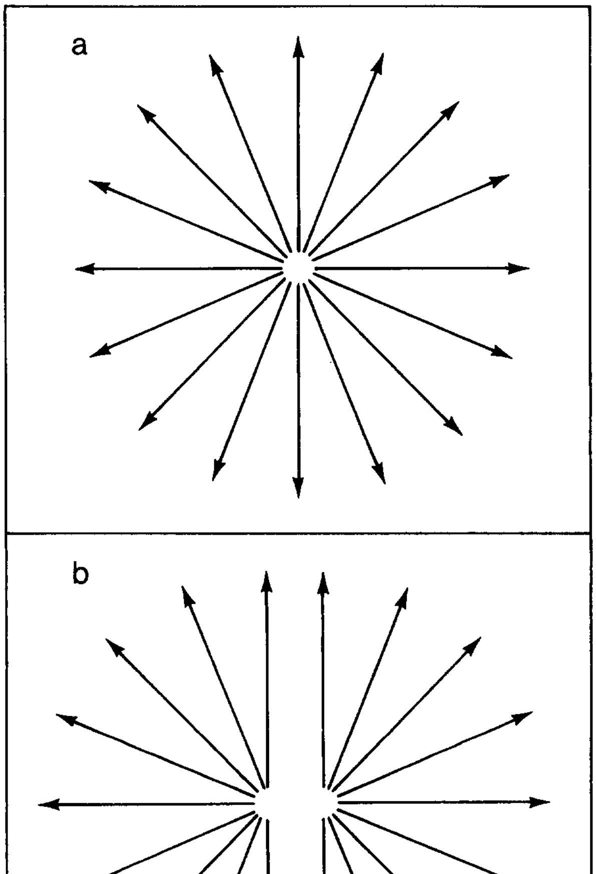

Figure 3 Both Fig. 3a and one-half of Fig. 3b represent an optically isotropic distribution of bonds. However, Fig. 3b results in a drift, in one direction, of the polymer chain imagined to be composed of such bonds. Fig. 3b enables one to establish a (weak) lower bound to the amount of chain folding

separation M. We have η_c chains each of length N_a within an area A. These chains begin at one surface and end at the other; otherwise they are free. We imagine the lattice to be completely full of polymer. We have:

$$f = \frac{MA}{N_a A} = \frac{M}{N_a} \tag{15}$$

$$f = \frac{\eta_c}{A} \tag{16}$$

Equation (16) defines f as the fraction of stems that are connected covalently to a random coil chain. Equation (15) states that the total number of CH_2 units fN_aA equals the total number of lattice sites MA. If every stem was the source of a chain, we would have N_aA CH_2 units; but this would overfill the space. Therefore, we begin with a fraction, f, of the stems as sources of chains. For each step of a chain which does not begin on the surface, we have a factor, Z, which is the coordination number of the lattice. For each step of a chain which begins on the surface, we have a factor Z'. For the simple cubic lattice $Z = 6, Z' = 5$. The total number of arrangements of the η_c chains is:

$$Q_{CT} = (Z')^{2A} Z^{(M-2)A} Z^{-(M-2)\eta_c} (Z')^{-2\eta_c} \tag{17}$$

The last two terms of equation (17) occur because there are M steps within each chain which are forced in one direction only. From:

$$Q_{CT} = Q_c^{\eta_c} \tag{18}$$

we obtain:

$$\begin{aligned} Q_c &= (Z')^{2A/\eta_c - 2} Z^{(M-2)A/\eta_c - (M-2)} \\ &= (Z')^{2(1/f-1)} Z^{(M-2)(1/f-1)} \end{aligned} \tag{19}$$

When $f = 1$, we have correct normalization. If we now maximize equation (19) subject to equations (15) and (16) we obtain:

$$\frac{N_a}{M^2} = \frac{\ln Z}{2\ln(Z/Z')} \tag{20}$$

which shows the thickness to vary as the square root of molecular weight. Or, equivalently:

$$f = \left(\frac{2\ln(Z/Z')}{\ln Z}\right)^{1/2} N_a^{-1/2} \tag{21}$$

which for the simple cubic lattice gives:

$$f = 0.45\, N_a^{-1/2} \tag{22}$$

The above treatment assumes the statistical length to be one monomer unit. A simple analysis shows that, more generally, we have:

$$f = \left(\frac{2\ln(Z/Z')}{\ln Z}\right)^{1/2} C_n^{1/2} N_a^{-1/2} \tag{23}$$

where C_n is defined and tabulated in *Table 1* of Flory's book[6].

We list here certain considerations not discussed in the derivation of equation (23).

(1) For $M = 1$, we should have a dependence on Z' but not on Z. Equation (19) shows this happens for $M = 2$ rather than $M = 1$. This is probably not serious.
(2) The treatment ignored packing and orientation effects. The isotropic packing effect (attrition due to competition for space) is not dependent on M and, therefore, has no effect on the minimization procedure. The change in packing due to orientation has been shown[7] to be of second order in M/N_a and does not affect the results.
(3) The treatment is for bridges only.
(4) The treatment ignores the surface energetics and the fold energies of the crystal. This affects the value of the coefficient in equation (21) but not the molecular weight dependence. The coefficient is calculated by published methods[7].
(5) The calculation is appropriate to diblock copolymers rather than to a homopolymer. We do not at this stage know what N_a is for a homopolymer (but see further on).

Other approximations to the evaluation of f. Those treatments of block copolymers which provide an estimate of the lamellar (block) thickness M, also by virtue of equation (15), provide an estimate of f. If both the blocks are amorphous, this estimate gives the fraction of the interface area between the two blocks that is covered by covalent links between the two blocks. For amphiphilic diblock copolymers, it is also the fraction of crystalline stems that project (are covalently connected) into the amorphous layer, $(1 - f)$ being the amount of folding. See below for quantitative estimates of f derived from experiment.

A treatment of amphiphilic block copolymers results in the following formulae for lamellar thickness[7]:

$$l_a = \frac{A r_a^{2/3}}{\rho_a^{1/3}} \tag{24}$$

$$l_c = \frac{A r_c \rho_a^{2/3}}{\rho_c r_a^{1/3}} \tag{25}$$

where A is a constant, containing energetics of the interface region. We mention these equations because amorphous thickness varies as $r_a^{2/3}$ rather than $r_a^{1/2}$. Hashimoto *et al.*[8] have shown experimentally that the 2/3 value is approximately correct and is consistent with the theories of Helfand[9] and Meijer[10] as well as the above theory[7]. The dependence of f on N_a is:

$$f \propto N_a^{-1/3} \tag{26}$$

which is a slower variation than that of equation (23).

Let us therefore consider the problem of bulk polymer near a surface more carefully. Specifically, we consider a bulk polymer consisting of free chains of length N_a between parallel plates. We shall assume that the attraction of the molecules for each other is so strong that all holes are squeezed out, with a resulting constant density across the material. Constant density is needed for the arguments which follow. The free energy is given by $F = U - TS$. U is calculated to be:

$$U = 2A\sigma_s \tag{27}$$

where σ_s is the surface energy.

To calculate S, we consider one molecule near the surface. When a segment of this molecule leaves the surface, there is no net energy change for the system since another segment from one of the polymers in the system will have taken its place. This is true, no matter what the value of σ_s is. Thus, the energetics of the surface for the freely-jointed polymer will have no effect on the shape of the molecule, no matter what its character and strength. This means that S is dependent only on the plate separation, M, the properties of the lattice, Z, Z', and N_a. It is dependent on temperature only through M.

To evaluate S, we modify the Flory–Huggins procedure. There are three distinct parts to the Flory–Huggins calculation.

(1) Location of the centre of mass of each molecule (or equivalently, location of the initial segment of each molecule).
(2) The calculation of the number of configurations of each molecule given the centre of mass.
(3) The competition for space.

The competition for space is treated here in the same way as for a bulk polymer without a surface. Because this third factor (sometimes called the attrition term) is independent of M, it can be ignored in any calculation of M. In the paper on block copolymers, the effect of bond orientation on the third factor is shown to be small[7].

Let us now calculate the contribution from factors (1) and (2). For the bulk polymer without the surface problem, we have for the centre of mass contribution of the η_c molecules of length N_a ($N = \eta_c N_a$):

$$\frac{S_{CMb}}{k} = \sum_{j=0}^{\eta_c} \ln(N - jN_a) = \int_0^{\eta_c} \ln(N - jN_a)\,\mathrm{d}j$$

$$= \eta_c \ln(\eta_c N_a) - \eta_c \tag{28}$$

Compare this with allowing each of the η_c molecules to have N sites as the possible location of the first segment. For this case, we have $S_{CMb}/k = \eta_c \ln(\eta_c N_a)$, which differs from equation (28) in the term $-\eta_c$. We now make the observation that the entropy due to effects (1) and (2) is η_c times the entropy of one molecule $-\eta_c$:

$$S_{CT} = \eta_c S_c - \eta_c \tag{29}$$

where S_{CT} does not include the attrition term. S_c includes both the location of its centre of mass and its number of configurations for each centre of mass. The use of equation (29) gives the Flory–Huggins result. We now make the assumption that equation (29) is valid also for a bulk polymer near a surface. For molecules near a surface, the localization entropy and configurational entropy for each molecule do not separate.

The calculation of the configurational entropy of a bulk polymer between two plates has now been reduced to that of calculating the entropy of one molecule between two plates; but this is done easily by the method of DiMarzio and Rubin[11]. The prescription is straightforward, although the numerical computation may be lengthy. There is only one parameter of the isolated polymer between two plates, i.e. the energy of attraction of the surface for the polymer. To determine it, we first observe that, over a long period of time, a given molecule will visit each place in the region between plates with equal probability; that is to say, the time–averaged segment density due to one molecule is a constant since the overall density is a constant. From the ergodic theorem, we know that the ensemble average density is also a constant. Therefore, we choose a value of surface energy for the calculation of the entropy of an isolated chain which results in constant segment density. However, it is known that this is the critical energy, or equivalently, the boundary conditions for constant density are the reflecting boundary conditions[11].

Another way[12] of arriving at this choice of boundary condition is to replace the effect of all of the other molecules on the molecule of interest by a potential energy $V(Z)$. We then ask what $V(Z)$ must be to result in constant segment density for the polymer chain. The answer is $V(Z) = 0$ between the plates and $V(Z) = \epsilon_c$ at the surfaces. Thus, we again arrive at the reflecting boundary condition for S_c.

Recapitulating, we have:

$$F = U - TS = 2A\sigma_s - T\eta_c S_c + T\eta_c \tag{30}$$

where S_c is the configurational entropy of one chain of length N_a between two plates of separation M. The value of M is obtained by minimizing F with respect to M. The calculation of S_c is performed by the method of DiMarzio and Rubin[11] at the critical energy, ϵ_c. This precise prescription when implemented should determine the power law for f.

The above prescription cannot be extended to include bridges, loops and cilia since these do not give constant density for the reflecting boundary condition[13]. The generalized problem thus remains unsolved. However, inspection of *Figure 2* of ref. 11 suggests an approximate procedure in the general case. One observes that the entropy is rather insensitive to boundary conditions. It goes through a shallow maximum at the absorbing boundary condition ($\theta = 0$) so that the entropy for the reflecting boundary condition ($\theta = 0.693$) and intermediate points is not much different from the values appropriate to the absorbing boundary. Thus, the free energy which we write symbolically as:

$$F = 2A\sigma_s - T\sum_{i=1}^{4} \eta_{ci} S_{ci}(\theta_i) \tag{31}$$

where i enumerates bridges, loops, cilia, and free chains will depend on θ_i only quadratically. S_{ci} indicates entropy and may include a small negative constant as in equation (30). Thus, it seems that the treatments of Meier[10] and Helfand[9] which seem so different (because of the use of the absorbing boundary condition by Meier and the reflecting boundary condition by Helfand) do not in fact give much different results. Meier's treatment minimizes free energy but does not take proper account of the density. Helfand's treatment takes better account of density contraints but does not minimize free energy. A treatment which minimizes the free energy (maximizes the entropy) with respect to θ_i, and subject to the constraint of constant density, is envisaged.

The method of Scheutjens and Fleer[14] is more general than the above in that it allows for variation in segment density. On the other hand, it is more difficult to implement.

All of the above considerations are useful for block copolymers where N_a is well defined, but they are less so for homopolymers. In the next section, we will use the methods of the Gambler's Ruin Problem of probability theory to gain insight into the homopolymer problem.

The statistics of the polymer chain portions (runs) residing in the amorphous regions of semi-crystalline homopolymers of lamellar morphology. The Yoon and Flory model[4] discussed above is equivalent to the Gambler's Ruin Problem of classical probability theory[15]. In turn, this latter problem is equivalent to the problem of a random walk on a line segment with absorbing boundary conditions on the ends. One starts a distance z from the one end (the gambler begins with z dollars) and steps up or down (wins and losses in units of a dollar) until one touches the bottom surface (he loses all his money) or the top surface (he wins an amount M). Let $u_{z,n}$ denote the probability that the process ends with the nth step at the barrier o (gambler's ruin at the nth trial). Let:

$$q_z = \sum_n u_{z,n} \qquad (32)$$

be the probability of a gambler's ultimate ruin and $(1 - q_z)$ the probability of winning a dollars. Then for one dimension we have:

$$q_z = 1 - \frac{z}{M} \qquad (33)$$

which reproduces equation (2.5) of Ch. XIV of Feller's book[15]. The case of a random walk on a simple cubic lattice gives a result identical to equation (33). Thus, if we start one step above the surface (with a stake of one dollar), $z = 1$, we have a probability of loop formation of:

$$P_{\text{loop}} = q_1 = \frac{M - 1}{M} \qquad (34)$$

and a probability of bridge formation of:

$$P_{\text{bridge}} = 1 - q_1 = \frac{1}{M} \qquad (35)$$

The expected duration of a game D_z is:

$$D_z = z(M - z) \quad \text{(one dimension)} \qquad (36)$$

$$D_z = 3z(M - z) \quad \text{(simple cubic lattice)} \qquad (37)$$

Equation (36) reproduces equation (3.5) of Ch. XIV of Feller[15] while equation (37) is obtained as a simple exercise from the same methods used by Feller to derive equation (36). For $z = 1$, we obtain an expression for the segment density in the amorphous regions by using the same argument which derived equation (3):

$$\rho = \frac{D_z}{M} = \frac{3(M - 1)}{M} \simeq 3 \qquad (38)$$

Thus, if one assumes unit density in the amorphous region, $f = 1/3$. This result should be compared to equation (22) which applies to chains of fixed length in the amorphous region. The results of Yoon and Flory quoted in the body of the text are equivalent to a biased gambler's ruin problem on a tetrahedral lattice, and as we saw, it led to a density of $\rho = 2$ and an f value of $1/2$. The above two estimates of f do not count any of the runs (loops) as adjacent re-entry loops, and since some undoubtedly exist, the value of f calculated here is an upper bound.

Notice that D_z for $z = 1$ is linear in M, rather than quadratic. This feature results in a density, ρ, which is independent of statistical length. Suppose we divide the M units into M/c units of length c each (this corresponds to our gambler betting M/c dollars each time rather than just 1). Then the duration of the game is:

$$D_1 = 3\left(\frac{M}{c} - 1\right) \simeq \frac{3M}{c} \qquad (39)$$

but the total number of dollars wagered is cD_1 and this number, which corresponds to the number of CH_2 units, is independent of c (the statistical length).

Another interesting feature of the equations is that a large fraction of the chains are loops rather than bridges, as equations (34) and (35) show. These equations are, however, sensitive to the choice of statistical length and M is to be replaced by M/c in both equations (34) and (35). It is now obvious that the large literature on the gambler's ruin problem can be used profitably to discuss the problem of the amorphous region of a polycrystalline system of lamellar morphology.

We must now ask the difficult question as to what the guarantee is that the Yoon and Flory scheme does give the proper statistics of chain segment occupation in the amorphous phase. The remainder of this section is intended to show that the Yoon and Flory statistics are correct for bulk polymers.

Let us first discuss the problem of an isolated polymer molecule of large molecular weight between two plates. This problem was solved both by a canonical and a grand canonical formalism (generating function method[11]). In general, the configuration statistics of a loop or bridge are dependent on the other loops and bridges in the same chain. However, a loop or bridge can be treated independently of the rest of the chain if its statistical weight is multiplied by $\exp(-\lambda n)$ where $\lambda = -\mu/\kappa T$. μ is the chemical potential. This is the essential content of the generating function method. Knowledge of the chemical potential allows us to treat loops and bridges as independent entities and ignore the fact that they are connected to other loops, bridges and trains[2,11]. A chain which starts at location 1, and ends up at 0 or a, has a generating function of the form[15]:

$$U(x) = \sum_{n=0}^{\infty} u_{1,n} \exp(-\lambda n) + \sum_{n=0}^{\infty} u_{a-1,n} \exp(-\lambda n)$$

$$= U_1(\lambda) + U_{a-1}(\lambda) \qquad (40)$$

where the first term on the right-hand side corresponds to the gambler's ruin (arrival at the lower surface which is equivalent to loop formation) and the second term corresponds to the gambler's winning (arrived at the upper surface which is equivalent to bridge formation). Equation (40) results from a simple application of equation (4.4) Ch. XIV of Feller[15]. Thus, one can consider loops and bridges as decoupled from the rest of the system (decoupled from its

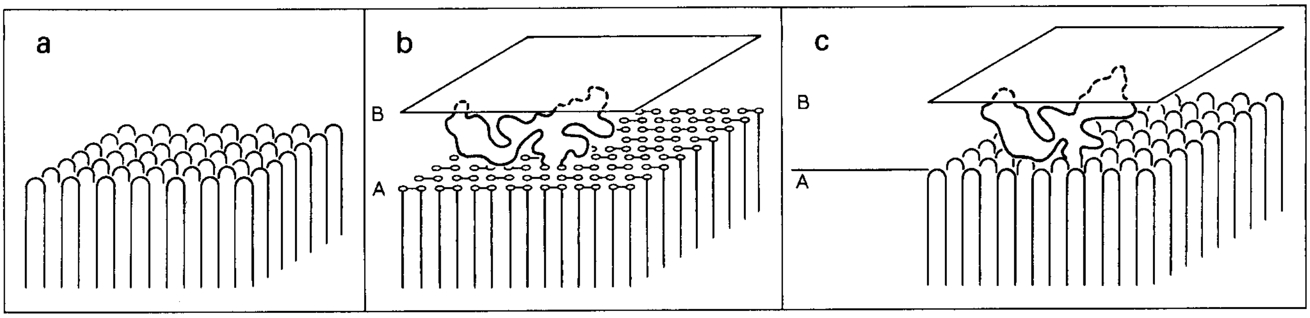

Figure 4 A regular array of tight loops, as in Fig. 4a, is a possible situation, but if each loop is made loose as indicated in Fig. 4b, the resulting density of the amorphous region would become too high. One can have loose loops only if one has simultaneously tight loops as indicated in Fig. 4c

environment) provided only that one adds a factor $\exp(-\lambda n)$ to the statistical weight. The above considerations extend the Yoon and Flory procedure to dilute solutions. We simply multiply the statistical weight of each configuration by the activity ($\exp(-\lambda n)$).

The Yoon and Flory procedure in the bulk is equivalent to the use of $\lambda = 0$ in equation (40). We first show that if the form of equation (40) is hypothesized, then $\lambda = 0$ for the bulk. Then we will discuss the hypothesis.

To determine λ, we use the condition that the average density of segments at each level in the amorphous region is constant:

$$\rho(z, \lambda) = c_1 \tag{41}$$

Whether some other condition might be used to determine λ is a moot point, since only one condition is necessary and constant density (equation (41)) suffices. We now observe that the random walk with reflecting barriers results in a constant density. But the random walk with reflecting barriers is nothing more than a succession of random walks with adsorbing boundaries. Each time the walk is terminated, one renews the walk by beginning a new walk, one step out from that adsorbing boundary which last adsorbed the walk. The average number of times level z is visited in each walk is a constant, independent of z, because the final density is a constant independent of z. The renewal procedure described above is exactly what Yoon and Flory did in their Monte Carlo simulation. They also obtained constant density.

Another way to show that constant density results from the unbiased gambler's ruin problem is to work in the continuum limit for which:

$$\frac{\partial \nu}{\partial t} = D\frac{\partial^2 \nu}{\partial x^2} \tag{42}$$

with boundary conditions:

$$\nu(0, t) = \nu(M,t) = 0 \tag{43}$$

and initial conditions:

$$\nu(z, 0) = \frac{\delta(z-1)}{2} + \frac{\delta(z-(a-1))}{2} \tag{44}$$

The initial condition corresponds to a gambler starting at $z = 1$ and $z = M - 1$ with equal probability, the game ending when he wins or loses. Integration of equation (42) from $t = 0$ to $t = \infty$ gives:

$$\nu(z, \infty) - \nu(z, 0) = D\frac{\mathrm{d}^2}{\mathrm{d}z^2}\int_0^\infty \nu(z, t)\mathrm{d}t = D\frac{\mathrm{d}^2\rho(z)}{\mathrm{d}z^2} \tag{45}$$

$$\begin{aligned} \rho(z) &= Az, & 0 \leqslant z \leqslant 1 \\ \rho(z) &= A, & 1 \leqslant z \leqslant a-1 \\ \rho(z) &= A(a-z), & a-1 \leqslant z \leqslant a \end{aligned} \tag{46}$$

The absorption boundary condition results in $\nu(z, \infty) = 0$ while the boundary condition, equation (43), the initial condition, equation (44), and the continuity of $\rho(z)$ results in equation (46). Notice that $\rho(z)$ is symmetrical about the midpoint of the line segment. Thus, we again arrive at the result that the gambler's ruin problem, i.e. equation (40) with $\lambda = 0$, results in constant density (except for the end points).

The final question is whether the hypothesis that the environment of a given loop or train can be accounted for by a factor $\exp(-\lambda n)$ is correct. This hypothesis cannot be proven, unless one were able to solve the problem of packing molecules exactly. We are far from solving that problem. However, it seems that, within the Flory–Huggins lattice approximation, the hypothesis is correct. The only effect of the environment on the loop or bridge in question is that an attrition factor exists (V_0 in the Flory approximation, S_0 in the Huggins approximation) per segment. This means that the effect of the other chains can be accounted for by a factor (V_0^n or S_0^n) which simply scales λ.

Observation II. Adjacent re-entry loops are very small and tight

Let us examine a surface consisting entirely of loops, to see if it is possible to have an amorphous–lamellar–crystalline complex with the amorphous part arising solely from a looseness in the loops. *Figure 4a* represents a structure with regular folding. There are a substantial number of publications that have argued that regular (tight) chain folding is sterically possible[16]. Some have suggested that staggering of the folds makes the packing easier[17]. Let us now try to accommodate an amorphous layer of folds by allowing disorder in the loops between planes A and B of *Figure 4b*. The same arguments used under *Observation I* apply here. The density of the amorphous region would become much

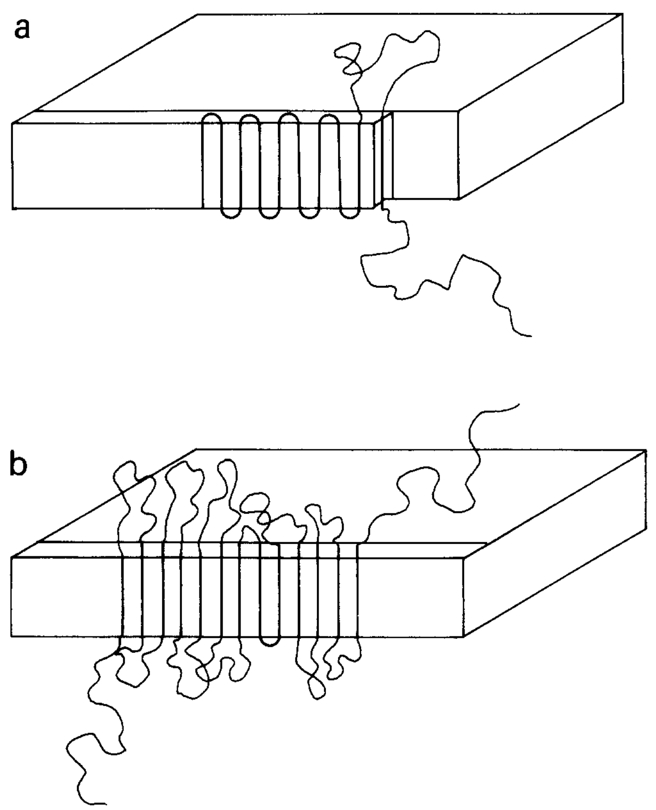

Figure 5 Two models of a polymer chain attaching to a polymer crystal at its periphery. See text for details

greater than that of the crystal. The only way to avoid this difficulty is to force some of the loops to be tight just below plane A (*Figure 4c*). One can have loose loops only if one also has tight loops.

Thus, there are only two possibilities; either one has tight loops only or one has a mixture of loose and tight loops. One never can have only loose loops.

Let us imagine each loop starting from one surface, stepping out to the other surface and then turning around and stepping back to the original surface. For stepping to the right, equation 11 is obeyed; for stepping to the left, an exactly analogous equation corresponding to the left hemisphere of *Figure 3b* is obeyed. It is easy to prove that, in such a case, only 1/4 of the crystal chain stems can be connected to loops and that (for large molecular weight) at least 3/4 must fold back. The amount of chain folding must be larger than 3/4 if the fundamental bond probility is some combination of that of equations (10) and (11). The proof follows the observation that such loops can be viewed as pairs of bridges.

The difficult problem of treating completely the crystalline–amorphous complex, with loops comprising the amorphous part and crystal stems the crystal part, has been attempted by Zachmann and Peterlin[18] and by Roe[19]. The treatment by Roe does not take into account the interaction between polymer chains and therefore, *a fortiori*, the competition of loops for the same space. In fact, if one were to assume, as Roe does, that the configurations of a loop are independent of the proximity of other loops, then the density of segments in the amorphous region near the crystal would greatly exceed the crystal density. To see this, one uses the distribution function for segment density in loops obtained previously[20], and multiplies it by the number of loops per unit surface area. The packing difficulties operative in our model are, therefore, also operative in the Roe model, and his estimates of loop sizes which are already small numbers must be considered to be upper bounds. The calculations of Zachmann and Peterlin must also be considered to give (weaker) upper bounds[21]. These models would undoubtedly serve as useful points of departure onto which we add the packing effects were we to attempt a quantitative theory of loop formation and distribution[22].

The above arguments deal with loops in the bulk of the crystal–amorphous complex (away from the edges). We will now show that at the growing edge of a crystal, loops are very small and tight. It is observed universally that polymer crystals grow by accretion to their perimeters[23]. Because of this, it is necessary to have sequential deposition of molecules for crystallization from dilute solution provided only that the crystal grows slowly. It violates no known fact to presume it to be true also for crystallization from the bulk. At the very least, in the limit of low undercooling the growth rate can be made so small that one must have sequential addition. The fact of sequential deposition allows us to use the models of isolated molecules at the edge of the growing crystal as displayed in *Figures 5a* and *5b*. The model of *Figure 5a* has been discussed previously[24] and that of *Figure 5b* is that of Roe[19]. In *Figure 5a*, the last stem (right-hand one) is attaching and detaching (in this model stems attach sequentially as well as molecules) and we ask what the expected loop size is. In *Figure 5b*, we allow all loops to change their sizes by pulling on each crystal stem and we ask what the average loop size is. An argument used previously[24] gives:

$$\langle j \rangle \simeq 3 \qquad (47)$$

for the model of *Figure 5a*, where j is the number of statistical segments in a loop. This argument assumed Gaussian statistics and no energetics within the loop. For the entropy of the loop, it used the calculation of the number of configurations appropriate to a polymer near a surface[2,19,20] The value $\langle j \rangle \simeq 3$ means the loops are so tight that the Gaussian approximation has been pushed to its limit and energetics of tight chain folds take over. It justifies the use of tight loops for previously incorporated stems in *Figure 5a*. The kinetic theories of chain folding which postulate a sequential deposition of stems within each molecule and a sequential deposition of molecules within each crystal are made credible by the fact that the loop lengths are small. Were the loop lengths to be large, one could imaging a large back pressure developing which would prevent further deposition.

The model of *Figure 5a* assumes no snaking around (reptation) once the crystal is formed. The model *Figure 5b* which allows reptation has been treated by Roe. The results of Roe are probably more applicable to the molecule on the crystal edge than to one in the crystal centre, since the interference between loops which was neglected by Roe is less extensive for loops on the edge of the crystal. Even so, the results of Roe show small loop size ($\langle j \rangle \simeq 7$) which again is to be viewed as an upper bound. In summary, the calculated loop sizes are small, even when interferences between loops are not taken into account; it is the alteration of random walk statistics in the presence of the surface that results in the small loop sizes. Details are given in refs. 19 and 24. Ref. 11 contains many references to the random walk problem in the presence of surfaces.

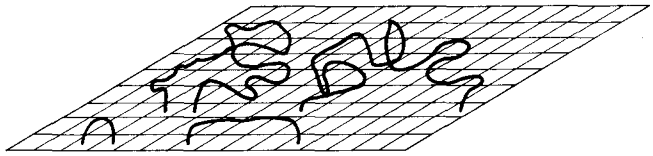

Figure 6 The four kinds of loops; adjacent-tight, non-adjacent-tight, adjacent-loose, and non-adjacent-loose

Observation III. The amount of non-adjacent re-entry is small

At this juncture, it is useful to classify loops as to whether they are loose or tight, adjacent or non-adjacent. In *Figure 6*, we display schematically each of the four possibilities. In the previous sections, we showed that the assumption of adjacent re-entry loops implies that a substantial fraction of them are tight. Here, we shall show that any combination of adjacent–loose, non-adjacent–loose, and non-adjacent–tight loops implies a substantial fraction of adjacent–tight loops.

First, let us show that *some* tight–adjacent loops are necessary. For an amorphous (or more properly, non-crystalline) region k units thick, we obtain by arguments similar to those leading to equation (3):

$$\rho = \frac{n}{V} = \frac{(\langle x\rangle + k)M^2}{kM^2} = \frac{\langle x\rangle + k}{k} \tag{48}$$

which applies to the model of *Figure 4b* where adjacent–loose, non-adjacent–loose and non-adjacent–tight loops from both the lower and upper crystalline lamellae fill the region between planes A and B. Here $\langle x\rangle$ is the average distance in numbers of segments between the stems which terminate a given loop (see *Figure 7*). The value k in the numerator arises from the presumption that, on average, the loops traverse the amorphous layer at the level $k/2$. The average number of segments in a loop is thus $\langle x\rangle + k$. Since the density of the non-crystalline region is experimentally less than 1, and since equation (48) gives $\rho > 1$, we always have some tight–adjacent folds. In the derivation, we used the shortest possible distance $\langle x\rangle$ between stems (tight–non-adjacent folds). The use of loose–non-adjacent folds would have resulted in an aven larger ρ, and would have implied even more tight–adjacent ren-entry loops.

However, it must be stressed that equation (48) was derived for the case where loops came from both surfaces into the amorphous region, and for the case where the average number of segments per loop is $\langle x\rangle + k$. If one of the surfaces is a non-polymer barrier (as for example in *Figure 4c*), then the estimate of ρ from equation (48) is halved and the bound becomes too weak to be of any value. Equation (48) is not useful for crystallization from dilute solution, since all loops forming the interface came from only one surface. A separate paper discussing the nature of the interface for such surfaces is in preparation.

Let us now estimate the expected amount of non-adjacent re-entry by calculation of $\langle x\rangle$. Our model is a varient of that of *Figure 5a*, in which we allow the last stem to settle at any location x (see *Figure 7*). We will assume that the energetics are the same for each placement of the stems. In dilute solutions, this is a poor assumption because the adjacent position ($x = 1$) is energetically favoured. Our estimate of $\langle x\rangle$ in this case will be larger than if we had taken energetics into account. However, in the bulk, we can imagine that each of the intervening, $x - 1$, positions are occupied by other stems of other molecules so that there should be no energetic preference. Therefore, we work only with the entropic contribution. At first, we imagine that the last stem can slap on and off many times before a new stem is added. This will allow us to make an equilibrium calculation. It has been suggested that this condition can be relaxed without affecting the results[24].

The probability distribution for the end-to-end length x can be given by[2]:

$$w_l \propto \frac{s_1^j \exp(-3x^2/2j_1 l^2)}{j_1^\theta} \quad \text{loops} \tag{49}$$

where θ depends on the nature of the surface near which the two end points lie. For no surface, $\theta = 3/2$, while, for the end points lying on a plane surface, $\theta = 5/2$. In equation (49), l is the length of a step and j_1 the number of them in a loop; s is the conformational freedom per step. If only one of the ends is pinned and the other is free to roam, then the corresponding factor for the cilia is:

$$w_c \propto s^j 2/j_2^\beta \quad \text{cilia} \tag{50}$$

with $\beta = 0$ for free space and 1/2 for a cilium on a surface and j_2 is the length of a cilium. The product of equations (49) and (50) is proportional to the total number of configurations consistent with i_1 segments in the loop, j_2 in the cilia and a non-adjacency index x. The expected value of x is obtained by:

$$\langle x\rangle = \frac{\int x W_l W_c \,\mathrm{d}j_1 \mathrm{d}x}{\int W_l W_c \,\mathrm{d}j_1 \mathrm{d}x} \tag{51}$$

where we have used the fact that $j = j_1 + j_2$ is a constant. If we let $\theta = 3/2$ and $\beta = 0$ (no surface), we obtain:

$$\langle x\rangle \simeq j^{1/2}/\ln j \tag{52}$$

This square-root dependence corresponds to an intuitive appreciation of random walk statistics. However, if we let $\theta = 5/2$ and $\beta = 1/2$ (a plane surface), we obtain:

$$\langle x\rangle \simeq t_1^{1/2} \tag{53}$$

where t_1 is the lower limit of the integration on j_1 and is the smallest number of bonds needed to make an adjacent re-entry loop. This result (equation (53)) may seem surprising

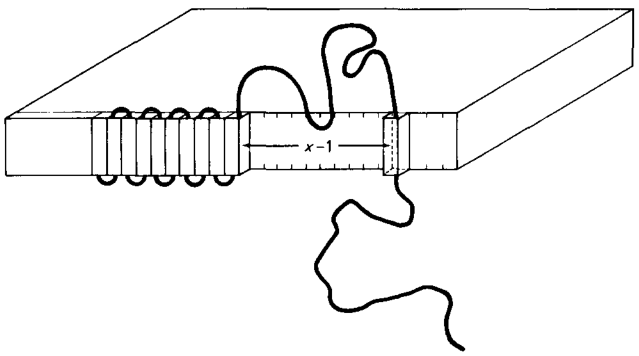

Figure 7 Model on which the calculation of the expected amount of non-adjacency, x, is estimated. The x-1 places between the two ends of the loop are imagined to be occupied by other stems of other molecules

to those not familiar with random walk statistics in the presence of a surface. The value we obtained for $\langle x \rangle$ is so small that we passed the limit of validity for the Gaussian method. Tight–adjacent re-entry loop energetics and other non-Gaussian characteristics are expected to take over at this stage. One can improve the procedure by (1) using discrete methods by adoption of the method of Roe to this problem and (2) allowing for the structure of the polymer. We shall not do so here because our only purpose is to show that *the presence of a surface strongly favours adjacent re-entry*.

It should be emphasized that Observations II and III have their greatest validity for the case of dilute solution crystallization, because the statistics of polymers near the surface that we used are known to be valid for isolated polymer molecules. If we focus our attention on a polymer together with the solvent around it, we see that a solvent molecule forced to move from the vicinity of the surface to the interior of the fluid by displacement by the polymer does not change its freedom and its contribution to the overall entropy. Now consider a polymer molecule which is surrounded by other polymers (bulk phase). When it approaches the surface, it loses freedom, just as if it were by itself. However, the other molecules (or pieces of molecules) which are displaced gain freedom as they move to the interior of the fluid. Thus, the overall effect on total entropy is smaller in this case. Thus, the statistics of a polymer molecule immersed in its own kind are different from one immersed in solvent, and equations (52) and (53) should be viewed as limiting forms, known to be valid only for dilute solutions.

EXPERIMENTAL CONFIRMATION OF PREDICTIONS

The experimental system of a diblock copolymer of polyethylene oxide and polystyrene allows us to make unambiguous statements about the amounts of randomness of the amorphous regions and folding in the crystalline regions. It has been studied extensively by Lotz and Kovacs[25] and by Lotz, Kovacs, Bassett and Keller[26]. (The triblock systems with the crystallizable portion in the middle are also useful, but experiments on such samples are not extensive).

In the diblock system, the two components are highly incompatible and the polyethylene oxide ends up being confined in the crystalline lamellae which alternate with lamellae consisting entirely of the amorphous polystyrene component. The chemical differences between the amorphous and crystalline regions enable us to make sone definite statements about the shape of the chains and the structure of the interface.

Consider the amorphous region first. The thickness of the amorphous lamellae ranges from about 20 Å to 54 Å, while the contour length of the polystyrene parts of the diblock range from about 208 Å to 582 Å. This means that only about 1/10 of the plane surface area separating the two regions is occupied by a molecule traversing the two regions (a covalent connection between the two adjacent regions). The result strongly suggests that the polystyrene chains approximate a random walk in the amorphous region. Similarly, the contour length of the polyethylene oxide portions ranges from about 670 Å to 1322 Å, while the lamellar thicknesses of the crystalline portions ranges from about 62 Å to 100 Å. Again, one calculates about 1/10 of the interface area occupied by chains traversing the two regions.

For the crystalline region, we have the added experimental observation that the chains must run (approximately) perpendicular to the lamella. Since the chains remain in the lamella, there must be folding (of the order of ten stems per molecule) ($f = 1/10$).

Regular adjacent re-entry folding has not been proved experimentally, only folding. To prove adjacent re-entry, one would need a more accurate density profile than is available presently. Yet, the experiment does rule out the switchboard model for this system.

For these systems, the chain folding lamellar morphology is the *equilibrium* situation. In crystallizable homopolymers, chain folding costs energy. Given enough time, the chain folds will anneal out of the system resulting in extended chain crystallization. However, in amphiphilic copolymer systems, this process can proceed only to a certain extent because the amorphous portions induce a strain energy which tends to pull the crystallizable portions apart. The crystalline chain portions tend to become fully extended, and, because they are connected covalently to the non-crystalline chain portions, they tend to extend the non-crystalline chain portions. But, the non-crystalline portions seek to be random in shape and the associated entropy force tends to pull the crystalline portions apart laterally. Thus, the balance between the two effects results in an equilibrium lamellar thickness. A prediction of lamellar thicknesses in terms of the relevant parameters is being published[7].

There will be regular chain folding in diblock copolymers whenever the following three conditions are satisfied simultaneously.

(1) There is a segregation of the crystallizable and non-crystallizable portions into a lamellar morphology.
(2) The contour length of the chain portions in each phase is longer than the thickness of the lamella.
(3) The crystallizable chain portions lie perpendicular to the lamellae.

ACKNOWLEDGEMENTS

We should like to thank J. D. Hoffman for many stimulating discussions and helpful suggestions. We also thank R. J. Rubin for the observation that the random walk between adsorbing boundaries *with renewal* is equivalent to a random walk with reflecting boundary conditions.

REFERENCES

1 DiMarzio, E. A. *Bull. Am. Phys. Soc.* 1978, **23**, 420: F. C. Frank in *Growth and Perfection of Crystals* (Proceedings of an International Conference on Crystal Growth held at Cooperstown, New York, August 27–29, 1958), Ed. Doremus, Roberts and Turnbull) Wiley, New York, 1958, discussion remarks, pp. 529 and 530
2 DiMarzio, E. A. and Bishop, M. *Biopolymers* 1974, **13**, 2331
3 Birshtein, T. M., Zhulina, E. B., and Skvortsov, A. M. *Biopolymers* in press; Birshtein, T. M. *Biopolymers* in press; Hoeve, C. A. J. *Prague Microsymposium*, 1976; DiMarzio, E. A. and Rubin, R. J. *J. Chem. Phys.*, Sect. V, 1971, **55**, 4318
4 Yoon, D. Y. and Flory, P. J. *Polymer* 1976, **18**, 509
5 Flory, P. J. *J. Am. Chem. Soc.* 1962, **84**, 2857
6 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969
7 DiMarzio, E. A., Guttman, C. M. and Hoffman, J. D. 'The calculation of lamellar thickness in a diblock copolymer, one of whose components is crystalline', *Macromolecules* In press
8 Hashimoto, T., Shibayama, M., and Kawai, H. private communication
9 Helfand, E. and Wasserman, Z. R. *Macromolecules* 1976, **9**, 879; 1978, **11**, 960; Helfand, E. *Macromolecules* 1975, **8**, 552

10 Meier, D. J. in 'Block and Graft Copolymers', (Eds. J. J. Burke and V. Weiss), Syracuse Univ. Press, New York, 1973

11 DiMarzio, E. A. and Rubin, R. J. *J. Chem. Phys.* 1971, **55**, 4318

12 A general relationship between segment density and effective field has been obtained by E. A. DiMarzio and C. M. Guttman, *J. Res. Nat. Bur. Std.* 1978, **83**, 165

13 Gaylord, R. J., Paisner, M. J. and Lohse, D. J. 'Chain distribution function and segment density, functions of polymer chains confined by absorbing or reflecting barriers', *Macromol. Sci.* in press

14 Scheutjens, J. M. H. M. and Fleer, G. J. *J. Phys. Chem.* 1979, **83**, 1619

15 Feller, W. 'An Introduction to Probability Theory and its Applications', Vol. 1, 2nd Ed. Wiley, 1961. The notation in this section conforms to that of Feller

16 Corradini, P., Petraccone, V. and Allegra, G. *Macromolecules* 1971, **4**, 770 and references therein

17 See discussion by F. Khoury and E. Passaglia in Ch. 6 of 'Treatise on Solid State Chemistry', Vol. 3. Ed. N. B. Hannay, Plenum Press, New York, 1976

18 Zachmann, H. G. and Peterlin, A. *J. Macromol. Sci.-Phys. Edn.* 1969, **3**, 495

19 Roe, R. J. *J. Chem. Phys.* 1970, **53**, 3026

20 The segment density distribution for a loop is given by E. A. DiMarzio, *Polymer Prepr.* 1968, **9**, 256

21 The difference in the results of the two methods probably arises from the different manner in which they distribute segments among the loops

22 Packing difficulties affect both the number of loops and the configurational properties of each loop. One can, as a first approximation, ignore the change in configurational properties of individual loops and use our density arguments to determine the number of loops $(\ldots \nu_j \ldots)$ of each kind. Each loop size distribution $(\ldots \nu_j \ldots)$ determines an average density, $\rho(\ldots \nu_j \ldots)$, and an average thickness, $d(\ldots \nu_j \ldots)$, of the amorphous region which, when put in as constraints on the total free energy minimization problem determine a set $\ldots \nu_j \ldots$ consistent with the constraints

23 See, for example, Blundell, D. J. and Keller, A. *J. Polym. Sci.* 1968, **6**, 433

24 Sanchez, I. C. and DiMarzio, E. A. *J. Chem. Phys.* 1971, **55**, 893

25 Lotz, B. and Kovacs, A. J. *Kolloid Z. Z. Polym.* 1966, **209**, 97

26 Lotz, B., Kovacs, A., Basset, G. A. and Keller, A. *Ibid.* 1966, **209**, 115