# Study of amorphous–crystal interfaces in polymers using the wicket model: estimates of bounds on degree of adjacent reentry

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(*Received* 20 *June* 1980)

An attempt to ascertain the structure of the crystal-amorphous interface in polycrystalline polymers of lamellar morphology is made by discussion of an idealization of loops called wickets. Equations which arise from the constraints of density at the interface are obtained that relate the various kinds of wickets to their lengths and to interface thickness. A measure of the degree of adjacent reentry is defined and bounds on the extent of adjacent reentry are obtained. It is found that the larger the assumed value of average loop size the larger the amount of adjacent reentry. Infinite average loop size results in complete adjacent reentry.

## INTRODUCTION

The question of the structure of the interface between the amorphous and crystalline regions in a semicrystalline polymer system of lamellar morphology is not yet solved. Flory has estimated that at most one-half of the chains emanating from the crystal can proceed into the amorphous region[1]. The other half must turn back or fold. He also suggested that it was possible for more than one-half to turn back, but not less. DiMarzio[2], DiMarzo, Guttman and Hoffman[3], and DiMarzio and Guttman[4] have presented estimates on the amount of folding which are considerably larger than the one-half figure. They have also given bounds on the amount and kind of folding possible for a variety of models of the amorphous phase. The above papers represent efforts to establish quantitatively a result explained qualitatively by Frank[5] in 1958.

Folding can be either adjacent or non-adjacent. The determination of the amount of folding is much easier than the problem of determining whether this folding is adjacent reentry or non-adjacent reentry. In ref 4 the amount of adjacent reentry folding was calculated to be large for polymer crystallization from dilute solution but experimental and other theoretical results confirming this conclusion are meagre. The amount and kind of folding in melt crystallized polymers is even less well known, though recent estimates based on neutron scattering data on quench-crystallized polyethylene suggest that the degree of adjacency is above one-half[6,7].

The question of the structure of the interface region of a semi-crystalline polymer system is amenable to both experimental and theoretical studies. One example of a system for which the properties of the interface (and therefore answers to questions on the character of chain folding) are experimentally accessible, is the diblock copolymer system of poly(ethylene oxide) (PEO) copolymerized with polystyrene (PS). These systems have been studied experimentally by Lotz, Kovacs, Keller, and Basset[8,9]. Here, the poly(ethylene oxide) portions are crystalline and the polystyrene portions are amorphous. By measurement of lamellar thickness of both the amorphous and crystalline regions and by knowledge of the molecular weight of the poly(ethylene oxide) and of the polystyrene portions, the authors found that the PEO chains are folded with about 10–13 stems per molecule. A theory of chain-folding in these amphiphilic systems has been developed which predicts the lamellar thicknesses in terms of the microscopic parameters of the system[10]. Furthermore, the nature of the interface in this system is experimentally ascertainable at least in part because one can determine the interface thickness. Kovacs[11] has seen many higher order reflections in the small-angle X-ray scattering data (10–15 orders). This observation suggests a narrow interface region for this system.

Interfaces of non-crystalline phase-separated polymer systems also appear to be narrow. Meier[12] and Helfand[13] have made theoretical estimates of about 15–20 Å for interface thickness of diblocks both of whose components are amorphous. Krause[14] has argued for even thinner interfaces (on the order of one monomer unit thick). These results suggest that in many polymer–polymer systems the interface region is narrow.

The nature of the total amorphous region of a semicrystalline polymer has been modelled in a variety of ways[15–17]. In any description we need to have a model which has adjacent folds, bridging chains (bridges), loops, cilia and free chains (or floating chains — chains unattached to any crystalline region). Each of these kinds of chains must participate in the amorphous phase and all must be included in a complete description of the interfacial region. Previous models of the amorphous crystal interface take extreme views of the numbers of each kind of these entities at the interface. In the fringed micelle model each stem yields a bridge (or cilia); this model results in high densities for the amorphous phase[4]. The switchboard model of Flory (recently called the random reentry model)[1,15,6] has its floppy loops and bridges which obey random statistics. It leads to too high a density in the amorphous phase[3,7,6] and to questions as to whether the morphology of single crystals is consonant

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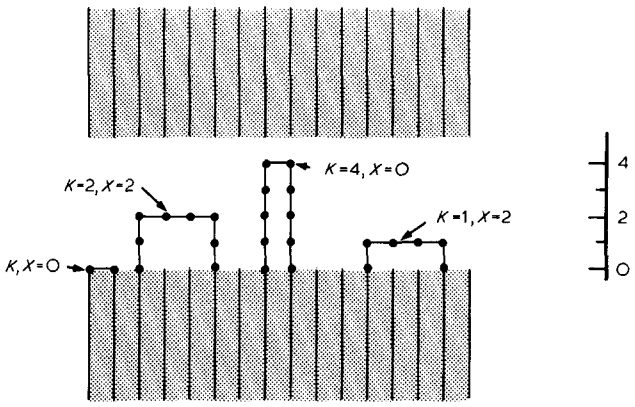


*Figure 1* Examples of various kinds of wickets in an interfacial region of $M = 4$

with such a model[18]. However, a model with complete adjacent reentry is not consistent with the neutron scattering data on highly quenched samples of polyethylene[15,7,19]. As we pointed out earlier[6,7] something intermediate to these models seems to be called for, but with a degree of adjacent reentry of somewhat over one-half.

In the present paper, we present a generalized model of the interface that deals with the intermediate situations. In this paper we propose to study what we shall call the wicket model. Wickets, as seen in *Figure* 1, are the simplest form of a loop. A chain walks $K$ steps directly away from the surface plane, then walks $x$ steps parallel to the surface, and then directly returns to the surface. This object which is indexed by both $K$ and $x$ is called a wicket. We study wickets because, with their simplicity of structure, equations relating to their packing densities may be written down and solved in special cases. However, even with their simplicity they have some random character in that for a given $K$ the distribution of $x$ and thus the reentry position of the wicket may be random. The solutions to the problems of the wicket model will yield insight into the problems of the packing of loops near a surface.

Wickets offer an opportunity to study a model of the interface which has both loops and adjacent folds. The loops modelled here can be tight loops as in the case where $x$ is small or loose loops as in the case where $x$ is large. In each case we may estimate the minimal amount of adjacency for each type of loop. Thus the study of such a model will hopefully offer a means to determine the relative amounts of randomness and adjacency that can coexist in the surface layer without violating simple packing considerations.

## THEORY OF WICKETS

We let $n_{K,x}$ be the number of wickets that go $K$ steps perpendicular to the lamellar phase and walk $(x+1)$ steps on level $K$, parallel to the lamellar plane. *Figure* 1 shows some examples of wickets. The interface region has $M+1$ levels labelled 0 to $M$ on which wickets may lie. At each level we allow the wickets to fill up the space to a density of $\rho(K)$. The wickets all come from the bottom lamellae. The case in which we have wickets coming from both surfaces is also interesting, but will not be treated here. The number of segments at level $K$ is given as:

$$\rho(M)L^2 = \sum_{x=0}^{\infty} x n_{M,x} + 2\sum_{x=0}^{\infty} n_{M,x} \tag{1}$$

$$\rho(K)L^2 = \sum_{x=0}^{\infty} x n_{K,x} + 2\left(\sum_{l=K}^{M}\sum_{x=0}^{\infty} n_{l,x}\right) \tag{2}$$

$$\rho(0)L^2 = \sum_{x=0}^{\infty} x n_{0,x} + 2\sum_{l=0}^{M}\sum_{x=0}^{\infty} n_{l,x} \tag{3}$$

where $L^2$ is the area in which the $n_{K,x}$ wickets are located. If we define:

$$n_l = \sum_{x=0}^{\infty} n_{l,x} \tag{4}$$

$$\bar{x}(l)n_l = \sum_{x=0}^{\infty} x n_{l,x} \tag{5}$$

$$m_l = n_l/L^2 \tag{6}$$

then the basic equations can be written as:

$$\rho(M) = \bar{x}(M)m_M + 2m_M \tag{7}$$

$$\rho(K) = \bar{x}(K)m_K + 2\sum_{l=K}^{M} m_l \tag{8}$$

$$\rho(0) = \bar{x}(0)m_0 + 2\sum_{l=0}^{M} m_l \tag{9}$$

Note that:

$$\bar{x}(0) = 0 \tag{10}$$

This condition is necessary, otherwise we could have wickets whose tops are below the level 0. Level zero is defined as that level which has no wickets below it. This also means that $\rho(0) = 1$. That is the bottom level has by assumption the crystal density. With these two conditions, we also have from equation (9) the relation:

$$\sum_{l=0}^{M} m_l = 1/2 \tag{11}$$

This is the statement that the stems of the wickets completely fill the crystalline region beneath the interface. Notice that the normalization is one-half rather than one.

By subtracting the equation for level $K+1$ from that for level $K$ we obtain:

$$m_K = \frac{\bar{x}(K+1)m_{K+1} - [\rho(K+1) - \rho(K)]}{(\bar{x}(K)+2)} \tag{12}$$

To simplify the equations, we assume that $\rho(K) = 1$ in the remainder of this paper. Thus we have:

$$m_K = \frac{\bar{x}(K+1)}{2+\bar{x}(K)} m_{K+1} \qquad 0 < K < M-1 \tag{13}$$

$$m_M = \frac{1}{2+\bar{x}(M)} \tag{14}$$

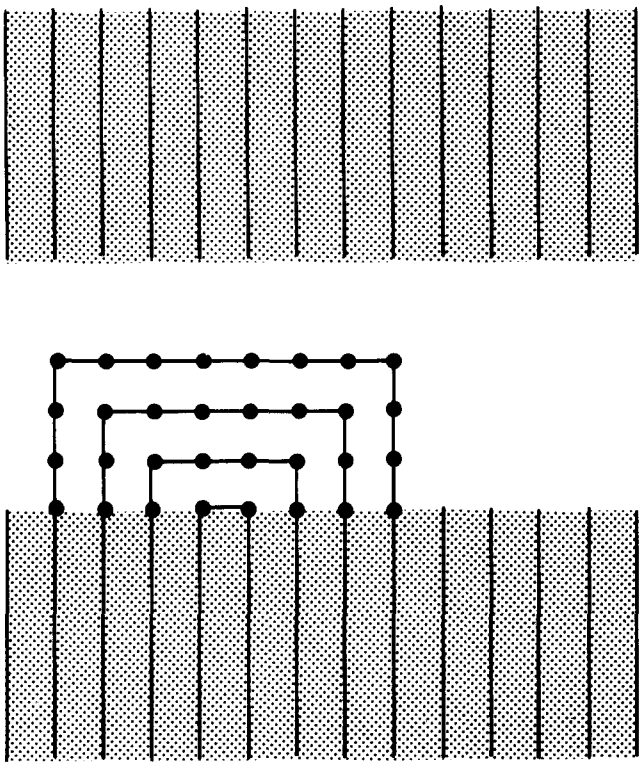

*Figure 2* Example of nested wickets which show surface structure

The above assumes that the density in the interface region is identical to the crystal density. A more sensible assumption would be that the density of the interface region smoothly goes from the crystal density to the amorphous density but this would complicate an already complicated set of equations. The fundamental equations (13 and 14) give the $m_K$ in terms of the $\bar{x}(K)$. These equations plus equation (10) are our complete set of equations.

We have $M+1$ ($m_K$) variables and $M$ [$\bar{x}(K)$] variables but only $M+1$ equations relating them. An important question is whether we can determine any other relations which help to constrain the possible values of $m_K$ and $\bar{x}(K)$. Clearly such relations exist, but in this paper we shall not attempt to quantify them. We have not yet solved this important problem, but we should like to mention some ideas that will need to be considered further to develop these constraints.

One constraint which may be experimentally accessible is the average loop length. The average loop length $\Omega$ is defined by:

$$\Omega = \sum_{K=0}^{M} [(\bar{x}(K)+2K]m_K \Big/ \sum_{K=0}^{M} m_K \qquad (16)$$

Summation of equations (7), (8) and (9) for all $K$ yields the numerator of equation (16). Assuming $\rho(K)=\rho(0)=1$, we obtain:

$$\Omega = 2(M+1) \qquad (17)$$

Thus the average loop length is twice the thickness. This result applies to models more general than the wicket model and to derive it one only needs to assume that loops and only loops are space filling in a interfacial region of thickness $M$.

We can now ask how each term on the r.h.s. of equation (16) contributes to $\Omega$. If the average $x$ is zero, that is:

$$0 = \sum_{K=0}^{M} \bar{x}(K) \Big/ \sum_{K=0}^{M} m_K \qquad (18a)$$

then from equation (13) we see that we have completely adjacent reentrant wickets at level $M$. Further if the average $K$ is zero, there are no wickets above the zeroth level:

$$0 = \sum_{K=0}^{M} Km_K \Big/ \sum_{K=0}^{M} m_K \qquad (18b)$$

then we have complete adjacent reentry. We might expect when we had:

$$\bar{x}(K) = 2K \qquad (18c)$$

(i.e. an isotropic case) we would have the minimum adjacent reentry.

Another constraint is the value of $M$. If it can be established that the interface region is on the order of 15 Å thick as has been suggested by the work on block copolymers[12-14] then a few layers are suggested ($M=1$ to 6). Such a small value of $M$ enormously simplifies the range of possible structures for the surface. The adsorption theories of Helfand[20], Roe[21] and Scheutjens and Fleer[22] show narrow interfaces for adsorption of polymers from solution. A recent work of Poser and Sanchez[23] shows $M$ values of about 5 which are largely independent of molecular weight for the case of a liquid–vapour interface. Finally, it is a characteristic of Cahn–Hilliard theory that interface thicknesses are small except near critical points. These facts suggest, but do not prove, that the energetic differences between amorphous and crystalline regions result in small $M$ values.

In addition to the energetic constraints we have two general classes of entropy constraints.

The first entropy constraint concerns the difficulty in packing the wickets when they are considered to be rigid objects. To see that there is a constraint, imagine that at layer $K$ we are packing rigid rods of length $\bar{x}(K)$ randomly within the layer. For such a system packing difficulties occur long before we reach a dense packing[24-26]. We can avoid these difficulties by aligning the rods (horizontal portion of the wickets) parallel within each layer. However, the vertical portions of the wickets will still have large interferences with the horizontal portions of other wickets. We conclude that there are great difficulties in packing rigid wickets. However, certain specialized nested structures like that of *Figure* 2 or variants of *Figure* 2 are not precluded, but significant ordering in the interfacial regime would be implied by such structures.

The second entropy constraint concerns the difficulty in packing the wickets when they are considered to be flexible objects. This problem has been thoroughly discussed in ref 4. The main conclusion is that the tendency to maximize entropy results in chains and chain portions in the amorphous region whose contour length $x$ is considerably in excess of $M$. That is to say, a substantial wandering of chains in the amorphous region occurs due to the increase in the number of configurations gained by such wanderings. Our selections of $\bar{x}(K)$ in the next section are made with the results of ref 4 in mind but they are not

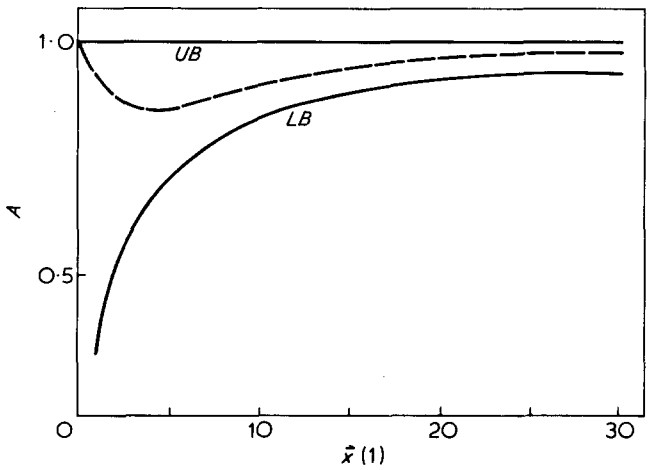


*Figure 3* Lower bounds (*LB*) and Upper bounds (*UB*) for the amount of adjacent reentry, *A*, as a function of wicket length for $M = 1$ (a two layer structure). The lower bound for $x = 0$ is 1. The dotted line schematically displays the true *A*

unambiguously determined by that work. The fact that entropy tends to result in large $x$ coupled with the constraints of density which are embodied in the equations (10–14) of this work can result in substantial adjacent reentry. This is shown in the next section.

There is another constraint arising from entropy which is noted in the Discussion below.

Although the above arguments suggest great difficulties in the formation of any but highly structured (nested) loops, quantitative proofs are lacking. A quantitative proof would require knowledge of $M$ relationships among the $\bar{x}(K)$ and $m_l$ in addition to those of equations (7)–(9). An immediate difficulty arises. Are these equations to be determined by kinetic or equilibrium considerations? Certainly lamellar thickness and degree of crystallinity, $\chi_c$, are determined by kinetic considerations. This means that at a fundamental level the $M$ additional relationships can be obtained only through (difficult) kinetic considerations. Alternatively a simple equilibrium procedure suggests itself. We assume the amorphous thickness $M$ and the crystalline thicknesses $M\chi_c/(1-\chi_c)$ as given. Although these quantities are determined by kinetics, we can know them through experiments and thereby circumvent difficult theoretical questions. We now assume that the free energy of the above lamellar system is a minimum. That is to say, there is enough mobility in the chains so that they can seek out the minimum free energy situation consistent with the constraint of $M$ and $\chi_c$. This procedure determines $\bar{x}(K)$ and $m_l$. The implementation of the above equilibrium approach is still a difficult problem which will be tackled at a later date. Although we will be forced in this paper to deal with an incomplete set of equations there is a sense in which this can be an advantage. The conclusions we draw, though limited in scope transcend any approximations that may be found necessary for the complete treatment. Thus we proceed to a discussion of our incomplete set of equations.

## FRACTION OF ADJACENCY, *A*, AND ITS BOUND

The amount of adjacency, $A$, is easily obtained for an $M$ level interface region as:

$$A = 2\sum_{K=0}^{M} m_{K,0} \tag{19}$$

where $m_{K,x}$ is defined as $n_{K,x}/L^2$ in analogy to equation (6). Thus we have:

$$m_K = \sum_{x=0}^{\infty} m_{K,x} \tag{20}$$

Now by equation (10), $m_0 = m_{0,0}$ and we obtain

$$A \geqslant 2m_0$$

Thus the fraction of folds on level zero is a lower bound to the amount of adjacency.

Since equations (7)–(9) only relate to average values of $x$ at level $K$, $x(K)$, we have no way from these equations to obtain values for $A$. The distributions of $x$ giving rise to each $\bar{x}(K)$, of course, determines the fraction of adjacent folds in each $K$th level. Some example distributions should be instructive at this point.

If the distributions of $x$s that lead to an $\bar{x}(K)$ is narrow then the amount of adjacency, $A$, is just given by $2m_0$ because no other $m_K$ contributes to $A$ ($m_{K,0}=0$)

$$A_{\text{narrow}} = 2m_0 \tag{21}$$

If the distribution of $x$s is homogeneous from 0 to $2\bar{x}(K)$ then the fraction of those adjacent folds are $1/[2\bar{x}(K)+1]$ for each $K$ and the amount of adjacency is:

$$A_{\text{homo}} = 2\sum_{K=0}^{M} \frac{m_K}{[2\bar{x}(K)+1]} \tag{22}$$

If the distribution is exponential then it is easy to show*:

$$A_{\text{exp}} = 2\sum_{K=1}^{M} \frac{m_K}{\bar{x}(K)} + 2m_0$$

## SOLUTION OF EQUATIONS (13) AND (14) FOR SOME SPECIAL CASES

(a) $M = 0$. We have $m_0 = 1/2$ as the only solution and this corresponds to perfect adjacent reentry.

(b) $M = 1$.

$$m_1 = 1/[2+\bar{x}(1)] \tag{23}$$

$$m_0 = x(1)/(2[2+\bar{x}(1)]) \tag{24}$$

For $\bar{x}(1) = \infty$ we have $m_1 = 0$, $m_0 = 1/2$ for perfect adjacent reentry. For $\bar{x}(1) = 0$, we have $m_1 = 1/2$, $m_0 = 0$ which again corresponds to perfect adjacent reentry but at level 1 rather than at level 0. *Figure* 3 displays the amount of adjacency $A$ along with its bounds.

(c) $M = 2$. This case is of interest because Sadler has suggested[27] that his neutron scattering data can be fitted with equal amounts of adjacent, next-to-adjacent and next-to-next-to-adjacent loops. This model would require

* This result is only true for large $\bar{x}(K)$ when integrals can replace sums. In general, for an exponential distribution

$$\rho(x) = e^{-\tau x}(1-e^{-\tau}); \qquad \tau = \ln\left(1+\frac{1}{\bar{x}}\right)$$

and $$l(0)(1-e^{-\tau}) = \frac{1}{1+\bar{x}(K)}$$

Thus $$A_{\text{exp}} = 2\sum_{K=0}^{M} \frac{m_K}{(\bar{x}(K)+1)}$$

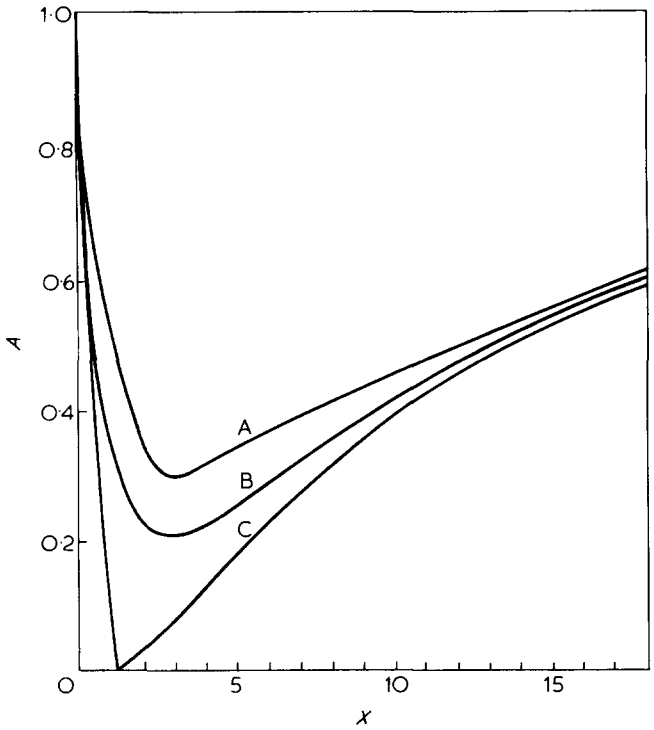


*Figure 4* Fraction of adjacent reentry, $A$, for three distribution functions as a function of the average length, $X$, of the wickets. The curves are asymptotic to $A = 1$ for $\bar{x} = \infty$. In the Figure, curve (A) is the fraction of adjacency for an exponential distribution of $x(K)$s with a mean value $X$ for any level $K$ for a 5 level system ($M = 5$). Curve (B) is the fraction of adjacency for a homogeneous distribution of $x(K)$ (see text) for the same system. Curve (C) is the fraction of adjacency for a narrow distribution of $x(K)$s for the same system

three levels ($M=2$). We have for this case:

$$m(2)=\frac{1}{2+\bar{x}(2)} \tag{25}$$

$$m(1)=\frac{\bar{x}(2)}{[2+\bar{x}(1)][2+\bar{x}(2)]} \tag{26}$$

$$m(0)=\frac{\bar{x}(1)\bar{x}(2)}{2[2+\bar{x}(1)][2+\bar{x}(2)]} \tag{27}$$

Any values of $\bar{x}(1)$ and $\bar{x}(2)$ are consistent with equation (9). If $\bar{x}(2)=\infty$ or if $\bar{x}(1)=0$ we again have a two level problem. It is easy to show that these equations are not inconsistent with Sadler's proposal.

(d) The case of constant $x(K)=X$

$$\bar{x}(K)=X \qquad M\geqslant K\geqslant 1$$

$$m_M=\frac{1}{2+X} \tag{28}$$

$$m_K=\frac{X^{M-K}}{(2+X)^{(M-K+1)}} \qquad 1\leqslant K\leqslant M \tag{29}$$

$$m_0=\frac{X^M}{2(2+X)^M} \tag{30}$$

For the case of $X$ large compared with $M$ we have $m_0 = 1/2$. More generally for large $X$ we have approximately:

$$m_0\simeq\frac{\exp(-2M/X)}{2} \tag{31}$$

Equation (31) shows that large average loop size implies extensive adjacent reentry. This is *catch* 22 for the switchboard model. The very assumptions of large loop size (large $X$) force us to have substantial numbers of tight loops (substantial adjacent reentry). See equation (31).

It is an inherent feature of the random switchboard model that a substantial number of the loops be short and tight. This feature arises solely from density requirements, and is not dependent on special features of the wicket model. Thus for example the application of Gamblers Ruin Methods[4] to a two-phase model of polymer semicrystalline systems leads to an average run length in the amorphous region of $3M$ which in turn[3] results in an amount of adjacency of 2/3 ($A=2/3$). Other methods[4,7] which are applicable to amphiphilic diblock copolymers result in even larger values for $A$. The actual values $\bar{x}(K)$ of the wicket model are, as we have observed, not yet known, but it is instructive to use the crude intuition that the loops randomly walk in the amorphous region before coming back to the surface. We then expect $X=aM^2$ and

$$m_0\simeq\exp\frac{(-2/aM^2)}{2} \tag{32}$$

This results in extensive adjacency. Please note that it is not the position of the authors that $X=aM^2$. We are simply making the observation that those who interpret the switchboard model in this way are forced to large amounts of adjacent reentry via equation (32) ($A>2m_0$).

For the case of small $X$, the picture is not as clear. For $X$ approaching zero we have adjacent reentry but all at level $M$. For $X=1$, the case of average near adjacency, we have:

$$A>\frac{1}{3^M} \tag{33}$$

For the three distributions of $x$s described above, we obtain for $X=1$:

$$A_{\text{narrow}}=\frac{1}{3^M} \tag{34a}$$

$$A_{\text{homo}}=\frac{1}{3}+\frac{2}{3}\times\frac{1}{3^M} \tag{34b}$$

$$A_{\text{exp}}=\frac{1}{2}+\frac{1}{2}\times\frac{1}{3^M} \tag{34c}$$

It is clear for all distributions but the narrow one that we have a considerable amount of adjacent reentry for $X=1$. For the narrow distribution with $M$ large there is little adjacent reentry. However, almost all the folds are next adjacent in this case and we still then expect a somewhat ordered surface. In *Figure* 4 we display the amount of adjacency, $A$, for each of the three models of $x(K)$ distributions for various values $X$ for $M=5$. $A_{\text{homo}}$ and $A_{\text{exp}}$ have their minimum values where $X$ is about 0.6 and 0.7 times $M$. For $M$ equal to 5 that minimum is about 20 to 30% adjacency. For $M$ larger, the percentage minimal adjacency will drop and for smaller $M$, the percent minimal adjacency will increase. Notice for all the models for $A$ we have over 50% adjacency at $X=14$ or 15 (2 or 3 times $M$). Thus we see that if the value of $X$ is less than $M$ we may not conclude that adjacent reentry is the predominant mode. However, we suggest that in such cases

the fold region is still highly structured. *Figure* 2 for example shows a system of nested folds in which $X$ and $M$ are proportional ($M = 3$).

## DISCUSSION

Because of the inherent difficulties of the wicket problem there are many things we have not done. A listing will help to circumscribe what we have accomplished as well as to suggest useful problems.

(1) We have ignored cilia, bridges, free chains and loose loops. It is easy to see that their inclusion results in more adjacent reentry than predicted by our equations. Let a bridge prolongate without change of direction perpendicular to the interface. Such chains have no effect on the equations. If we had started with an area of $L'xL'$ and then reduced it to one of $LxL$ by subtracting away all the bridges, then the solution is as we have given. Likewise, it is easy to see that any wandering of the bridge in directions parallel to the surface of the lamellae would take up space needed by the wickets, thus resulting in fewer wickets with large $x$ and/or $K$. Similarly cilia, free chains, and loose loops above the surface take up needed space and result in more of the adjacent reentry wickets.

(2) We have allowed chains to emanate from one surface only. If we allowed them to emanate from both the top and bottom surfaces of the crystals which enclose the amorphous region then we could formulate the problem along the lines of the development of this paper. Although we have not solved this problem, it is easy to see that a larger amount of adjacent reentry is implied. First, notice that the upper surface of *Figure* 2 can be thought of as consisting entirely of adjacent reentry wickets. If we view the solved problem of this paper as a double surface problem we have solutions which correspond to substantial amounts of adjacent reentry in the bottom layer and complete adjacent reentry in the upper layer. Thus, we can expect that the double surface problem results in considerably more adjacent reentrant wickets. We are not forced to this conclusion rigorously because we can imagine the double surface emanation problem with $2M$ layers to consist of two single surface problems, each of $M$ layers placed back to back. However, this formulation is unrealistic because it does not allow for penetration of lower loops into upper regions and *vice versa* which is sure to occur due to entropic considerations. As a general rule we can surely state that twice as many wickets competing for the same space result in enhanced adjacent reentry in the two surface problem compared with the one surface problem.

(3) The determination of loop size distribution from entropic and energetic considerations was not attempted. This is an integral and essential part of the problem. The authors believe that the theory of the thermodynamics at interfaces has to be further developed before its application to the nature of chain-folding can be made on the surface. We have, however, pointed out in previous works[2-4] that if the chains in the amorphous regions are random then they overfill the space unless extensive folding occurs. Thus, packing considerations argue against loose loops. As we pointed out in the Theory above, tight non-adjacent loops also have difficulties.

(4) Another important thermodynamic effect is the growth of cilia (the two ends of the molecules) at the expense of loops. A simplified model in ref 4 shows this effect clearly but the effect also occurs in biopolymers[28], adsorption of polymers on surfaces[22], and in a model of crystallization by Roe[29]. This effect results in tight loops.

(5) In describing the surface of a crystal obtained by the specific kinetic process of polymer crystal growth, we must include the requirements that the kinetic process places on the properties of the crystal interface. This certainly has not been done here and awaits a more complete picture of the growth kinetics.

## CONCLUSIONS

We have used a simplified model of a loop to estimate the amount of strict adjacency or near adjacency which is necessary to fulfill packing requirements at the interface between the crystalline and amorphous portions of a polymer. We have shown that in general even the simplest model of a loop leads to packing difficulties unless we allow for some adjacency. We have offered some models which do not require strict adjacency but these have much near adjacency. Finally, we have shown that large loops as required by some versions of the switchboard model imply substantial adjacent reentry.

## ACKNOWLEDGEMENT

We should like to thank David Sadler for several helpful suggestions.

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