Modelling the amorphous phase and the fold surface of a semicrystalline polymer—the Gambler's Ruin method

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A semicrystalline polymer with lamellar morphology consists of alternating amorphous and crystalline regions. If sufficiently long, each molecule in this system traverses both the crystalline and amorphous zones. The amorphous portion is comprised of portions of a molecule that form loops that re-enter the same lamella at some distance from the point of emergence, and bridges that form connections between two different crystal lamellae. (A tight fold is not considered to be a loop). The statistics of loops and bridges are shown to be identical to the classical Gambler's Ruin problem in mathematical statistics. This is a useful observation because the extensive existing literature on the Gambler's Ruin problem allows us immediately to transcribe results to the polymer system. Using this approach, the ratio of the number of loops to the number of bridges is determined to be M, the thickness of the amorphous zone in unit statistical steps. Also, the average number of steps comprising the amorphous run is determined to be $3M+1$ for a simple cubic lattice in three dimensions. This modelling leads to a calculation of the minimal fraction of crystal stems involved in tight folding in a semicrystalline polymer. For a simple cubic lattice this is found to be 2/3. The effects of crystal structure and stiffness of the chain in the melt on this bound are discussed.

INTRODUCTION

The amorphous phase of a bulk-crystallized, high crystallinity, semicrystalline polymer has recently undergone experimental study[1]. The focus of much theoretical work in semicrystalline polymers has been, however, on the crystalline aspects of these systems. Significant theoretical studies on the amorphous phase have been largely lacking. Yoon and Flory[2] have developed a computer model for semicrystalline polyethylene. It is their representation of the amorphous phase of a semicrystalline polymer that we shall generally use as a starting point for the theoretical developments which follow. From our models, which are mathematically exact, we shall determine properties, such as the number of lengths of loops and ties in the amorphous phase between the crystal lamellae. We shall find that these properties of the amorphous phase influence properties of the crystal–amorphous interface. To anticipate our results, we shall find that one is able to place significant lower bounds on the probability of adjacent re-entry of a chain into a crystal face. Generally such probabilities of adjacency are found to be greater than 2/3. These bounds arise out of density arguments. This result is fully consistent with models of tight loops (called wickets) which we previously developed[3].

The mathematical development presented here shows why the switchboard[4] or random re-entry model[2,5] always must yield a density in the amorphous region higher than that in the crystal. This point was first made by Frank[6] in 1958 and has been developed further semiquantitatively by him recently[7] and by the present authors[8]. Here, we shall give a more detailed and more quantitative discussion of the subject.

Our purpose is to study that amorphous part of a semicrystalline polymer which resides between the crystalline lamellae in the spherulites of a bulk grown polymer. Most of the earlier discussion on this amorphous phase of a semicrystalline polymer has focussed on the nature of the amorphous–crystalline interface. It is convenient to discuss the nature of this interface in terms of two extreme views. These will now be discussed in order to provide both a vocabulary and a perspective for the present work.

The two extreme views of the amorphous crystal interface in semicrystalline polymers are usually designated as the random switchboard model and the fully-adjacent re-entry model. In the random switchboard model, the chain generally traverses the crystalline lamella only once; it then emerges from the crystal lamella into in the amorphous phase, where its trajectory obeys random walk rules. Generally, all the portions of a chain in the amorphous phase in this model are either ties (chains attached to different lamellae) or loops (chains attached to the same lamella at points that are never or practically never adjacent to each other). The point of re-entry into the crystal phase is completely determined by amorphous chain statistics. The point of re-entry of an emergent chain back into the crystal phase is thought by the advocates of this model to occur at some distance from the exit point.

The view that the switchboard model with no (or virtually no) adjacent re-entry is the correct physical representation of the interface in a melt-crystallized semicrystalline polymer was advanced many years ago[4,9] and is still strongly held[2,10]. The principal arguments favouring this model are based on (1) the fact that it can be used to interpret small-angle neutron scattering (SANS) data; (2) the belief that molecular motion in the melt is too

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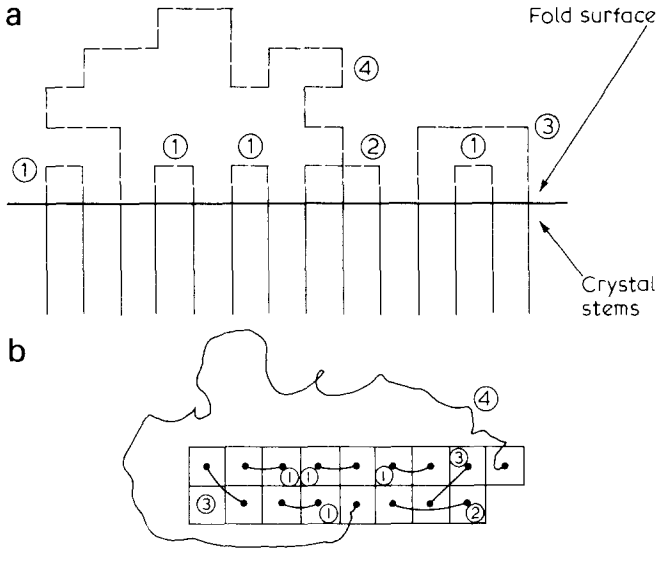

Figure 1 Schematic of different types of folding. (a) A variety of tight loops (regular folds) and a loose loop is shown in a single given fold plane. Folds marked ① are adjacent folds and counted in p_{ar}. Folds marked ② and ③ are near adjacent folds and are counted in p_{aar}. Folds ① ② and ③ all contribute to p_{tf}. Loose loops like ④ are not counted in p_{tf}. (b) A variety of regular folds and loose loops shown on the plane perpendicular to the fold plane. Folds marked ① are adjacent folds and are counted in p_{ar}. The folds marked ② are an example of a next near adjacent fold. Folds marked ③ are examples of tight folds resulting in fold plane roughening. Folds ① ② and ③ count in p_{tf}. The loose loop marked ④ is not counted in p_{tf}

slow to allow any regular folding; and (3) the view that the switchboard model provides a natural explanation for the existence of an amorphous component. As we have noted, a principal objection to the switchboard model is that the model has been thought to yield much too high a density in the amorphous region[3,6-8,11,13]. In the present work, we shall formally show that this objection is both well-founded and compelling.

Consider now, for the purposes of discussion, the other extreme view of the crystal–amorphous interface, the *fully*-adjacent re-entry model. In this extreme case, as each stem emerges from the lamella, it folds back into the crystal of origin with a more or less tight loop or a sharp fold. It is generally thought that the work to complete the fold is intimately involved in the nucleation rate and substrate completion rate that govern the growth kinetics[13]. This idealized model has been used extensively to deal with the kinetics of crystallization[14,15], as well as a variety of morphological features, such as sectorization[16], that are seen both in solution-grown and melt-grown crystals under appropriate circumstances. One clear concern about this extreme fully-folded model is that, except for cilia, the model, has no amorphous phase in its sharp fold version, and only a limited amount of amorphous material if some of the adjacent re-entry folds are not tight. Partly because of this, models with mixtures of adjacent and non-adjacent re-entry (i.e. loops or bridges) had been advocated earlier[17]. Recently, the theory of niche separation[13], which is an application of the kinetic nucleation theory of polymer crystal growth, has been used to estimate quantitatively the amorphous component of semicrystalline polymers at large undercoolings.

Two further objections to the fully-adjacent re-entry model should be noted. One is the contention of Flory and Yoon[10] that the crystallizing chain cannot be extracted from the melt in a short enough time to allow any significant degree of adjacent re-entry during substrate completion. This has been disputed by both our work[18] and that of Klein and Ball[19] which indicates that reptation provides a tenable mechanism, allowing the force of crystallization to reel in a molecule onto the substrate with a high degree of adjacent re-entry. The remaining objection of Flory and Yoon[10] is that SANS studies on quench-crystallized bulk polyethylene, while subject to dispute on some details, makes it clear that the fully-adjacent re-entry model does not apply. Our analysis of the SANS data[11-13], which does not have a density anomaly in the interfacial region, indicates that the probability of tight folding (mostly adjacent re-entry) is actually about 0.65 for highly quenched samples used in the SANS experiments.

One may conclude from the above. The first is that neither of the extreme cases discussed above is precisely correct, and that models (such as the ACA of Guenet *et al.*[20], or the central core model, or the variable cluster model[11,12]) which avoid density anomalies should be given consideration. Arguments concerning the issues noted above have been made in some detail in a current Faraday Discussion[21] and will not be reviewed here.

The above discussion brings out the importance of defining a parameter that denotes the degree or probability of adjacency or tight folding. With such a parameter, one has an index of whether a system or model under study more closely approximates the random switchboard or the fully-adjacent re-entry type of model. This parameter which has been used to characterize the crystal–amorphous interface is the probability of adjacent re-entry, p_{ar}[11,13]. It is the fraction of stems which return adjacent to the previous crystal stem in the same chain with only a few segments used in the interfacial region to form a tight fold (8 to 20 for PE). Two other quantities which shall be used to characterize the surface need to be defined. The fraction of stems which return near adjacent or next near adjacent but always with tight folds (loops using only a few segments) is given by p_{aar}, the probability of close adjacency. The quantity which measures the sum of adjacent, near adjacent or next near adjacent stems, all with tight folds, shall be called the probability of tight folding, p_{tf}. We have:

$$p_{tf} = p_{ar} + p_{aar} \tag{1}$$

These quantities are defined also in *Figure 1*. Each grouping of adjacent, near adjacent and next near adjacent stems connected by tight folds shall be called a cluster of stems. The average cluster size, $\langle n_c \rangle$, for an infinite molecular weight chain is related to p_{tf} by:

$$\langle n_c \rangle = (1 - p_{tf})^{-1}$$

In this work we shall not be able to distinguish between p_{ar} and p_{tf}. What we can compute is the fraction of stems participating in a cluster of folds which are so tight that the folds do not significantly contribute to the amorphous density. We shall characterize the surface from these models by p_{tf} alone.

As noted earlier this paper will focus on the issue of whether it is possible for a chain to retain its random coil character and keep the correct amorphous density for

switchboard-like models. The most important theoretical conclusion to be drawn from our results is that lower bounds on the probability of tight folding can be obtained. This guide to both experimental and other theoretical studies leads us to reject any $p_{tf}=0$ model and thus any switchboard-like model. For the case where the crystal stems are perpendicular to the fold surface where the chain bond vector is parallel to the crystal stem, and where the amorphous phase has the normal configurational properties of a random walk, the lower bound for the probability of tight folding is shown rigorously to be 2/3. This bound is changed only slightly by zigzag or by normal changes in crystal lattice, or by chain stiffness in the amorphous phase. The effects that can lower or raise this lower bound are discussed below.

In the next section we shall review and considerably expand a part of an earlier paper[8] showing that the Yoon and Flory model of the amorphous chain in a semicrystalline matrix obeys Gambler's Ruin statistics. With this insight, and some generalization of the above, we shall determine the properties of the chains in the amorphous phase assuming that phase is isotropic. Effects of introducing some anisotropy are then explored. In all our developments, we shall consider what minimal requirements for p_{tf} are given by the various models.

THE YOON AND FLORY MODEL OF AN AMORPHOUS POLYMER IN A SEMICRYSTALLINE MATRIX AND ITS RELATION TO THE GAMBLER'S RUIN PROBLEM

The Yoon and Flory[2] computer model of semicrystalline polyethylene was developed to explain SANS experiments on this material. In doing so they have offered a model for the portion of a chain in the amorphous phase of a semicrystalline polymer and we use that model as a focus for the present work on the amorphous phase of a semicrystalline polymer. We focus on their models without reflecting walls buried in the amorphous phase[2]. Lamellar morphology is assumed: that is, sets of parallel planes which separate crystal and amorphous regions are established. The polymer stem is first placed in the crystal phase. After the chain has gone through the crystal phase it emerges into the amorphous phase, obeying so-called real chain statistics (modified random walk). Its amorphous ramblings do not include any self-exclusion effects[22]. When the chain touches either of the planes separating the crystal and amorphous phase the chain is them immediately absorbed into the crystal to form a stem. The process is then repeated. For simplicity we shall consider their model for an infinite molecular weight chain. That is, end effects are not considered. The chain has no cilia, only loops and ties. In a later paper, cilia will be included in the modelling and calculations.

We note here the assumption in this model and in Yoon and Flory's model that the spherulitic lamellar structure of a highly crystalline, semicrystalline polymer can be represented by parallel sheets of an alternating amorphous and crystalline structure. For the configuration of a given chain this assumption is most likely valid. However, when we want to estimate the number of segments participating in the amorphous fraction from crystallinity, this assumption may be in error. This is, for example, because of the amorphous material built up at the spherulite interface. This latter effect cannot be taken into account in the Yoon and Flory modelling or in ours.

For the case of no cilia, the rules for the Yoon and Flory model for an amorphous phase of M unit steps are repeated in *Table 1* along with the equivalent rules for the Gambler's Ruin problem (with renewal). An inspection of *Table 1* immediately shows that the Gambler's Ruin problem (*GRP*) and the Yoon–Flory model of the amorphous phase are identical. In *Figure 2a* we show the traverse of a single chain through various lamella structures. In *Figure 2b* we show how the properties of the chain can be viewed as separate walks of a gambler between losing and winning. It is assumed in doing this that the chains in each amorphous phase are representative, and the loops and ties do not depend where in physical space and to what chain they are tied. The walk is one without exlusion in the amorphous phase (no memory or long range volume exclusion effects) as is normal in the Flory description of the melt[9].

The Yoon and Flory infinite molecular weight case has been identified with the Gambler's Ruin problem where the gambler starts with \$1 as discussed in *Table 1*. Now we establish a dictionary to compare properties of the Gambler's Ruin problem and properties of the amorphous chain in a lamellar morphology.

Our dictionary is presented in *Table 2*. We remind the reader that in this paper we are looking at modelling for infinite molecular weight chains only. Thus we have not defined properties of cilia. In the Appendix, we collect the equations and their solutions for all dimensions for the Gambler's Ruin problem. We refer the reader to it for details of derivations. In the rest of this section we shall expand on the definitions given in *Table 2*, which will be used in this paper.

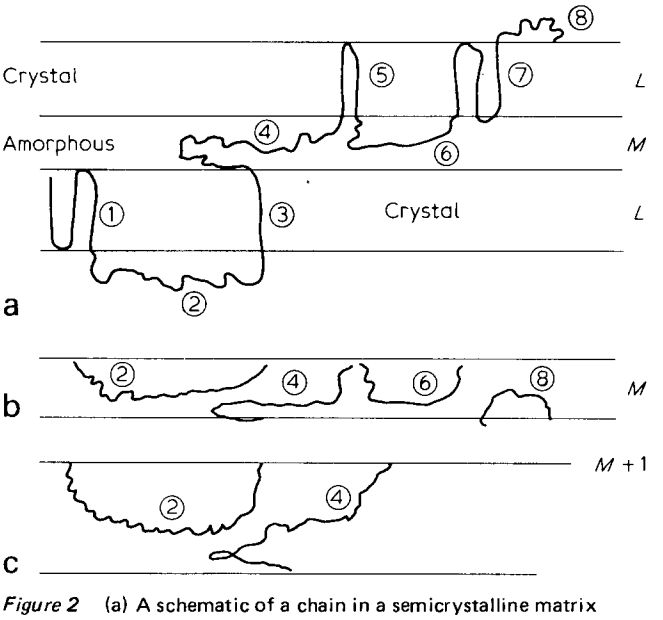

Figure 2 (a) A schematic of a chain in a semicrystalline matrix obeying Yoon and Flory rules. Sections of chain marked ① ③ ⑤ and ⑦ are runs in crystalline regimes of thickness L. n_1, n_3, n_5 and n_7 are the number of segments in these runs. Sections of the chain marked ②, ④, ⑥ and ⑧ are runs in the amorphous region. n_2, n_4, n_6 and n_8 are the number of segments in these runs. (b) Only the amorphous sections of the chain drawn in (a). These parts of the chain make up the Gambler's Ruin walk. (c) Expanded view of a loop, ②, and a tie, ④

Table 1 The rules of Yoon and Flory computer model of amorphous phase

1. The chains traverse an amorphous region whose thickness is equivalent to $M+1$ statistical steps of the chain. At any point in its walk it has a z coordinate between $z=0$ and $z=M+1$, $z=0$ being the lower crystal–amorphous boundary and $z=M+1$ being the upper crystal–amorphous boundary
2. The chain starts from the edge of the crystal and behaves as a random walker (with proper real chain statistics) while it is in the amorphous phase
3. When the chain touches the crystal–amorphous interface it is absorbed into the crystal and forms a stem. If it reaches the lamella it left, the chain is said to form a loop. If it reaches the other lamella, it is said to form a tie (see *Figure 2c*)
4. The chain traverses the crystal region (r times) and then returns to the amorphous phase again as a random walker
Rules for classic Gambler's Ruin problem with renewal
1. To win, a gambler must have total winnings of $M+1$ dollars; to lose, his total winnings are zero dollars. The gambler always has in his possession during the game between 1 and M dollars
2. Gambler starts the game with z dollars; our gambler is special since he starts the game with 1 dollar. He gambles $1 for each trial
3. When the gambler has 0 dollars he is said to have lost the game. When he has $M+1$ dollars he is said to have won the game; in either of these two instances we say one game has been played
4. Having won or lost a game the gambler always starts a new game (Gambler's Ruin with renewal)

There is a symmetry for the chain in the amorphous phase that does not occur in the Gambler's Ruin problem. In both the rules and the dictionary for the Gambler's Ruin problem we have, for simplicity, assumed the gambler always starts with $1. This is the same as assuming the chain can only enter into the amorphous phase from the bottom face of the amorphous phase. Since we assume the chain can enter equally with equal probability from the top or bottom face of the amorphous phase we must assume it is equally likely that the gambler starts with $1 or $$M$. In the case he starts with $$M$ a loop is when he wins $$(M+1)$ and a tie is when he loses. This symmetrizing of the *GRP* will be done as we derive various equations. It simply means the gambler has an equal probability of starting with $1 or $$M$.

The meaning of the fraction of loops and ties is evident. However, the meaning of the average duration, D_1, needs to be related to other properties and shall be done here. Consider a lamellar system with l_a the thickness of the amorphous layer and l_c the thickness of the crystal layer. If ρ_a is the density of the amorphous phase and ρ_c the crystal density, then the mass crystallinity for a lamellar system is given by:

$$\chi_c = \frac{l_c\rho_c}{l_a\rho_a + l_c\rho_c} \tag{2}$$

Now, let r_c be the average number of monomers in a run of the chain in the crystal before it executes a Gambler's Ruin walk and let r_a be the number of steps of the Gambler's Ruin walk: then the mass crystallinity, the total number of monomers in the crystal, is τr_c for τ repeats of crystalline runs followed by amorphous runs. The number of steps in the amorphous phase is τr_a if every chain in the interlamellar amorphous phase participates in the crystal phase. Thus, the mass crystallinity is:

$$\chi_c = \frac{r_c}{r_c + r_a} \tag{3}$$

for an infinite molecular weight polymer.

We immediately have from equations (2) and (3):

$$\frac{l_a\rho_a}{l_c\rho_c} = \frac{r_a}{r_c} \tag{4}$$

Let us say that the chain traverses the lamella $f+1$ times to form a cluster of $f+1$ stems for each run r_c. As noted before, this cluster, or these $f+1$ traverses, must be made up of tight folds which do not contribute segments to the amorphous phase. In fact, we shall assume these folds contribute only to the crystal run. Let us say there are $\bar{k}$ segments in the average fold. Then the contribution to the crystal run from these is $f\bar{k}$. We may now relate r_c to l_c. If the run r_c is made up of $f+1$ traverses of crystal lamella, then:

$$r_c = (f+1)l_c/b' + f\bar{k} \tag{5a}$$

$$r_c = (f+1)\left(l_c/b' + \frac{f}{f+1}\bar{k}\right) \tag{5b}$$

where $(b')^{-1}$ is the number of crystal segments per unit of length perpendicular to the lamellar surface. In the simplest case b' is the projection of one monomer bond on the axis perpendicular to the lamella. b' not only includes the effects of chain zigzag, like those found in polyethylene, but also includes chain axis tilt. Any other crystal structure effects also come into b'.

In *Figure 3* we show various crystal structure effects which can change b'. Such effects contribute to increasing the cross-sectional surface area of each chain in the crystal as it exits the lamella. The effects of b' and related effects on the surface are largely local effects and cannot easily be discussed in detail in this generalized mathematical treatment of the amorphous phase. However, a few more comments seem appropriate at this juncture.

As we shall see in what follows, the assumption that a chain leaves the crystal amorphous interface as a random

Table 2 Some properties of the Gambler's Ruin problem and analogous properties of amorphous chains in interlamellar regions (Gambler always starts at $z=1$ for these definitions)

Probability of failure	<– – –>	Probability of a loop
Probability of winning	<– – –>	Probability of a bridge (tie)
Expected duration of a game	<– – –>	Average number of steps in an amorphous walk (loop or tie)
Expected duration of a game which is finally lost	<– – –>	Average number of steps in a loop
Expected duration of a game which is finally won	<– – –>	Average number of steps in a tie (bridge)
Probability that gambler wins z' dollars	<– – –>	Average number of segments (in one dimension) at point z' in region

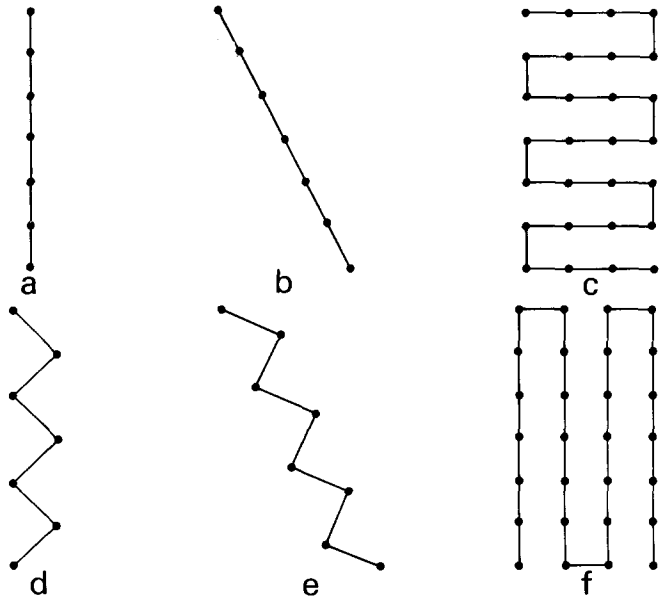

Figure 3 A variety of ways the crystal adjusts to increase its surface area per stem to avoid density problems in the amorphous phase. (a) Single stem no density avoidence. (b) Tilted single stem affects area like a $\cos\theta$ angle of tile. (c) Crystal makes horizontal passes as well as vertical ones. (d) Zigzag in crystal. (e) Tilted zigzag. (f) Folding

walker leads to the conclusion that the effective number of segments per run in the amorphous phase of that chain is much larger than simply the density from a rod-like walk. This will be seen from quantities such as duration of the walk and from the segment density per chain exit from the crystal. In order for the crystal and the amorphous phase to have nearly identical densities, we must then invoke some effect to correct values of the densities in the amorphous and crystal region. This paper is mainly concerned with whether there is any way this can be done by adjusting the amorphous phase. However, as is evident from *Figure 3* there are a number of ways the crystal can be adjusted to alleviate this problem. All the ways explored in *Figure 3* except tight folding require an adjustment within the bulk of the crystal. Tight folding alone is a crystal interfacial property. In general we might expect only interfacial phenomena to be affected by the amorphous phase density or packing problems and this is the general presumption of this paper. However, it is possible that the amorphous packing problems *do* lead to changes in the bulk crystal state, but this issue will not be dealt with here.

What we shall do is to take the view that b' is near b, the bond distance. That is, we assume that the crystal stems are perpendicular to the interfacial plane. For cases where (b'/b) is not near one appropriate corrections to the equations in those sections will be necessary.

From equations (4) and (5) we obtain:

$$f+1=\frac{\rho_c}{\rho_a}\left(\frac{b'}{b}\right)\frac{r_a}{(l_a/b)}\times\left(1+\frac{f}{f+1}\frac{\bar{k}b'}{l_c}\right)^{-1} \tag{6}$$

$r_a/(l_a/b)$ is, of course, to be determined by the Gambler's Ruin calculation.

In general, we expect the number of units in a crystal stem to be much larger than that in the fold. Thus:

$$\frac{\bar{k}b'}{l_c}\ll 1$$

ρ_c/ρ_a is generally greater than one but by only 10 to 20%. Therefore, f depends largely on r_a/l_a and (b'/b), $r_a(l_a/b)$ will be determined in the next sections.

From f we may also determine the probability of tight folding p_{tf}. Since the cluster size is $f+1$, then for infinite chain length:

$$p_{tf}=\frac{f}{f+1}=1-\frac{1}{1+f} \tag{7}$$

Thus, we have a relationship between the probability of tight folding, the density of each phase, and the ratio of the thickness of the amorphous phase to the duration length of the walk in the amorphous phase.

Until now we have considered local or structural effects only in the crystal phase as described by b'. We now wish to discuss structural effects in the amorphous phase. These are twofold—the effect of varying statistical length and a local structural effect near the crystal–amorphous interface. Generally both effects await more detailed studies: Monte Carlo calculations looking into aspects of these effects are currently in progress. However, for the effect of varying statistical length, we offer the following general arguments.

We wish to consider the effect of varying the statistical length of the step in the amorphous phase. Our current dictionary connects the Gambler's Ruin properties to the walk in the amorphous phase: each step is of unit length and each truly random. If we have a real chain we must include the effects of chain structure in the bulk. Although we cannot deal with this problem in detail in this paper we can take into account the major effects of structure by considering the effect of a varying statistical length on our calculations. If we consider a gambler who gambles C dollars on each throw of the dice, then he wins when he wins $(M+1)/C$ dollars and loses when he gets to zero. For example, we have the duration of a run, r'_a, in steps of length C is:

$$r'_a=R_a((M+1)/C) \tag{8a}$$

where $R_a(x)$ is the functional form for the duration of a walk in an amorphous phase of thickness x. The duration of walks in steps of unit length, r_a, is:

$$r_a=C\,r'_a \tag{8b}$$

and thus:

$$r_a=C\,R_a((M+1)/C) \tag{8c}$$

Thus any function which is a linear function of M will not depend on the statistical step length for large M. As we shall see in the next section both the average duration of a run in the amorphous phase and the average number of steps (monomers) in a loop are linear functions of M and thus will show no effect of statistical length for large M.

The density at each amorphous level must be considered in a little detail here. Let us say we have an average run. We allow a chain to emerge from a crystal and after r_a steps, the chain returns to the crystal. That average run will have $L(k)$ segments at each level k. Therefore, the density we consider is the density at level k per exit from the crystal.

Finally, let us discuss a minor modification of the model. In what has been discussed before and in what we shall discuss we always assume that each time the chain

touches the crystal–amorphous interface it is absorbed into the crystal. This need not be the case. Let us say rather the chain has a probability θ of being absorbed upon touching and a probability of $1-\theta$ of not being absorbed (being reflected). Then the duration, $r_a^{(\bar{n}_0)}$ of a walk which has $(\bar{n}_0-1)$ equal to the number of times the chain touches before it is absorbed is given by

$$r_a^{(\bar{n}_0)}=\bar{n}_0 r_a^{(1)} \tag{9a}$$

$$r_a^{(1)}=r_a \tag{9b}$$

where $r_a^{(1)}$ is by definition the number of segments in a run of a chain absorbed upon touching only once. It is easy to show for an infinite chain:

$$\bar{n}_0=\frac{1}{1-\theta} \tag{10}$$

Furthermore, the density per exit of a stem for such a run $L^{(n_0)}(k)$ is given by:

$$L^{(\bar{n}_0)}(k)=\bar{n}_0 L^{(1)}(k) \tag{11a}$$

$$L^{(1)}(k)=L(k) \tag{11b}$$

It was clear that replacing r_a with $r_a^{(n_0)}$ in equation (6) will increase the folding by about $\bar{n}_0$ and thus increase the probability of tight folding. We shall not discuss this further in this paper except to point out that $\bar{n}_0$ is always equal to, or greater than, one. Any modification of the equations to make $\bar{n}_0$ greater than one will always be in the direction of increasing p_{tf} and of increasing the density arising from each stem of crystal which goes into the amorphous phase. Thus it would seem that any modification of the model like this goes in the direction of increasing the amount of folding.

GAMBLER'S RUIN PROBLEM—THE CASE OF THE CHAIN IN A CUBIC LATTICE WITH A COMPLETELY ISOTROPIC AMORPHOUS ZONE

We consider the case of a gambler in a cubic lattice in d dimensions. As we argued earlier, this is not a serious limitation for we may scale all our results by using concepts of statistical steps. Further, we pointed out that those quantities which are linear in the number of steps in the thickness of the amorphous phase are largely independent of the statistical step size. As we shall see soon, this linearity is true for important properties like the duration of the game (the average number of steps in a run in the amorphous phase).

We have, for a completely isotropic amorphous zone:

$$\begin{aligned} &p+q+\alpha=1 \\ &p=q \\ &\alpha=(d-1)/d \end{aligned} \tag{12}$$

where d = dimensionality of lattice. (p, l, α and D_z are defined in Appendix A, A1.) For a one dimensional lattice $p=q=1/2$; for a three dimensional lattice $p=q=1/6$.

Figure 2a shows an example of a single chain crossing various crystal and amorphous regions. The average length of a run in the amorphous phase r_a—the average number of steps of a single run in the amorphous region in *Figure 2a*—is given by:

$$\bar{r}_a=(n_2+n_4+n_6+n_8)/4 \tag{13}$$

where n_i is the number of segments in the walk labelled i in the amorphous phase.
$\bar{r}_a$ is given in this case by:

$$\bar{r}_a=(D_1+D_M)/2+1 \tag{14}$$

where we have presumed the chains do not know the top of the lamellae from the bottom and so there are equally as many chains emanating from the top of any lamella as from the bottom. M is the number of statistical steps measuring the thickness of the amorphous phase. We then have by Appendix A:

$$\bar{r}_a=\frac{M}{(1-\alpha)}+1 \tag{15}$$

M is equal to the thickness of the amorphous phase, l_a, in a cubic lattice with a statistical step length of one. We noted before that p is the probability of stepping in the $+z$ direction, q the probability of stepping in $-z$, and $\alpha/4$ the probability to step in $+x$, $-x$, $+y$ or $-y$ directions. For a cubic lattice:

$$p=q=\frac{1-\alpha}{2}=1/6 \tag{16a}$$

$$r_a=3M+1 \tag{16b}$$

We now use the previous equation to estimate the amount of folding. Following equation (6) we obtain for f, the amount of folding for any lattice:

$$1+f=\frac{\rho_c}{\rho_a}\left(\frac{b'}{b}\right)\frac{r_a}{(l_a/b)}\left(1+\left(\frac{f}{f+1}\right)\frac{\bar{k}b'}{l_c}\right)^{-1} \tag{17}$$

For a cubic lattice with $\bar{k}b'<l_c$, $b'=b$, and $l_a=(M+1)b$, we have:

$$1+f=\frac{\rho_c}{\rho_a}\left(\frac{M}{1-\alpha}+1\right)\frac{1}{M+1}-1 \tag{18}$$

For large M in three dimensions:

$$1+f=3\frac{\rho_c}{\rho_a} \tag{19}$$

In general $(\rho_c/\rho_a)>1$. Thus,

$$f>2 \tag{20}$$

By equation (7) we obtain, by the same reasoning:

$$p_{tf}>2/3 \tag{21}$$

for a cubic lattice. Notice that our results are bounds. p_{tf} of 2/3 for a cubic lattice is a lower bound. As long as the chain abides by the assumptions made here this is a rigorous bound.

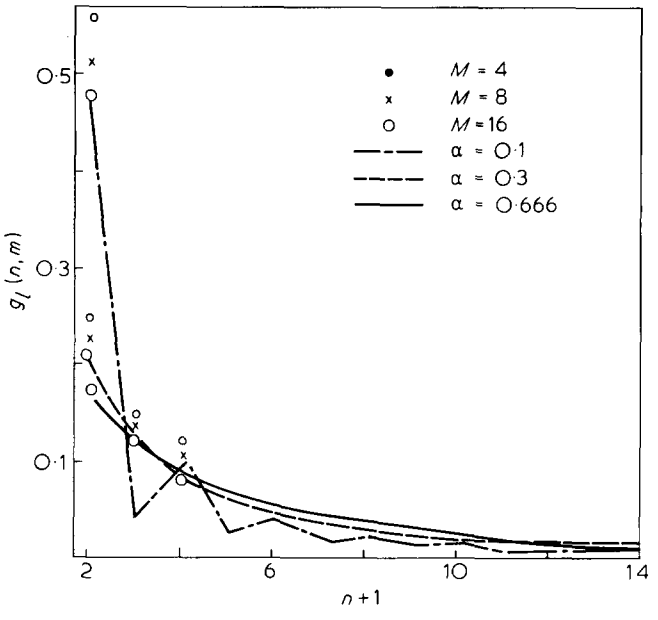

Figure 4 Fraction of loops of length n for various values of α, $g_L(n, M)$. Values of α marked on Figures. Points on Figure near $n+1=2, 4, 6$ show the effect of differing M. The effect is largest for n small

Equations (16b) and (21) are fundamental equations for our discussion of the inadequacies in the switchboard (or random re-entry) model. Equation (16b) tells us that each random walk exit from the crystal takes three times the number of segments as the thickness of the amorphous phase. Thus the random walk exit takes the space of three crystal-like stems in the amorphous phase. We see this again in equation (21) when we see that we need at least two folds to avoid any density problems.

This estimate of p_{tf} in equation (21) is consistent with the value obtained in an analysis of the SANS experiment on models for PE that Guttman *et al.*[11,12] obtained previously. They estimated $p_{tf}=0.6$ to 0.8 to fit the data and their models. Recall that the specimens used in the SANS experiments were quench-crystallized, which would maximize the randomness of the surface, i.e. promote the highest possible degree of non-adjacent re-entry.

Runs in the amorphous phase are made up of loops and bridges. From equation (A11b)—see Appendix—the fraction of walks which are loops is given by:

$$P_L=\frac{M}{M+1} \tag{22}$$

while the fraction which are bridges are by equation (A12b)—see Appendix:

$$P_B=\frac{1}{M+1} \tag{23}$$

The probabilities of loops or bridges are independent of α and dependent only on the thickness of the amorphous region. Thus, the number of ties in this model increases as the thickness of the amorphous layer decreases. If, as is often supposed[23], the ultimate strength of a semicrystalline polymer depends on the number of ties per unit area then this completely random walk model of the amorphous phase in semicrystalline polymers would predict that as the amorphous region thickness decreases the polymer strength increases if all other parameters are kept fixed.

We may also estimate the average loop and bridge length. From equations (A22) and (A23) the average loop length $\langle L\rangle$ is for a cubic lattice:

$$\langle L\rangle=\frac{2M+1}{3(1-\alpha)}+1=2M+2 \qquad (\text{for } \alpha=2/3) \tag{24}$$

while the average tie length $\langle B\rangle$

$$\langle B\rangle=\frac{(M+1)^2-1}{3(1-\alpha)}+1=(M+1)^2 \qquad (\text{for } \alpha=2/3) \tag{25}$$

The average number of segments in a loop depends linearly on the thickness while the number in a tie depends quadratically. If for the tie we use the analogy that the ties control the ultimate extension of a semicrystalline polymer plaque[24] then we find that the polymer may be pulled out to an extension ratio proportional to its amorphous thickness. What this value may be is not exactly clear but it does say that the thicker the amorphous phase the weaker is the material and the more extensible it should be.

It is interesting to consider here the size distribution of loops. Let us define $g_L(n,M)$ as the fraction of loops of length n for a thickness M of the amorphous phase. Analytical expressions for these are given in the Appendix and graphical data are given in *Figure 4*. For loops with $\alpha=2/3$ we see that although the average number of segments in a loop depends on the thickness of the amorphous phase, M, the loop distribution is always peaked at the very smallest loop sizes and has only a weak dependence on M. The fraction of loops of only two segments, $g_L(2,M)$:

$$g_L(2,M)=\frac{1}{6}\left(\frac{M+1}{M}\right) \tag{26}$$

is about 17%. The fraction of loops of 3 segments is about 12% and of 4 segments, 10%. Thus loops which are adjacent or near adjacent account for nearly 30% of the loops even in a random walk model. Thus approximately 1/4 of the stems in the crystal which lead to no folding (random walks) return adjacent or near adjacent. With a p_{tf} of 0.6 as in equation (21) the number of adjacent stems is closer to 0.75 in this view.

The above discussion of loop distribution for small loops shows the major inadequacy of the Gambler's Ruin approach; that is, being a true random walk, neither local structure nor short range exclusion nor long range excluded volume are included. The effects of the lack of short range exclusion are most apparent in the loops of 2 segments and 4 segments. Loops of 2 segments can never occur due to local exclusion effects for a real chain (walks with self-reversals are not allowed). From similar considerations, about 2/3 of the loops with 4 segments are also not allowed. Thus treatments where more local structure is put into the models is required. As we have pointed out above this is not easily done analytically. However, computer simulation can be carried out on part of this problem and we are currently doing this. At this

juncture let us only say that in a previous paper to compute the SANS of semicrystalline polyethylene[11], calculations were made of some quantities reported here using models that include some effects of local structure. The results of those simulations are similar to results reported here when the distances are measured in steps of statistical lengths.

Now, $L(k)$, the average number of segments at level k for each exit from the crystal for such a set of ruin problems is given by:

$$L(k)=\frac{1}{(1-\alpha)}\left(\frac{M+1-k}{M+1}+\frac{k}{M+1}\right) \tag{27}$$

Equation (27) is obtained from equations (A47a) and (A47b). In deriving equation (27) we have used the fact that on average there are equal numbers of exits from the lamella at the top and the bottom of the amorphous phase. For a lattice in three dimensions:

$$L(k)=3 \tag{28}$$

Thus, there are three segments on each level of the amorphous phase independent for each exit from the crystal. If the crystal and amorphous density are the same for this lattice there must be on the average three stems in the crystal for each time the chain emerges into the amorphous phase; that is, the crystal must have two folds and these folds must be tight so as not to go into the amorphous phase and contribute to its density. These folds must be tight and are most probably adjacent. This result is consistent with the results of equations (19)–(21) and again emphasize the fact that a model in which each stem emerges from the crystal as a random walk is not possible.

The fact that the Gambler's Ruin procedure gives constant density (equation 28) as a function of z is absolutely necessary for the correct modelling of the polymer system. In the bulk amorphous phase a polymer chain must on the average show a constant density. Had $L(k)$ not been a constant, the Gambler's Ruin problem would not have been a good model for polymer chains.

CUBIC LATTICE WITH AN ANISOTROPIC AMORPHOUS ZONE AND $p=q$

We assume the probabilities of stepping in $+z$ and $-z$ are identical to each other, but not identical to the probabilities of making x or y steps. For this case we have $\alpha \neq 2/3$; α can take any other value from near zero (almost no stepping in the x or y direction) to a value close to one (nearly all the steps are parallel to the xy plane).

We can obtain immediately the following equations for the duration of the walk (from equation 15):

$$\bar{r}_a=\frac{M}{(1-\alpha)}+1 \tag{29}$$

for the average number of segments in a loop:

$$\langle L\rangle=\frac{2M+1}{3(1-\alpha)}+1 \tag{30}$$

for the average number of segments in a bridge:

$$\langle B\rangle=\frac{(M+1)^2-1}{3(1-\alpha)}+1 \tag{31}$$

and for the amount of folding, equation (18):

$$1+f=\frac{\rho_c}{\rho_a}\left(\frac{M}{1-\alpha}+1\right)\frac{1}{M+1} \tag{32}$$

For the density of the amorphous phase when each stem of a crystal goes into the amorphous phase we have:

$$L(k)=\frac{1}{1-\alpha} \tag{33}$$

For the probability of adjacency, from equations (7) and (32):

$$p_{tf}=\frac{\left(\frac{M}{1-\alpha}+1\right)-\frac{\rho_a}{\rho_c}(M+1)}{\left(\frac{M}{1-\alpha}+1\right)} \tag{34}$$

For M large we have:

$$p_{tf}=\alpha\frac{\rho_a}{\rho_c}+\frac{\rho_c-\rho_a}{\rho_c} \tag{35}$$

while for $\rho_c=\rho_a$

$$p_{tf}=\alpha \tag{36}$$

From an inspection of these equations, it would appear that considerable non-adjacent folding is allowed for the case of α near zero. In what follows we shall show that α near zero is a disallowed case; that is, the random walk model fails near $\alpha=0$. Furthermore, we shall show that when α is near zero, what appears to be random walks are, in reality, adjacent folding. Finally, we shall try to estimate minimal values allowed for α.

Consider the case of $\alpha=0$. For $\alpha=0$ we have walks only on the line perpendicular to the lamellar plane and with $p=q$. In this case, both the local excluded volume problem, the fact that a step cannot walk back on itself, and the global excluded volume problem are violated in the extreme. This kind of walk, corrected for excluded volume effects, would not be random but rather an extension of the crystal.

When α is close to, but not equal to, zero the violations of excluded volume are nearly as serious. The minimal requirement that we have correct configurations is to have at least one step parallel to the x–y plane (the lamellar plane) in a loop. Let us define the average number of steps in a loop which are in the xy plane as $\langle L_{x,y}\rangle$. Since α is the fraction of steps in the x–y plane*:

$$\langle L_{xy}\rangle=\alpha\langle L\rangle \tag{37}$$

$$\langle L_{xy}\rangle=\frac{\alpha(2M+1)}{3(1-\alpha)} \tag{38}$$

and by the same argument the number of segments in the z direction, $\langle L_z\rangle$, is:

* Notice $\langle L_{xy}\rangle$ is α times the duration of a walk starting at $z=1$ since those steps of a loop which are equally probable are only those in the loop which start one step above the plane. To form the loop, the step up to one level above the plane must be made. This means that $\langle L_z\rangle$ is 1 α times the duration of the loop starting one step above the surface plus 1.

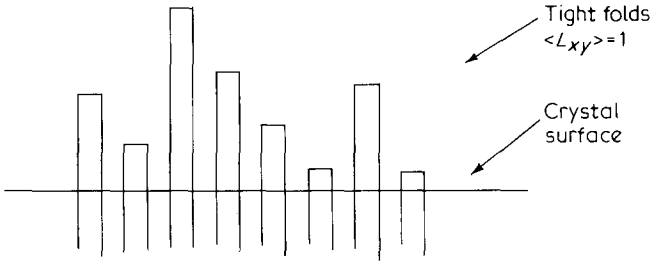

Figure 5 Needle-like tight loops making up surface for the case $\langle L_{xy}\rangle = 1$

$$\langle L_z\rangle = \frac{(1-\alpha)(2M+1)}{(1-\alpha)\quad 3} + 1 \tag{39}$$

$$= \frac{2M+1}{3} + 1 \tag{40}$$

Now for a loop $\langle L_{xy}\rangle$ must have a value of at least 1. If $\langle L_{xy}\rangle$ is 1 then the loop is like those in *Figure 5*. Notice these are the only configurations which do not have the excluded volume problem for $\langle L_{xy}\rangle = 1$. If $\langle L_{xy}\rangle = 1$ then we have for α_m, the minimal value of α,

$$\alpha_m = \frac{3}{2M+4} \tag{41}$$

Now α_m is a lower bound on α. We should recall that M is not in unit steps of polymer segments but in statistical steps. As we have pointed out earlier for the Yoon and Flory calculation, M is about 10 for an amorphous phase of 90 Å. α_m, the minimum α for their case is about 0.124. However, this small α does not imply p_{tf} is small since all the loops that make α_m, for $\alpha_m = 0.124$, although they occur by a random process, must be tight. This is because to have $\langle L_{xy}\rangle = 1$, only loops of one step in xy direction are allowed since no loops of $L_{xy} = 0$ are allowed in the average. No larger values of L_{xy} can be allowed otherwise $\langle L_{xy}\rangle$ would have to be greater than one. Larger values of $\langle L\rangle$ are allowed where we have loops with longer extensions in the z direction. These loops are all tight adjacent folds with long needle-like excursions into the amorphous region as shown in *Figure 5*. Thus for this case the fold surface is very rough, but with very tight folds. Although α is small, p_{tf} is 1.

As α increases the number of loops with L_{xy} greater than one increases. For small α we have:

$$\alpha = \frac{3\langle L_{xy}\rangle}{(2M+1+3\langle L_{xy}\rangle)} \tag{42}$$

The probability of adjacency p_{tf} may be examined in the light of equation (42) as follows. First, we estimate the fraction of adjacent folds required by the fact that for a given α we have a density defect which requires that we have tight folding amongst many stems, p_{arn}. We can estimate p_{arn} from equation (34) as:

$$p_{arn} = \frac{\left(\frac{M}{1-\alpha}+1\right) - M\rho_a/\rho_c}{\left(\frac{M}{1-\alpha}+1\right)} \tag{43}$$

Second, we estimate those random walks which are in reality tight folds because α is a value near zero—what we have in the past called accidental adjacency, p_{ara}, can be estimated for a given α from the fraction of those stems which yield three segment walks. This fraction can be estimated by subtracting from the normalization the fraction of two step walks since these are certainly disallowed. This estimate, which is a lower bound, is:

$$p_{ara} = \frac{(1-\alpha)g_L(2,M)}{(1-g_L(1,M))} \tag{44}$$

where $g(n,M)$ is given graphically by *Figure 4* or by equations (A29)–(A36). Thus,

$$p_{tf} = p_{arn} + p_{ara} \tag{45}$$

This equation is plotted for various M as a function of α, assuming $\rho_c/\rho_a = 1.15$ (the value for PE) in *Figure 6*.

From *Figure 6*, we see that the probability of adjacency rapidly obtains values over 0.5 for small α. We should remember that this result is a lower bound. Thus realistic cases would be expected to yield larger p_{tf}.

Finally, we should observe that there is an entropy force tending to randomize the orientation of bonds (which of itself results in $\alpha = 2/3$). The only force which could conceivably cause asymmety ($\alpha \neq 2/3$) arises from the packing entropy (competitions of chains for space). However, an estimate of this force for the closely related problem of diblock copolymers has recently been made[25] and in that case α deviates only slightly from the symmetrical ($\alpha = 2/3$) value.

We have shown that p_{tf} is sensibly greater than 0.5 no matter what the value of α. These results show that anisotropy in the chain orientation of this kind cannot result in small p_{tf}.

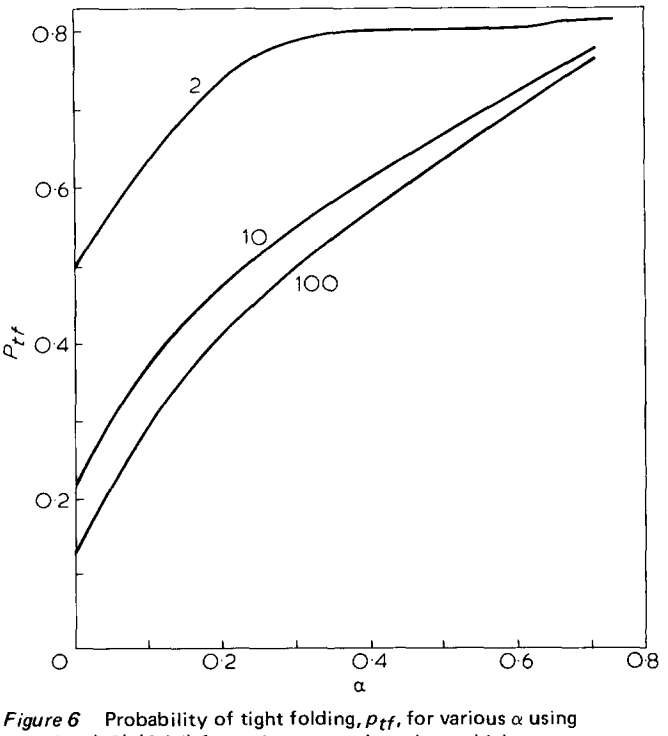

Figure 6 Probability of tight folding, p_{tf}, for various α using equation (45) (4.17) for various amorphous layer thicknesses M (M = 2, 10 and 100)

DISCUSSION AND CONCLUSIONS

We have shown here that the Gambler's Ruin problem may be used as a model for the amorhpous phase of a semicrystalline polymer. We have shown that from the analysis of this problem a number of significant new ideas emerge about properties of an amorphous phase that is bounded by crystal lamellae.

It has been demonstrated that for a case where every crystal stem leads to a run in the amorphous phase that one must expect a higher amorphous density than crystal density. To avoid this dilemma we invoke a considerable amount of tight folding for the chains on the surfaces of the crystal. In those cases in which tight folding is not required by packing considerations in the amorphous phase, the case of α near zero, we have shown that the random walk itself yields large amounts of adjacent or tight folding. This phenomenon is called by us 'accidental adjacency'.

Further we have shown that density problems occur for models in which each amorphous run is allowed to touch the crystal without being taken in as a crystal stem upon each touch. We show that our results yield a lower bound to the density arising from each stem that exist from the crystal phase and therefore this modification of the model can only require still more tight folding.

The model is also able to predict properties of chains in the amorphous phase. For example the fraction of loops and ties are available to us as well as their average length in numbers of monomers and the distribution of these lengths.

Earlier preliminary Monte Carlo experiments on 'real chain' models for polyethylene show for a 100 Å thick amorphous phase that about 1/10 of every chain that exits from the crystal as a random walker will lead to a tie and 9/10 will lead to a loop. For models with correct density profiles and with $p_{tf} = 2/3$, 3% of all crystal stems lead to ties and 30% of all stems lead to loops. The rest of the stems are involved in tight folds.

We have shown that if one assumes an isotropic amorphous phase, or only x y anisotropy, that the switchboard or random re-entry model leads to packing problems, as have been discussed before. These packing problems can only be avoided by crystal modifications, such as tilt, helicity, or tight folding.

Finally, we should review what needs to be done to extend this work. The effects of local structure in the chain and in the presence of a surface in the amorphous phase needs to be studied. A paper is in preparation presenting the results of Monte Carlo studies of chains which obey rotational isomeric statistics (so called 'real chain model') which are between two absorbing walls. These studies show that the arguments given in equation (8) of this paper are essentially correct. Thus for a polyethylene-like chain the duration of the run per chain exiting from the crystal is predicted by equation (16) where M is measured in polyethylene bond distances. The density of the amorphous phase for a switchboard model of polyethylene is then found to be about $2.5\rho_c$ (ρ_c = density of the crystal phase). This result differs from $3\rho_c$ predicted in this paper due to the fact that (b'/b) does not equal one.

The long range exclusion effects should also be studied. The effect of orientation in the amorphous phase ($p \neq q$) needs to be studied.

Finally, the effects of cilia on all this work must be considered. These effects will begin to show chain molecular weight effects.

REFERENCES

1 D'Esposito, L. and Koenig, J. L. *J. Polym. Sci. (Polym. Phys. Edn.)* 1976, **14**, 1731; and Mitchell, G. R., Lovell, R. and Windle, A. H. *ASC Symp. Ser.* 1980, **141**, 215; and Voight, G. and Kimmich, R. *Polymer* 1980, **21**, 1001

2 Yoon, D. Y. and Flory, P. J. *Polymer* 1976, **18**, 509

3 DiMarzio, E. A., Guttman, C. M. and Hoffman, J. D. *Polymer* 1980, **21**, 1379

4 Flory, P. J. *J. Am. Chem. Soc.* 1962, **84**, 2857

5 Yoon, D. Y. and Flory, P. J. *Faraday Soc. General Discussion No. 68* 1979, 288

6 Growth and Perfection of Crystals, Proceedings of an International Conference on Crystal Growth held at Cooperstown, New York, August 27 29, 1958, (Eds. Doremus, Roberts and Turnbull), Wiley, New York, 1958. Discussion remarks of F. C. Frank and P. J. Flory, pp. 529 and 530

7 Frank, F. C., *General Introduction. Faraday Soc. General Discussion 68*, 1979, 7

8 DiMarzio, E. A. and Guttman, C. M. Polymer 1980, **21**, 733

9 Comments by Flory, P. J., in Ref. 6

10 Flory, P. J. and Yoon, D. Y. *Nature* 1978, **272**, 226

11 Guttman, C. M., Hoffman, J. D. and DiMarzio, E. A. *Faraday Soc. General Discussion 68*, 1979, 297

12 Guttman, C. M., Hoffman, J. D. and DiMarzio, E. A. *Polymer 1981, 000*

13 Hoffman, J. D., Guttman, C. M. and DiMarzio, E. A. *Faraday Soc. General Discussion 68*, 1979, 177

14 Hoffman, J. D., Davis, G. T. and Lauritzen, J. I., Ch. 7 in 'Treatise on Solid State Chemistry, Vol. 3', (Ed. N. B. Hannay), Plenum Press, New York, 1970

15 Frank, F. C. and Tosi, M. *Proc. Roy. Soc. (A)* 1961, **263**, 323

16 Khoury, F. and Passaglia, E., Ch. 6 in 'Treatise on Solid State Chemistry, Vol. 3', (Ed. N. B. Hannay), Plenum Press, 1976

17 Hoffman, J. D. *Soc. Plastics Eng. Trans.* 1964, **4**, 315

18 DiMarzio, E. A., Guttman, C. M. and Hoffman, J. D. *Faraday Soc. General Discussion 68*, 1979, 210

19 Klein, J. and Ball, R. C. *Faraday Soc. General Discussion 68*, 1979, 198

20 Guenet, J. M., Picot, C. and Benoit, H. *Faraday Soc. General Discussion 68*, 1979, 251. Also see Guenet, J. M. and Picot, C. Polymer 1979, **20**, 1483

21 *Faraday Soc. General Discussion 68*, 1979

22 Flory, P. J., 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1969

23 Backman, D. K. and DeVries, K. L. *J. Polym. Sci. (A-1)* 1979, **7**, 2125

24 Peterlin, A. *Polymeric Materials* 1981

25 DiMarzio, E. A., Guttman, C. M. and Hoffman, J. D. *Macromolecules* 1980, **13**, 1194

26 Feller, W., 'An Introduction to Probability Theory and Its Applications', 3rd Edn., Wiley, New York, 1968, Vol. I, Ch. XIV

27 Cox, D. R. and Miller, H. D., 'The Theory of Stocastic Processes', Ch. 2, Wiley, New York, 1965

APPENDIX

Gambler's Ruin results: connection with polymer chain statistics

Introduction

To avoid rederiving the equations for the Gambler's Ruin problem (*GRP*) as we apply it to the polymer between two lamellae, we have made use of derivations and discussion of the *GRP* in the textbooks Feller[26] and Cox and Miller[27]. Equations derived by them are reported here.

We have chosen to use these two books for didactic considerations. Feller, although less complete in his treatment of the problem, is easier to read and gives this reader more insight into the meaning of his results. All results of interest to us are given in Cox and Miller.

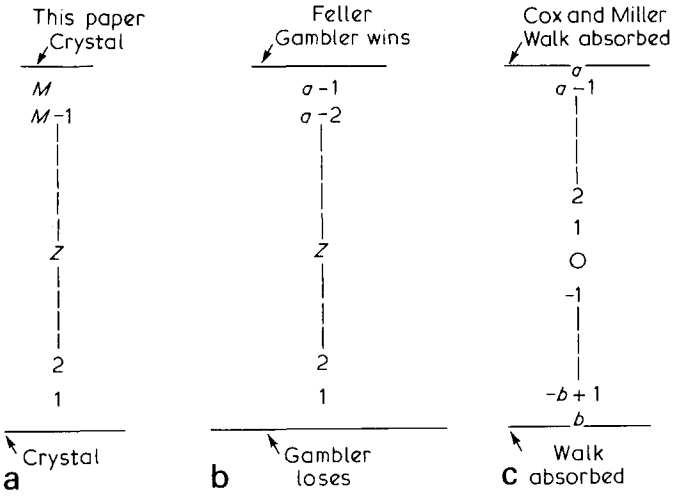

Figure (A1) Comparison of notational differences and coordinate systems amongst this work, Feller[26] and Cox and Miller[27]

There are significant notational differences between Feller and Cox and Miller. These differences are most apparent in their choice of where the absorbing wall is. That difference is discussed here to help the reader. In our discussion the number of levels in the z direction in the amorphous phase are numbered from 1 to M. Our pointer to a given level is called z. Thus the crystal starts at level 0 and $M+1$ (the absorbing walls). In Feller, the gambler walks freely from 1 to $a-1$ and wins or loses his game when he has \$0 or \$$a$ respectively. His pointer is also z. In Cox and Miller the absorbing walls are at $-b$ and $+a$ while the pointer is at zero. *Figure A1* shows these differences. In the equations that follow we shall use our convention 0,z and $M+1$.

Average length of loops and ties

Here, we derive the various properties of the chain in an amorphous crystalline lamellar system in a cubic lattice in three dimensions.

Feller has derived the equations for the duration of the bgame for a Gambler's Ruin problem in one dimension. We now consider a chain in three dimensions. Consider a chain on a cubic lattice with a probability to step in the $+z$ direction of p (gambler wins) and q in the $-z$ direction (gambler loses). The chain has the probability of walking in any of the other directions α_{+x} for the $+x$, α_{-x} for the $-x$, α_{+y} for the $+y$ and α_{-y} for $-y$. We define:

$$\alpha=\alpha_{+x}+\alpha_{-x}+\alpha_{+y}+\alpha_{-y} \tag{A1}$$

and thus have:

$$p+q+\alpha=1 \tag{A2}$$

A chain which is allowed to walk in directions other than z is equivalent to a gambler who participates in a game that has α as the probability of neither winning nor losing on a given bet. Then following Feller (p. 341) the duration of a game starting at any z', $D_{z'}$, is given by:

$$D'_z=pD_{z'+1}+qD_{z'-1}+\alpha D_{z'}+1 \tag{A3}$$

with the boundary conditions: $D_0=0$; $D_{M+1}=0$. Since the amorphous phase is M units thick we have:

$$a=M+1$$

(that is the gambler 'wins' when his winnings reach \$$a$). Following Feller for $p\neq q$ it is easy to show the one dimensional result is unchanged for $\alpha\neq 0$. We have:

$$D_z=\frac{z}{q-p}-\frac{M+1}{q-p}\times\frac{1-(q/p)^z}{1-(q/p)^{(M+1)}} \tag{A4}$$

D_1 is the duration of the walk starting one step above the absorbing wall. The average length, r_a, of a run leaving one side of the amorphous phase is thus:

$$r_a=D_1+1 \tag{Z5a}$$

$$r_a=\frac{1}{q-p}+\frac{M+1}{p}\times\frac{1}{(1-(q/p)^{M+1}}+1 \tag{A5b}$$

where $M+1$ is the thickness of the amorphous phase in unit steps. For $p=q$ we have a slightly different result than in one dimension. The formal solution of equation (A3) is $-z^2/(1-\alpha)$ and then we obtain:

$$D_z=\frac{1}{(1-\alpha)}z(M+1-z) \tag{A6}$$

or for $p=q$ we have for r_a:

$$r_a=\frac{M}{1-\alpha}+1 \tag{A7}$$

For the cubic lattice with all steps equally probable we have $\alpha=2/3$, and therefore:

$$r_a=3M+1 \tag{A8}$$

This equation is similar to one already derived by DiMarzio and Guttman[8] earlier except the '1' was left out of their results. The reader is reminded that r_a is the average number of steps for a run in the amorphous phase whether it be a loop or a tie. Later we shall derive the average length of a loop $\langle L\rangle$ or the average length of a bridge $\langle B\rangle$.

Probability of loops and ties (bridges)

As noted in the text, the probability of a loop is the probability of a ruin for a gambler that starts with \$1 while the probability of a bridge is the probability of a win of \$$a$ for a gambler starting with \$1. (For a gambler starting with \$$(a-1)$ then the probability of a loop is the probability of a win of \$$a$ and the probability of a bridge is that of ending the game with \$0.) It is easy to show for the three dimensional case if, as in Feller:

q_z = probability of gambler starting with \$$z$ ultimate ruin

p_z = probability of gambler starting with \$$z$ ultimate win

$$q_z=\frac{(q/p)^{M+1}-(q/p)^z}{(q/p)^{M+1}-1} \quad \text{for } p\neq q \tag{A9}$$

and

$$q_z=1-z/(M+1) \quad \text{for } p=q \tag{A10}$$

This along with:

$$p_z + q_z = 1, \text{ all gamblers finally win or lose}$$

determines our results. The probability of a loop, p_L, is then

$$p_L = \frac{(q/p)^{M+1} - (q/p)}{(q/p)^{M+1} - 1}, \quad p \neq q \tag{A11a}$$

$$p_L = \frac{M}{M+1}, \quad p = q \tag{A11b}$$

The probability of a bridge, p_B, is then:

$$p_B = \frac{(q/p) - 1}{(q/p)^{M+1} - 1}, \quad p \neq q \tag{A12a}$$

$$p_B = \frac{1}{M+1}, \quad p = q \tag{A12b}$$

Average length of loops or bridges

We now wish to obtain the average number of steps in a loop, or bridge or cilia. Following Feller, p. 349, $u_{z,n}$ is the probability that a gambler starting with \$$z$ ends up with \$0 in n tries; $u_{1,n}$ is then the probability of a loop of length n; $u_{M,n}$ is the probability of a bridge of n steps; $u_{z,n}$ is the probability of a cilia which starts at z and ends up at zero in n steps. The equations for $u_{z,n}$ are found in Feller.

The average value of a loop $\langle L \rangle$ is then:

$$\langle L \rangle = \sum_{n=0}^{\infty} n u_{1,n} \Big/ \sum_{n=0}^{\infty} u_{1,n} + 1 \tag{A13}$$

where the loop starts at $z = 1$. For a cilia that starts at z and lands on $M+1$ the equation remains the same except p and q interchange and z goes to $M+1-z$. For a loop that starts at $M+1-1$ we simply need $u_{1,n}$ with p and q interchanges. The average value for the number of segments in a bridge $\langle B \rangle$ is given by:

$$\langle B \rangle = \sum_{n=0}^{\infty} n u_{M,n} \Big/ \sum_{n=0}^{\infty} u_{M,n} + 1 \tag{A14}$$

Feller obtains equations for $u_{z,n}$ using a generating function technique. By his equation (4.5):

$$U_z(s) = \sum_{n=0}^{\infty} u_{z,n} s^n \tag{A15}$$

It is then obvious that

$$s\left(\frac{\partial \ln U_1(s)}{\partial s}\right) = \frac{\sum_{n=0}^{\infty} n u_{1,n} s^n}{\sum_{n=0}^{\infty} u_{1,n} s^n}$$

or we have:

$$\langle L \rangle = s\left(\frac{\partial \ln U_1(s)}{\partial s}\right)_{s=1} + 1 \tag{A16}$$

and

$$\langle B \rangle = s\left(\frac{\partial \ln U_{a-1}(s)}{\partial s}\right)_{s=1} + 1 \tag{A17}$$

Detailed algebra for the solution of these equations for the case of $1 - p - q = \alpha$, $\alpha \neq 0$ is given by Cox and Miller* (p. 30–33). From these calculations we obtain for $q \neq p$ for a gambler who starts with \$$z$ and finally loses all his money (a chain that starts at z and goes to the 0 edge):

$$\langle C_z^0 \rangle = \frac{d}{p-q} \times \frac{p^d + q^d}{p^d - q^d} - \frac{d-z}{p-q} \times \frac{p^{d-z} + q^{d-z}}{p^{d-z} - q^{d-z}} \tag{A18}$$

(where $d = M+1$)

and for the gambler that starts with \$$z$ and finally wins \$$(M+1)$ (a chain that starts at z and goes to the $M+1$ edge):

$$\langle C_z^{M+1} \rangle = \frac{d}{q-p} \times \frac{q^d + p^d}{q^d - p^d} - \frac{z}{q-p} \times \frac{q^z + p^z}{q^z - p^z} \tag{A19}$$

(where $d = M+1$)

Then the length of a loop which starts on either the top (at $z = M$) or bottom (at $z = 1$) is given by:

$$\langle L \rangle = \frac{d}{p-q}\left(\frac{p^d + q^d}{p^d - q^d}\right) - \frac{d-1}{p-q}\left(\frac{p^{d-1} + q^{d-1}}{p^{d-1} - q^{d-1}}\right) + 1 \tag{A20}$$

(where $d = M+1$)

The same is true for a bridge. A bridge (tie) starts at one and goes to $M+1$ or starts at M and goes to 0, giving for its length:

$$\langle B \rangle = \frac{d}{p-q}\left(\frac{p^d + q^d}{p^d - q^d}\right) - \frac{1}{p-q}\left(\frac{p+q}{p-q}\right) + 1 \tag{A21}$$

(where $d = M+1$)

In a later paper when we deal with the effects of orientation we shall present a fuller interpretation of these results. Here we only report them.

For the case of $p = q$ one may not simply go to the limit in equations (A18) to (A21). We must return to the original representation in terms of $U_z(s)$ and go to limits carefully. In going to the limit, we must first let $p = q$, the let $s = 1 - \varepsilon$. Assuming ε is small, we can carry out a small ε expansion. Notice we have a series in $\varepsilon^{1/2}$, and we must keep terms up to $\varepsilon^{3/2}$. For the loop $\langle L \rangle$:

$$\langle L \rangle = \frac{2M}{3(1-\alpha)} + 1 \tag{A22}$$

and for the bridge $\langle B \rangle$:

$$\langle B \rangle = \frac{(M^2 + 2M)}{3(1-\alpha)} + 1 \tag{A23}$$

For future reference, from the chain that starts at z and goes to 0 we obtain:

* In Cox and Miller $u_{z,n}$ is called as $f_{0,a}^{(n)}$.

$$\langle C_z^0 \rangle = \frac{z}{3(1-\alpha)}[(2M+1-z)] \tag{A24}$$

For the chain which starts at z and goes to $M+1$, we have:

$$\langle C_z^{M+1} \rangle = \frac{(M+1)^2 - z^2}{3(1-\alpha)} \tag{A25}$$

Probability of a loop or tie of length n

Now from an estimation of $u_{1,n}$ we can find the fraction of loops of each size, i.e. the loop size distribution; from $u_{M,n}$ we can obtain the distribution of ties. Feller gives for $u_{z,n}$ the equation (his equation (4.1)):

$$u_{z,n+1} = pu_{z+1,n} + qu_{z-1,n} \tag{A26}$$

with boundary conditions:

$$u_{0,n} = u_{M+1,} = 0 \text{ for } n > 1$$

Although this cannot be solved in simple closed form we can obtain numerical values for the $u_{z,n}$.

More generally, we can solve the Cox and Miller equations for $f_{0,a}^n$ for the case $\alpha \neq 0$. Cox and Miller's $f_{0,n}^{(n)}$ reduce to Fellers $u_{z,n}$ for $\alpha = 0$. In Cox and Miller a loop is found by setting $a = 1$ in their 'f' derived for absorption at the 'a' wall.†

Cox and Miller give an equation for $f_{0,a}^{(n)}$ as a finite sum. However, a careful rederivation of this shows that their equations are in error. Specifically, their equation (25), p. 33, should be written as:

$$f_{0,a\,(\text{correct})}^{(n)} = f_{0,a\,(\text{Cox and Miller})}^{(n)} \times 4(pq)^{1/2} \tag{A27}$$

where

$$f_{0,a(\text{Cox and Miller})}^{(n)} = \frac{1}{2(a+b)}\left(\frac{p}{q}\right)^{a/2} \times$$

$$\sum_{v=1}^{a+b-1} (-1)^{v+1} \sin\left(\frac{bv\pi}{a+b}\right) \sin\left(\frac{v\pi}{a+b}\right) s_v^{n-1} \tag{A28}$$

$$(s_v)^{-1} = 1 - p - q + 2(pq)^{1/2} \cos\left(\frac{v\pi}{a+b}\right)$$

In what follows we always use $f_{0,a(\text{correct})}^{(n)}$.

Since we may expect the sum of the f's for a loop to yield p_L as in equations (A11) we have:

$$p_L = \sum_{n=1}^{\infty} f_{0,1}^{(n)} \tag{A29}$$

since Cox and Miller $a = 1$ yields a loop. In the same way for a bridge $a = M+1$ and we obtain for p_B:

$$p_B = \sum_{n=M}^{\infty} f_{0,M+1}^{(n)} \tag{A30}$$

† The reader should remind himself of the difference between the Feller a and the Cox and Miller a as explained earlier.

Now let us define the fraction of loops of a given size as $g_L(n,M)$. The we have:

$$g_L(n,M) = \frac{f_{0,1}^{(n)}}{p_l} \tag{A31}$$

In the same way for bridges we have:

$$g_B(n,M) = \frac{f_{0,M}^{(n)}}{p_B} \tag{A32}$$

is always one larger than n.

In *Figure 4* we display the results of numerical calculation for loops on $g_L(n,M)$. We show only the case for $p = q = 1 - \alpha/2$ for various α and for various M. There is little effect on $g_L(n,M)$ of the thickness of the amorphous phase, M. As we see in *Figure 4* for $\alpha = 0.1$, 0.3 and 0.666 this same phenomenon holds. That is, there is little dependence on the thickness of the amorphous phase. In fact for the case of $n = 1$, we find the case of maximum numerical effect as a function of M. It is easy to show this effect is $(M+1)/M$. Upon doing the sums analytically for $n = 1$, we obtain:

$$f_{0,a}^{(1)} = (pq)^{1/2}(p/q)^{a/2} \tag{A33}$$

and for $p = q$:

$$g_L(1,M) = p\frac{M+1}{M} \tag{A34}$$

$$g_L(1,M) = \frac{1-\alpha}{2}\frac{M+1}{M} \tag{A35}$$

This is the case for a loop of two steps. For a loop of three steps we obtain:

$$f_{0,1}^{(2)} = p(1-p-q) \tag{A36a}$$

for $p = q$ we have:

$$g_L(2nM) = p(1-2p)\frac{M+1}{M} = \frac{\alpha(1-\alpha}{2}\frac{M+1}{M} \tag{A36b}$$

Similar calculations may be undertaken for the bridge. In this case the distributions are functions of M peaking around $n = M^2$. This will not be done here.

For future reference we write down the equation for the absorption on the $-b$ wall. By Cox and Miller that is:

$$f_{0,a\,(\text{Cox and Miller})}^{(n)} = \frac{1}{2(a+b)}\left(\frac{p}{q}\right)^{a/2} \times$$

$$\sum_{v=1}^{a+b-1} (-1)^{v+1} \sin\left(\frac{av\pi}{a+b}\right) \sin\left(\frac{v\pi}{a+b}\right) s_v^{n-1} \tag{A37}$$

Density of the amorphous phase as a function of position

We wish to obtain the average number of times the gambler has k dollars having started with z dollars. This is equivalent to determinint the times a walk visits a given level k in the amorphous zone having been begun at level z and ending at either side of the zone. As we show in the main text, this is equivalent to obtaining the density (number of segments) of the chain at any level in the amorphous layer per exit from the crystal.

To derive this quantity we follow Feller again. By a modification of Feller we may write the finite difference equation for $v_{k,n}^{(z)}$ the probability that a walker starting at z will arrive at level k after n steps:

$$v_{k,n+1}^{(z)} = p\,v_{k-1,n}^{(z)} + q\,v_{k+1,n}^{(z)} + \alpha v_{k,n}^{(z)} \qquad \text{(A38)}$$

For a walk starting at z we have:

$$v_{k,0}^{(z)} = 0, \quad k \neq z \qquad \text{(A39a)}$$

$$v_{k,0}^{(z)} = C_z, \quad k = z \qquad \text{(A39b)}$$

C_z is the number of walkers which leave level z. By the condition that the walk is absorbed at walls at $z=0$ and at $z=a$ we have:

$$v_{k,n}^{(z)} = 0 \qquad \text{(A40)}$$

for all n. As before: p = probability of step in $+z$ direction; q = probability of step in $-z$ direction; α = probability of step in other directions parallel to lamellae.

Now let us define the mean number of times walkers arrive at level k if C_z started at level z as $L^z(k)$. The we have:

$$L^z(k) = \sum_{n=0}^{\infty} v_{k,n}^{(z)} \qquad \text{(A41)}$$

Summing equation (A38) over n we obtain:

$$L^z(k) - v_{k,0}(z) = pL^z(k-1) + q\,Lz(k+1) + \alpha\,L^z(k) \qquad \text{(A42)}$$

where we note:

$$\sum_{n=0}^{\infty} v_{k,n+1}(z) = L^z(k) - vk,n(z) \qquad \text{(A43)}$$

The boundary conditions are for $C_z = 1$:

$$L^z(M+1) = 0; \quad L^z(0) = 0$$
$$v_{k,0}(z) = \alpha_{k,z} \qquad \text{(A44)}$$

The solution to these equations for $p \neq q$ is:

$$L^z(k) = \left(\frac{p^z - q^z}{p^{M+1} - q^{M+1}}\right)(p^{k-z})\left(\frac{p^{M-k+1} - q^{M-k+1}}{p-q}\right) \qquad \text{(A45)}$$

for $k > z$

$$L^z(k) = \frac{p^{M-z+1} - q^{M-z+1}}{p^{M+1} - q^{M+1}} q^{z-k}\left(\frac{p^k - q^k}{p-q}\right) \qquad \text{(A46)}$$

for $k \leqslant z$. For $p = q$ we obtain:

$$L^z(k) = \frac{1}{q}\left(\frac{M+1-z}{M+1}\right)k, \quad k \leqslant z \qquad \text{(A47a)}$$

$$L^z(k) = \frac{1}{q}\left(\frac{M+1-k}{M+1}\right)z, \quad k \geqslant z \qquad \text{(A47b)}$$

Properties of cilia

A cilia is like a loop or tie which does not start near the surface; that is, it is a gambler who starts with $\$z$ where $\$z$ is anywhere from \$2 to $\$(M-1)$. Thus, to compute the properties of a cilia, one need only compute the properties of $z \neq 1$ or $z \neq a-1$. In general these properties of the cilia are dependent, from the Gambler's Ruin point of view, on when the cilia ends (or starts) – where its last segment lands.

Thus, we obtain from the equations for the duration with waiting α (i.e. equations A4 and A6):

$$D_z = \frac{1}{(1-\alpha)}z(M+1-z), \quad \text{for } p = q \qquad \text{(A48)}$$

$$D_z = \frac{z}{q-p} - \frac{M+1}{q-p} \times \frac{1-(q/p)^z}{(1-(q/p)^{(M+1)})} \qquad \text{(A49)}$$

for $p \neq q$

The duration at z is the number of segments in the cilia starting from z. Notice a cilia starting at $z=1$ and being absorbed at the $z=0$ wall has one less step than a loop grong from $z=0$ to $z=1$ and returning to $z=0$. The properties computed in *Probability of loops or ties* and *Average length of loop or tie* are characterized by which side of the lamellae (upper or bottom) the cilia goes to and shall not be discussed here.

However, the calculation of the fraction of cilia of length n leaving from z and which are absorbed on one wall or the other is of interest. We shall call this quantity $h_c(z,n)$. Using the Cox and Miller notation this is:

$$h_c(z,n) = f_{0,a(\text{correct})}^{(n)} + f_{0,-b(\text{correct})}^{(n)} \qquad \text{(A50)}$$

From equations (A27), (A28) and (A37) we obtain $h_c(z,n)$ in terms of M and z. Since:

$$p_z = \sum_{n=0}^{\infty} f_{0,a(\text{correct})}^{(n)} \qquad \text{(A51)}$$

and

$$q_z = \sum_{n=0}^{\infty} f_{0,b(\text{correct})}^{(n)} \qquad \text{(A52)}$$

then $h_c(z,n)$ is automatically normalized to one, i.e.:

$$1 = \sum_{n=0}^{\infty} h_c(z,n) \qquad \text{(A53)}$$

The contribution to the density of a cilia starting at z is given by equations (A45)–(A47) which shall not be repeated here.