This equation has been used throughout the model calculations presented in this paper. It should be mentioned that this equation for $\bar{m}$ gives the upper limit of the volume V_k. In the real system the topologically next neighbor as well as the next neighbor in the other chain direction (Figure 1) will hinder the spatial mobility of the kth unit. Thus the efficient available volume would be even smaller. However, complexed junctions are not fixed but fluctuate around mean positions, similar to junction fluctuations in covalent polymer networks.[23] Such a fluctuation increases V_k and thus may partly compensate for neglecting the influence of both nearest neighbors.

Symbols

β	parameter that describes the breadth of the distance distribution between free functional groups
C^∞	characteristic ratio
d_u	average distance between two free functional groups
$f_{\text{red.}}$	factor by which the mole fraction of complexed units is reduced due to topological restrictions
i	number of functional groups per chain
K_0	equilibrium constant
l	length of monomer repeating unit
m	average number of monomer units between the kth functional group and the next complexed group
n	degree of polymerization
P_i	probability that a chain has i functional groups
$p(k)$	probability of the kth functional group of a chain to form a complex when $k-1$ functional groups are complexed
$Q(k)$	$W(R_k)$ = reduced probability for the kth functional group of a chain to form a complex if $k-1$ groups are complexed
ρ	number of functional groups per unit volume
R_k	average radius that defines the sphere in which the kth functional group can move
$[U_0]$	concentration of functional groups (mol/L)
u	degree of modification (fraction of monomer units that carry functional groups)
V_k	volume available for the kth unit
x_2^0	mole fraction of complexed functional groups without topological restrictions
x_2^{eff}	mole fraction of complexed functional groups

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A Continuum Gambler's Ruin Model

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ABSTRACT: A continuum version of the gambler's ruin model is presented. The following functions are derived: end-to-end vector distributions of both loops and ties and their Fourier transforms, chain length distributions of both loops and ties, and their Laplace transforms. A few of the lower moments of these distributions are also calculated. Gambler's ruin models lack sufficient detail to accurately predict the degree of adjacent reentry but nevertheless predict that most chains return to the crystal very near the point of departure. For example, on the basis of this model, we predict that $^3/_4$ of the chains in polyethylene return to the same crystallite within about 14 Å.

Introduction

The statistics of random walks between two absorbing parallel planes provides an important model of the amorphous domains of semicrystalline polymers. This model is admittedly deficient in accounting for the detailed packing of chains in the amorphous domains but has the benefit of mathematical tractability and accounts for chain packing in a certain mean-field sense in that it yields a uniform segment density throughout the amorphous domain.[1-3] Guttman, DiMarzio, and Hoffman[1,2] were the first to apply the concept to semicrystalline polymers, adopting the expression "gambler's ruin" model. The gambler's ruin model is expected to be valid and useful to the extent that polymer chains in the amorphous domains are ideal random walks.

Guttman, DiMarzio, and Hoffman first considered random walks on the simple cubic lattice[1] and later extended these results to more general random walks.[2] In

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Table I

	tight loops	amorphous loops	ties
fraction	$1 - \Phi$	$\Phi(1 - s/L)$	$\Phi s/L$
no. av no. of bonds, N_n	0	$(sL/3D_2)F_1F_2$	$(L^2/6D_2)F_3$
wt av no. of bonds, N_w	0	$(2L^2/15D_2)(F_4/F_2)$	$(7L^2/30D)_2(F_5/F_3)$
N_w/N_n	undefined	$(2L/5s)(F_4/F_1F_2^2)$	$^7/_5(F_5/F_3^2)$
mean square throw length	0	$(4D_1sL/3D_2)F_1F_2$	$(2D_1L^2/3D_2)F_3$
end-to-end vector distributn	$P_{TL} = \delta(\mathbf{r})$	$P_{AL}(\mathbf{r})$	$P_T(\mathbf{r})$
end-to-end vector Fourier transform	$C_{TL} = 1/4\pi^2$	$C_{AL}(\mathbf{k})$	$C_T(\mathbf{k})$
bond distributn function	$B_{TL} = \delta(t)$	$B_{AL}(t)$	$B_T(t)$
bond distributn Laplace transform	$b_{TL} = 1$	$b_{AL}(q)$	$b_T(q)$

this paper we present a continuum gambler's ruin model, considering random walks as solutions of the diffusion equation. We find that a few of the results obtained by Guttman and DiMarzio[2] in generalizing the simple cubic lattice model to general random walks are incorrect.

The amount of adjacent reentry in semicrystalline polymers has been a matter of controversy for a number of years, but new studies are leading to a concensus on at least one issue: A large number of chains must return to sites within a few unit cells of their point of departure to avoid severe overcrowding of the amorphous domains. The original gambler's ruin treatment yields a probability of adjacent reentry of $^2/_3$.[1,2] Other treatments,[3-9] including both Monte Carlo calculations,[4] mean-field lattice models,[5-8] and off-lattice gambler's ruin calculations[3,9] also indicate that most chains return to sites near their point of departure. The details of chain structure at the interface depend strongly on such things as chain stiffness and fold energy; nevertheless, all these models indicate a high degree of near adjacent reentry. For example, the Monte Carlo calculations indicate that the amount of strictly adjacent reentry (i.e., nearest-neighbor returns in the lattice) becomes relatively small if chain packing at the interface is treated exactly and if a reasonable energy is assigned to strictly adjacent folds. However, the combination of nearest-neighbor and near-neighbor reentry is always predicted to be on the order of $^2/_3$ or so. The model considered here indicates that the precise folding structure cannot be predicted by gambler's ruin models but is in agreement with previous treatments in predicting a large degree of near adjacent reentry. The value of $^2/_3$ for the amount of adjacent reentry is obtained only for lattice models; off-lattice versions of the gambler's ruin model, including freely jointed walks[3,9] and the present treatment, predict values in the vicinity of $^2/_3$ but do not point to any specific value.

In what follows, we give expressions for the distribution functions of the end-to-end vector of loop and tie chains, the distribution functions of the number of bonds in loop or tie chains, the Fourier or Laplace transforms of these distribution functions, and several averages taken over these distributions.

Computation of Distribution Functions Etc.

We consider the statistics of continuum random walks between two absorbing barriers, determined by the diffusion equation

$$\frac{\partial W}{\partial t} = D_1\frac{\partial^2 W}{\partial x^2} + D_1\frac{\partial^2 W}{\partial y^2} + D_2\frac{\partial^2 W}{\partial^2 z} \qquad (1)$$

where $W(x,y,z,t)$ is the probability of finding the random walk at position (x,y,z) and where t represents, in the present context, not time but the number of backbone bonds. We assume the existence of absorbing plane barriers at $z = 0$ and $z = L$ for L the thickness of the amorphous domain. Note the use of different "diffusion" coefficients in directions parallel and perpendicular to the lamellar plane. This is done to afford greater generality to the analysis and reflects our belief that such anisotropies exist.[10,11] The case of an isotropic amorphous phase is obtained by setting $D_1 = D_2 = D$, and in that case one makes a connection between the "diffusion" coefficient and the characteristic ratio by writing $D = C_\infty l^2/6$ since in the absence of absorbing or reflecting boundaries solutions to eq 1 obey $\langle R^2 \rangle = 6Dt$. We consider random walks initiated at the site $(0,0,s)$ that continue until they are absorbed at one of the faces $z = 0$ or $z = L$. We let s be arbitrary but require $s \ll$ L. The solution to eq 1 for these boundary conditions has been given in ref 12. Also in ref 12 expressions are given for two functions $f_L(\mathbf{r},t)$ and $f_T(\mathbf{r},t)$, respresenting probabilities of finding amorphous loop and tie chains, respectively, with a given end-to-end vector $\mathbf{r}$ and given number of bonds t. The results given here are all obtained by appropriate integrations over f_L or f_T. We assume that a fraction, Φ, of the crystalline stems present in the system are followed by random walks initiated at the site $(0,0,s)$, adjusting Φ so that the amorphous domain has the correct density. Then we assume that the remaining fraction $1 - \Phi$ of crystalline stems are followed by very tight loops having (effectively) 0 bonds and making no contribution to the amorphous domain. The value of Φ necessary to give the correct density is[12,13]

$$\Phi = (1 - s/L)^{-1}\frac{2D_2\rho}{l_n s} \qquad (2)$$

where ρ is the ratio of amorphous to crystalline density and l_n is the average projection of a bond onto the direction normal to the lamellar plane (defined as l_c/N_b, for N_b, the number of bonds in a stem, and l_c, the crystal thickness). The model comprehends changes in tilt angle, i.e., the angle between the crystalline stem and the direction normal to the lamellar plane, through the tilt angle dependence of l_n.

Each crystalline stem is followed, therefore, by one of three different types of objects: a tight loop, an amorphous loop, or a tie. The tight loops are the zero length loops required to give the correct density, while the amorphous loops and ties are the random walks having statistics given by eq 1, segregated according to the plane at which they are absorbed. In Table I we summarize the properties of all these various objects. The first row of Table I gives the fraction of crystalline stems followed by one of the three types of object. The second and third rows give the number- and weight-average number of bonds contained in each object. The fourth row gives the polydispersity ratio of each type of object. The fifth row gives the mean-square distance $\langle x^2 + y^2 \rangle = \langle r^2 \rangle$ where $(x,y,0)$ (for loops) or (x,y,L) (for ties) is the point at which the random walk returns.[14] The sixth and seventh rows gives the probability distribution[15] of the two-vector $(x,y) = \mathbf{r}$, and its Fourier transform, respectively.[16,17] The eighth and ninth rows give the probability distribution of the number of bonds in each type of object and its Laplace transform, respectively.[17] We give the Fourier and Laplace transforms here because, first, closed-form, exact expressions can be given and because, second, such functions are expected to be important in the theory of neutron scattering by semicrystalline polymers. The following functions appear in Table I

$$P_{AL}(\mathbf{r}) = (1 - s/L)^{-1}\frac{D_2}{L^2 D_1}\sum_{j=1}^{\infty} j \sin\left(\frac{\pi j s}{L}\right) K_0\left[\left(\frac{D_2}{D_1}\right)^{1/2}\frac{\pi j r}{L}\right] \quad (3)$$

$$P_T(\mathbf{r}) = \frac{D_2}{D_1 s L}\sum_{j=1}^{\infty}(-1)^{j-1} j \sin\left(\frac{\pi j s}{L}\right) K_0\left[\left(\frac{D_2}{D_1}\right)^{1/2}\frac{\pi j r}{L}\right] \quad (4)$$

$$C_{AL}(\mathbf{k}) = \frac{1}{4\pi^2}(1 - s/L)^{-1}\frac{\sinh\,[(D_1/D_2)^{1/2}kL(1 - s/L)]}{\sinh\,[(D_1/D_2)^{1/2}kL]} \quad (5)$$

$$C_T(\mathbf{k}) = \frac{1}{4\pi^2}\,\frac{L}{s}\,\frac{\sinh\,[(D_1/D_2)^{1/2}ks]}{\sinh\,[(D_1/D_2)^{1/2}kL]} \quad (6)$$

$$B_{AL}(t) = \frac{2D_2\pi}{L^2}(1 - s/L)^{-1}\sum_{j=1}^{\infty} j \sin\left(\frac{\pi j s}{L}\right)\exp\left(\frac{-D_2 t \pi^2 j^2}{L^2}\right) \quad (7)$$

$$B_T(t) = \frac{2D_2\pi}{\mathrm{s}L}\sum_{j=1}^{\infty}(-1)^{j-1} j \sin\left(\frac{\pi j s}{L}\right)\exp\left(\frac{-D_2 t \pi^2 j^2}{L^2}\right) \quad (8)$$

$$b_{AL}(q) = (1 - s/L)^{-1}\frac{\sinh\,[(qL^2/D_2)^{1/2}(1 - s/L)]}{\sinh\,[(qL^2/D_2)^{1/2}]} \quad (9)$$

$$b_T(q) = (L/s)\frac{\sinh\,[(qs^2/D_2)]}{\sinh\,[(qL^2/D_2)]} \quad (10)$$

where K_0 represents the zeroth modified Bessel function of the second kind and sinh represents the hyperbolic sine. These quantities (all unity to first order in s/L) also appear in Table I.

$$\begin{gathered} F_1 = (1 - s/L)^{-1} \qquad F_2 = 1 - 3s/2L + s^2/2L^2 \\ F_3 = 1 - s^2/L^2 \\ F_4 = 1 - 5s^2/2L^2 + 15s^3/8L^3 - 3s^4/8L^4 \\ F_5 = 1 - 10s^2/7L^2 + 3s^4/7L^4 \end{gathered} \quad (11)$$

At first glance, the results in Table I are rather disconcerting. Most of the quantities shown there are given in terms of the arbitrary parameter s. Setting $s = 0$ does not help, since as eq 2 shows, this causes Φ to diverge, while clearly Φ must be less than 1. The s dependencies in Table I are examples of the "Vonk paradox"[3,9] which states that many of the properties of random walks between two absorbing barriers initiated at or near one of the boundaries are dependent on the precise way in which the walks are initiated. This result is paradoxical because we do not expect, nor is it desirable, that the results of the gambler's ruin model for any global properties depend on details such as s. The resolution of this paradox lies in the fact that the division of the set of all loops into subsets of tight and amorphous loops is artificial. For example, suppose we increase s. This would remove a number of very short walks from the set of amorphous loops. However, as eq 2 demonstrates, increasing s causes a decrease in Φ or an increase in the fraction of tight loops. The addition of tight loops offsets the removal of short amorphous loops for all properties insensitive to the small changes in loop size. By removing the segregation between tight loops and amorphous loops, we should expect the s dependencies to drop out of all global properties, at least to first order in s/L.

Table II

	loops	ties
fractn	$\epsilon = 1 - \Phi s/L$	$\omega = \Phi s/L$
no. av no. of bonds, N_n	$(\Phi sL/3D_2)(F_2/\epsilon)$	$(L^2/6D_2)F_3$
wt av no. of bonds, N_w	$(2L^2/15D_2)(F_4/F_2)$	$(7L^2/30D_2)(F_5/F_3)$
N_w/N_n	$(2L/5\Phi s)(\epsilon F_4/F_2^2)$	${}^7/_5(F_5/F_3^2)$
mean square throw length	$(4D_1\Phi sL/3D_2)(F_2/\epsilon)$	$(2D_1L^2/3D_2)F_3$
end-to-end distributn functn	$P_L(\mathbf{r})$	$P_T(\mathbf{r})$
end-to-end Fourier transform	$C_L(\mathbf{k})$	$\mathrm{C_T}(\mathbf{k})$
bond distributn functn	$B_L(t)$	$B_T(t)$
bond distributn Laplace transform	$b_L(q)$	$b_T(q)$

This is indeed the case, as Table II indicates. There we list the properties of loops and ties, where the new classification of loops represents the combination of tight and amorphous loops. The first five rows of Table II are global properties. In these rows, s always appears in the combination $s\Phi$ (except for the weak s dependence of F_j), and since we can write

$$s\Phi = \frac{2D_2\rho}{l_n}F_1 \quad (12)$$

we conclude that these global properties exhibit no s dependence to leading order in s/L. We have the two definitions

$$\omega = \Phi s/L \qquad \epsilon = 1 - \omega \quad (13)$$

giving the total fraction of ties and loops, respectively.

The various distributions or transforms in the loops column of Table II are weighted sums of functions appearing in Table I

$$Q_L = \epsilon^{-1}[(1 - \Phi)Q_{TL} + \Phi(1 - s/L)Q_{AL}] \quad (14)$$

where Q_L is a generic name for one of the functions P_L, C_L, B_L, or b_L, similarly for Q_{AL} and Q_{TL}. Note that s dependencies still occur in the various distributions or their transforms. This is to be expected as long as the s dependencies are limited to small values of r and t or large values of k and q. Whenever $ks \ll 1$ we may write

$$C_L(\mathbf{k}) = \frac{1}{4\pi^2\epsilon}[1 - \omega\Omega \coth \Omega] \quad (15)$$

and

$$C_T(\mathbf{k}) = \frac{\Omega}{4\pi^2}\operatorname{csch}\Omega \quad (16)$$

where

$$\Omega = kL(D_1/D_2)^{1/2} \quad (17)$$

Likewise, whenever $qs^2/D_2 \ll 1$ we have

$$b_L(q) = \epsilon^{-1}(1 - \omega\Psi \coth \Psi) \quad (18)$$

and

$$b_T(q) = \Psi \operatorname{csch}\Psi \quad (19)$$

where

$$\Psi^2 = qL^2/D_2 \quad (20)$$

Since eq 15–20 are devoid of s dependencies, we conclude that global properties are indeed s independent.

In Table III we display expressions for a number of properties in the isotropic limit $D_1 = D_2 = C_\infty l^2/6$. Table

Table III

	loops	ties
fractn	$\epsilon = 1 - \omega$	$\omega = C_\infty l^2 \rho / 3Ll_n$
no. av no. of bonds, N_n	$2L\rho/3l_n$	$L^2/C_\infty l^2$
wt av no. of bonds, N_w	$4L^2/5C_\infty l^2$	$7L^2/5C_\infty l^2$
N_w/N_n	$2/5\omega$	$^7/_5$
mean square throw length	$4\omega L^2/3$	$2L^2/3$
mass fractn	$^2/_3$	$^1/_3$

III omits lower order terms in s/L. Note the complete absence of s dependence.[18]

Interesting approximations to $P_L(\mathbf{r})$ and to $B_L(\mathbf{t})$ can be written by replacing the summations in eq 3 and 7 with integrations. We obtain[19]

$$P_L(\mathbf{r}) \simeq \epsilon^{-1}\left[(1 - \Phi)\delta(\mathbf{r}) + \left(\frac{\Phi s}{2\pi}\right)\left(\frac{D_2}{D_1}\right)\left(\frac{D_2}{D_1}r^2 + s^2\right)^{-3/2}\right] \tag{21}$$

$$B_L(\mathbf{t}) \simeq \epsilon^{-1}\left[(1 - \Phi)\delta(\mathbf{t}) + \frac{\Phi s}{2}D_2^{-1/2}t^{-3/2}\pi^{-1/2}\exp(-s^2/4D_2t)\right] \tag{22}$$

Note that these expressions become independent of s at either large r or large t. Aside from the δ function peak at the origin, we summarize the behavior of these approximate distributions as follows: $P_L(r)$ falls off as r^{-3} for $r^2 \gg s^2$ and is independent of r for $r^2 \ll s^2$. $\mathrm{B}_\mathrm{L}(\mathrm{t})$ falls off like $t^{-3/2}$ for $D_2t \gg s^2$, goes through a maximum at $t = s^2/6D_2$, and then falls off to zero as $t \to 0$.

We also consider the following two integrated distributions:

$$iP_L(r) = \int_0^r \mathrm{d}r'\, 2\pi r' P_L(r') \tag{23}$$

$$iB_L(t) = \int_0^t \mathrm{d}t'\, B_L(t') \tag{24}$$

representing respectively the fraction of loops with throw distance less than r and number of bonds less than t. Employing eq 21 and 22 yields

$$iP_L(r) \simeq \epsilon^{-1}[1 - \Phi s(s^2 + r^2D_2/D_1)^{-1/2}] \tag{25}$$

$$iB_L(t) \simeq \epsilon^{-1'}[1 - \Phi \operatorname{erf}(s/2D_2^{1/2}t^{1/2})] \tag{26}$$

Note the absence of s dependence at large r or t. (The s dependence of eq 26 disappears because $\operatorname{erf}(x)$ is proportional to x for small x.)

Table IV
Probability of Nonadjacent Reentry

definitn	general probability	probability in isotropic limit	min r or t necessary for universal behavior
throw length > r	$(\Phi s/r)(D_1/D_2)^{1/2}$	$\Phi s/r$	$(D_2/D_1)^{1/2}r > 4s$
no. of bonds, > t	$\Phi s/(\pi D_2 t)^{1/2}$	$(\Phi s/l)(6/\pi t C_\infty)^{1/2}$	$D_2t > 2.5s^2$

Previous gambler's ruin treatments have taken a value equivalent to $1 - \Phi$ as the probability of tight folding or of adjacent reentry. However, since the distinction between tight folds and short amorphous walks is vague, it should be recognized that the probability of tight folding or of adjacent reentry is ill-defined within the context of gambler's ruin models. For example, the simple cubic lattice treatment of Guttman et al. gives $^2/_3$ for the probability of adjacent reentry,[1] but if one also counts the shortest amorphous walks, then the amount of tight folding increases by 5%. The equivalent of $1 - \Phi$ for freely jointed walks with the first step having an arbitrary orientation and a length chosen to be an arbitrary fraction of a complete bond is $^1/_2$, but one can obtain a probability greater than $^2/_3$ by including all amorphous walks with total length less than two bonds.[3,9] We have implied elsewhere[3] that one can only expect to get the correct result if walks are initiated after penetrating the amorphous domain a distance equal to the statistical segment length of the chain. However, this is still vague. For example, employing freely jointed walks in which the first step is a whole bond oriented normal to the lamellar plane yields a value of about $^3/_4$.[20]

The difficulty lies, ultimately, in the inability to extract local information, i.e., the probability of adjacent reentry, from models that can only give information concerning long-range properties. It is not even clear that a gambler's ruin model based on a walk that is a good representation of the local θ-state structure (e.g., a rotational isomeric state model) would permit a reasonable estimate of the adjacent reentry probability. One could argue that details of intermolecular chain packing or considerations of crystallization kinetics are also important in determining short-range structure at the interface. The best that we can do to estimate the amount of nonadjacent reentry is to specify the fraction of loops having throw length greater than some arbitrary r for r large enough for the s dependencies to be absent or to specify the fraction of loops having greater than t bonds for t also arbitrary but large enough to see no s dependencies. These are given by $1 - iP_L$ or $1 - iB_L$ and are summarized in Table IV. We also display in Table IV the r or t value considered large enough to observe universal behavior (i.e., behavior independent of s). These are taken as the r values required for the term $(D_2r^2/D_1 + s^2)^{-3/2}$ in eq 21 to be within 90% of $(D_2r^2/D_1)^{-3/2}$ and the t values required for the term $\exp(-s^2/4D_2t)$ in eq 22 to be within 90% of unity. The value $\Phi s/r$ is the fraction of loops having throw lengths greater than r. We see that the distance Φs controls the amount of near-adjacent reentry.

As an example, consider quantities appropriate for polyethylene ($C_\infty = 6.7$, $\rho = 0.85$, $l = 1.54$ Å, $l_n = 1.27$ Å) in the isotropic limit. We obtain $\Phi s = 3.5$ Å. Then we predict (3.5 Å)/r for the fraction of loops having throw lengths greater than r, valid for $r > 14$ Å. We predict $1.2t^{-1/2}$ for the fraction of loops having more than t bonds, valid for $t > 12$. Clearly, even though we are unable to accurately specify an adjacent reentry probability, we do predict that the large majority of the chains return to sites near the point of departure.[21]

Since $C_L(k)$, $C_T(k)$, $b_L(q)$, and $b_T(q)$ are generating functions for the moments $\langle r^{2j}\rangle_L$, $\langle t^j\rangle_L$, $\langle r^{2j}\rangle_T$, and $\langle t^j\rangle_T$, respectively, expressions for these moments valid to leading order in s/L may be obtained by expanding eq 15, 16, 18, and 19 in powers of k or q. (We let $\langle ...\rangle_L$ and $\langle ...\rangle_T$ represent averages for loops and ties respectively.) We obtain

$$\langle t^j\rangle_L = \left(\frac{j!2^{2j}B_j}{(2j)!}\right)\frac{\Phi s}{\epsilon}L^{2j-1}D_2^{-j} \tag{27}$$

$$\langle t^j\rangle_T = \left(\frac{2j!(2^{2j-1} - 1)B_j}{(2j)!}\right)L^{2j}D_2^{-j} \tag{28}$$

$$\langle r^{2j}\rangle_{L,T} = \frac{\pi^{1/2}(2j)!}{\Gamma(j + 1/2)}D_1^{\,j}\langle t^j\rangle_{L,T} \tag{29}$$

where B_j represents the Bernoulli numbers.[22] Note that

$$\frac{\langle t^{2j}\rangle_L}{\langle t^j\rangle_L^{\,2}} \propto \frac{L}{\Phi s} = \omega^{-1} \tag{30}$$

while

$$\langle t^{2j}\rangle_T / \langle t^j\rangle_T^{\,2} = \text{constant} \tag{31}$$

(The $j = 1$ values of these ratios are just N_w/N_n and are given in Tables I–III.) The large value of the ratios in eq 30 or of N_w/N_n in Tables I–III indicates that the loops have a very broad distribution of lengths. This indicates that most of the material in the amorphous domains is contained in a small number of very long chains, either loops or ties. Another indication of this is the fact that loops and ties have mass fractions of the same order of magnitude.

Conclusions and Discussion

The gambler's ruin model is very useful in predicting global properties of semicrystalline polymer chains, for example, the fraction of tie chains or the radius of gyration.[23] It also indicates that a large fraction of the chains leaving a given crystal must return shortly to avoid overcrowding of the amorphous domains. However, it cannot predict the precise structure of folding on a local scale. Even though only a small number of chains leave the vicinity of their departure points, these chains are on average very long and contribute most of the density of the amorphous domains.

One new result derived here are the expressions for the Fourier transforms C_L and C_T. These functions permit the approximate calculation of scattering structure factors that are important in the theory of neutron scattering by these polymer systems. Structure factor calculations are currently under way.

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References and Notes

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(12) See the appendix to ref 10.

(13) The factor $(1 - s/L)^{-1}$ appearing in eq 2 was neglected in ref 12, but retained here, where we explicitly retain terms to all orders in s/L unless stated otherwise.

(14) Upon integration one encounters Fourier series whose sums are given in: Gradshteyn, I. S.; Ryzhik, I. M. *Table of Integrals, Series, and Products*; Academic: New York, 1980; pp 38–40. Alternatively, expressions for N_n, N_w, and $\langle r^2\rangle$ may be obtained by expanding the appropriate Fourier or Laplace transform in series, since these transforms are generating functions for the moments.

(15) To compute P_{AL} and P_T we employ the identity

$$\int_0^\infty \mathrm{d}x\ x^{-1} \exp\left(\frac{-\beta}{4x} - \gamma x\right) = 2K_0(\beta^{1/2}\gamma^{1/2})$$

which may be obtained by differentiating both sides of eq 3.324.1 of Gradshteyn, I. S.; Ryzhik, I. M. *Tables of Integrals, Series, and Products*; Academic: New York, 1980, p 307 with respect to β.

(16) To obtain $C_{AL}(\mathbf{k})$ and $C_T(\mathbf{k})$, we first integrate $e^{i\mathbf{k}\cdot\mathbf{r}} f_L(\mathbf{r},t)$ or $e^{i\mathbf{k}\cdot\mathbf{r}} f_T(\mathbf{r},t)$ over $\mathbf{r}$ and then over t, after which ref 14 above applies.

(17) We employ the following definitions for Fourier and Laplace transforms:

$$C(\mathbf{k}) = (2\pi)^{-1} \int \mathrm{d}\mathbf{r}\ e^{i\mathbf{k}\cdot\mathbf{r}} P(\mathbf{r}) \quad \text{(two-dimensional Fourier)}$$

$$b(q) = \int_0^\infty \mathrm{d}t\ e^{-qt} B(t) \quad \text{(Laplace)}$$

(18) Some of the results given in Table III disagree with results obtained in ref 2. For example, the quantities C_∞ and l should only appear in the combination $C_\infty l^2$ while the combination $C_\infty l$ appears in ref 2.

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(21) It should be noted that the failure of polyethylene to achieve Gaussian statistics over such short chains is a source of error in this calculation.

(22) Definitions of the Bernoulli numbers differ slightly in the literature. Here we employ the definition given in: Dwight, H. B. *Tables of Integrals and other Mathematical Data*, 4th ed.; MacMillan: New York, 1961.

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