Lattice models of semicrystalline polymers: the Flory theorem implies that mean-field predictions are exact

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The statistical properties of several different ensembles of properly packed (i.e. non-mean-field) lattice chain systems that model the amorphous domains of semicrystalline polymers are studied by Monte Carlo calculations. The models are shown to obey accurately mean-field predictions as long as comparisons are limited to isotropic regions. This is seen as a direct consequence of the Flory theorem. In fact, this calculation is a particularly sensitive computer simulation test of the Flory theorem, because it permits calculations to be performed in the absence of chain ends.

(Keywords: Monte Carlo calculations; semicrystalline polymers; Flory theorem; computer simulation)

INTRODUCTION

There have appeared over about the last decade a number of models of the amorphous domains of semicrystalline polymers. These all represent the chain segments of the amorphous domains as walks between two parallel planes, the two planes representing the boundaries between amorphous and crystalline domains. These models fall into three general categories. The simplest category, usually called gambler's ruin models[1-6], represents the amorphous chains as purely ideal random walks, placed into the domain between the two planes with no direct regard for chain packing considerations except in the mean-field sense that the overall segment density is uniform and matches the experimental density of the amorphous domains. The second category of models still treats the packing problem in a mean-field fashion, but builds non-uniformities into the chain segments near the boundaries to account for the gradual dissipation of crystalline order[7-13]. The third category of models treats the packing problem exactly by Monte Carlo generation and sampling of properly packed lattice systems[14,15]. This paper reports a comparison between the properties of the properly packed models and the mean-field models. The properly packed models prove to follow accurately the predictions of the mean-field models.

MONTE CARLO CALCULATIONS

A previously described algorithm[14] was used to generate and sample a set of six different properly packed lattice chain ensembles. The different ensembles are characterized by Hamiltonians that are functions of three parameters: a chain bending energy, a packing energy tending to align adjacent bonds, and a hairpin turn energy. These are denoted a, b and c, respectively. See ref. 14 for details of the Hamiltonian. *Table 1* lists the values of a, b and c assigned to the six ensembles. The chains are laid out on a simple cubic lattice with the two planes $z = 0$ and $z = 31$

representing the crystal–amorphous boundary. The domain is bounded on the lateral sides by the planes $x = 0$, $x = 31$, $y = 0$, $y = 31$, with periodic boundary conditions across these lateral faces. At regular sampling intervals the structure of chains in the system is sampled as follows: two planes are drawn at the levels $z_1 = n$ and $z_2 = 31 - n$, for $n = 0, 1, 2, \ldots, 14$. This gives successively thinner and thinner slices of thickness $L = z_2 - z_1 = 31, 29, 27, \ldots, 3$. Chain segments stepping into the domain from either the level z_1 or z_2 are followed until they once again leave the domain; those leaving via the same face through which they entered are classified as loops, those leaving through the opposing face as ties. The average chain length of both loops and ties, M_L and M_T, respectively, and the fraction of ties, t, are thereby estimated as a function of L for each of the six ensembles. M_L and M_T are both defined so that all lattice bonds lying entirely in the range $z_1 < z < z_2$ contribute to the loops or ties. In other words, bonds lying entirely in the planes $z = z_1$ or $z = z_2$ do not contribute to loops or ties defined between those planes.

DERIVATION OF MEAN-FIELD PREDICTIONS

Assume that the two planes at z_1 and z_2 cut through isotropic regions. Let M be the total number of lattice sites in each plane. Now imagine stepping through the lattice, stopping at each lattice site and counting the number of bonds seen entering or leaving that lattice site and that lie entirely in the region $z_1 < z < z_2$ (i.e. we do not count bonds parallel to the z planes at $z = z_1$ or $z = z_2$). At each of the levels $z = z_1 + 1, z_1 + 2, \ldots, z_2 - 1$ we count two bonds at each lattice site, yielding a contribution of $2M$ per level. At each of the two levels $z = z_1$ and $z = z_2$ we only count $M/3$ per level since only one bond in six on these levels points into the domain. The total count is $2M(3L - 2)/3$. This counting procedure counts each bond in the domain exactly twice, so there are $M(3L - 2)/3$ bonds in the domain. Also each of the $2M/3$ bonds counted in the layers $z = z_1$ or $z = z_2$ defines

Table 1

Ensemble	a	b	c	C_∞	K_1	K_2	K_3	Q^a
1	0	0	0	1.664	0.50	0.77	-0.82	-0.04
2	-0.10	-0.10	0	1.661	0.32	0.82	-0.74	-0.09
3	0.25	0.25	0	1.707	0.68	0.77	-1.04	-0.03
4	0.30	0.30	0	1.663	0.68	0.58	-0.42	0.07
5	0.50	0	0	1.439	0.59	0.49	-0.50	0.07
6	0	0	4	2.738	1.68	1.08	-3.21	-0.01

^{a} Q is defined as $K_1 + C_\infty K_2 + K_3/C_\infty - 2C_\infty + 2$, which, according to equation (6), should be zero

the end of either a loop or a tie, so there are $M/3$ loops or ties in total. Therefore, the average number of bonds in either a loop or a tie is $3L - 2$. We therefore may write:

$$t M_T + (1 - t) M_L = 3L - 2 \tag{1}$$

We note that equation (1) depends only on the assumption that the melt in the region $z_1 < z < z_2$ is isotropic; it holds, therefore, for both the mean-field and the properly packed models whenever these are isotropic.

The appropriate gambler's ruin prediction for the three quantities M_L, M_T and t can be obtained from the first two rows of Table 1 of ref. 5. The relevant entries in that table involve the following parameters: Φ, s, L, D_2, F_1, F_2 and F_3. As described in ref. 5, we can write $F_1 = F_2 = F_3 = 1$ and $D_2 = C_\infty l^2/6$ (or just $C_\infty/6$ using units such that $l = 1$), where C_∞ is the characteristic ratio of the chain. The parameter Φ is essentially a normalization factor, which can be neglected in the present application. (It was necessary in that paper to renormalize the fractions of loops and ties to include tight folds. That renormalization is not needed here so we set $\Phi = 1$.) L is the domain thickness. The value s is a parameter with a specific significance for continuous random walks, but only a vague significance, at present, for lattice chains. An appropriate value for s will become apparent shortly. The following expressions are the appropriate gambler's ruin predictions for the three quantities M_L, M_T and t:

$$M_L = 2sL/C_\infty + K_1 \tag{2}$$

$$M_T = L^2/C_\infty + K_2 L \tag{3}$$

$$t = s/L + K_3/L^2 \tag{4}$$

The three terms K_1, K_2 and K_3 are included because we have come to expect model-dependent terms in descending powers of L in all gambler's ruin calculations. They will also serve as adjustable parameters.

Now we insert equations (2)–(4) into (1) and equate equal powers of L. This leads to the appropriate identification of the parameter s in the context of lattice walks:

$$s = C_\infty \tag{5}$$

and to a relationship between the subdominant parameters:

$$K_1 + C_\infty K_2 + K_3/C_\infty - 2C_\infty = -2 \tag{6}$$

Inserting equation (5) into equations (2)–(4) leads to these predictions:

$$M_L = 2L + K_1 \tag{7}$$

$$M_T = L^2/C_\infty + K_2 L \tag{8}$$
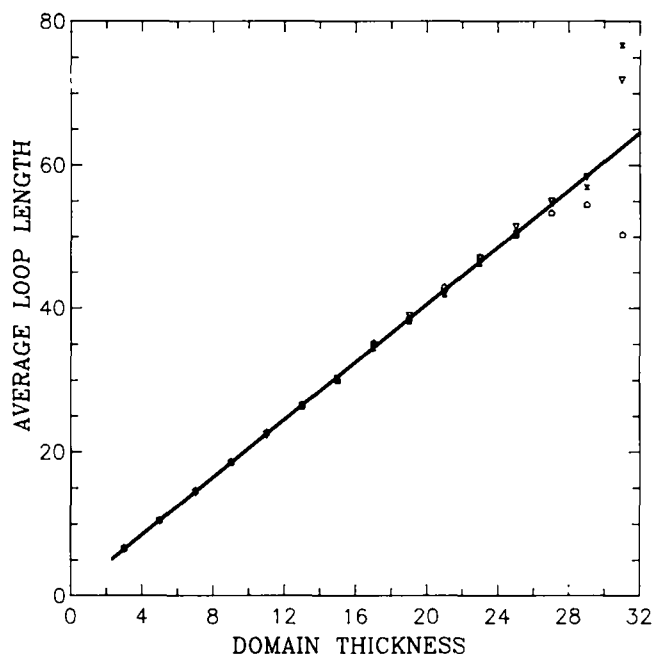
$$t = C_\infty/L + K_3/L^2 \tag{9}$$

Figure 1 The function M_L for ensembles 1, 2 and 3 as computed by Monte Carlo method (symbols) and by equation (7) (full curves)

The above are the appropriate mean-field predictions for the present lattice models. It is important to note that although we have proven equation (1) rigorously, the above three equations have only been established for mean-field models.

COMPARISON BETWEEN MEAN-FIELD PREDICTIONS AND MONTE CARLO RESULTS

The values of M_L, M_T and t obtained from the Monte Carlo simulations were fitted to equations (7)–(9) by adjusting C_∞, K_1, K_2 and K_3. The resultant fits are shown in *Figures 1–6*, and the parameters C_∞, K_1, K_2 and K_3 yielding the fits are shown in *Table 1*. The fits are always excellent, except at either large or small L. Departures at large L occur for z_1 and z_2 values near 0 and 31, respectively, where the amorphous domains are anisotropic. Departures at small L occur when the two planes lie within the correlation length of the melt. We conclude that equations (7)–(9) are excellent representations of properly packed (i.e. non-mean-field) isotropic systems. Note also (consult the column labelled Q in *Table 1*) that the fitted parameters C_∞, K_1, K_2 and K_3 satisfy equation (6) to within the limits expected given sampling and fitting uncertainties, although no attempt was made, during fitting, to force such agreement.
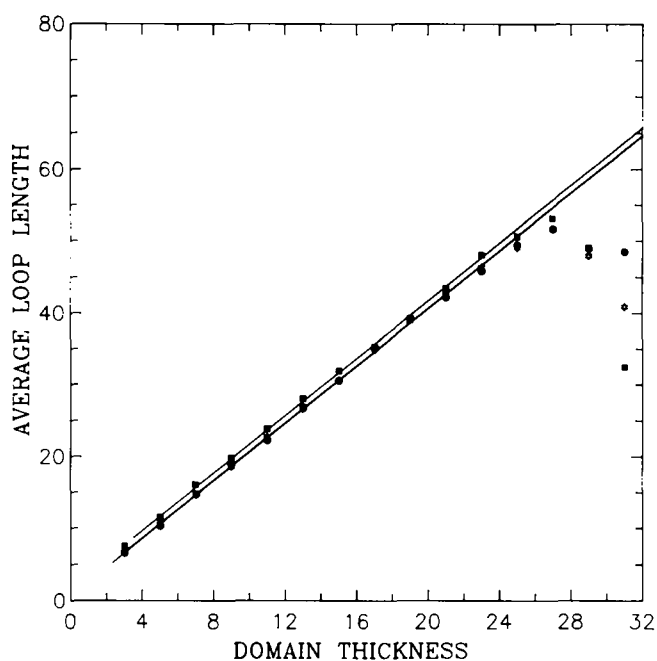
For reasons that are not understood, the first four

Figure 2 The function M_L for ensembles 4, 5 and 6 as computed by Monte Carlo method (symbols) and by equation (7) (full curves)
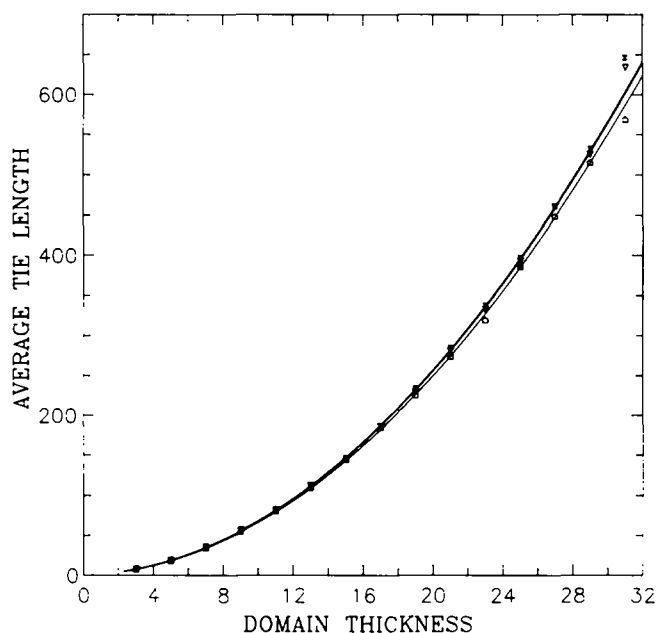

Figure 3 The function M_T for ensembles 1, 2 and 3 as computed by Monte Carlo method (symbols) and by equation (8) (full curves)

ensembles exhibit almost identical behaviour, so no attempt has been made to label individual curves in *Figures 1, 3* and *5*. The characteristic ratios of these four ensembles are all very nearly 5/3, suggesting, at least, that 5/3 might be the exact result. The six curves for M_L all lie very close together, so individual curves have also not been labelled in *Figure 2*. This is of course predicted by equation (7), which indicates that all the M_L curves should agree up to an additive constant of order unity.

DISCUSSION

In retrospect, the fact that the properly packed models agree so well with mean-field predictions comes as no surprise. It is simply a manifestation of what has come

to be known as the Flory theorem, i.e. the concept that molten chains are ideal[16-18]. An earlier attempt[14] at comparing the two classes of models failed on two accounts: first of all, the two planes z_1 and z_2 were drawn through anisotropic regions of the domain; and secondly, the attempted comparison was done between a mean-field model with $C_x = 1$ and a properly packed model with $C_x = 1.66$.

Attempts at verifying the Flory theorem by computer simulation have been less than completely satisfying[19,20]. Effective molecular size exponents, i.e. v in the expression $\langle R^2 \rangle^{1/2} \sim N^v$, are usually computed to be quite near to, but consistently larger than, 1/2. In the opinion of this author, this is because of the presence of chain ends at
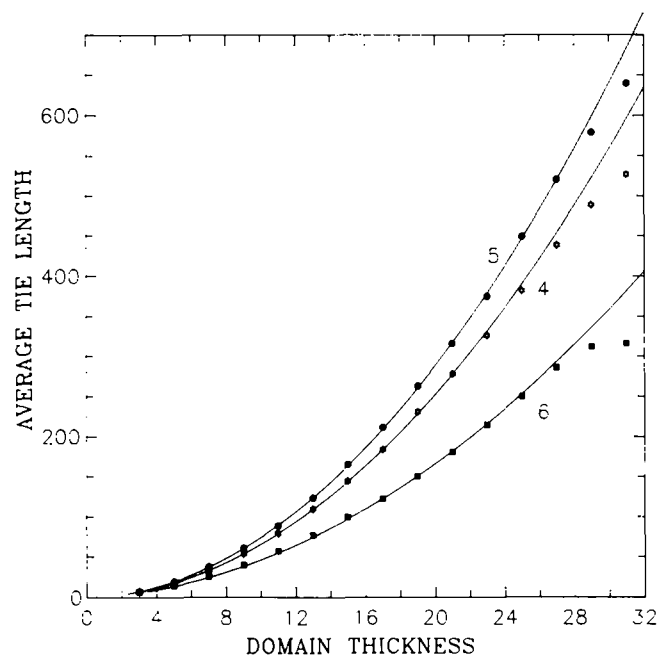

Figure 4 The function M_T for ensembles 4, 5 and 6 as computed by Monte Carlo method (symbols) and by equation (8) (full curves)
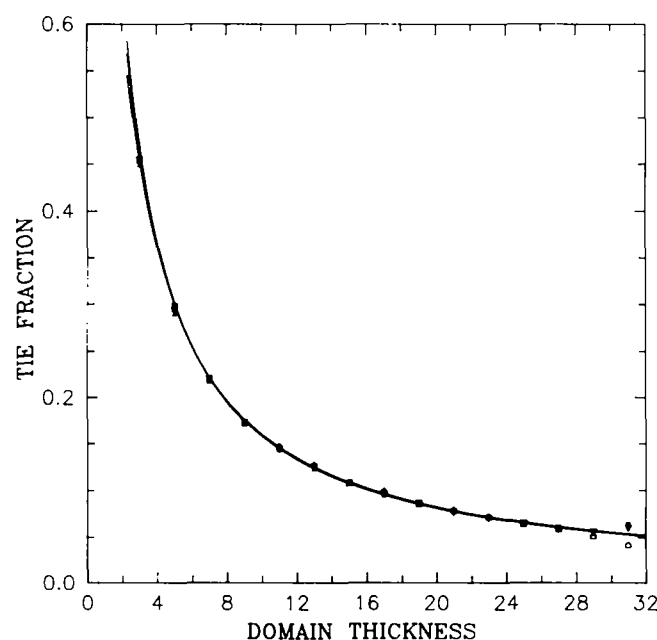

Figure 5 The function t for ensembles 1, 2 and 3 as computed by Monte Carlo method (symbols) and by equation (9) (full curves)
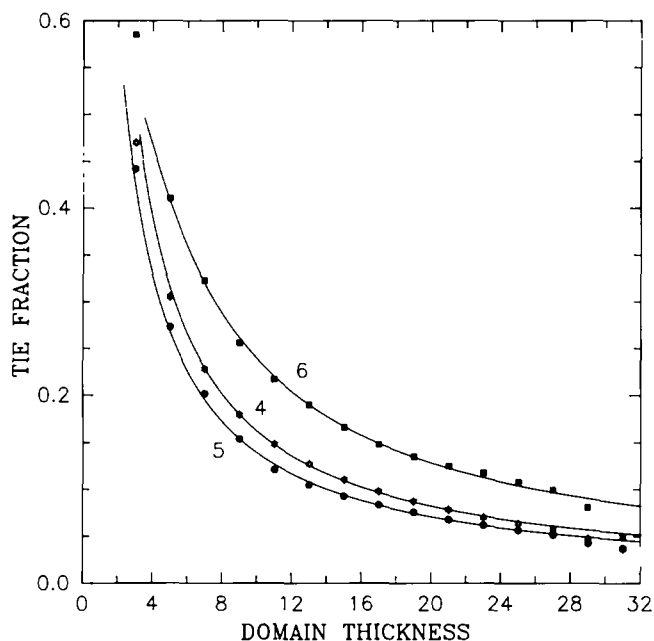
Figure 6 The function t for ensembles 4, 5 and 6 as computed by Monte Carlo method (symbols) and by equation (9) (full curves)

finite molecular weights. The Flory theorem should be mathematically rigorous in the limit $N \to \infty$, i.e. in the absence of chain ends. To see this, consider a polymer melt constructed from infinitely long chains. The sum:

$$\sum_{j=-\infty}^{+\infty} \langle \boldsymbol{v}_i \cdot \boldsymbol{v}_j \rangle$$

$\boldsymbol{v}_i$ and $\boldsymbol{v}_j$ being bond vectors, undoubtedly converges. (We could argue, for example, that $\boldsymbol{v}_i$ and $\boldsymbol{v}_j$ for $|i-j|$ large cannot possibly be correlated unless they happen to lie in close proximity. This suggests $|\langle \boldsymbol{v}_i \cdot \boldsymbol{v}_j \rangle| < |i-j|^{-3/2}$, which would imply that the sum converges absolutely.) If

$$\sum_{j=-\infty}^{+\infty} \langle \boldsymbol{v}_i \cdot \boldsymbol{v}_j \rangle$$

converges, the chain is necessarily ideal. (The quantity $\langle \boldsymbol{v}_i \cdot \boldsymbol{v}_j \rangle$ is entirely analogous to the velocity auto-correlation function of a particle. If the integral over time

of the autocorrelation function exists, then the particle executes Brownian dynamics[21].) The convergence of the sum and subsequent ideality of the chains devolve, ultimately, from the complete translational and rotational symmetry of the polymer melt, which in turn only exists as $N \to \infty$. For finite N, an occasional chain end will disrupt the complete translational symmetry and therefore invalidate the theorem. Computer tests of the Flory theorem would best be carried out on systems of infinite molecular weight. That is, of course, unfeasible. The next best calculation would be the study of finite-sized domains from which all chain ends have been eliminated. This is, in fact, what has been achieved. In summary, these calculations demonstrate the validity of mean-field treatments of semicrystalline polymer systems, and provide a satisfying test of the Flory theorem.

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