The Interphase in Lamellar Semicrystalline Polymers†

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ABSTRACT: A lattice theory is developed to describe in detail the transition from perfect crystalline order to the isotropy of the adjoining amorphous state in a lamellar semicrystalline polymer. The required dissipation of chain flux causes a majority, ca. 70%, of the chains to reenter the same lamellae from which they emerge. However, even in the most favorable circumstance in which the interface is normal to the stems of chains in the crystal, fewer than 20% of these chains are engaged in adjacent folds with immediate reentry. Most of the reentry in the first three lattice layers adjoining the crystal surface occurs at sites that are nearby, but nonadjacent, to the site of exit. The interphase in which order persists is predicted to be 10–12 Å in thickness, in agreement with experiments. The interfacial free energy, 55–70 erg cm^{-2}, calculated from the persistence of order beyond the crystal interface is compared with deductions from observed depressions of melting temperatures due to the finite thickness of the lamellae.

Introduction

Semicrystalline polymers formed from the melt generally consist of lamellar crystals separated by amorphous regions. Axes of the chains are transverse to the faces of the lamellae, which normally are 100–500 Å in thickness; their lateral dimensions are much larger. The regions between the crystal lamellae, measuring 50–200 Å in thickness, exhibit properties approximating those of the amorphous, noncrystalline polymer, although vestiges of order in the transitional regions are indicated by various measurements.[1-4] Typically, the lengths of the polymer chains are many times greater than the lamellar thickness. Hence, each molecule must pass through the same or different lamellae many times. The manner in which this requirement is met is obviously of the foremost importance in regard to the molecular morphology of the crystal–amorphous interphase.

The regularly folded model according to which the long-chain molecule reverses its direction immediately upon emerging from the face of the lamella and returns to it in adjacency to the crystalline "stem" of the previous passage has been discredited by an abundance of evidence,[1,5,6] most compellingly by results of neutron scattering experiments on deuterated chains of polyethylene or of isotactic polypropylene dispersed in, and cocrystallized with, the corresponding protonated polymer.[7-12] It is well established, therefore, that the preponderance of the chains protrude from the crystalline lamellae and proceed into the interphase for a distance that is significantly beyond what may be regarded as the surface of the crystal.

In the fully disordered amorphous state the polymer chains assume their characteristic random configurations as is predicted by theory and well confirmed by experiments.[13] Transition from the virtually perfect order of the crystal to the isotropy and randomness of the amorphous, or liquid, state cannot occur abruptly. The continuity of the long polymer chains imposes severe constraints on the transition. These constraints have no counterpart in the crystal–liquid interface for low molecular weight substances. Moreover, the crystalline–amorphous polymer interface, or interphase, here considered differs importantly from the polymer interfaces treated by Helfand,[14] namely, those between two incompatible amorphous polymers and between an amorphous polymer, or polymer solution, and a wall.

The flux of chains emanating from the 001 face of the crystal is large; it may reach the maximum that spatial requirements of the chains will allow (if the conformation in the crystal and the crystal structure so dictate). This flux must be diminished substantially as a necessary prerequisite for attainment of random disorder. The mere requirement of isotropy of the distribution of bond directions necessitates a reduction of the surface density of chains by a factor of one-half if the chains in the crystal are normal to the interface and if the difference in densities of the phases is ignored.[15] The flux of chains emerging from the crystal must somehow be reduced at least by this factor, if order is to be fully dissipated. If the chains are sufficiently long to warrant neglect of occurrence of chain ends, then the required attenuation can only be achieved through return of a substantial proportion of the emanant chains to the crystal from which they emerged.[15] Their reentry need not be immediate or adjacent, however.[16]

Treatment of the crystal–amorphous interphase on the assumption that random configurations are adopted immediately upon emergence of the chains from the crystal lamella leads at once to an excessive density in the vicinity of the surface.[17,18] This is a consequence of disregard of the deduction asserted above according to which the chain flux must undergo attenuation before randomness may ensue.[15] From an alternative point of view, the constraint on the bulk density on the one hand and the continuity of the chains on the other preclude immediate dissipation of the flux of chains from the surface of the crystal. To ascribe random chain statistics to the emergent chains[17,18] is to disregard these constraints which are responsible for the very features that are peculiar to the interphase.

The lattice model is eminently suited to the treatment of the interphase in a way that takes account of the constraints incident thereon.[19,20] It is deficient, however, in its manifestly unrealistic idealization of the chain configuration relative to that of the real chain. This well-known shortcoming of the lattice model for representing real chain molecules does not disqualify it for our immediate purpose of exploring the general features of the dissipation of order in the vicinity of the phase boundary. We present here a theoretical treatment of the interphase using the lattice model in a way which should reveal the principal characteristics of chain configurations in the interphase. The method of treatment has much in common with the pro-

† We take special pleasure in dedicating this paper and the one that follows to Walter H. Stockmayer on the occasion of his 70th birthday.

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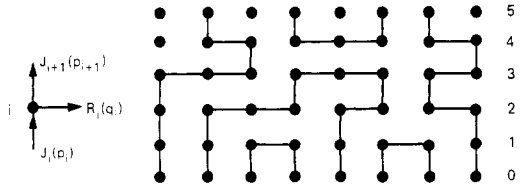

Figure 1. Schematic cross-sectional view of the interphase in a lamellar semicrystalline polymer. The layers are numbered from the crystal surface ($i = 0$), and $J_{i+1}(p_{i+1})$, $J_i(p_i)$, and $R_i(q_i)$ denote the number densities (fractions) of different connections of lattice segments.

cedures used recently[19] for the treatment of monolayers and bilayers comprising chain molecules with polar head groups and for the similar treatment of micelles.[20]

Theory

Model. We consider a system of long molecular chains that emanate from the face of a perfect crystal transverse to the axes of the chains, e.g., from the 001 face of the crystal. Attention is focused on the interphase region between the perfect crystal and the amorphous phase in which isotropy is attained. The chains are assumed to be in a state of equilibrium subject to the constraints imposed by their connections to the crystal and by their mutual coexistence at bulk density. The density of the interphase is assumed to be the same as that of the crystal. Appropriate corrections could be introduced to take account of the gradation of density between the crystalline and amorphous phases if this should be warranted. The molecules are assumed to be of such lengths that occurrence of chain ends in the interphase is so rare as to be negligible.

The system is represented by chains of linearly connected segments, each of which is assigned to one of the sites of a cubic lattice. Representation in this manner requires that the segments be isodiametrical so that one of them is eligible to occupy a lattice site (exclusively) regardless of its orientation. The lattice dimension, and hence the size of a segment, is dictated therefore by the diameter of the chain. In the case of polymethylene this dimension is ca. 4.5 Å and the segment comprises ca. 3.5 CH_2 groups.

One of the axes of the lattice is oriented parallel to the chain axis in the crystal. Layers of segments transverse to this direction are indexed by i commencing with the layer adjacent to the 001 face of the crystal; all layers $i \leq 0$, which occur within the crystal, are assumed to be perfectly ordered. The mutual alignment in each perfectly ordered layer ensures that the succeeding layer, in the absence of defects, must likewise be perfectly ordered. At the *first* interphase layer ($i = 1$), chain folds that reverse the chain direction (folds with adjacent reentry in the first layer; cf. seq.) admit of attrition of the flux of chains into the next layer. To the extent that such folds occur, a corresponding degree of disorder can be accommodated in the following layer. Disorder begets further attrition in the "flux" of chains, especially through the tolerance of larger loops leading to reversals of the chain trajectory and eventual reentry of the crystal at a site generally some distance from the point of emergence. The model, reduced to two dimensions, is illustrated in Figure 1.

Constraints: Conservation and Continuity. It is expedient to focus attention on bonds between consecutive segments of the lattice chain, instead of on the segments. We distinguish horizontal bonds within a given lattice layer parallel to the interface from vertical bonds connecting neighboring segments occupying sites in adjoining layers. Let J_i denote the number of vertical bonds per unit area between segments in layers $i - 1$ and i. Included are all vertical bonds regardless of the chain direction, which need not be specified.[36] If N_0 is the number of sites per unit area in a layer, then $J_0 = N_0$. The number density R_i of horizontal bonds in layer $i > 0$ is related to the densities of vertical bonds entering and leaving that layer according to the *conservation condition*

$$R_i = N_0 - (J_i + J_{i+1})/2 \tag{1}$$

Expressed in terms of the fractions $p_i = J_i/N_0$ and $p_{i+1} = J_{i+1}/N_0$ of vertical bonds attached to layer i and the fraction $q_i = R_i/N_0$ of horizontal bonds in that layer, this relation becomes

$$q_i = 1 - (p_i + p_{i+1})/2 \tag{2}$$

$$= 1 - \bar{p}_i \tag{2'}$$

where $\bar{p}_i N_0$ is the mean of the number of vertical bonds per unit area at the two faces of layer i.

A chain reaching layer i via one of the J_i vertical bonds from layer $i - 1$ may be succeeded by another vertical bond and thus pass through layer i continuing at once to the next layer, i.e., to layer $i + 1$. Alternatively, the vertical bond from layer $i - 1$ may be succeeded by one or more horizontal bonds in layer i, after which it may resume its previous vertical direction via a bond leading to layer $i + 1$. In either case the given chain is counted in J_{i+1} as well as in J_i.

Alternatively, the sequence of horizontal bonds initiated by a vertical bond from layer $i - 1$ may be terminated by a vertical bond that returns the chain to layer $i - 1$. The direction of the chain is thereby reversed, and the number density J_{i+1} of vertical bonds in the next interlayer is reduced by two. We designate a trajectory of this kind as a negative, or downward, reversal. The number of sequences of this character per unit area in layer i will be denoted by S_i^{--}.

A sequence of one or more horizontal bonds may similarly be terminated at both of its ends by vertical bonds extending upward, i.e., from layer i to $i + 1$. Such positive, or upward, reversals increase J_{i+1} by two compared to J_i. Their number per unit area will be denoted by S_i^{++}.

It will be apparent that the attrition in J from one interlayer to the next will depend on the difference between S^{--} and S^{++} in the intervening layer. Thus, *continuity* of the chains requires that

$$J_{i+1} - J_i = 2(S_i^{++} - S_i^{--}) \tag{3}$$

or

$$p_{i+1} - p_i = 2(S_i^{++} - S_i^{--})/N_0 \tag{3'}$$

The combined number density of horizontal sequences consisting of one or more bonds in layer i is

$$S_i = S_i^{++} + S_i^{--} + S_i^{\pm} \tag{4}$$

where $S_i^{\pm}$ is the number density of sequences in layer i that are bound at one end by a vertical bond to layer $i - 1$ and at the other by a vertical bond to layer $i + 1$.

The incidence q_i of horizontal bonds is a primary measure of disorder in layer i. It is uniquely related to the combined incidences p_i and p_{i+1} of vertical bonds from adjacent layers according to the conservation condition expressed by eq 2 or 2'. The apportionment of $1 - q_i$ between p_i and p_{i+1} depends on the difference between the numbers S_i^{--} and S_i^{++} of sequences engaged in negative and positive reversals in layer i. The progression of the dissipation of order through successive layers depends explicitly on these differences according to the continuity equation, eq 3. Thus, it depends on two factors: the

number of horizontal sequences in the given layer and the bias favoring "negative" connections over "positive" ones.

Statistical Distribution of Configurations in the Interphase. The connections occurring at the two ends of a horizontal bond are assumed to be mutually independent except in cases where the given bond is joined to two vertical bonds extending in the same direction. We take account of the likelihood that such adjacent returns may be subject to specific conformational constraints affecting chain folding in this manner by introducing a parameter h to modify this incidence. In other respects the distribution of bond connections is taken to be Bernoullian. Accordingly, we represent the relative incidences of various configurations, ++, +−, etc., for horizontal bonds by elements of the matrix

$$\mathbf{U}_i = \begin{bmatrix} hu_+^2 & u_+u_- & u_+u_0 \\ u_-u_+ & hu_-^2 & u_-u_0 \\ u_0u_+ & u_0u_- & u_0^2 \end{bmatrix}_i \tag{5}$$

where u_+, u_-, and u_0 are weighting factors for junctions at the terminus of a horizontal bond with an "upward" vertical bond, with a "downward" vertical bond, and with a horizontal bond, respectively. The incidences of adjacent returns ++ and −− are assumed to be affected by the same factor h. The serial index i for the layer in question is appended to the matrix; it applies to each of the quantities therein. The matrix of a priori *probabilities* of occurrences of the various states of horizontal bonds is

$$\mathbf{F}_i = C_i\mathbf{U}_i \tag{6}$$

where C_i is the normalization factor equal to the reciprocal of the sum of the elements of $\mathbf{U}_i$; i.e.

$$C_i^{-1} = (u_{i+} + u_{i-} + u_{i0})^2 - (1 - h_i)(u_{i+}^2 + u_{i-}^2) \tag{7}$$

Since only the relative magnitudes of the elements of $\mathbf{U}_i$ are important, we are at liberty to let

$$u_{i+} + u_{i-} + u_{i0} = 1 \tag{8}$$

Then

$$C_i^{-1} = 1 - (1 - h_i)(u_{i+}^2 + u_{i-}^2) \tag{9}$$

The a priori *incidences*, f_{i+}, f_{i-}, f_{i0}, of the several kinds of connections of horizontal bonds in the given layer are obtained by summing the rows (or columns) of $\mathbf{F}_i$. From eq 5 and 6 we thus obtain, with the aid of eq 8

$$\begin{aligned} f_{i+} &= C_iu_{i+}[1 - (1 - h_i)u_{i+}] \\ f_{i-} &= C_iu_{i-}[1 - (1 - h_i)u_{i-}] \\ f_{i0} &= C_iu_{i0} \end{aligned} \tag{10}$$

The *conditional probabilities* for the various states of horizontal bonds are given by the elements of $\mathbf{f}_i^{-1}\mathbf{F}_i$, where $\mathbf{f}_i$ is the diagonal matrix comprising the a priori incidences given by eq 10. It follows that the number density of negative sequences containing l horizontal bonds in layer i is

$$\begin{aligned} S_{i;l}^{--} &= R_iC_ih_iu_{i-}^2, \qquad l = 1 \\ S_{i;l}^{--} &= R_iC_iu_{i-}^2u_{i0}^{l-1}, \qquad l > 1 \end{aligned} \tag{11}$$

Summation over l gives

$$S_i^{--} = R_iC_iu_{i-}^2(u_{i+} + u_{i-})^{-1}[1 - (1 - h_i)(u_{i+} + u_{i-})] \tag{12}$$

Similarly, one obtains

$$S_i^{++} = R_iC_iu_{i+}^2(u_{i+} + u_{i-})^{-1}[1 - (1 - h_i)(u_{i+} + u_{i-})] \tag{13}$$

$$S_i^{\pm} = 2R_iC_iu_{i+}u_{i-}(u_{i+} + u_{i-})^{-1} \tag{14}$$

and

$$\begin{aligned} S_i &\equiv S_i^{++} + S_i^{--} + S_i^{\pm} \\ &= R_i(1 - C_iu_{i0}) \end{aligned} \tag{15}$$

The average number $\langle l_i^{--}\rangle$ of horizontal bonds in a negative reversal in layer i is

$$\sum_{l=1}^{\infty} lS_{i;l}^{--}/S_i^{--}$$

with corresponding expressions for $\langle l_i^{++}\rangle$ and $\langle l_i^{+-}\rangle$. Evaluation of the respective summations using eq 11 and its analogues yields

$$\langle l_i^{--}\rangle = \langle l_i^{++}\rangle = (u_{i+} + u_{i-})^{-1}\left[\frac{1 - (1 - h_i)(u_{i+} + u_{i-})^2}{1 - (1 - h_i)(u_{i+} + u_{i-})}\right]$$

$$\langle l_i^{+-}\rangle = (u_{i+} + u_{i-})^{-1} \tag{16}$$

Substitution of eq 12 and 13 in eq 3′ and introduction of q_i for R_i/N_0 gives

$$p_{i+1} - p_i = 2q_iC_i(u_{i+} - u_{i-})[1 - (1 - h_i)(u_{i+} + u_{i-})] = 2q_iB_i \tag{17}$$

where B_i, defined by comparison with the preceding equation, is given by

$$B_i = (u_{i+} - u_{i-})[1 - (1 - h_i)(u_{i+} + u_{i-})]/[1 - (1 - h_i) \times (u_{i+}^2 + u_{i-}^2)] \tag{18}$$

after substitution of eq 9 for C_i. Substitution of eq 2 for q_i in eq 17 yields

$$p_{i+1} = [2B_i + (1 - B_i)p_i]/(1 + B_i) \tag{19}$$

In conclusion, the configuration distribution in layer i may be specified by the number density $R_i = q_iN_0$ of horizontal bonds, the numbers $f_{i+}R_i$ and $f_{i-}R_i$ of positive and negative junctions, and the numbers $F_{i++}R_i$ and $F_{i--}R_i$ of positive and negative adjacent returns. These specifications are consistent with the constraints and they take account of the bias affecting adjacent reversals, or regular folds. Of the stochastic variables q_i, f_{i+}, f_{i-}, F_{i++}, and F_{i--} that specify the distribution in layer i, the last four are fully determined by the quantities u_{i+}, u_{i-}, and h_i according to the relations above; q_i depends on values of the stochastic variables in preceding layers through the conservation and continuity conditions (cf. seq.).

Configuration Partition Function. The partition function Ω for the interphase is formulable as the product of factors Ω_i for successive layers; i.e.

$$\Omega = \prod_i \Omega_i \tag{20}$$

In order to derive Ω_i it will be necessary to introduce a priori *statistical weights* (not to be confused with a priori *incidences* introduced above) that complement the stochastic variables, identified above, which specify the actual distribution. Before proceeding, however, we observe that Ω_i representing layer i in the partition function Ω comprises two subsidiary factors: $\Omega_{\mathrm{I},i}$ that depends on the allocation of the bonds between horizontal and vertical orientations, and $\Omega_{\mathrm{II},i}$ that takes account of the distribution of connections involving the horizontal bonds. These factors reflect the constraints imposed by the conditions of conservation and continuity, respectively; see eq 2 and 3.

The a priori statistical weights for horizontal and vertical orientations in the cubic lattice are $^2/_3$ and $^1/_3$, respectively. It follows that

$$\Omega_{\mathrm{I},i} = (2/3)^{R_i}(1/3)^{\bar{J}_i}\binom{N_0}{R_i} \tag{21}$$

where $\bar{J}_i \equiv (J_i + J_{i+1})/2 = N_0 - R_i$ according to eq 1, or

$$\bar{J}_i \equiv N_0\bar{p}_i \tag{22}$$

With reduction of the combinatory factor in eq 21 using Stirling's approximation, one obtains

$$\Omega_{I,i} = [(2/3q_i)^{q_i}(1/3\bar{p}_i)^{\bar{p}_i}]^{N_0} \quad (23)$$

Formulation of the second factor requires specification of the *a priori weights* for the various connections involving horizontal bonds in the isotropic state. The relative probabilities for connection of the terminus of such a bond to another horizontal bond, to a vertical bond reaching the preceding layer, and to a vertical bond reaching the succeeding layer are expressible, respectively, as σ, $(1 - \sigma)/2$, and $(1 - \sigma)/2$ in the absence of effects that perturb the incidence of adjacent reversals. The parameter σ may be related to the statistical weight τ for a bend relative to unity for a collinear connection. In the cubic lattice

$$\sigma = (1 + 2\tau)/(1 + 4\tau) \quad (24)$$

(For a completely flexible chain $\tau = 1$ and $\sigma = {}^3/_5$ in the cubic lattice.) We introduce the additional parameter η for the a priori weighting factor for an adjacent return. Then, in the isotropic state the a priori probabilities of various junctions involving horizontal bonds, derived by repetition of the procedure leading to eq 10, are

$$\phi_+ = \phi_- = \Gamma[(1 - \sigma)/2][1 - (1 - \eta)(1 - \sigma)/2]$$
$$\phi_0 = \Gamma\sigma \quad (25)$$

where

$$\Gamma = [1 - (1/2)(1 - \eta)(1 - \sigma)^2]^{-1} \quad (26)$$

(compare eq 9). The a priori probability of an adjacent return of either sign is

$$\Phi_{++} = \Phi_{--} = \Gamma\eta(1 - \sigma)^2/4 \quad (27)$$

(compare eq 6). Hence, the conditional probability applicable to connection of a horizontal bond with a vertical one when the opposite terminus of the horizontal bond is joined to a vertical bond of the same sign is

$$\Phi_{++}/\phi_+ = \Phi_{--}/\phi_- = \eta[(1 - \sigma)/2][1 - (1 - \eta)(1 - \sigma)/2]^{-1}$$

The second factor in the partition function for layer i may therefore be written

$$\Omega_{II,i} = \{(\Phi_{++})^{F_{++}}(\Phi_{--})^{F_{--}}(\phi_+ - \Phi_{++})^{f_+ - F_{++}}(\phi_- - \Phi_{--})^{f_- - F_{--}}(\phi_0)^{f_0}\}_i^{R_i} \times \left(RF_{++}, RF_{--}, R(f_+ - F_{++}), R(f_- - F_{--})\right)_i^R \quad (28)$$

where the subscripts i index all quantities enclosed within braces or parentheses. Resolution of the combinatory factor in this equation through use of Stirling's approximation, substitutions from eq 6, 10, 25, and 27 for the various quantities occurring therein, and combination with eq 23 for $\Omega_{I,i}$ yields[37]

$$\omega_i = \Omega_i^{1/N_0} = [(2/3q_i)^{q_i}(1/3\bar{p}_i)^{\bar{p}_i}](\Gamma/C_i)^{q_i}\left\{\left[\frac{(1 - \sigma)^2\eta}{4h_iu_{i+}^2}\right]^{h_iu_{i+}^2} \times \left[\frac{(1 - \sigma)^2\eta}{4h_iu_{i-}^2}\right]^{h_iu_{i-}^2}\left[\frac{1 - \sigma^2}{4u_{i+}(1 - u_{i+})}\right]^{u_{i+}(1-u_{i+})} \times \left[\frac{1 - \sigma^2}{4u_{i-}(1 - u_{i-})}\right]^{u_{i-}(1-u_{i-})}\left[\frac{\sigma}{u_{i0}}\right]^{u_{i0}}\right\}^{q_iC_i} \quad (29)$$

The interfacial free energy attributable to order in the interphase is given by

$$\gamma = -(kT/a)\sum \ln \omega_i \quad (30)$$

where a is the cross-sectional area of a lattice cell, which may be equated to the cross section of the crystal per chain stem.

Analytical and Computational Procedures

Since $q_i = 0$ and $p_i = 1$ for all $i \leq 0$, eq 2 with $i = 0$ yields the obvious result $p_1 = 1$ for the reduced density of vertical bonds reaching the first layer above the crystal surface. According to eq 2 with $i = 1$

$$1 - p_2 = 2q_1 \quad (31)$$

It follows from eq 17 that $B_1 = -1$. Hence, from eq 18

$$(u_{1-} - u_{1+})\left[\frac{1 - (1 - h_1)(u_{1+} + u_{1-})}{1 - (1 - h_1)(u_{1+}^2 + u_{1-}^2)}\right] = 1 \quad (32)$$

The unique solution of this equation for $h_1 > 0$, $u_{i+} \geq 0$, $u_{1-} \leq 1$, and $0 \leq (u_{1+} + u_{1-}) \leq 1$ is $u_{1-} = 1$ and $u_{1+} = 0$, from which it follows also that $u_{10} = 0$. Thus, all horizontal bonds in the first layer beyond the crystal must be allocated to hairpin folds, i.e., returns with tight, adjacent reentry to the crystal. Sequences in this layer are exclusively of unit length and all of them are terminated by vertical bonds from the preceding layer. These restrictions do not apply to succeeding layers, provided, of course, that $q_1 \neq 0$. The foregoing arguments do not establish the value of q_1 and, hence, the number of adjacent folds in the first layer of the interphase. This quantity may be determined, however, by assigning it the value that maximizes the partition function for the interphase as a whole; see below.

According to the results deduced in the preceding paragraph, $C_1 = h_1^{-1}$. It follows from eq 29 that the factor $\omega_1 = \Omega_1^{1/N_0}$ entering the partition function per chain, i.e.

$$\omega = \prod\omega_i = \Omega^{1/N_0} \quad (33)$$

as the contribution for the first layer is

$$\omega_1 = \frac{1}{3}\left[\frac{\Gamma(1 - \sigma)^2\eta}{2q_1}\right]^{q_1}\left[\frac{1}{1 - q_1}\right]^{1-q_1} \quad (34)$$

It depends exclusively on q_1, apart from the parameters σ and η that characterize the lattice chain. The value assigned to q_1 determines p_2 according to eq 31. Values assigned to u_{2+}, u_{2-}, and h_2 then determine p_3 according to eq 18 and 19, and hence $\bar{p}_2 = (p_2 + p_3)/2$; eq 2 or 2′ furnishes q_2. The factor ω_2 for the second layer follows from eq 9, 26, and 29. Assignment of u_{3+}, u_{3-}, and h_3 permits similar evaluations for the third layer, etc.

The set of quantities u_{i+}, u_{i-}, and h_i for each layer $i \geq 2$, together with q_1 for the first layer, define the distributions of bonds and their connections in successive layers of the interphase. They thus describe the transition from the perfect order of the crystal to the disorder prevailing in the amorphous phase some distance removed from the crystal. The partition function ω, or Ω, for the interphase is fully defined by these quantities. Their values at equilibrium, subject to the boundary conditions incident on the interphase, may be established by maximization of ω. The number of variables precludes performance of the task by analytical methods. Inasmuch as the number of layers required for dissipation of order turns out to be fairly small, maximization is well within the capabilities of computational methods, however.

The numerical computations were carried out primarily by using the FMND subroutine of the SL-MATH package,[21]

Table I
Characteristics of Successive Layers in the Interphase for $\sigma = 0.60$ and $\eta = 0.01$

	layer i				
	1	2	3	4	5
p_i	1.000	0.810	0.443	0.336	0.332
q_i	0.095	0.374	0.611	0.666	0.668
u_{i+}	0.000	4.0×10^{-5}	0.141	0.198	0.200
u_{i-}	1.000	0.998	0.276	0.203	0.198
h_i		1.2×10^{-5}	7.5×10^{-3}	9.5×10^{-3}	0.010
S_i^{++}/N_0	0.000	0.000	0.019	0.043	0.044
S_i^{+-}/N_0	0.000	7.2×10^{-3}	0.126	0.145	0.144
S_i^{--}/N_0	0.095	0.184	0.072	0.045	0.043
$2\sum_{j=1}^{i} S_j^{--} N_0$	0.190	0.558	0.702		
$2\sum_{j=1}^{i} S_{j;1}^{--}/N_0$	0.190	0.192	0.193		
$\langle l_i^{--} \rangle$	1.00	2.00	3.39		

which is based on Powell's algorithm.[22] Some of the results thus obtained were checked by using the VA10A subroutine of Fletcher's solution.[23] Excellent agreement was obtained. The constraints $q_1 > 0$ together with $0 \leq u_{i+1} \leq 1$, $0 \leq u_{i-} \leq 1$, $0 \leq u_{i0} \leq 1$, and $h_i \geq 0$, in each layer $i \geq 2$ were applied in maximizing the partition function Ω given by eq 20, 29, and 34. All numerical results presented below were obtained for a lattice comprising a total of $L = 10$ layers. Calculations carried out for $L > 10$ show no perceptible differences from those for $L = 10$.

Numerical Results

The results obtained with the lattice parameters $\sigma = 0.6$ and $\eta = 0.01$ are listed in Table I. These parameters correspond to the cubic lattice with no preference for the straight "trans" junction over right-angle "gauche" junctions and with a conformational energy of 3.66 kcal mol^{-1} at 400 K opposing tight folds. These results show that the perfect orientational order of the crystalline region ($p_1 = 1$) is dissipated rapidly within the first three layers, isotropy being attained in the fourth layer (i.e., $p_4 \simeq {}^1/_3$ and $q_4 \simeq {}^2/_3$). That is, the interphase adjoining the lamellar crystallite subject to the values of the parameters quoted above consists of only three lattice layers. In the case of polyethylene, for example, the thickness of this interphase corresponds to a layer about 10 Å in thickness.

The course of the transition from perfect alignment to random disorder is indicated in Table I by the values of S_i^{++}/N_0, S_i^{+-}/N_0, and S_i^{--}/N_0 for the incidences of the several kinds of horizontal sequences in each of the first three layers. Nearly all of these sequences in the first two layers are negative reversals (S_i^{--}). Approximately 56% of the chains emanating from the crystal terminate in reversals within the first two layers; see the third from last row in Table I. All of the returns in the first layer necessarily occur through adjacent reentry, as the analysis presented above shows. In the second layer, adjacent folds account for attrition of only 0.2% of the initial flux of chains from the crystal (compare the figures in the penultimate row of Table I). In the third layer adjacent folds account for only 0.1% of the initial flux. Nearly all of the reversals in the second layer consist of two horizontal bonds that leapfrog[24] adjacent folds in the first layer, either along or across them. consequently, the average length $\langle l_2^{--} \rangle$ of a horizontal negative sequence in the second layer is very nearly 2.00. Additional reversals occur in the third layer, but with an average length of 3.4. Of all the chains

Table II
Effects of Adjacent Reversals on Characteristics of the Interphase for $\sigma = 0.60$

	η				
	0.0001	0.001	0.01	0.1	1.0
$q_1 = S_1^{--}/N_0$	0.087	0.089	0.095	0.117	0.210
S_2^{--}/N_0	0.154	0.178	0.184	0.203	0.130[a]
$\langle l_2^{--} \rangle$	2.00	2.00	2.00	2.01	2.45
S_3^{--}/N_0	0.105	0.081	0.072	0.052	
$\langle l_3^{--} \rangle$	3.13	3.34	3.39	3.34	
γ,[b] erg cm^{-2}	61.2	55.6	53.8	46.5	35.9

[a] Of these, 0.042 are adjacent reversals. [b] Calculated for a lattice with cross-sectional area per cell of $a = 18.3$ Å^2, corresponding to the polyethylene chain.

Table III
Effects of Adjacent Reversals on Characteristics of the Interphase for $\sigma = 0.80$

	η				
	0.0001	0.001	0.01	0.1	1.0
$q_1 = S_1^{--}/N_0$	0.072	0.075	0.085	0.098	0.167
S_2^{--}/N_0	0.145	0.148	0.169	0.190	0.137[a]
$\langle l_2^{--} \rangle$	2.00	2.00	2.00	2.01	3.11
S_3^{--}/N_0	0.097	0.093	0.070	0.049	0.046
$\langle l_3^{--} \rangle$	4.28	4.41	5.10	5.65	4.94
γ,[b] erg cm^{-2}	66.5	65.8	60.2	53.9	44.7

[a] Of these, 0.015 are adjacent reversals. [b] See footnote *b* in Table II.

emanating from the crystal, ca. 70% undergo reversal without proceeding beyond the third layer; see Table I. Of these, only 19.3% become engaged in adjacent folds.

Characteristics of the interphase for various values of the parameter η expressing conformational restraints on adjacent reversals are presented in Table II for $\sigma = 0.60$ and in Table III for $\sigma = 0.80$. Corresponding values of the statistical weight for a right-angle bend are $\tau = 1$ and ${}^1/_6$, respectively; see eq 24. These values cover the range that is appropriate for most real chains. Adjacent reentry, evidenced by q_1, increases with η, as expected. At $\eta = 1.0$ and $\sigma = 0.60$ it accounts for 42% of the emanant chains. A further 8.4% terminate in adjacent reversals in the second layer; see footnote *a* in Table II. For $\eta < 0.1$, a condition universally fulfilled by real polymer chains, adjacent reversals are confined almost exclusively to the first layer. Fewer than about 20% of the emanating chains are so involved. Only for $\eta > 0.1$ does the average length $\langle l_2^{--} \rangle$ of reversals in the second layer exceed 2.0 perceptibly. The average lengths $\langle l_3^{--} \rangle$ in the third layer increase with η for small η, but reach maxima in the vicinity of $\eta = 0.1$, depending on σ.

The effect of σ is comparatively small, as is apparent from comparison of Tables II and III. The preference for collinear junctions of units signified by the increase in σ from 0.60 to 0.80 decreases adjacent reentry in the first layer and, simultaneously, decreases the already rare occurrence of adjacent returns in succeding layers; compare footnotes *a* in Tables II and III. The average lengths $\langle l_3^{--} \rangle$ of negative horizontal sequences increase with σ.

The interfacial free energies γ calculated according to eq 30 and given in the last rows of Tables II and III decrease with increasing η. They are increased by increasing σ from 0.60 to 0.80.

The results above serve to specify the value in each layer of the order parameter defined as usual by

$$s_i \equiv 1 - (3/2)\langle \sin^2 \psi \rangle_i$$

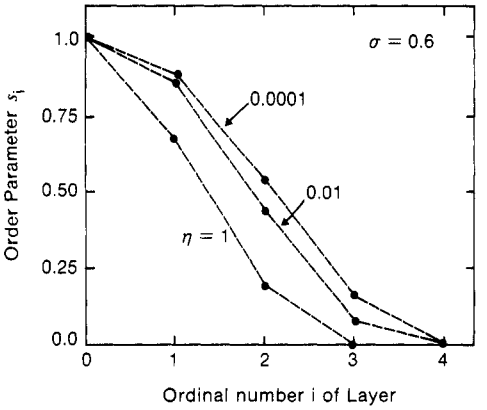

Figure 2. Variation of the (orientational) order parameter of chain segments in consecutive interfacial layers, calculated for $\sigma = 0.60$ and the values of η indicated. The dashed lines connecting the points are shown for convenience only.

where ψ is the angle between a bond and the normal to the crystal surface. Thus

$$s_i = 1 - 3q_i/2 \tag{35}$$

values of which are shown in Figure 2 for $\sigma = 0.60$ and the three values of η indicated therein. The decrease of the order parameter through the successive layers is rapid, but the rate of decrease diminishes with decrease in η. Thus, the thickness of the interphase increases with decrease in η, i.e., with increasing restraints on the occurrence of adjacent reversals and, hence, with decrease in adjacent reentry at the first layer.

Discussion

The parameter that is foremost in its effect on the calculations presented is η. Estimation of η from the free energy associated with the formation of an adjacent fold in a polymethylene chain leads to values in the range 0.005–0.02,[25] depending on the plane of the fold relative to the crystal lattice; it is certainly less than 0.05. Similar values are likely for other crystalline polymers. According to the lattice calculations presented above for values of η in the indicated range, ca. 70% of the emergent chains return to the face of the crystal from which they emerged without passing beyond the third layer. This result (±5%) is insensitive to the parameters η and σ within their allowable ranges, as may be seen by evaluating $2\sum_{i=1}^{3} S_i^{--}/N_0$ from the data in the columns of Tables II and III. Only a small fraction (given by $2q_1$) of these "return loops" are adjacent folds in the first layer. Their proportion depends on η and to a lesser extent on σ. Within the admissible range of η they account for fewer than 20% of the emergent chains. This deduction from the lattice model is consistent with results of measurements of neutron scattering by semicrystalline polyethylene[7,8,10-12] and isotactic polypropylene[9,12] over the intermediate range of scattering vectors (from 0.05 to 0.4 Å^{-1}). It is confirmed also by analysis of the infrared spectra of mixtures of protonated and deuterated polyethylenes.[26]

Monte Carlo calculations on lattice chains in the crystal–amorphous interphase reported recently by Mansfield[27] may be compared with these results. For values of Mansfield's parameters that correspond to our preferred values ($\eta \approx 0.01$ and $\sigma = 0.6$–0.8), his results are in approximate agreement with ours. Most of his calculations were carried out with no restraint on adjacent folds. Under this condition (i.e., $\eta = 1$) and for a bending energy of zero ($\sigma = 0.6$) he finds the incidence of adjacent folds to be 0.79, which is much greater than the results of our analytical treatment, according to which the combined fraction of chains engaged in adjacent folds should then be ca. 0.50, inclusive of those in the second layer as well as in the first; see Table II. The Monte Carlo procedure employed by Mansfield is nonergodic;[27] the effect this circumstance may have on his results is unclear.

For plausible values of η and σ the calculations here presented show that the parallel order of emergent chains is largely dissipated at the third layer, and it is vanishingly small at the fourth; see Figure 2. An interphase thickness of 10–12 Å is therefore indicated. This result stands in agreement with experimental determinations from Raman[3,28] and NMR[2,4] spectra of semicrystalline polyethylenes having lamellar morphologies.

Interfacial free energies γ given in Tables II and III range from 50 to 65 erg cm^{-2} for values of the parameters in the admissible ranges. The effect of lamellar thickness on the melting point for polyethylene leads to estimates[29-31] of 90–300 erg cm^{-2}, depending on the molecular weights. The fact that the theoretical estimates are close to those deduced for lower molecular weights[31] (with lamellar rather than extended-chain morphology) lends support to the view that persistence of order beyond the face of the crystal is the major source of the comparatively large interfacial free energy associated with the 001 face of the lamellar crystallite. The considerably larger values deduced for high molecular weights may be attributable to departures from equilibrium due to the rapidity of the crystallization process[6,32] (see below).

Several aspects of the analysis and calculations presented here require comment. First, the theory and the procedures followed in its application do not preclude the occurrence of cyclic conformations beyond the crystal and not engaged therein. The very small values of S_2^{++} in the second layer ensures that such rings residing in two or more layers of the interphase must be rare. Statistical considerations lead to the conclusion that the number of planar cyclic conformations within a given layer must be negligible as well.

Secondly, the theory addresses states of equilibrium in the lamellar interphase. To the extent that kinetic limitations on the process of crystallization from a melt consisting of entangled chains prevent attainment of equilibrium,[6,32] the partially ordered interphase may extend farther beyond the crystal surface with concomitant increase in the interfacial free energy. Also, the incidence of adjacent returns may simultaneously be reduced below the predictions of theory.

Finally, we have assumed throughout this paper that the surface of the lamellar crystallite is normal to the axes of the chains within the crystal. In fact, the lamellae are often tilted considerably, up to ca. 40° in the case of polyethylene,[33,34] from orthogonality to the axes of chain sequences, or "stems", within the crystal. The surface density of chains in the first layer of the interphase is thereby reduced, and the urgency of adjacent reentry in order to diminish the flux of chains is consequently relieved. This aspect and its effect on the character of the interphase are treated in detail in the following paper,[35] which deals also with other ramifications of the theory presented here.

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(36) The J_i used here corresponds to the quantities represented by the same symbol in previous papers.[19,20] Designation of them as fluxes in the present paper is inappropriate inasmuch as chains proceeding in both vertical directions are included.
(37) It is unnecessary to distinguish collinear from rectilinear connections between bonds in a given layer inasmuch as the distribution between horizontal connections of these two kinds is not subject to constraint. A factor representing this distribution has not been included in the partition function expressed by eq 29. Allowance for free equilibration between the two types of horizontal bond connections would reduce the factor to unity.

Chain Packing at Polymer Interfaces

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ABSTRACT: The lattice theory presented in the preceding paper is applied to various polymer interfaces of general interest. The reduction of surface chain density in lamellar semicrystalline polymers due to tilting of the interfacial plane from orthogonality to the chain sequences within the crystal allows the incidence of adjacent folds to diminish markedly; it may become negligible for a tilt angle >25°. Chain configurations in the noncrystalline region between two lamellar crystallites are little affected by the entry of chain sequences from the more remote surface if the interlamellar separation is greater than 4–5 lattice layers, or ca. 20 Å. In lamellar single crystals, the sites of chain reentry are separated predominantly by two or three lattice steps, according to the theory. For polymer melts bounded by a hard wall, the theory predicts a rather narrow interphase comprising no more than two lattice layers. The chain sequences tend to orient along the surface in the first layer adjoining the wall, whereas in the second layer they exhibit a slight preference for orientation normal to the surface. Similar characteristics of chain configurations hold for a thin layer between two walls, or in a thin film, unless the thickness approaches that of a monomolecular layer.

Introduction

In the preceding paper[1] (referred to as I hereafter), we present a lattice theory that describes chain packing in the interphase of a lamellar semicrystalline polymer. The molecular weight of the polymer is assumed to be sufficiently high to justify disregard of chain ends. Essential to this theory is the treatment of packing of polymer chains in the interfacial layers subject to two conditions of constraint: one of conservation and the other of continuity. The conservation condition (eq I-2 or I-2′) requires that all lattice sites be occupied discretely by segments, with the number of "horizontal" bonds joining segments in a given layer consistent with the "fluxes" of chains between this layer and those adjoining it. The continuity condition (eq I-3 or I-3′) asserts that the change in chain fluxes from one interlayer to the next must be equal to the difference between S^{--} and S^{++}, the numbers of negative and positive reversals, respectively, of chain directions involving one or more horizontal bonds in the given layer. Subject to these constraints, the configuration distribution is specified by the initial flux p_1 into the first layer and the set of quantities u_{i+}, u_{i-}, and h_i expressing the fractional occurrences of various connections of horizontal bonds in each interfacial layer i.

The treatment of interphase configurations in this manner and the derivation of the configurational partition function that follows (eq I-29) do not rest on specific assumptions concerning the nature of the interface. In principle, the theory is applicable to interfaces of any kind at which long polymer chains are the principal constituents. The interphase in lamellar semicrystalline polymers, discussed in the preceding paper, is treated by applying the boundary condition $p_1 = 1$ in the first layer, since the chains are taken to be perfectly aligned within the crystal

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