

Kinetics of Crystallization in Multicomponent Systems: II. Chain-Folded Polymer Crystals

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Using polyethylene as an example, the kinetics of growth of chain-folded polymer crystals is treated using a theory for the kinetics of growth of chains in multicomponent systems. The kinetic chain is considered to be a chain-folded strip growing on the lateral face of a chain-folded lamella, and the various components are the possible lengths l_j the polymer chain may form on folding at the end of the growing strip. Thus, the number of components is in principle infinite, but it is sufficient to take a number of the order of 20–50 for the calculations. By an iteration procedure, the calculations are carried out so that the average thickness of the strip is the same as that of the chain-folded lamella on which it grows. This necessitates modification of the rate constants that would be used without this requirement. The rate of growth, average thickness and its standard deviation, and the pair distribution are calculated as a function of undercooling and other relevant parameters of the system. The results for the rate of growth and thickness are similar to those of simpler theories, provided that the constant end-surface free-energy of those theories is replaced by a temperature dependent “effective” surface free-energy. The standard-deviation of the thickness is larger than commonly believed, values of 8 to 14 Å being typical. Consequently, the crystals as grown may have quite rough fold surfaces, although the equilibrium roughness will be less.

Key Words: Chain-folded crystals, Crystal growth, kinetics, multicomponent systems, surface free-energy.

1. Introduction

In the preceding paper in this issue [1]¹ (henceforth referred to as I) we demonstrated how a theory [2] (henceforth referred to as LDP) of the kinetics of growth of chains in multicomponent systems could be applied to the kinetics of crystallization in binary systems. The chain is considered to be a layer of molecules deposited at a growth step. The system chosen for study in I was that composed of the *n*-paraffins C₂₄H₅₀ and C₂₆H₅₄. It was shown in I that it is relatively easy using the LDP method to calculate the total flux, the composition of crystal growing from a given composition of liquid, and the pair distribution. Phase diagrams at equilibrium (total flux zero) and kinetic conditions (total flux greater than zero) were calculated, and the behavior of the flux with temperature deduced.

In I, there is some question about the relationship between the calculated flux and the crystal growth rate. In the present case a layer of chain-folded segments growing at the lateral surface of a chain-folded lamella forms the kinetic chain. This layer is expected to have only a very small number of kinks (if any) and hence the kinetics of growth of such a layer will quite accurately represent the rate of crystal growth. Indeed, this is the usual approach

taken in theories of polymer crystallization [3, 4, 5].

It is our purpose, then, to apply the LDP theory to the problem of the kinetics of formation of chain folded polymer crystals. Several quite adequate theories for this problem are available [3, 4, 5], but they all have some deficiencies. These arise primarily from the methods of treating fluctuations in the lamellar thickness. In the theory of Hoffman and Lauritzen [3], fluctuation is not treated directly. Under given conditions, it is assumed that a uniform lamella (or, in the sense of I, a uniform strip) will grow. The growth rate as a function of the thickness is calculated, and this is maximized with respect to thickness. The thickness which gives the maximum rate is considered to be the thickness growing under those conditions, and its value is given by the well-known equation, derived for small undercoolings,

$$l_g^* = \frac{2\sigma_e T_m^0}{\Delta h \Delta T} + \frac{kT}{a\sigma} \quad (1)$$

where l_g^* is the thickness, σ_e the end surface free-energy, Δh the heat of fusion per unit volume of crystal, σ the lateral surface free-energy, a the lateral dimension of the unit cell, T_m^0 the melting point of the infinitely thick lamella, T the absolute temperature, ΔT the undercooling and k Boltzmann's constant. The distribution in thickness of these uniform strips

¹ Figures in brackets indicate the literature references at the end of this paper.

about this maximum rate thickness is also calculated and shown to be relatively small [3].

Clearly, this treatment is not completely adequate. Rather than *assuming* that a uniform strip grows, and consequently laying down segments of uniform length at the end of the growing strip, the deposited segment length should be permitted to vary, so that each deposited segment should have all possible lengths. This larger problem was attacked by Frank and Tosi [4] in their extension of the Hoffman-Lauritzen theory by permitting a single fluctuation in the segment length.

In addition to this, Frank and Tosi investigated the effect of change in substrate thickness, as discussed in I in the section on the effect of the two-dimensional character of crystallization, but again by allowing only a single fluctuation. This treatment led to the disquieting result that crystallization cannot occur at an undercooling less than

$$\Delta T = \sigma T_m^0 / a \Delta h. \quad (2)$$

The only complete attack on the problem was made by Price, who permitted all possible lengths for each segment deposited at the end of the growing strip. However, Price adapted a formalism developed by Mullins [6] for the distribution in Markov chains any step of which may go into any of n states, and this method is useful only when equilibrium obtains in the growing chain. (This equilibrium does not, of course, pertain to the whole lamella, for the equilibrium thickness implicitly assumed in all the kinetic theories is infinite.) It should thus be exactly applicable only when the crystallization rate is zero, although for very small undercoolings not too much error is likely to be made, as pointed out in I. For polymer crystallization, however, rather large undercoolings are easily attainable (indeed, they are the rule) and under these conditions significant differences between this equilibrium treatment and a truly kinetic theory may arise. Moreover, the equilibrium theory cannot, of course, say anything about the rate of crystallization.

In this paper we solve a problem which in our view is a more reasonable theoretical approximation to the true situation in polymer crystallization than any of the previously given treatments. The problem is best formulated with reference to figure 1. We have a substrate, which represents an already-grown chain folded lamella, of thickness l_s . On the edge of this lamella a new strip of chain folded material is initiated and grows. The thickness of the initial segment of the strip laid down is l^1 ; the molecule then folds and lays down a segment of thickness l^2 ; this in turn folds and lays down a segment of thickness l^3 , etc. Each of the thicknesses l^1, l^2, l^3 , etc. may have any value. We wish an answer to these questions: (a) What is the rate of growth (at steady state) of the strip as a function of the relevant parameters of the system? (b) What is the average thickness of the strip? (c) What is the width and nature of the distribution about

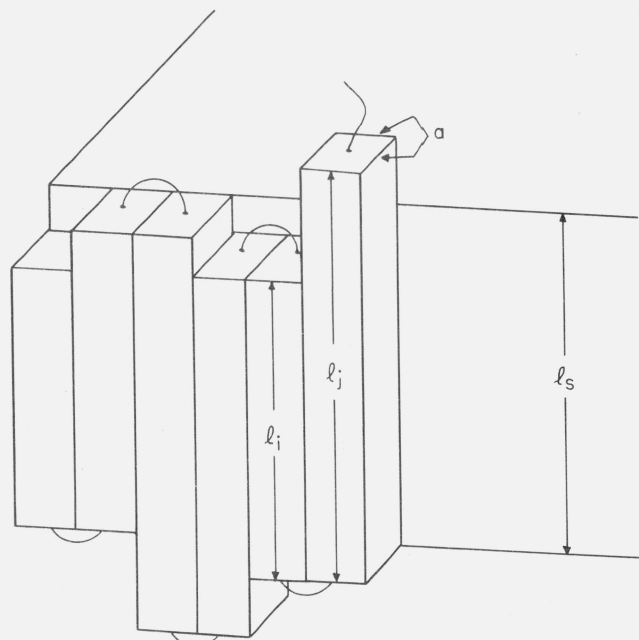


FIGURE 1. Schematic diagram for the model of a chain folded strip growing on the lateral face of a chain-folded lamella of uniform thickness.

The growing strip is the kinetic chain of the LDP theory [2], and the segment lengths (or thicknesses) l_i and l_j are the various components of the system.

this average? (d) What are the pair distributions, i.e., how much correlation is there between segments of various thicknesses?

It is clear that this problem is one that may be solved by the LDP theory. The "chain" in that theory is represented by the "strip" in this problem, and the components are the possible thicknesses l_j . These various thicknesses l_j are then considered as various "species" j , each species being one of the components of the system, and in what follows we will use the words "chain" and "strip," and "species j " and "thicknesses l_j " interchangeably. Considered in this sense, the "species" are evanescent things; they do not exist in the liquid phase and come into existence only when the random coil polymer chain in the liquid phase folds with the thickness l_j onto the lateral face of the growing crystal. Except for this character of the "species" this is, then, similar to the problem solved in I, but the number of components is, of course, larger than two. Indeed it is, in principle, infinitely large for an infinite molecular weight polymer. Since the LDP theory cannot easily be adapted to an infinite number of components, for the calculations a number of sufficient size must be taken so that the results are not affected by taking a larger number. This will be discussed more fully below.

An outline of the method by which these calculations may be made has already been given in I and in reference [2] and will not be repeated here. We will, however, give some pertinent equations which are necessary for the subsequent exposition. The LDP theory assumes only nearest neighbor interactions,

and assumes knowledge of the rate constants α_0^j , β_1^j , α^{ij} and β^{ij} , which are rate constants for the forward and backward processes for, respectively, the initial and subsequent steps in the chain. The kinetic equations for chain growth at steady state are solved in terms of quantities λ^j defined by

$$\lambda^j = \sum_{i=1}^n \frac{\alpha^{ij} \lambda^i}{\beta^{ij} + \lambda^i} \quad (3)$$

where n is the number of components in the system. The total flux is given by

$$S_T = \sum_{j=1}^n \frac{\alpha_0^j N_0 \lambda^j}{\beta_1^j + \lambda^j} \quad (4)$$

where N_0 is simply a scaling factor. The fraction f_i of species i in the grown chain is given by

$$f_i = \frac{\lambda^i N^i}{S_T} \quad (5)$$

and the N^i in turn are obtained from the recursion relation

$$N_\nu^i = \sum_{j=1}^n \frac{\alpha^{ij} N_{\nu-1}^j}{\beta^{ij} + \lambda^i} \quad (6)$$

with N_1^i given by

$$N_1^i = \frac{\alpha_0^i N_0}{\beta_1^i + \lambda^i} \quad (7)$$

For large ν , eq (6) becomes independent of ν and becomes the matrix equation

$$N^i = \sum_{j=1}^n \frac{\alpha^{ij} N^j}{\beta^{ij} + \lambda^i} \quad (8)$$

The pair distribution function, f_{ij} , which gives the fraction of i, j pairs in the system is given by

$$f_{ij} = \frac{\lambda^j \alpha^{ij} N^i}{\beta^{ij} + \lambda^j} \cdot \frac{1}{S_T} \quad (9)$$

With these equations, and knowing the rate constants, the complete problem may be solved, and the description of the method of calculation will be given in a subsequent section.

There are two processes conceptually possible in the chain fold problem that are not considered by the LDP theory, and one of which is not possible in I. These are processes by which a given species at a given position in the chain may be replaced by an

other species. In the LDP theory, the only way in which a certain species j (thickness l_j) at a given position ν in the chain (position in the strip) can change to species i is by removal of all species from positions $\nu, (\nu+1)$, etc. (i.e., "melting" of the strip back to position $(\nu-1)$) and then replacing species j at position ν with species i at that position. In the present problem, however, it would seem relatively easy to change species at a given location by readjustment in the lengths of segments between folds, provided only that the contour length of the deposited polymer chain remain unaltered. (In I such a change of species would require an actual interchange of molecules.) This process, which is not considered in this treatment, may, as will be discussed below, have important consequences in the experimental correlation of values of surface energies obtained from crystallization experiments with those obtained from melting point experiments. In the second process, the change of species j to species i at position ν can be accomplished by only *incomplete* removal of species j and subsequent refolding to the length appropriate to species i . The importance of this process is difficult to assess without a detailed theory in which it is incorporated.

Of these two processes the first clearly is not part of the sequential growth process of the strip, and arises from rearrangements after the strip has grown. Its effect in the present treatment will not change the growth rate, insofar as this can be considered as determined by the sequential deposition of segments at the lateral face of the growing lamella. Nor, in fact, will it change the average thickness of the strip, for the contour length of the polymer chain must be preserved. But it may have an important bearing on the ultimate *distribution* of thicknesses in the strip and will affect the pair and higher distributions. We will return to this point later; for the present it should be borne in mind that the distributions we compute are those determined by the kinetic process of growth and not necessarily those obtaining after rearrangements occur.

For the calculations we use parameters appropriate to polyethylene, since the crystallization behavior of this polymer is better understood than that of any other. Unlike the approach in I, our aim in this paper is an intensive study of this well-known system. The results are illustrative of what happens in polymer crystallization in general.

2. The Rate Constants

2.1. Preliminary Considerations

In order to apply the LDP theory we need to know the rate constants α_0^j , β_1^j , α^{ij} and β^{ij} , which are, respectively, the rate of initiation of new strips by depositing from the melt or solution the species l_j on a fresh substrate; the rate of dissolution of this back to melt or solution; the rate of adding species j to a strip whose

terminal element is species i ; and the rate of removal of species j from a strip whose terminal elements are i and j . Under kinetic conditions, these rate constants are impossible to deduce without knowing the exact details of the elementary processes involved in adding and subtracting species from the chain. However, it is shown in LDP that at equilibrium (total flux or rate of crystallization zero) the ratios of α_j^j/β_1^i and α^{ij}/β^{ij} are given by

$$\frac{\alpha_0^j}{\beta_1^j} = \exp [(\mu_j - \epsilon_j^0)/kT] \quad (10a)$$

$$\frac{\alpha^{ij}}{\beta^{ij}} = \exp [(\mu_j - \epsilon_{ij})/kT] \quad (10b)$$

where μ_j is the chemical potential of species j in the liquid phase, and ϵ_j^0 and ϵ_{ij} are, respectively, the free energies of initiating a chain and of adding species j to a chain terminating in species i . Clearly, the arguments of these exponentials are the changes in free energy of the system which result from removing the species j from solution or melt and placing it on the substrate, divided by kT .

These equations give only the ratio of the rate constants; without more knowledge we do not know how to apportion this free energy change between the forward and backward rate-constants. Frank and Tosi [4] considered the problem of apportionment and came to the conclusion that it was reasonable to assign all the free energy change to the energetically more unfavorable step. As in I, we, however, adopt a somewhat more empirical approach. We first *assume* that under kinetic conditions, the rate-constant ratio is still given by eqs (3). Then we carry out calculations for various arbitrary assignments of the free energy change.

The calculation of this free energy change is easily carried out by a method similar to that used by Price [5] and outlined in I. More elaborate and more accurate methods could doubtless be used. In particular, for crystallization from solution, the Flory-Huggins theory [7] of polymer solutions could be used to evaluate μ_j , but to enter into this much detail at this stage of our knowledge of polymer crystallization adds a detail which is unnecessary for the understanding of the elements of the problem. In the method used by Price each species added to the growing strip is considered to be a rectangular parallelepiped. We assumed it to have a square cross-section with an area one half the area of the (001) cross section of the polyethylene unit cell. This parallelepiped is considered to have a surface free energy σ per unit lateral area and σ_e per unit end area. Then, if the strip grows on a substrate of thickness l_s , and with reference to figure 1, we may write

$$\begin{aligned} \mu_j - \epsilon_j^0 = a^2 l_j \frac{\Delta h \Delta T}{T_m^0} - 2a l_j \sigma \\ - 2a \sigma U(l_j - l_s) + kT \ln \Delta l / \delta \end{aligned} \quad (11a)$$

$$\begin{aligned} \mu_j - \epsilon_{ij} = a^2 l_j \frac{\Delta h \Delta T}{T_m^0} - 2a^2 \sigma_e - 2a \sigma U(l_j - l_i) \\ - 2a \sigma U(l_j - l_s) + kT \ln \Delta l / \delta \end{aligned} \quad (11b)$$

where Δh is the heat of fusion per unit volume of crystal, T_m^0 is the melting point of the infinitely thick lamella, $\Delta T = T_m^0 - T$, and $U(x)$ is the function

$$U(x) = x \quad x \geq 0$$

$$U(x) = 0 \quad x \leq 0$$

Except for the term $kT \ln \Delta l / \delta$ (which is discussed below) these are the same energies used by Price, although he symmetrized the matrix composed of them because of the requirements of the Mullins treatment, and which in any case is the correct procedure at equilibrium. In our own case it will be noticed that the $\mu_j - \epsilon_{ij}$ matrix is not symmetric.

It will be noticed that in eq (11a) we do not have a term involving the end surface energy. This is not an omission. In our view, the first segment attached to the substrate has a length of dangling polymer chain on each end. One end (or possibly both) will subsequently fold, but we take the energy necessary for this into account in the energy for the next step (eq 11b, and see below under Apportionment of Free Energy). The first step, as we count them, does not involve folding. What *should* be added is a term involving the localization of the chain, but such a term is difficult to calculate. Moreover, the initial rate constant is important primarily in determining the temperature dependence of the total flux, and such terms as this would add negligibly to this temperature dependence. We also note that if the end of the polymer chain is considered to lie flush with the edge of the substrate (in our view a highly unlikely event) then this would involve a surface energy more like σ than σ_e .

The term $kT \ln \Delta l / \delta$ does not arise from fundamental causes but only because of computational limitations. In this term δ represents the minimum length difference between unlike species (generally the length of one unit cell c dimension) and Δl represents the difference in length between two adjacent species chosen for the computation, i.e., $\Delta l = l_{j+1} - l_j$. For very broad distributions, as are found in this problem as will be discussed fully under Results, it is necessary to have a very wide range of lengths. Now, the number of components in the system is this range of lengths divided by the difference in length between adjacent species. This length difference should be the "natural" length δ , but this makes the number of components greater than the capacity of the computer (on the order of 50 components). Hence, it is necessary to use a larger length, Δl . This in turn causes an underestimation of the free-energy change on crystallization because each "species" chosen for the calculation represents $\Delta l / \delta$ "natural" species, resulting in an incorrect estimation of the entropy of

$k \ln \Delta l / \delta$. When comparing calculations carried out for various Δl it is important to include this term.

The rigid-rod approximation for the species used in calculating these free energies is expected to be only a crude approximation to the true energies involved. This approximation will be worse the larger the length of species j is compared to the substrate. For large differences (what might be called large "overhangs") the portion of the chain extending above the substrate will doubtless be some type of random loop, and the use of the rigid-rod approximation should not be taken to imply that this is our view of the true physical state of these overhanging chains. The rigid-rod approximation is in our view, however, a good approximation for those chains shorter than the substrate and those only slightly longer. We use it for all lengths because it is difficult to know exactly at what lengths to begin treating the overhanging chains as random coils, and because such treatment would in itself be subject to considerable uncertainty. All that we can say with certainty about these greatly overhanging chains is that their free energy is higher than that of the same chains in the crystalline state and the rigid-rod approximation adequately takes this into account. Moreover, to treat properly large loops of random coils on the surface would involve more than nearest neighbor interactions, and a thorough treatment of the problem would become quickly intractable.

As have previous authors, we neglect those (presumably rare) occasions where l_j may be less than l_s but still protrude beyond the substrate.

2.2. The Effect of the Two-Dimensional Nature of the Problem

As already discussed in I, the process of crystallization has a two-dimensional character that makes it difficult to treat by the one-dimensional LDP theory. Thus, when the composition of the growing strip is calculated by the LDP theory, there is no assurance that its average thickness, defined as

$$\bar{l} = \sum_j f_j l_j \quad (12)$$

where f_j is the fraction of species j in the grown strip, is the same as that of the substrate. Clearly, if our calculations are to represent a real physical process of crystallization, this is a minimum requirement. It would appear that this physical process could easily be represented by choosing a substrate thickness l_s , growing a strip on it, using this strip as a substrate for a subsequent strip and continuing the process until $l_s = \bar{l}$. This is essentially the procedure used by Price. This would meet the requirement that the thickness of the growing crystal would be constant, but would not assure us that the pair and higher distributions in the strip and the substrate would be the same; but it would be a first and reasonable approximation to the true physical situation.

If this process is carried out with the rate constants calculated by eqs (10) using the energies in eqs (11), it is found that crystallization does not proceed at temperatures above by some finite undercooling, essentially as was found by Frank and Tosi. Above these temperatures the thickness converges to a value below that stable for that undercooling and the flux drops to zero. This does *not* occur if the thickness of the substrate is not allowed to vary.

In this problem, as also in I, when rate constants appropriate to a one-dimensional problem are used for a two-dimensional one, difficulties are encountered. In particular, we would expect our theory to predict crystallization at temperatures near the melting point for it is at these temperatures that the steady-state conditions assumed would be most likely to obtain. Thus, the result that crystallization does not proceed at a temperature *above* a relatively large undercooling (about 33 degrees) seems to us to be the result of an incorrect treatment of an essentially two-dimensional problem by a one-dimensional theory, and results as an artifact of the treatment. However, it should be noted at this time, that in the process of correcting this difficulty we trade it for another, but perhaps more explicable one. This is discussed fully in the section on the Total Flux.

The only proper way to overcome this difficulty would be to construct a truly two-dimensional theory. This would be a truly formidable task. As in I, we adopt a more realistic course of action and ask if there is some way of modifying the rate constants so that physical results will be obtained over the entire temperature range.

In order to answer this question, the same type of variational analysis carried out in the appendix to I may be carried out for this problem. That is, an ensemble consisting of crystals of various thicknesses each with strips of various thicknesses and lengths growing on them is considered. The free energy of this system is expressed in terms of the number of strips and their lengths, compositions, thickness and substrate thicknesses. This free energy is minimized with respect to these variables. Then, using the principle of detailed balance it may be shown that the rate constant ratio that minimizes this free energy *at equilibrium* (total flux zero, but not necessarily at the melting point) is given by

$$\frac{\alpha_j^0}{\beta_j^0} = \exp \frac{1}{kT} \left[a^2 l_j \frac{\Delta h \Delta T}{T_m^0} - 2a\sigma l_j - a\sigma |l_j - l_s| \right] \quad (13a)$$

$$\frac{\alpha_j^0}{\beta_j^0} = \exp \frac{1}{kT} \left[a^2 l_j \frac{\Delta h \Delta T}{T_m^0} - 2a^2 \sigma_e - 2a\sigma U(l_j - l_i) - a\sigma |l_j - l_s| \right]. \quad (13b)$$

During this derivation it was necessary to assume that the distribution of species in the strip was symmetric. This will not necessarily be the case under kinetic conditions.

These rate constants are very similar to those in eqs (11), the only difference being the replacement of the term $2a\sigma U(l_j - l_s)$ with $a\sigma|l_j - l_s|$. The term $2a\sigma U(l_j - l_s)$ arose because we had a very definite process in mind of placing species of thickness l_j on a substrate of thickness l_s . It is in just this step that the two-dimensional character of the problem becomes apparent, and, as already pointed out, we cannot take this two-dimensional character exactly into account. Now, if instead of considering the *formation* of a crystal in the dimension normal to the growing strip we were asked to calculate the free-energy of an already grown crystal, we should use a term just like $a\sigma|l_j - l_s|$. This makes the appearance of this term somewhat more plausible.

In a somewhat more empirical vein, it should be noted that, in the ratio of $\alpha^{\dot{v}}/\beta^{\dot{v}}$ in eqs (11) (which determines the composition of the growing strip) either of the U functions may be replaced by an absolute value function. Of the four possibilities only that expressed by eqs (13) leads to the result that crystallization proceeds continuously to T_m^0 , whatever the distribution of free-energy to forward and backward rate constants. Moreover, symmetrizing the rate constants as was done by Price also leads to a cessation of crystallization at all temperatures above a finite undercooling. In short, the rate constants given by eqs (13) are the only ones that do not lead to a cessation of crystallization above a finite temperature below T_m^0 .

Without further discussion, then, we take the same approach as in I and *assume* that these rate-constant ratios, which are derived for equilibrium, will also hold under kinetic conditions. We then have left the problems of the apportionment of the free-energies and the treatment of interfacial transport terms.

2.3. The Apportionment of the Free Energies

As previously discussed, without a detailed model of the processes involved in the deposition of species on the growing strip, it is not possible to know how the free-energy changes in crystallization are to be apportioned to the forward and backward rate constants. Rather than assume such a model, or try to derive it, we adopt a more empirical approach and carry out calculations for various arbitrary apportionments.

First, we have the problem of apportioning the free-energy to the rate constants for the initial step in the chain, viz, $\alpha_i^{\dot{v}}$ and $\beta_i^{\dot{v}}$. These rate constants do not affect the composition of the chain, but they do strongly affect the total flux. We cannot hope to predict this accurately in any case, and all we can do is try to predict its dependence on temperature.

There are two extreme cases to be considered: (a) All the free energy in the forward reaction rate constant and (b) all in the backward rate constant. In the former case, $\beta_i^{\dot{v}}$ in unity; in the latter, $\alpha_i^{\dot{v}}$ is unity, and it is easy to derive the relationship between the total flux in the two cases. If we let S_T^{α} and S_T^{β} represent the fluxes in the two cases we may write from eqs (4) for the total flux in each case

$$S_T^{\alpha} = \sum_j \frac{N_0 \alpha_i^{\dot{v}} \lambda^j}{1 + \lambda^j}$$

$$S_T^{\beta} = \sum_j \frac{N_0 \lambda^j}{\beta_i^{\dot{v}} + \lambda^j}$$

Now, for the second case, $\beta_i^{\dot{v}}$ is $(\alpha_i^{\dot{v}})^{-1}$ for the first case. Hence we may write

$$S_T^{\beta} = \sum_j \frac{N_0 \alpha_i^{\dot{v}} \lambda^j}{1 + \alpha_i^{\dot{v}} \lambda^j}$$

Now, if both λ^j and $\alpha_i^{\dot{v}}$ are much less than unity, both fluxes are approximately the same. Near T_m^0 , $\lambda^j \ll 1$, and $\alpha_i^{\dot{v}}$ is always much less than unity. At rather large undercoolings λ^j is no longer small, and may be as high as 0.2. Nevertheless, we only carry out calculations in which all the energy is assigned to the forward rate constant and take $\beta_i^{\dot{v}} = 1$. In a sense this is physically reasonable, since it makes the free energy a "barrier" to be overcome in the initial step of the chain, and is the apportionment that Frank and Tosi derived as being correct.

For the subsequent steps in the chain we envision the following process. When a polymer chain has laid a segment on the growing strip, before it can lay down another segment on the strip it must form a fold. This requires an energy approximately of the amount $2a^2\sigma_e$ which therefore acts as a "barrier" to subsequent growth of the strip. We thus put this term in the $\alpha^{\dot{v}}$. The remainder of the energy we apportion in arbitrary ways, as was done in I. If we let E_{ij} be the argument of the exponentials in eq (13b) then we take

$$\alpha^{\dot{v}} = \exp[-2a^2\sigma_e/kT] \exp[\varphi(E_{ij} + 2a^2\sigma_e)/kT] \quad (14a)$$

$$\beta^{\dot{v}} = \exp[(\varphi - 1)(E_{ij} + 2a^2\sigma_e)/kT] \quad (14b)$$

where φ is an arbitrary parameter the value of which can range from zero to unity. We shall see that the value of φ has a significant effect on the results, particularly at high undercoolings.

2.4. The Effect of the Interfacial Transport Term

The rate constant ratios expressed by eqs (13) were derived at equilibrium (total flux zero) and as a result do not contain terms expressing the rate of transport or diffusion of species from the melt or solution to the growing interface. If this diffusion or transport depends upon both the diffusing species (j) and the species at the end of the chain (i), then the rate constants given by eqs (12) should be multiplied by factors a_{ij} and b_{ij} , as already pointed out in I. Unfortunately, it seems almost impossible at this time to decide what these factors ought to be.

A simpler but less correct approach is to assume that a_{ij} and b_{ij} are independent of i and j . If this is done, then, as discussed in I, the composition and

distribution in the chain is not affected. The only result is that the total flux as calculated by the LDP theory should be multiplied by a transport term. Because this term will have an Arrhenius or WLF [8] temperature dependence, the temperature dependence of the total flux calculated here will be somewhat in error, and this error will become greater the greater the undercooling and the closer to the glass-transition temperature the conditions become. However, as will be seen below, other effects intervene at such large undercoolings. Nevertheless, it will be understood that where we discuss the temperature dependence of the total flux we do not include this transport term.

3. Method of Calculation

The constants, parameters and the variables and their ranges used in the computations are given in table 1. The equilibrium melting point, heat of fusion and lateral dimension are those of polyethylene. The parallelepiped shown in figure 1 was assumed to have a square cross section, but this is expected to have no significant effect on the calculations. Three different values of the end and lateral surface energies were used, although most of the calculations were carried out with the values $\sigma_e = 60$ ergs/cm² and $\sigma = 10$ ergs/cm². The values of σ_e given in the literature cover a wide spectrum, with the value 60 ergs/cm² being on the low side [4, 5, 9, 10, 11]. As we will see, however, the actual value of this constant is less important than the value of a parameter derived from it. The value of 10 ergs/cm² is a normal value from several different sources [9, 12]. The number of components was usually taken to be 21, although often the calculations were repeated with 50 components, particularly under those conditions where the deposited layer had a broad distribution of lengths. With the value of Δl shown, these numbers of components gave ranges of lengths of 105, 250, 210, and 500 Å. Usually the combinations $n = 21$, $\Delta l = 5$, or $n = 50$, $\Delta l = 5$ were used.

TABLE 1. Value and range of parameters for calculation

Temperature	360–415.2 °K
$\Delta h/k$	21.2 °K/Å ³
T_m^0	415.2 °K
Δl	5 ^a , 10 Å
Number of Components	21, 50
σ_e	82.8, 60, 41.4 ergs/cm ²
σ	5, 10 ^a , 20 ergs/cm ²
φ	0, 1/2, 1
a	4.285 Å

^a Most commonly used values.

The calculations were carried out as follows. First, for the temperature in question, a substrate thickness l_s close to the final expected layer thickness was chosen. The lengths l_j were chosen so that the shortest length was given by $l_s - \left(\frac{n-1}{2}\right) \Delta l$ for n odd, and

$l_s - \frac{n}{2} \Delta l$ for n even. If this minimum length was less than zero, the value 5 Å was chosen. With this value of substrate thickness, lengths l_j , and the other relevant parameters, α_j^i , β_j^i , α^{ij} and β^{ij} were calculated from eqs (14). From these, the values of λ^j defined by eq (3) were calculated by the iteration procedure outlined in I and LDP until convergence to one part in 10⁷ was obtained. From these λ^j , the N_j^i were calculated by the recursion formula eq (6) until again convergence to one part in 10⁷ was obtained, and then the f_i were calculated by eq (5). From these last quantities the average thickness \bar{l} of the grown strip was computed by eq (12). This was now compared to l_s . If the difference was greater than one part in 10⁷, the whole procedure was repeated using \bar{l} as the new l_s . A new set of lengths l_j was chosen by the procedure already outlined, which had the advantage in most cases of having one of the l_j equal to \bar{l} when convergence between \bar{l} and l_s was obtained. When \bar{l} was the same as l_s within one part in 10⁷, the iteration was discontinued and S_T and the f_i computed by eqs (4) and (5) respectively. For those computations with $n = 21$, f_{ij} (eq (9)) were also computed. In addition to these, two other quantities of interest were calculated. The first, which we denote by s_l , is the standard deviation in l , and is defined by

$$s_l = \left(\sum_i f_i (l_i - \bar{l})^2 \right)^{1/2}.$$

This gives a measure of the spread in the distribution. The second, which we denote by \bar{g} , is the average free energy per segment in the strip, and is given by

$$\begin{aligned} \bar{g} = \bar{l} a^2 \frac{\Delta h \Delta T}{T_m^0} + kT \sum_j f_j \ln f_j - kT \sum_{i,j} f_{ij} \ln f_{ij} \\ - a\sigma \sum_j f_j |l_j - l_s| - a\sigma \sum_{i,j} f_{ij} |f_i - f_j| \\ - 2a^2 \sigma_e + kT \ln \Delta l / \delta. \end{aligned} \quad (16)$$

We will now discuss in some detail the behavior of the various quantities calculated. We are particularly interested in the total flux, S_T ; the average length, l ; and the composition of the chain, f_i and f_{ij} .

4. Results

4.1. The Average Thickness and Its Standard Deviation

A plot of \bar{l} against the reciprocal of the undercooling is given in figure 2 for $\sigma = 10$ ergs/cm², $\sigma_e = 60$ ergs/cm², and for the three values of φ .

The curves are similar to those already presented by Price and Frank and Tosi. They have a linear portion at low undercooling, fall to a minimum value at an undercooling of 20 to 25 degrees, and then rise rapidly to very large values. We will henceforth denote the temperature at which the thickness diverges by T_a . The behavior in this region depends markedly on

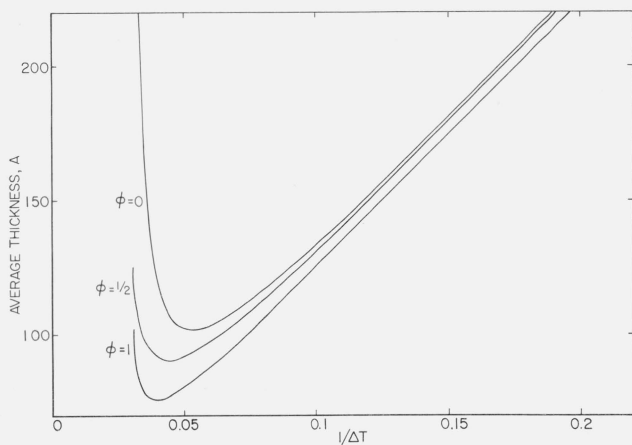


FIGURE 2. Plots of average thickness of chain folded crystals against reciprocal of the undercooling for $\sigma = 10$ ergs/cm², $\sigma_e = 60$ ergs/cm², and for three values of ϕ .

The almost linear portion at low undercoolings extends to the melting point.

the value of ϕ , but discussion of these curves will be postponed until we have presented the results for s_l .

The results for s_l against undercooling are given in figure 3 for $\sigma_e = 60$ ergs/cm² and $\sigma = 10$ ergs/cm² for the three values of the parameter ϕ . It will become clear from the subsequent discussion in this section that s_l is independent of σ_e (over any reasonable range of values), the experimental value of which has considerable uncertainty, but is strongly dependent on σ , which fortunately is somewhat better known. The behavior of s_l varies considerably with ϕ . In all cases, the value of s_l approaches 8.133 Å at T_m^0 , but below this temperature the curves diverge considerably. For $\phi = 1$ and $\phi = 1/2$, the change of s_l with temperature is not very great, but for $\phi = 0$, s_l becomes very large as the temperature at which \bar{l} goes to infinity is approached (figure 2). In fact, detailed investigation in this region indicates that not only does \bar{l} approach infinity, but, for $\phi = 0$, the width of the distribution f_j also approaches infinity, with a consequent divergence of s_l at this temperature.

It is interesting to compare our results for the value of "surface roughness" as expressed by figure 3 with those of Price. On the figure there is indicated the equilibrium² value of s_l , which is closest to the curve for $\phi = 1$, but in any case this is considerably larger than the 1 to 2 Å roughness quoted by Price. Indeed, the minimum values of 8 to 10 Å obtained here for $\phi = 1/2$ and $\phi = 1$ are relatively large for crystals of ordinary thickness (125 to 150 Å), to say nothing of the case for $\phi = 0$, which would predict very furry crystals indeed at large undercoolings. However, for experimental purposes, the differences in these curves may be less important, for at the normally attainable undercoolings (for polyethylene) of 10 to 15 °C,

² The "equilibrium" value of s_l is the value of s_l that minimizes the free energy of a chain folded crystal when the thickness of the crystal is maintained constant. The method of calculation will be presented in a subsequent publication.

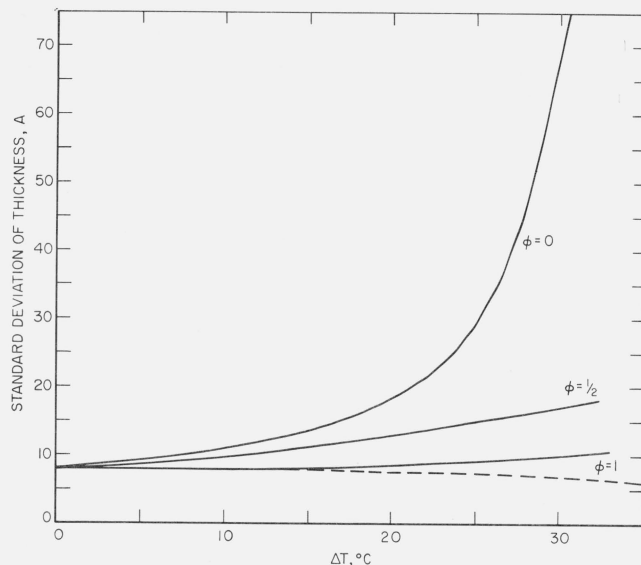


FIGURE 3. Plots of standard deviation of thickness (eq 15 of the text) of chain folded crystals against undercooling for $\sigma = 10$ ergs/cm² and for three values of ϕ .

The standard deviation of the thickness is essentially independent of σ_e for reasonable values of thickness. The dashed curve represents the value of s_l that minimizes the free energy of a chain folded crystal when the mean thickness of the crystal is maintained constant.

s_l varies only from 8.5 to 14 Å for the various values of ϕ .

We now return to a discussion of the curves in figure 2. The linear portion of the curves makes it tempting to analyze their behavior by an equation analogous to eq (1). We accordingly define two parameters σ_{eff} and δl , and express the average thickness at any temperature T by the equation

$$\bar{l} = \frac{2T_m^0 \sigma_{\text{eff}}(T)}{\Delta h \Delta T} + \delta l(T). \quad (17)$$

This is of the same form as eq (1), with $\delta l(T)$ replacing $kT/a\sigma$, and with σ_e replaced by a temperature dependent σ_{eff} . The parameter σ_{eff} is amenable to non-arbitrary definition; hence the form of eq (17). That is, $\sigma_{\text{eff}}(T)$ may be defined, in analogy to the theory of Lauritzen and Hoffman, by

$$2a^2 \sigma_{\text{eff}} = \frac{a^2 \bar{l} \Delta h \Delta T}{T_m^0} - \bar{g} \quad (18)$$

where \bar{g} is defined by eq (16). From this equation it will be seen that σ_{eff} is given by

$$2a^2 \sigma_{\text{eff}} = 2a^2 \sigma_e - kT \sum_j f_j \ln f_j + kT \sum_{i,j} f_{ij} \ln f_{ij} + a\sigma \sum_j f_j |l_j - l_s| + a\sigma \sum_{i,j} f_{ij} |f_i - f_j| - kT \ln \Delta l / \delta. \quad (19)$$

In the theory of Lauritzen and Hoffman, σ_e is of course essentially temperature independent, and in the present work it is interesting to compare σ_e and σ_{eff} .

Accordingly, in figure 4 we show a plot of $\sigma_e - \sigma_{\text{eff}}$ for several different values of the lateral surface energy σ , and for several different values of the parameter ϕ . First, it will be noticed that since σ_e is a constant, σ_{eff} is rather strongly temperature-dependent. Secondly, it will be noticed from the curves for $\sigma=10$ that there is a strong dependence on ϕ , which, however, becomes progressively smaller as ΔT approaches zero, and disappears entirely at T_m^0 . Thirdly, it will be noticed that the difference between σ_e and σ_{eff} is dependent upon σ , and is a significant fraction of σ_e . From the definition of σ_{eff} , it is clear that if f_i and f_{ij} are independent of σ_e , then $\sigma_e - \sigma_{\text{eff}}$ will also be independent of it. But from the definition of the rate constants, the term in $\bar{l}2a^2\sigma_e/kT$ is simply a multiplicative factor independent of i and j and hence does not influence the distribution. We have the result, then, that $\sigma_{\text{eff}} - \sigma_e$ is a measure of the width of the distribution, which is strongly influenced by σ , as is evident from the expressions for the rate constants. Thus, $\sigma_{\text{eff}} - \sigma_e$, measures, so to speak, the same thing s_l does, but is somewhat more basic, for, as will be discussed in the section on the total flux, σ_{eff} controls this quantity.

There is a rather simple physical explanation for the behavior of $\sigma_e - \sigma_{\text{eff}}$. For a rough surface, a great deal of extra lateral surface is exposed, and this would tend to make the effective surface free-energy greater than the surface energy of the smooth surface, σ_e . This is expressed by the terms $a\sigma \sum_i f_i |l_i - l_s|$ and

$a\sigma \sum_{i,j} f_{ij} |f_i - f_j|$ in the definition of σ_{eff} . These terms would tend to raise the free energy of the solid phase compared to the (higher) free-energy of the liquid phase. But the introduction of this rough surface introduces a "mixing entropy" expressed by the terms

$kT \sum f_i \ln f_i$ and $kT \sum f_{ij} \ln f_{ij}$. The mixing entropy arises from the various configurations a polymer in the crystal may adopt. These terms tend to lower the free-energy of the solid as compared to the liquid. At the equilibrium these latter terms must win out and override the effect of the lateral surface terms, for if they did not there would be no mixing. Thus, at the melting point $\sigma_e - \sigma_{\text{eff}}$ is positive, rather than negative as might be expected from considerations of surface energy alone. However, for highly nonequilibrium distributions, such as occur with $\phi=0$ near the divergence temperature T_d (see fig. 3), the lateral surface terms win out and $\sigma_e - \sigma_{\text{eff}}$ is negative, and hence $\sigma_{\text{eff}} > \sigma_e$. Note that σ_{eff} can be equal to σ_e under two conditions. The first and obvious one is when all the species are of the same length and the distribution is therefore a delta function. This is the Hoffman and Lauritzen case. The second, and less obvious, is when for kinetic reasons sufficient lateral surface is exposed that the terms relating to those in eq (19) just balance the mixing terms. This, as explained above, cannot happen at equilibrium.

The value of δl calculated from eq. (17) at each temperature is shown in figure 5 plotted against undercooling for the same values of the parameters as figures 2 and 3. The values for $\phi=0$ and $1/2$ are about the same up to undercoolings of approximately 20 degrees and then the $\phi=0$ curve rapidly increases, as would be expected from the behavior of the curves of figure 2. The curve for $\phi=1$ is somewhat lower over the whole range, but also diverges at T_d .

It is interesting to compare the values of δl in the range of 0 to 20 degrees undercooling with the term $kT/a\sigma$ in eq (1). The values of δl in this range of ΔT vary from about 18 to 35 Å, whereas $kT/a\sigma$ in this range by comparison is constant and equal to 12.9 Å.

The undercooling at which \bar{l} approaches infinity is given by $\sigma T_m^0/a\Delta h$ for all values of ϕ , although this is

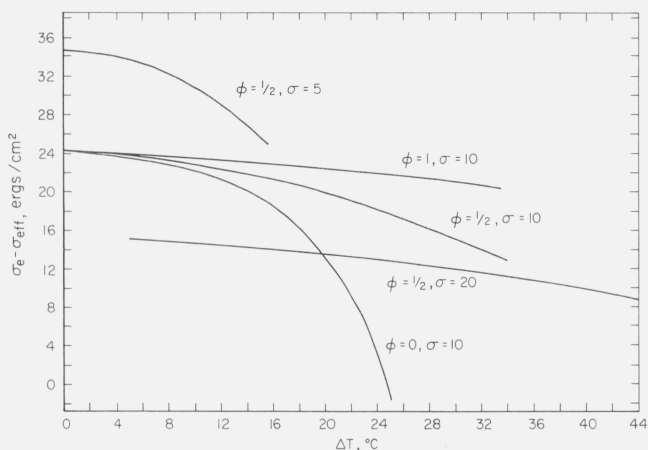


FIGURE 4. Plots of $(\sigma_e - \sigma_{\text{eff}})$ (eq 19 of the text) versus undercooling for various values of σ and ϕ .

The quantity $(\sigma_e - \sigma_{\text{eff}})$ is not appreciably dependent on σ_e unless σ_e is very small.

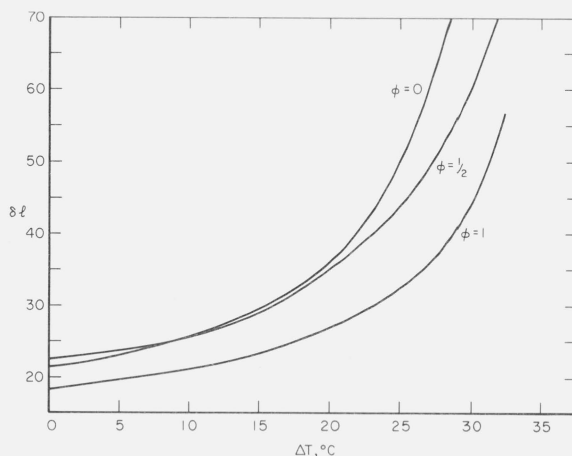


FIGURE 5. Plots of δl (eq 17 of the text) versus supercooling for $\sigma = 10$ ergs/cm², and for three values of ϕ .

These plots are independent of σ_e unless σ_e becomes too small. The curves for $\phi=0$ and $\phi=1/2$ do not actually cross one another, the $\phi=0$ curve being above the $\phi=1/2$ curve throughout the whole range.

difficult to prove analytically except for $\varphi=1$, and is as much a deduction as a proof. It is interesting to note in this regard, however, that this is the same undercooling at which Price found such a divergence, but is *half* the undercooling at which Frank and Tosi found it. The existence of this divergence is not the result of a fluctuation treatment of the problem, for it is also found in an extension of the Hoffman-Lauritzen treatment [13]. In that treatment as in that of Frank and Tosi it occurs at twice the undercooling found here. For $\sigma=10$ ergs/cm², the undercooling at which the divergence occurs in our work is 33.14 °C.

This is a rather high undercooling which is very difficult or perhaps impossible to achieve experimentally in crystallization from the melt, but can be achieved in crystallization from solution. Nevertheless at such high undercoolings it may be that the steady-state conditions required by the theoretical treatment are never attained. We return to this point when discussing the behavior of the total flux.

We will not attempt at this time to fit experimental results with our theoretical treatment. This rather long and involved task will be reported in a subsequent publication. It will be shown there that in order to fit the known experimental results (with any theory, not necessarily our own) it is necessary to invoke a small temperature dependence for σ as well as the temperature dependence for σ_{eff} and δl found here.

As a result of this analysis we can say that over most of the range of interest, the variation of lamellar thickness with temperature may be represented by an equation of the form of eq (1), namely eq (17). However, the parameters σ_e and δl must be considered temperature dependent, the exact amount of this dependence depending on the value of φ appropriate to the problem.

4.2. The Total Flux

The behavior of the total flux, S_T , which, except for transport terms, is representative of the rate of crystallization, is best analyzed by an equation analogous to that derived by Frank and Tosi. In our notation this may be written

$$S_T = S_T^0(\varphi, T) \left[\exp\left(\frac{a\Delta h\Delta T}{\sigma T_m^0}\right) - 1 \right] \exp\left(\frac{-4a\sigma\sigma_e T_m^0}{\Delta h\Delta T k T}\right). \quad (20)$$

In this expression the preexponential term $S_T^0(\varphi, T)$ is expected to have only a slight temperature dependence as compared to the exponential terms, as it should if this representation is to be of value. Moreover, it is expected that the dominant term is

$$\exp\left(-4a\sigma\sigma_e T_m^0 / \Delta h\Delta T k T\right),$$

the other having only a minor effect. We anticipate that σ_e in eq (20) should be replaced by σ_{eff} .

A plot of $\Delta T \log S_T$ against ΔT is given in figure 6 for the same value of the parameters as in figures 2 and 3. For low to moderate undercoolings, the

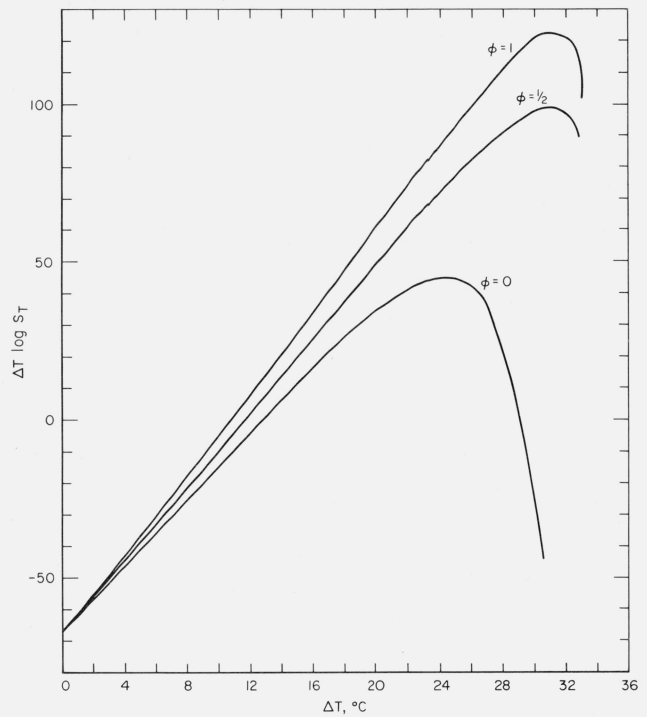


FIGURE 6. Plots of $\Delta T \log S_T$ versus undercooling for $\sigma = 10$ ergs/cm², $\sigma_e = 60$ ergs/cm², and for three values of φ . The curves are very nearly linear at low undercoolings.

curves are very nearly linear with an average slope that depends on φ . This near linearity indicates that in this range the terms $S_T^0[\exp(a\Delta h\Delta T/\sigma T_m^0) - 1]$ are indeed of negligible variation compared to the other term in eq (20). However, near T_d the curves have a maximum. For the $\varphi=0$ curve, this maximum is caused in fact by the very large values of σ_{eff} , but in the other curves it is caused by a fall-off of the S_T^0 term. It is to be noted that this maximum exists *without* a transport term and is not occasioned, as usually accepted, by the activation energy for transport becoming the dominant factor in the nucleation process. The flux falls to zero at an undercooling of $\sigma T_m^0/a\Delta h$, and we will return to this important point at the end of this section.

In spite of this maximum in the total flux, over a large range of undercooling the curves are approximately linear, which indicates that over this range $S_T^0(\varphi, T)$ is indeed approximately constant. To illustrate this, in figure 7 we show the value of $\log S_T^0(\varphi, T)$ plotted against undercooling for a range of ΔT of 30 °C. (The temperature T_d corresponds to a ΔT of 33.14 °C.) Over this range $S_T^0(0, T)$ shows a variation of about one order of magnitude, while $S_T^0(1/2, T)$ and $S_T^0(1, T)$ show a variation of about one half order of magnitude. Compared to the variation in the exponential factors, this variation is completely negligible. In fact, over the range of undercoolings considered, the variation of

$$(\exp[a\Delta h\Delta T/\sigma T_m^0] - 1),$$

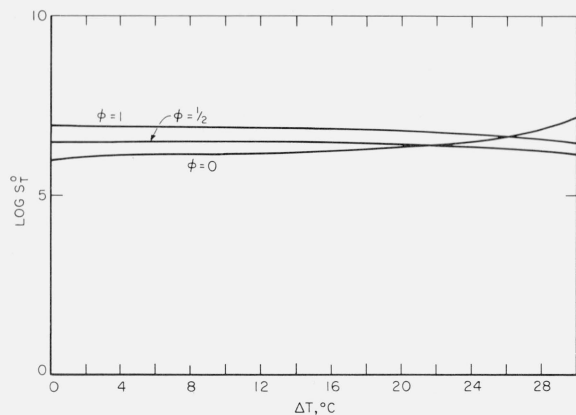


FIGURE 7. Plots of $\log S_f^0$ (eq 20 of the text) versus undercooling for $\sigma = 10 \text{ ergs/cm}^2$, $\sigma_e = 60 \text{ ergs/cm}^2$, and for three values of ϕ .

is also negligible, as is indeed the variation with ϕ . Thus we conclude that the total flux, for an undercooling of as much as 30 °C is given with more accuracy than is usually necessary for the interpretation of growth rate data by the expression

$$S_T = S_f^0 \frac{a\Delta h\Delta T}{\sigma T_m^0} \exp\left(\frac{-4a\sigma\sigma_{\text{eff}}T_m^0}{\Delta h\Delta T kT}\right) \quad (21)$$

where S_f^0 is a constant.

Now, eq (21) has an important consequence for the interpretation of growth rate data, for it indicates that to the extent that this theory is representative of the processes involved in the growth of chain folded polymer crystals, $\sigma\sigma_{\text{eff}}$ is the parameter that controls the temperature dependence of the growth rate, and not $\sigma\sigma_e$. As we have seen, for low undercoolings, σ_{eff} may be quite small compared to σ_e and independent of ϕ .

With this interpretation, there is no reason to expect the value of the end surface free-energy computed from crystal growth data to be the same as the value of the end surface free-energy obtained from, for example, experiments on melting point against lamellar thickness. The reason for this is as follows: the parameter σ_{eff} is a measure of both the free energy of making a fold and of the irregularity of the folded surface, as is evident from eq (19). If the surface is perfectly regularly folded, σ_{eff} is equal to σ_e , but for surfaces that are not perfectly regular, the value of σ_{eff} is dependent upon the particular distribution of fold lengths. For the values of σ_{eff} quoted here this distribution is *determined by the kinetics of the growth process*. Now, it is quite possible that although when a lamella is freshly grown it may have this kinetic distribution of fold lengths, upon subsequent storage, and particularly upon heating to the melting point, this distribution will very likely change and approach some other distribution, even though \bar{T} may remain unchanged. If the distribution approaches a perfectly sharp distribution, then the surface energy measured will indeed be σ_e . However, it is much more likely that the distribution would approach the *equilibrium* distribution charac-

teristic of the particular temperature in question, and the end surface energy would be the value characteristic of that distribution. In short, kinetic experiments such as growth-rate measurements, lead to a value of σ_{eff} characteristic of a *kinetic* distribution, while "equilibrium" type experiments lead to a value characteristic of an *equilibrium* distribution.

The difference between the two types of experiments should not, however, be overemphasized. In particular, in the worst case, namely $\phi = 0$, for $\sigma_e = 60 \text{ ergs/cm}^2$ the value of σ_{eff} varies from about 36 ergs/cm^2 at very low undercoolings to about 46 ergs/cm^2 at an undercooling of 20 deg. The value characteristic of the equilibrium distribution over this whole temperature range is approximately 36 ergs/cm^2 . As may be seen from figure 4, the variation for $\phi = 1/2$ and $\phi = 1$ is somewhat less.

We now turn to a discussion of the maximum in S_T , and the decrease of S_T to zero at an undercooling of $\sigma T_m^0/a\Delta h$. This, of course, is the same undercooling at which Frank and Tosi found a cessation of crystallization, but there is one important difference between our results and theirs. In our case, crystallization proceeds relatively normally above this temperature, whereas in theirs crystallization proceeds only below it. Moreover, at this temperature our thickness diverges, while theirs is regular. Nevertheless, by our choice of rate constants, we have traded the disquieting result that crystallization does not proceed *above* a certain undercooling for the equally disquieting result that crystallization does not proceed below it. Of the two possibilities we prefer the latter, although it would seem to be contrary to experience. After all, we know from experiments on homogeneous nucleation that crystal growth can occur at undercoolings greater than $\sigma T_m^0/a\Delta h$. The reason for our preference is that these theories of crystallization presume that steady-state exists. Now, it is much more likely that steady-state can be obtained near the melting point where processes are slow, than at large undercoolings where processes are rapid and more complex. While we are by no means certain that this is the proper explanation of the difference between our results and observed behavior, we can suggest that at undercoolings approaching our divergence temperature, steady state never obtains in the real physical case, and our treatment (and any other) becomes inapplicable. To see how this rationalizes the results, we note first that if the thickness of the growing layer is finite, the total flux is not zero, as will be evident from our expressions for α_0^j/β_1^j and α^j/β^j . If we now imagine a strip nucleating on a substrate formed, for example, from a homogeneous nucleus, it may start with some finite thickness, and begin to increase to the thickness determined by the steady state equations, which may be infinite. If it could achieve this, its rate of growth would drop to zero (eq. (13a)), but it is entirely likely that before it reaches this thickness it might encounter another strip growing in the same manner on the same substrate and hence never approaches this steady-state

thickness. Clearly, to solve this problem correctly (in one dimension), one would have to solve the full time dependent equations given in LDP. We know of no way to do this, and the only conclusion we can come to is that the reason our treatment does not reproduce reality in the range of undercoolings of T_d and below is that steady state is never attained.

We note also that the inclusion of transport terms to slow down the overall rate will not necessarily help matters any. It is not the absolute magnitude of the flux which is important, but the relative rates of initiation and growth of strips (in our notation, essentially the relative magnitudes of α_i^j/β_i^j and α^{ij}/β^{ij}). Thus, unless the transport terms affect initiation and growth in significantly different ways (which we consider unlikely) the retardation of the whole process by transport will not change the achievement of steady state materially.

4.3. The Distribution

Having discussed the effect of the distribution as exemplified, e.g., by s_i and σ_{eff} , we now give some detailed examples of it.

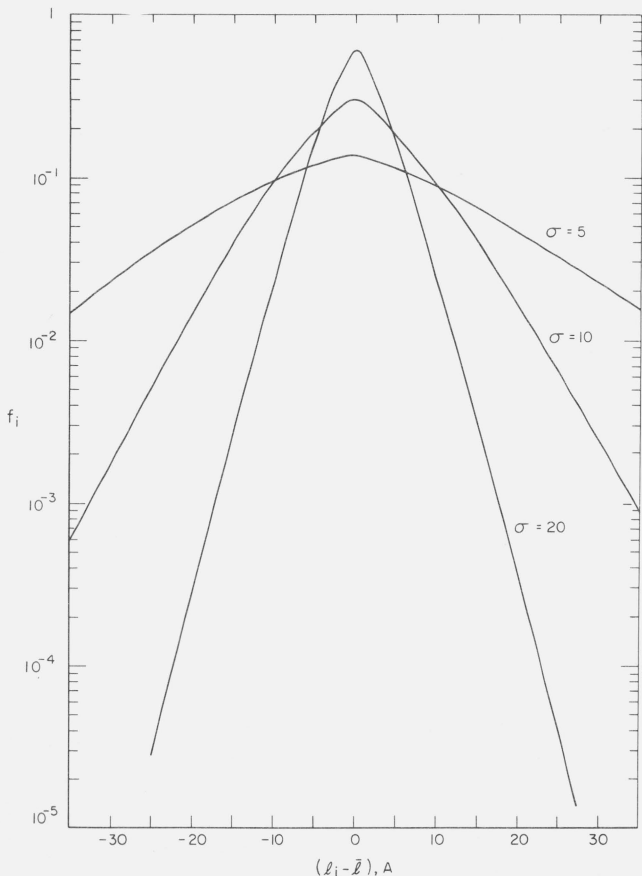


FIGURE 8. Plots of f_i , the fraction of species i (eq 5 of the text), versus the deviation of l_i from its mean value for $\Delta T=3$, $\varphi=1/2$, and three values of σ .

This plot is essentially independent of the value of σ_e , except that \bar{l} is different for the different values of σ_e . At higher undercoolings the curves are similar but broader.

Figure 8 gives a plot of f_j against $l_j - \bar{l}$ at an undercooling of 3 degrees for three different values of the lateral surface energy term σ and for $\varphi=1/2$. The curves have a peak at the value of $l_j = \bar{l}$, and fall off on both sides of this value at a rate which is dependent on the value of the lateral surface energy σ . These curves are very similar to those already presented by Price. The curves are not affected by the value of σ_e , although \bar{l} of course is strongly dependent on it. The higher the value of lateral surface energy the sharper the distribution, as would be expected, for the higher the value of σ , the more energetically unfavorable is the exposure of lateral surface, and this results in a smoother surface. The values of s_i , which is characteristic of the distribution, are 3.745, 8.548, and 18.519 Å respectively, for $\sigma=20$, 10, and 5 ergs/cm².

Figure 9 gives an example of the pair distribution function, f_{ij} . This is plotted from the results for $\varphi=1/2$, $\Delta T=15^\circ\text{C}$, $\sigma_e=60$ ergs/cm², $\sigma=10$ ergs/cm². The plot is made so that the origin is at $l_j = l_i = \bar{l}$. At this point, as is expected, f_{ij} is a maximum and falls off monotonically in all directions.

Not too much can be said about the figure, but some things should be pointed out. First, in any plane $l_j = \text{constant}$, or $l_i = \text{constant}$, the maximum value of f_{ij} occurs at the value of l_i or l_j equal to \bar{l} . This indicates that correlation with the substrate thickness is the most important factor in determining f_{ij} . Second, a shoulder is noticeable in the region $l_i > \bar{l}$, $\bar{l} \leq l_j \leq l_i$. (The same shoulder appears opposite the origin,

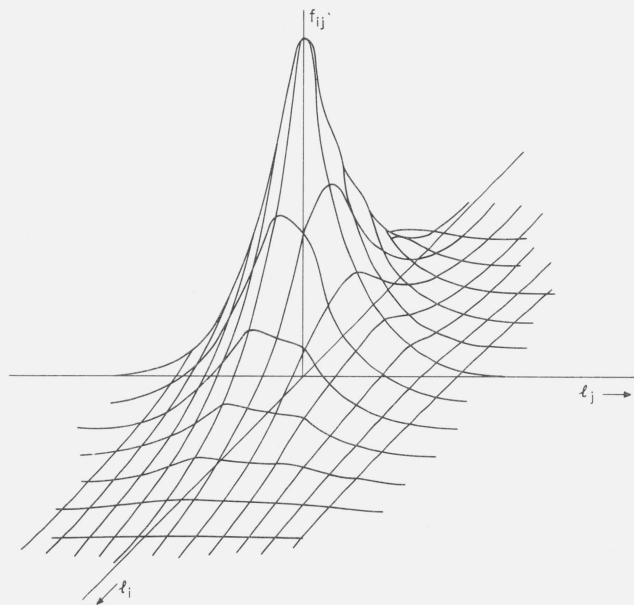


FIGURE 9. Plot of f_{ij} , the pair distribution (eq 9 of the text) versus l_i and l_j for $\Delta T=15$, $\varphi=1/2$, and $\sigma=10$ ergs/cm².

This plot was calculated for $\sigma_e=60$ ergs/cm², and is essentially independent of σ_e provided the origin is at $l_i=l_j=\bar{l}$. The peak in the plot is at the origin, and is more pronounced at lower undercoolings.

i.e., where $l_i < \bar{l}$, $\bar{l} \geq l_j \geq l_i$.) This indicates that correlation occurs with \bar{l} and all lengths between l_j and \bar{l} , but falls off very rapidly for $l_j > l_i$. Similarly, f_{ij} falls off very rapidly with l_j as l_j becomes smaller than \bar{l} for $l_i < \bar{l}$. All these remarks have their counterparts for $l_i < \bar{l}$.

This behavior is what would be expected on physical grounds. Imagine a segment $l_i > l_s = \bar{l}$ deposited at the end of the growing strip. The next segment to be deposited, l_j , will be energetically most favored if it is the same thickness as \bar{l} . For any thickness less than \bar{l} , not only is the bulk free-energy term $\alpha^2 l_j \Delta h \Delta T / T_m^0$ in eq (13b) less than if $l_j = \bar{l}$, but the term $\alpha \sigma |l_j - l_s|$ further reduces it. If $l_j > l_s$ but less than l_i , the bulk free energy term $\alpha^2 l_j \Delta h \Delta T / T_m^0$ tends to favor accretion as compared to $l_j = l_s$, but the term $\alpha \sigma |l_j - l_s|$ more than compensates for it except near T_a . Finally, for $l_j > l_i$, the term $2\alpha \sigma U(l_j - l_i)$ is added to the term $\alpha \sigma |l_j - l_s|$ and the probability of accretion falls off rapidly with increasing l_j . The same remarks, with proper changes, apply when $l_i < l_s$.

We may compare f_{ij} with the pair-distribution that would occur for random mixing, as was done in I. For the random case we have,

$$f_{ij}^r = f_{ij} = f_{ji}^r$$

where f_{ij}^r is the (symmetric) pair distribution when random mixing occurs. From this we may construct the difference

$$\delta f_{ij} = f_{ij} - f_{ij}^r = f_{ij} - f_{ji}^r.$$

The results for this difference are difficult to present graphically. However, in the difference matrix the following behavior is observed at low undercoolings (3 °C). The maximum occurs at f_{ii} where $l_i = \bar{l}$, as is to be expected. Now, if for the purposes of discussion a cartesian coordinate system is laid on the matrix with origin at f_{ii} , and the x axis along the direction of increasing j , then for small ΔT the first and third quadrants are negative and the second and fourth positive, and the coordinate axes are positive. Said less graphically but more precisely

$$\delta f_{ij} > 0, l_i \geq \bar{l}, l_j \geq \bar{l}$$

$$\delta f_{ij} > 0, l_i \leq \bar{l}, l_j \leq \bar{l}$$

$$\delta f_{ij} < 0, l_i > \bar{l}, l_j < \bar{l}$$

$$\delta f_{ij} < 0, l_i < \bar{l}, l_j > \bar{l}.$$

For ΔT somewhat larger (15 deg) these quadrants are predominantly of the same signs as for lower ΔT , but deviations occur for l_j or l_i considerably larger or smaller than \bar{l} , i.e., away from the origin but near the coordinate axes. The δf_{ij} matrix is almost symmetrical but definitely not so, and thus the f_{ij} matrix

is also not. This is as expected from the matrix of the α_{ij} and β_{ij} .

4.4. The Approach to the Steady-State Thickness

It will be recalled that in the section on the method of calculation, we described that beginning with a substrate of thickness \bar{l}_s we grow on it at a given temperature a strip the thickness of \bar{l} which in general will be different from l_s . This is then used as a substrate for a subsequent strip, and the process continued until $\bar{l} = l_s$. This amounts to a theoretical analog of the well-known experiment in which a crystal growing at a given temperature is cooled to another temperature and growth permitted to proceed with the formation of a step. Our procedure gives a profile of this step. This type of information has already been given by Price, and although we have not pursued this matter thoroughly, preferring to replace the above iteration scheme with a considerably more efficient one mathematically, we will present one result both because it is different from what Price has already presented and because it may be of some experimental interest. Accordingly, we show in figure 10 the approach to the final thickness when a substrate 133.1 Å thick is used as a substrate for growth at a temperature at which the final thickness is 113.8 Å. This corresponds to having grown a crystal at 405.2 °K and continuing growth on it at 402.2 °K. It will be noticed that the decrease in thickness is monotonic, arriving smoothly at the final result. After 24 steps the thickness is within 1 Å of the final result, but it takes 81 steps to arrive at within one part in 10^7 of the final thickness. It is interesting to note that some recent results of Bassett, Blundell, and Keller [14] obtained by gold deposition on surfaces, show a different behavior of the gold in a region approximately 100 Å wide near a step than in other regions. Twenty-four layers corresponds to 103 Å; however, before more can be said, detailed calculations for the particular conditions in question would have to be carried out, and a knowledge of just what this gold deposition technique measures in the region of the step would have to be known.

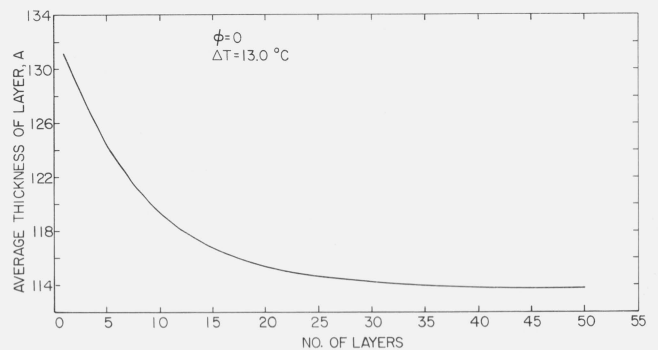


FIGURE 10. Plot of average layer thickness versus the number of layers as the layer thickness approaches its final steady state value.

This calculation was made for $\sigma = 10$ ergs/cm², $\sigma_s = 60$ ergs/cm², $\phi = 0$, $\Delta T = 13$. The original substrate thickness was 133.1 Å and corresponds to an undercooling of 10 deg.

5. Conclusions

We have shown that the LDP theory for the kinetics of the growth of chains in multicomponent systems may successfully be applied to the problem of the growth of chain-folded polymer crystals. In this problem each of the possible folded segment lengths deposited at the end of the growing strip is considered a component and the strip itself is the chain. Over most of the temperature range of interest, it is necessary to take the number of components so defined to be of the order of 50.

The most difficult aspect of this application of the LDP theory is its adaptation to the two-dimensional character of crystal growth, but it should be pointed out that this same problem arises in all previous theories of polymer crystallization. In the present instance, this adaptation was accomplished by appropriate modification of the rate constants, using as a criterion the fact that crystallization, given some type of nucleus, should occur at small undercoolings.

The problem of the apportionment to forward and backward rate constants of the free energy changes occurring in the process of accretion of elements at the end of the growing strip has not been solved. Instead, calculations were carried out for various arbitrary apportionments, with significant differences in the results. In our views, this is an outstanding theoretical problem in the treatment, but is not one likely to be solved without detailed knowledge (or at best a detailed model, which is a different thing) of the microscopic process by which a polymer chain adds to the growing crystal.

Perhaps the most intriguing result of this treatment is the roughness of the crystal surface as grown. This produces a standard deviation in the thickness of some 8 Å at the melting point and increases to more than ten angstroms at normal undercoolings, the exact amount depending strongly on the exact apportionment of the free energy changes. There are some experiments, notably density [15] and heat of fusion measurements [16], which have as one interpretation such a rough surface, but it should be borne in mind that the roughness calculated here is that occurring during the kinetic processes of growth and not necessarily the equilibrium roughness appropriate to the temperature in question. Nevertheless, unless a smooth surface is energetically favored over a rough surface (which could be theoretically accomplished, for example, by incorporating into the theory what might be called a "lock-in" energy, that is, an energy that would favor adjacent segments in the growing layer being of the same thickness and the same thickness as the substrate) such smooth crystallographic surfaces as are seen in isolated polyethylene lozenges [17] are likely to remain inexplicable on the basis of this theory, and probably any other statistical mechanical theory.

Over the range of undercoolings of usual experimental interest, the thickness grown as a function of temperature and the total rate of crystallization (neglecting transport or diffusion terms) can be analyzed

by equations previously derived by others (eqs (1) and (18) of the text) provided that the end-surface free energy σ_e in those theories is replaced by an "effective" end surface free energy σ_{eff} . This latter quantity is intimately related to the roughness of the surface, and is temperature dependent, the exact amount of this dependence depending on the apportionment of the free energy to forward and backward rate-constants. Near the melting point, where the results are independent of this apportionment, the difference between σ_e and σ_{eff} is about 24 ergs/cm² for $\sigma = 10$ ergs/cm² and independent of σ_e , with σ_{eff} being smaller. This difference becomes smaller as undercooling is increased, and varies with the value of σ .

At undercoolings approaching $\sigma T_m^0/a\Delta h$, the grown length approaches a minimum and then becomes infinite at this undercooling. For all the free-energy in the backward rate constants ($\varphi = 0$ in eqs (14)) the distribution also becomes infinitely broad, while for all the energy in the forward or equally divided between forward and backward rate constants the distribution remains finite, and the approach to the infinite length is logarithmic, as was found also by Frank and Tosi, although at twice the undercooling. The distribution for $\varphi = 0$ is thus very different from the equilibrium distribution and in a sense represents a very inefficient mode of crystallization. Indeed, for crystals with such very rough surfaces, the use of the LDP theory can be questioned, for nonnearest-neighbor interaction should most likely be taken into account.

At the same temperatures where the grown thickness reaches a minimum, the growth rate, or total flux, reaches a maximum and then falls off, even in the absence of transport terms. Again this effect is most pronounced for $\varphi = 0$, and again the relevance of these results to reality in this region may be questioned for under conditions of such rapid growth, steady state may never be reached. The same criticism, however, applies to all other theories and this situation is likely to remain, for to solve the kinetic equation under nonsteady-state conditions is a truly formidable task.

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6. References

- [1] J. I. Lauritzen, Jr., E. Passaglia and E. A. DiMarzio, *J. Res. NBS* **71A4**-457, 245 (July-Aug. 1967).
- [2] J. I. Lauritzen, Jr., E. A. DiMarzio and E. Passaglia, *J. Chem. Phys.* **45**, 4444 (1966).

- [3] J. I. Lauritzen, Jr., and J. D. Hoffman, J. Res. NBS **64A** (Phys. and Chem.) No. 1, 73 (1960); J. D. Hoffman and J. I. Lauritzen, Jr., J. Res. NBS **65A** (Phys. and Chem.) No. 2, 297 (1961).
- [4] F. C. Frank and M. Tosi, Proc. Roy. Soc. **A263**, 323 (1961).
- [5] F. P. Price, J. Chem. Phys. **35**, 1884 (1961).
- [6] W. W. Mullins, Phys. Rev. **114**, 389 (1959).
- [7] P. J. Flory, Principles of Polymer Chemistry (Cornell Univ. Press, Ithaca, N.Y., 1953).
- [8] M. L. Williams, R. F. Landel and J. D. Ferry, J. Am. Chem. Soc. **77**, 3201 (1955).
- [9] J. D. Hoffman, SPE Transactions, P. 327 ff (1964).
- [10] R. G. Brown and R. K. Eby, J. Appl. Phys. **35**, 1156 (1964).
- [11] B. Wunderlich and A. Arakawa, J. Polymer Sci. A, **2**, 3697 (1964).
- [12] D. Turnbull and R. L. Cormia, J. Chem. Phys. **34**, 820 (1961).
- [13] F. Gornick and J. D. Hoffman, Ind. Eng. Chem. **58**, 41 (1966).
- [14] G. A. Bassett, J. D. Blundell, and A. Keller, J. Macromol. Sci. (Physics), in press.
- [15] G. M. Martin and E. Passaglia, J. Res. NBS **70A** (Phys. and Chem.) No. 3, 221 (1966).
- [16] H. Hendus and K. H. Illers, Kunststoffe, to be published.
- [17] D. C. Bassett and A. Keller, Phil. Mag. **8**, 345 (1961).

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