Crystal growth kinetics and the lateral habits of polyethylene crystals

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The lateral growth habits of lamellar crystals of polyethylene grown from solution can be typified in terms of the aspect ratio, r, which is the ratio of the dimension of the crystals in the b-axis direction to that in the a-axis direction. The aspect ratio depends on crystallization temperature, undercooling, solvent, polymer concentration and molecular weight. At steady state growth, r can be expressed in terms of the ratio of growth rates normal to the {110} and (200) faces. Expressing the growth rates in terms of the kinetic theory of polymer crystal growth yields an expression which is used to analyse experimental results on the effect of temperature and concentration on the lateral growth habits of crystals grown from xylene. Using as two adjustable parameters the ratio of end surface free energies for the two growth surfaces and the ratio of the lateral surface free energies to fit the r versus ΔT data permits the determination of these ratios with high sensitivity. The actual values obtained are dependent upon concentration, the assumed growth regime, and, most importantly, ϕ, the parameter in the growth rate equations apportioning the bulk free energy change to the forward and backward steps in the stem deposition process.

INTRODUCTION

In the kinetic theory of polymer crystal growth[1], which is a nucleation theory, the growth rate normal to a lateral face of a chain-folded crystal is largely determined by the undercooling, the heat of fusion, the lateral and end (fold) surface free energies, and the interfacial transport of material. The thickness of the crystals is determined by the surface free energies, the undercooling and the heat of fusion.

The theory has accounted successfully for the temperature dependence of the growth rate and the thickness of the lamellar crystals formed from solution and from the melt[1,2]. Until recently, however, it has not been applied to the analysis of the lateral habits of polymer crystals. This is of particular interest in the case of polyethylene crystals grown from solution. The lateral habit of crystals of this polymer has long been known to vary depending on the growth temperature, undercooling, polymer concentration and molecular weight, as well as the nature of the solvent[3-17]. The reported variations in habit, which reflect changes in the ratio of the growth rates of the {110} and (200) faces (see later, Figure 1), imply that the parameters that control the growth rates (principally the surface free energies) are different for these faces. A priori, the surface free energies would be expected to differ because the faces involved are crystallographically distinct from one another. These surface free energies might also be expected to vary with temperature, solvent, and with the concentration and the molecular weight of the polymer. Indeed, evidence that these factors affect the surface energies has been reported[18-24]. There has, however, been no information concerning the possibility that these various factors affect the surface free energies

associated with growth at the {110} and (200) faces differently.

This paper is concerned with the quantitative determination of some of the aforementioned factors by applying the kinetic theory of polymer crystal growth to the analysis of the variation, with temperature and concentration, of the lateral habit of polyethylene crystals grown from solution in xylene. The experimental data analysed are those of Blundell and Keller[12] and Valenti and Pedemonte[14] for crystals of Marlex 6009 polyethylene. Principally, this

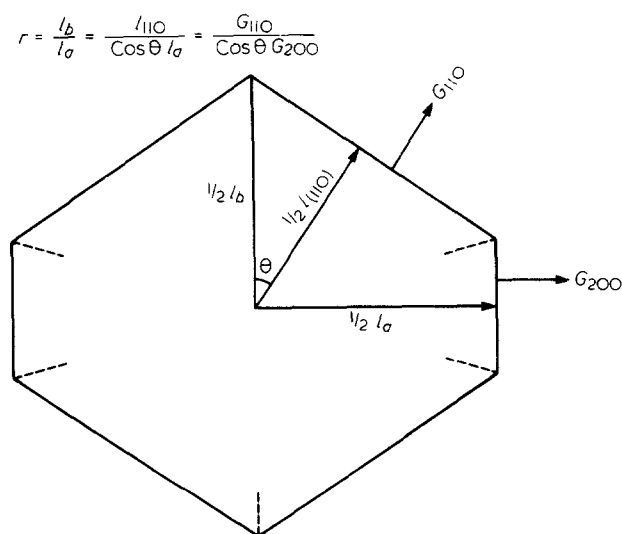$$r = \frac{l_b}{l_a} = \frac{l_{110}}{\cos\theta\, l_a} = \frac{G_{110}}{\cos\theta\, G_{200}}$$

Figure 1 A schematic representation of the c-axis projection of a truncated polyethylene crystal. The aspect ratio r is defined as the ratio of the dimension of the crystal in the b to that in the a crystallographic direction. At steady-state growth, this ratio is given in terms of the growth rates G_{110} and G_{200} as shown

paper is concerned with the difference in the end surface free energy, σ_e, and in the lateral surface free energy, σ, between the {110} and (200) faces, and with the variation of these differences with temperature and solution concentration. A parallel intent is to investigate the effects of two additional parameters of the kinetic theory. These are the 'substrate length' for regime I growth[1,25] and ϕ (ref. 26, denoted by Ψ in ref. 1), the apportionment of the bulk free energy change between the forward and backward steps in the process of stem deposition along a growth face. It is established from this analysis that an accounting of the variation of growth habit with undercooling based on the kinetic theory in its present stage of development provides a sensitive method of constraining and determining the mentioned parameters. In particular, the analysis serves as a very sensitive 'null point' method for determining the relative (but not absolute) values of surface energies. These relative values are, however, dependent upon the growth regime and the value of ϕ.

While this paper was in manuscript form, an abstract of a recent paper presented by Alfonso, Fachetti and Pedemonte[27] became available. These authors have also analysed the lateral growth habits of polyethylene crystals in terms of the kinetic theory of polymer crystal growth, Their analysis is more limited than that presented here in that a simplified form of the rate equations from the kinetic theory is used which precludes an examination of the effects of ϕ, and only Regime I growth is considered.

The method of analysis described here can, of course, be applied to crystals of polyethylene grown from solvents other than xylene, as well as to other polymer crystals which are bounded laterally by crystallographically different growth faces by virtue of the low symmetry (e.g. orthorhombic, monoclinic, or triclinic) of the polymer crystal structure. Initially, the theoretical basis of the method of analysis is given. It will be readily apparent that the treatment is an application in two dimensions of the more general three-dimensional treatment of Hartman and Bennema[28].

THEORETICAL BASIS

Derivation of principal equations

This method of analysis considers a polyethylene crystal growing under steady-state conditions, i.e. at constant temperature and constant polymer concentration in the mother liquor. The effect of this steady-state assumption on the analysis of the experimental data is dicsussed later. First, the parameter used to describe the lateral habits of the crystals is defined and the equations which express this parameter in terms of the growth rates of the different lateral growth faces, are then derived.

A schematic diagram of a 'truncated' polyethylene single crystal is shown in *Figure 1*. This crystal which is six-sectored and can be presumed flat for the purposes here, is bounded laterally by {110} and (200) growth faces. Taking l_a and l_b to be the crystal lengths in the [100] and [010] directions, the lateral habit of the crystal in terms of the *aspect ratio, r,* is:

$$r = l_b/l_a \qquad (1)$$

where

$$l_b = l_{110}/\cos\theta \qquad (2)$$

$$\theta = \tan^{-1} b/a \qquad (3)$$

and b/a is the ratio of the dimensions of the b- and a-axes of the polyethylene unit cell. Denoting the growth rates normal to the respective growth faces by G_{110} and G_{200}, and taking these rates to be constant with time (in agreement with experiment[23,29-32] and the steady-state assumption) then:

$$G_{110} = dl_{110}/dt \qquad (4)$$

$$G_{200} = dl_a/dt \qquad (5)$$

Assuming further that the lateral dimensions of the seeds from which the crystals evolve are negligible compared with the size of the crystals which develop from them[33], or that they have the same aspect ratio, and that the seeds do not influence the lateral habit of the crystals grown at different temperatures[14], it follows that:

$$r = G_{110}/G_{200}\cos\theta \qquad (6)$$

In some papers[11,12,14] the lateral habits of polyethylene crystals have been expressed in terms of geometric ratios which are different from but are easily converted to the aspect ratio r.

There is one feature concerning r which it is necessary to introduce at this stage in anticipation of the description and discussion of the experimental results on crystals grown from xylene which are analysed. It is established that, for the same polymer molecular weight, concentration and solvent, r becomes larger the higher the crystallization temperature[5,9,12-15], although the range of aspect ratios shifts to higher or lower values of r depending on the molecular weight of the polymer, its concentration and the solvent. The noteworthy feature is that in the limit of the lowest temperatures ($\simeq 70°C$) at which polyethylene crystals can be grown from solution in xylene under isothermal conditions, the crystals exhibit the familiar lozenge habit. These crystals, which are four sectored, are bounded laterally by {110} faces only, and their aspect ratio $r = \tan\theta = b/a$ (which is slightly dependent on temperature because of the thermal expansion of the unit cell) is ≈ 0.66. This value is the lowest limit of r for polyethylene crystals* and it will be denoted r_l in ensuing parts of this paper.

In considering r in terms of the growth rates of the {110} and (200) faces it is evident that (200) faces will not develop and lozenge-shaped crystals, $r_l = b/a \approx 0.66$, will be formed not only when $G_{110}/G_{200} = \sin\theta \approx 0.554$ but also when $G_{110}/G_{200} < 0.554$. In both these circumstances incipient (200) faces 'grow out' of the crystal. Analytical calculations yielding values of $r < r_l$ are described later. In these circumstances the results can be interpreted as indicating that the crystals formed are of the lozenge-shaped variety.

Having defined the habits of the crystals in terms of the aspect ratio r, the dependence of this ratio on $G_{110}/G_{200}\cos\theta$ may now be expressed in terms of the growth rates as given by the kinetic theory[1]. Later, the growth regime which governs the lateral development of the crystals is examined from both a consideration of the

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* Below $\approx 70°C$, isothermal crystallization from xylene is not possible. Micro-faceted dendritic crystals are formed, the lateral propagation of which is characterized by the successive development of sectored outgrowths at leading corners of lamellae and the overall growth of the lamellae occurs preferentially parallel to the a-axis[34]. Under these conditions of high undercooling at which diffusion becomes a controlling factor in the growth, the kinetic theory of polymer crystal growth on which the analysis here of habits is based is not applicable

Lauritzen 'z test'[25] and the experimental data, but initially both regime I and regime II kinetics are considered. In either case, the growth rate of a lateral crystal face may be expressed as a product of two factors:

$$G = FE \qquad (7)$$

The term designated E is a product of two exponential functions that contain the details of the nucleation and growth processes involved in the initiation and propagation of successive 'ribbons' of folded chains on a lateral face of the crystal. This term depends strongly on temperature. The term F contains terms related to transport and weakly temperature-dependent terms. As it is clear from equation (6) that the ratios of growth rates for the {110} and (200) faces of the crystal are considered, the variation of F with crystal face is of importance. For regimes I and II, the term F is given by the following expressions[1]:

$$F^I = d_n/d_p(kT/h)LP/l_u c \, \exp\left[-\Delta F^*/kT\right] \qquad (8a)$$

$$F^{II} = d_n(kT/h)(QP/l_u)^{1/2}c \, \exp\left[-\Delta F^*/kT\right] \qquad (8b)$$

Somewhat different expressions are given in ref. 2, but the conclusions are not altered.

The terms are as follows:
d_n, d_p = the width of the deposited stem normal and along the crystal face respectively
k = Boltzmann's constant
T = absolute temperature
h = Planck's constant
L = substrate length for nucleation and growth in regime I[1,25]
P, Q = complicated expressions involving the lateral surface free energy
l_u = length of a monomer unit
c = a function of the concentration
ΔF^* = the free energy of activation for transport at the growing interface

The only terms in equations (8a) and (8b) that vary with the crystal face are d_n, d_p, L (which may be the length of the crystal face), and P and Q which depend on the lateral surface free energy. However, this energy would not be expected to be greatly different for the {110} and (200) faces, an expectation which is confirmed later by the results. Computations show that a change of a few per cent in lateral surface free energy causes a slightly higher percentage change in P and a slightly smaller percentage change in Q. Compared, however, with the substantially larger effect of similar small changes in lateral surface energy on the exponential term E, the effects of any differences in P and Q between crystal faces are negligible and will be ignored.

Substituting the full expressions for the growth rates into equation (6):

$$r^I = \frac{2d_{110}}{a} \frac{2bL_{(110)}}{aL_{(200)}} \exp \frac{ab\phi\sigma_e^{110}}{kT} (1-\rho)$$

$$\times \exp \frac{4d_{110}\sigma_e^{110}\sigma^{110}}{\Delta h\, \Delta TkT/T_d^0} \left(\frac{a}{2d_{110}}\gamma\rho - 1\right) \qquad (9a)$$

$$r^{II} = \frac{2b}{a} \exp \frac{(2\phi-1)(a/2)b\sigma_e^{110}}{kT} (1-\rho)$$

$$\times \exp \frac{2d_{(110)}\sigma_e^{110}\sigma^{110}}{\Delta h\, \Delta TkT/T_d^0} \left(\frac{a}{2d_{110}}\gamma\rho - 1\right) \qquad (9b)$$

In these expressions the symbols have the following meanings:

r^I, r^{II} = the aspect ratio for regime I and regime II crystallization
a = the length of the unit cell a-axis
b = the length of the unit cell b-axis
d_{110} = the spacing between {110} planes in the unit cell
σ_e^{110} = the end surface free energy associated with the folding of molecules located on a {110} face
σ^{110} = the lateral surface free energy associated with the deposition of a stem on a {110} face
$\gamma = \sigma^{200}/\sigma^{110}$
$\rho = \sigma_e^{200}/\sigma_e^{110}$ with σ_e^{200} and σ^{200} defined analogously to σ_e^{110} and σ^{110}
Δh = the heat of fusion
ϕ = a parameter that apportions the free energy of crystallization to the forward and backward steps in the stem deposition process[26]. (Denoted by ψ in ref. 1.) Its value varies from 0 to 1. For zero, all the free energy is allocated to the backward step, and for unity to the forward step
T_d^0 = the temperature of dissolution of the extended chain crystal of the specified molecular weight at the specified concentration
$\Delta T = T_d^0 - T$ = the undercooling

All other symbols have the meanings defined previously.

These are the principal equations that will be used in the analysis. Clearly, in writing them in this manner, it has been anticipated that both the lateral and end surface free energies may be different for the two growth faces. Also, the free energy differences are expressed as the ratios γ and ρ, and these ratios have been 'scaled' to the surface free energies for the (110) face. Considering the ratios of surface free energies (and their temperature dependence) rather than differences is more convenient for the purposes here. As shown later, the experimental results are a very sensitive function of these ratios, and for given values of ϕ and the other parameters in the theory, they can be determined with great precision (but not accuracy, of course).

It should be noted at this point that, in their analysis, Alfonso et al.[27] omitted the first of the exponential terms of equation (9). It is shown later that these terms are, in fact, important.

The question of growth regime and the value of L

As indicated previously, the term L in the case of regime I growth is the length of the substrate on which an individual nucleation event with subsequent rapid propagation of a strip of folded molecules takes place. If this length is identified as the length of the crystal face then the growth normal to the face would be non-linear with time in regime I. This is certainly not the case for crystallization from the melt[1], nor does it appear to be the case for crystallization from solution where the growth rate has been reported to be constant with time at low levels of depletion of the polymer from the solution[23,29-32], and analysis of the temperature de-

pendence of the growth rate indicates regime I growth at low undercoolings[1]. Linear growth in regime I is accounted for by identifying L as a 'persistence length' that is smaller than the crystal edge and is constant independent of the size of the crystal[1].

It is noteworthy that even if the growth were non-linear, i.e. L is identified as the length of the growing face, the aspect ratio of the crystal would approach a stable value, for accelerating growth normal to a longer face would correspondingly increase the length of an adjoining shorter one, causing it to grow more rapidly. Under these conditions it may be shown that the outward growth of a given face would change exponentially with time, and the aspect ratio would approach a limiting value. However, in view of the experimental evidence for constant growth rate the possibility of alternatives are not considered further in this paper.

In principle it would be possible to leave the ratio L_{110}/L_{200} in the expression for the aspect ratio for the regime I growth case as an undetermined parameter. This, however, would add another adjustable parameter to a formulation that already includes at least two others and, furthermore, there is no basis to select a value for L_{110}/L_{200} which is either greater than or smaller than unity. Accordingly, pending further developments in understanding the physical meaning of L, the ratio L_{110}/L_{200} is assumed to be unity.

Lauritzen[25] has shown that the dimensionless quantity:

$$Z = iL^2/4g \qquad (10)$$

in which i is the rate of initiation of new growth strips on a lateral surface of the crystal and g is the growth rate of those strips along the face (it may be used as a criterion for determining whether growth is in regime I or regime II. For values of $z \leqslant 0.01$, growth is certain to be in regime I, while for values of $z \geqslant 10$, growth is in regime II. Using expressions for i and g from the kinetic theory[1,2], z may be calculated as a function of undercooling for the system of polyethylene in xylene. These calculations show that for an undercooling of $\approx 25°C$, the growth is mostly in a mixed mode at first, in accord with experiment[23], and approaches regime II as the crystals become reasonably large (size greater than a few micrometres). For undercoolings of $\leqslant 20°C$, growth is in regime I. The undercoolings in the experiments analysed here cover a range of $\approx 12-30°C$[12,14]. Hence, the growth in some of the experiments was probably in a mixed regime range, and in others, perhaps most, in regime I. There is no way of analysing data in a mixed regime mode; therefore, the analysis is carried out for both regimes. As shown later, the principal conclusions regarding an accounting of the variation of r with the crystallization conditions in terms of γ and ρ are relatively independent of the regime.

DATA USED IN THE ANALYSIS

Before proceeding with the analysis of the selected experimental data for r, it is necessary to describe and discuss this and other data which enter into the analysis.

Experimental data for r

As indicated previously, the analysis is limited to data on polyethylene crystals grown from xylene. The reason is
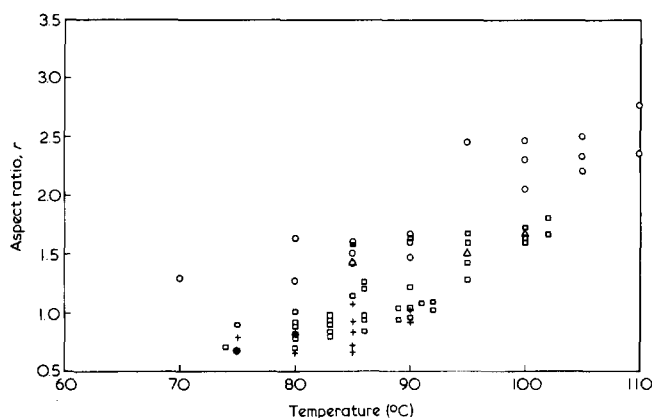

Figure 2 The aspect ratio as a function of the crystallization temperature for crystals of polyethylene of various molecular weights, grown from various solvents and at various concentrations, from the data of O, Keith[9]; +, Blundell and Keller[12]; □, Valenti and Pedemonte[14]; and △, Kawai and Keller[10]

that there is extensive knowledge of T_d^0 for polyethylene in xylene as a function of both molecular weight and concentration[35-37]. As shown in equations 9(a) and 9(b), such detailed knowledge, which is lacking for other solvents at present, is necessary for the analysis to be applicable.

Figure 2 is a plot of the values of r as a function of crystallization temperature collected from four investigations[9,10,12,14] on the effect of various crystallization conditions on r. The data include results of Blundell and Keller[12], Valenti and Pedemonte[14] and Keith[9] on crystals grown from various solvents at various concentrations ($\leqslant 0.5$ g/100 ml) and of polymer of different molecular weights, as well as some results of Kawai and Keller[10]. Blundell and Keller[12] grew crystals of polyethylene (Marlex 6009) from xylene at different temperatures and concentrations. Valenti and Pedemonte[14] studied crystals of the same polyethylene, and a number of fractions, grown from solutions having different concentrations of polymer in xylene, n-octane and n-decane. Keith[9] crystallized two fractions of different molecular weights from solutions in n-octadecane and n-dotriacontane containing relatively higher polymer concentrations. The aspect ratios in *Figure 2* range from ≈ 0.66 to 2.8.

Notwithstanding the fact that the effects of solvent, molecular weight, and concentration on r (see later) have been ignored in the plot shown in *Figure 2*, the data considered collectively indicate an overall upward trend in r with increasing crystallization temperature. Results of Khoury and Bolz[15-17] on crystals grown in the range $95°-115°C$ from 0.01% solutions of polyethylene fractions in the relatively poor solvents heptyl acetate and dodecanol are consistent with this trend. Crystals with an aspect ratio of ≈ 6 were grown from dodecanol at $115°C$.

The noteworthy feature is that crystals with aspect ratios ranging from 0.66 to 6 have been grown from dilute solutions. Here, the data analysed are those of Blundell and Keller[12] and Valenti and Pedemonte[14] for crystals of Marlex 6009 polyethylene grown from xylene using the 'self-seeding' technique. Their data, expressed here in terms of r, for crystals grown from 0.01 g/100 ml and 0.1 g/100 ml solutions are plotted in *Figure 3* as a function of crystallization temperature. *Figure 3* shows the close agreement between these two independent studies, with regard to both the effect of changing growth temperature
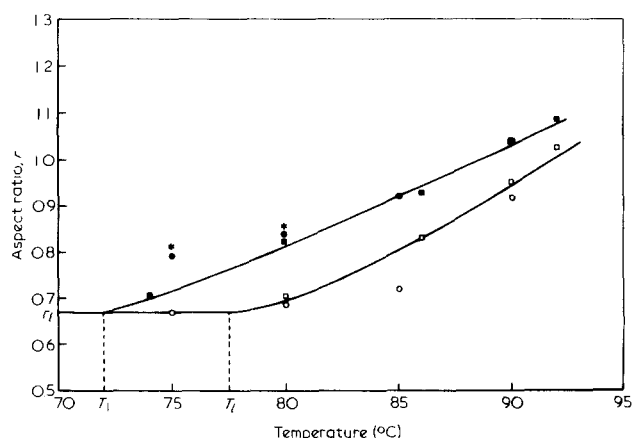
Figure 3 The data on the aspect ratio for crystals of polyethylene (Marlex 6009) grown in xylene, from ●, ○, Blundell and Keller[12]; and ■, □, Valenti and Pedemonte[14]. Solution concentrations: ■ and ●, 0.1; □, ○, 0.01 g polymer/100 ml solvent. The points marked r_l and T_l are, respectively, the value of the aspect ratio for the lozenge habit ($r \approx 0.66$) and the highest temperature (obtained by extrapolation) at which the lozenge can be obtained. For the points marked by an asterisk, the authors[12] indicate that crystallization may have occurred at a higher temperature

and that of changing concentration on r. The data for each solution concentration illustrate the now familiar increase in r with increase in temperature, i.e. with decrease in ΔT. Overall, the values of r range from 0.66 corresponding to the lozenge habit at a low temperature (one data point on the 0.01 g/100 ml solution curve) to 1.09 at 92°C (0.1 g/100 ml solution curve). As comparison with *Figure 2* shows, the data in *Figure 3* are at the lower end of the range of aspect ratios which polyethylene crystals grown from dilute solutions have been observed to exhibit.

A noteworthy feature in this connection is that in crystals with higher aspect ratios (i.e. $\geqslant 2$) and in which the (200) faces are longer than the {110} faces, the (200) faces exhibit distinctly curved profiles[9,13,15–17]. This phenomenon does not arise in the data analysed here; it is, however, a factor which must be taken into account in any future analysis of the growth habits of crystals with larger aspect ratios. A discussion of the causes of this feature which, *inter alia*, is probably associated in some measure with non-steady-state growth effects, is beyond the scope of the present paper.

One of the important points to be derived from the data in *Figure 3* in connection with this analysis is the highest temperature at which lozenge-shaped crystals ($r = r_l$) would still be formed under the prevailing conditions; this temperature is denoted T_l. From visual extrapolation of the data, T_l was taken to be 77.5°C for the 0.01 g/100 ml solution, and 72°C for the 0.1 g/100 ml solution.

A feature of the results of Blundell and Keller[12] and Valenti and Pedemonte[14] which is illustrated in *Figure 3* is the effect of concentration, i.e. that for the same molecular weight and crystallization temperature r increases with increasing concentration. This effect is not peculiar to crystals grown from xylene; it has also been observed in crystals grown from n-octane, and n-decane, and it becomes progressively less pronounced with increasing concentration[14]. Some results reported by Keith[9] on crystals grown from n-dotriacontane also exhibit an upward trend in r with increase in con-

centration at constant temperature although the changes do not appear to be monotonic.

The implications of this effect of concentration on r is considered further later in conjunction with considerations of the effect of concentration and molecular weight on another parameter involved in the analysis, T_d^0.

Finally, it is necessary to consider the effects of non-planarity. The basic equations are for planar crystals, or for the c-axis projection of non-planar, hollow pyramidal-shaped crystals. The reported measurements are for collapsed crystals when the crystals are non-planar. Pleating during collapse will tend to make the measured dimensions closer to the dimensions of the c-axis projection. It is believed that any error arising from this factor will not impair the principal conclusions.

Effect of concentration and molecular weight: value of T_d^0

An examination of equations (9a) and (9b) shows that at constant temperature, changes in concentration and molecular weight can affect r by affecting the surface energies and the surface energy ratios, and by affecting T_d^0 and, hence, ΔT. The effect on the surface energies is not predictable with present knowledge, but the effect on T_d^0 is easily calculated by the methods given by Sanchez and DiMarzio[35]. These authors give for T_d^0:

$$T_d^0 = \frac{T_m^0}{1 - \zeta} \tag{11}$$

where T_m^0 is the 'equilibrium' melting point, i.e. the melting point of extended chain crystals of the polymer of the given molecular weight, and ζ (called r in ref. 35) is given by:

$$\zeta = \frac{RT_m^0 \ln a(T_d^0)}{\Delta H(T_m^0)} \tag{12}$$

where $\Delta H(T_m^0)$ is the heat of fusion at the melting point of the extended chain polymer crystals, and $a(T_d^0)$ is the activity coefficient of the polymer in solution. This latter is a function of concentration and molecular weight. Using the data as given by Sanchez and DiMarzio[35] which in turn were obtained from Flory and DeVries[36] and Pennings[37], T_d^0 has been calculated as a function of molecular weight and concentration for polyethylene in xylene. The results are given in *Table 1*. The polyethylene–xylene system appears to be the only one for which sufficient data are available to make such a calculation possible. The results are as expected: T_d^0

Table 1 T_d^0 for various concentrations and molecular weights for polyethylene in xylene

C/MW	10^4	2×10^4	5×10^4	10^5	5×10^5	10^6
10^{-3}	373.0	380.1	385.4	387.6	390.1	390.6
10^{-2}	374.0	380.6	385.6	387.7	390.1	390.6
10^{-1}	374.9	381.1	385.8	387.8	390.1	390.6
1	375.8	381.6	386.0	387.8	390.1	390.6
10	376.7	382.0	386.2	388.0	390.2	390.6
T_m^0	413.2	415.9	417.6	418.1	418.6	418.6

C Concentration (g polymer/100 ml solvent)
MW Molecular weight

increases with both molecular weight and concentration, but the effect of both factors decreases as the molecular weight increases. Indeed, above a molecular weight of 5×10^5, the effect of concentration is negligible.

As noted previously, the data which will be analysed (*Figure 3*) are for crystals of Marlex 6009 polyethylene which unfortunately is not a fraction. It is not clear under these circumstances which molecular weight average (if any) controls the crystallization process. However, as solution theories are based on number-average molecular weight this average was used for the calculation of T_d^0. The number-average molecular weight of Marlex 6009 is 1.5×10^4 (ref. 38). From this, T_d^0 for the two concentrations was interpolated from *Table 1*. The values are 377.9 K and 378.5 K for the 0.01 g/100 ml and 0.1 g/100 ml concentrations, respectively. Shifting both of these values to slightly higher or lower temperatures affects the results of the analysis of the experimental data insignificantly.

From equations (9a) and (9b) it is evident that, at constant temperature, T, the effect of increasing concentration or molecular weight is to increase T_d^0 and, hence, ΔT. This clearly predicts a decrease in aspect ratio at the same T with increase in concentration of molecular weight. This is contrary to the experimentally observed effect of concentration illustrated in *Figure 3* and also demonstrated in other cases[9,14] mentioned previously. From these reported experimental results it is possible to conclude that the effect of concentration cannot be explained by changes in T_d^0 and, hence, can only be explained by changes in the surface energy ratios with concentration. It is noteworthy in this connection that Cooper and Manley[23] have indicated significant changes in the product $(\sigma\sigma_e)^{110}$ with concentration as well as molecular weight for growth at the {110} faces of polyethylene crystals formed in xylene solutions. In addition, in their recent analysis of polyethylene crystal habits Alfonso et al.[27] concluded that the term $[\frac{1}{2}a\sigma^{200}\sigma_e^{200} - d_{110}\sigma^{110}\sigma_e^{110}]$ (using the notation here) is dependent on concentration and molecular weight but is apparently independent of temperature.

It is shown later that only very small changes in the ratios of γ and ρ are necessary to explain the effect of concentration on r exhibited by the data shown in *Figure 3*. Although not concerned with an analysis of data on the effects of molecular weight on r in the present paper, the method of analysis and the results derived therefrom concerning the effect of concentration on r are relevant to reported observations on the dependence of r on molecular weight[12-15], as discussed later.

The effect of steady state

The derivations given previously are based on crystals growing at steady state. This clearly is not the case for the experimental data in *Figure 3*, for the concentration changes during the growth of the crystals. In addition, it would be expected that fractionation on the basis of molecular weight would occur, with the higher molecular weight components crystallizing first. These particular experiments were carried out with whole polymer, although experiments on fractions[14] show the same trends. Unfortunately, no experiments are known to us where crystal shapes have been determined under conditions of steady-state growth. Fortunately, analysis of equations (9), and the experimental results themselves, show that the

aspect ratio is not a very strong function of concentration. Thus, from the data in *Figure 3*, a change in concentration by a factor of ten changes r by a maximum of ≈ 0.1, by which time 90% of the polymer in solution has been crystallized. It would not be expected that further deposition of polymer would change the aspect ratio substantially. Therefore, the data in *Figure 3* are analysed as if they represented steady-state growth with the recognition that values of parameters calculated from these results are probably not exactly correct. This is justified by noting that the intention here is to illustrate the method of analysis rather than to obtain precise numerical results.

Other parameters

Lattice parameters. Equations (9) show that the values of the lattice parameters enter into the arguments of the exponentials, the variation of which with temperature is critical. Particularly important is the quantity $a/2d_{110}$, which is the coefficient of the product of the surface free energy ratios $\gamma\rho$. For this reason, the temperature dependence of the lattice parameters was specifically taken into account as follows. There are four quantities that appear in equations (9). These are $a/2d_{100}$, $2b/a$, $\frac{1}{2}ab$, and d_{110}. These were calculated as a function of temperature from the data of Davis, Eby and Colson[39] and of Swann[40]. For temperatures > 338 K, these were fitted with a straight line, which gives a good fit and is sufficient for the purposes here. The values used are given in *Table 2*.

Surface energies. As mentioned previously, there are data in the literature on the values for the temperature dependence of the surface free energies. Using the equations:

$$\sigma = \sigma_0[1 + x \Delta T] \tag{13}$$

and

$$\sigma_e = \sigma_{e0}[1 + y \Delta T] \tag{14}$$

Hoffman et al.[22] deduced the values 0.01 for x and 0.0135 for y. It became clear from later work[1], that a temperature dependence of σ_e was necessary to fit new and more accurate data, and the value for y was given as 0.014. To examine the effect of the temperature dependence of σ_e in the analysis here, calculations were carried out both with σ_e independent of temperature, and temperature dependent with $y = 0.014$. For an undercooling of 30°C, this causes a substantial change of over 40% in σ_e and, hence, of the arguments of the exponentials in equation (9), and causes significant changes in the results of the analysis. The lateral surface energy was taken to be constant in temperature. The actual values used were: $\sigma_{e0} = 90$ ergs cm^{-2} and $\sigma\sigma_e = 1280$ erg cm^{-4} at T_d^0 (see *Table 2*)*.

The value of ϕ. The value chosen for ϕ has marked effects on the results. To illustrate its effects, detailed calculations for $\phi = 1, \frac{1}{2}$ and 0 have been carried out and results for all values of ϕ have been obtained in less detail.

RESULTS OF THE ANALYSIS

The principal aim here is to derive values of γ and ρ from fitting the experimental data. There are, however, three

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* $1 \text{ erg} \equiv 10^{-7} \text{ J}$

Table 2 Values of parameters used in the analysis

Parameter	Values used
$a/2d_{110}$	$0.9057 [1 + 2.36 \times 10^{-4} (T - 338)]$
d_{110} (Å)	$4.1251 [1 + 0.892 \times 10^{-4} (T - 338)]$
$ab/2$ (Å^2)	$18.490 [1 + 0.308 \times 10^{-3} (T - 338)]$
$2b/a$	$1.3236 [1 - 0.343 \times 10^{-4} (T - 338)]$
σ_e, (ergs cm^{-2})	$90 [1 - y\Delta T]; y = 0, 0.014$
$\sigma \sigma_e$, (erg^2 cm^{-4})	$1280 [1 + y\Delta T]; y = 0, 0.014$
ϕ	$1, 1/2, 0$
T_d^0 (K)	377.9 for 0.01 g/100 ml, 378.5 for 0.1 g/100 ml
Δh, (ergs cm^{-3})	2.80×10^9
k (ergs K^{-1})	1.38×10^{-16}
Lozenge temperature, T_l (K)	350.7 for 0.01 g/100 ml, 345.2 for 0.1 g/100 ml

other parameters involved in the analysis, and it is important also to establish how the derived values of y and ρ vary with them. These parameters are the regime (I or II), the value of σ_e^{110}, and the theoretical parameter ϕ. Accordingly, y and ρ have been determined under the following conditions:

(a) Regime I and regime II crystallization, i.e. by assuming that the crystallization occurs in either of these two regimes despite the fact that the bulk of the evidence indicates that regime I prevails at least over most of the temperature range covered by the data.

(b) For σ_e^{110}, values derived from crystallization from the melt are used (see *Table 2*), and calculations are carried out for it independent of temperature and with a temperature dependence[1].

(c) For the parameter ϕ, the results of calculations for $\phi = 0, \frac{1}{2}$ and 1 are considered in detail and the effect on y and ρ for all values between 0 and 1 is also examined.

Before proceeding with the actual determination of y and ρ, the following is noted. If both y and ρ were allowed to have a linear temperature dependence, there would be four quantities to determine: their values at some specified temperature and their temperature coefficients. Clearly, these are too many parameters to derive from the data available, so y and ρ are assumed to be independent of temperature; therefore, there are only two quantities to determine. In effect, this amounts to choosing values of y and ρ that give both the value of the aspect ratio at a specified temperature and its temperature dependence. First, however, it is necessary to establish if it is possible, by using the temperature dependent and independent values of σ_e^{110} (*Table 2*) to fit the data for both regimes, and for all values of ϕ, with one of the quantities y or ρ constant and the other adjustable.

Case 1: $y = 1$, ρ not temperature dependent. This is an example of the general case where one of the quantities y or ρ is fixed and the value of the other is determined. Here, y is fixed at a value equal to unity. Other reasonable values of y could have been chosen with equivalent results. In this illustrative case, the primary aim was to establish whether r versus ΔT curves could be calculated which exhibited qualitatively the proper temperature dependence, *viz*, that r increases as ΔT decreases, and that somewhere in the range of ΔT between zero and fifty, r was equal to r_l, i.e. ≈ 0.66.

The results are shown in *Figure 4* for regime I for $\phi = 1$, $\frac{1}{2}$ and 0, and in *Figure 5* for Regime II for $\phi = 1$ and $\frac{1}{2}$.
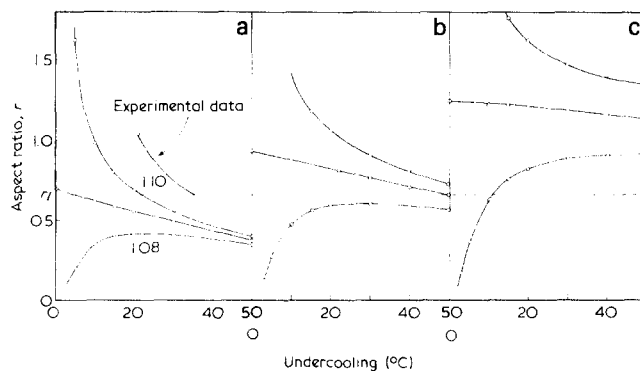

Figure 4 Calculated curves of aspect ratio *versus* undercooling for regime I, σ_e^{110} temperature dependent, and three values of ϕ for the case where $y = 1$ and ρ is the only adjustable parameter. In each case, $\rho = 1.10$ for the upper curve and 1.08 for the lower curve. The middle curve is for $\rho = 2d_{110}/a$ at T_d^0. Only for $\phi = 1$ can both the proper trend in the temperature dependence of r and an aspect ratio corresponding to the lozenge habit ($r \approx 0.66$) in this range of ΔT be obtained. (a) $\phi = 1$; (b) $\phi = \frac{1}{2}$; (c) $\phi = 0$
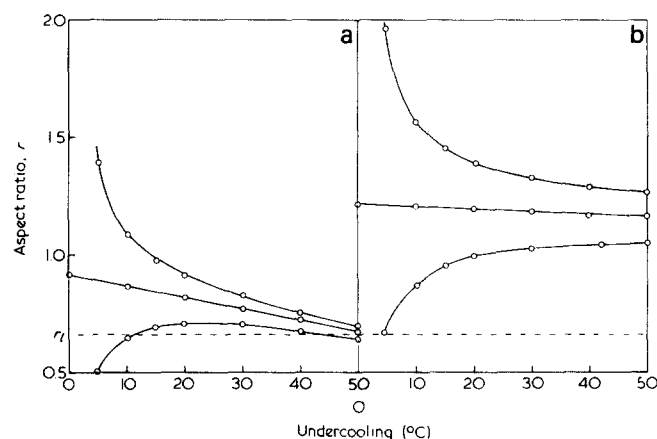

Figure 5 Similar calculations as in *Figure 4*, but for regime II and $\phi = 1$ (a) and $\frac{1}{2}$ (b). In each case $\rho = 1.10$ for the upper curve, and 1.08 for the lower curve. The middle curve is the $\rho = 2d_{110}/a$ at T_d^0. The corresponding curves for $\phi = 0$ occur at higher values of r than those shown. In all these cases the proper trend in the temperature dependence of r in addition to a value for r corresponding to the lozenge habit ($r \approx 0.66$) in this range of ΔT could not both be obtained

These curves were calculated for σ_e^{110} temperature dependent with $y = 0.014$ (see *Table 2*). Similar curves, but with a less pronounced temperature dependence are obtained with σ_e^{110} independent of temperature. They lead, however, to the same conclusions. In considering the results in *Figures 4* and *5*, the values of r which are less than $r_l = 0.66$ can be interpreted as indicating that the corresponding habit of the crystals will be the lozenge habit ($r_l = 0.66$), as discussed previously. In each of the cases shown in *Figures 4* and *5*, curves are shown for three values of ρ. In each case, for the upper curve, $\rho = 1.10$, and for the lower curve, $\rho = 1.08$. For the middle curve, ρ has the value of $2d_{110}/a$ at T_d^0. This value of ρ divides the behaviour into two regions. For ρ greater than this value, the curves have the proper temperature dependence, while for ρ less than this, they do not. This behaviour is, of course, clear from equation (9). For $y\rho = 2d_{110}/a$ at T_d^0, the argument of the second exponential approaches a finite limit at $\Delta T = 0$, as does r. For $y\rho$ greater than this, $r \rightarrow \infty$ as $\Delta T \rightarrow 0$, while for $y\rho$ less than this value, $r \rightarrow 0$ as

$\Delta T \to 0$. Hence, from the requirement of proper temperature dependence of r:

$$\gamma \rho \geqslant \frac{2d_{110}}{a} \approx 1.091 \qquad (13)$$

Thus, a qualitative criterion has yielded a quantitative result.

Also, somewhere in this range of ΔT, a value of $r = r_1 \approx 0.66$ is required. For the example chosen, $y = 1$; therefore, this is possible in only one case, i.e. for regime I, $\phi = 1$, and even here, as shown later, the experimental results can only be fitted approximately by adjusting ρ only. If σ_e^{110} is taken as independent of temperature, then the experimental results cannot be fitted even approximately, but the other conclusions (i.e. equation (13)) are the same. Clearly, to reproduce even the qualitative observations in all cases except one, and in that case to reproduce the experimental data accurately, γ must be an adjustable parameter. Thus, at least two adjustable parameters are necessary to fit the data.

It is noteworthy that it is possible to fit the data for $\gamma = 1$ if ρ is permitted a temperature dependence. There is no *a priori* reason, however, to stipulate this value of γ. Indeed, calculations of interaction energies[41] indicate that γ is not unity. In addition, stipulating the value of γ and fitting with a temperature dependent ρ would, in effect, be using three parameters for the fit: the value of γ, and that of ρ and its temperature coefficient. This is not a desirable procedure. Hence, although calculations of this type have been carried out, they are not presented here. The temperature dependence of ρ is considered later.

Perhaps the most significant result of even these preliminary calculations is the marked effect of ϕ. Although detailed discussion of this is not possible until a full analysis is completed, a few points are applicable here. Mathematically, the effect of ϕ is evident from equation (9). The second exponential in these equations principally controls the temperature dependence of r, and its argument must be positive for r to exhibit the proper temperature dependence. However, at high ΔT, the first exponential markedly influences the magnitude of r. The magnitude of the argument of this exponential clearly depends directly on the value of ϕ, and, indeed, for regime II, changes sign at $\phi = \frac{1}{2}$. This is the mathematical origin of the strong dependence of the results in *Figures 4* and *5* on ϕ, which is shown also in subsequent results. The physical origin is, unfortunately, not as clear.

Case 2: γ and ρ adjustable, but temperature independent. These calculations were carried out by requiring that the aspect ratio be r_1 at T_1. This gives a relation between ρ and γ. The actual values of ρ and γ were then obtained by requiring a good fit to the data. No analytical means were used for this fitting, for, as shown later, the method is very sensitive and allows reasonably precise determination of the values of γ and ρ.

Before proceeding to the numerical results, there is an important point to be noted from equation (9): for regime I, $\phi = 0$, and regime II, $\phi = \frac{1}{2}$, the argument of the first exponential term becomes zero. What remains available for fitting is the product $\gamma \rho$ in the second exponential, and, as a result, only one adjustable parameter is available in these two cases. As in the case of regime I, $\gamma = 1$, $\phi = 1$ mentioned previously, the data cannot be fitted with only

one parameter. The result is that for regime I, $\phi = 0$, and for regime II, $\phi = \frac{1}{2}$, only a temperature dependence of the product $\gamma \rho$ can be used to explain the results.

Typical results of the fitting procedure for a case other than the two mentioned previously are given in *Figures 6* and *7* for the 0.01 g/100 ml and the 0.1 g/100 ml solution data, respectively. These results were calculated for the case of σ_e^{110} temperature dependent, for regime I, and $\phi = 1$. The results are very similar for all other cases. As described previously, choosing the value of ρ also fixes the value of γ for it is necessary that the curve always passes through the $r_1 - T_1$ point.

Each of the Figures shows three curves: one of which is considered to be a good fit to the data, and two for which ρ had to be changed by $\approx \pm 2\%$. These latter two curves, which clearly do not fit the data, constitute a 'sensitivity analysis' for the procedure. It is evident that the values of γ and ρ are easily established to better than 1%.
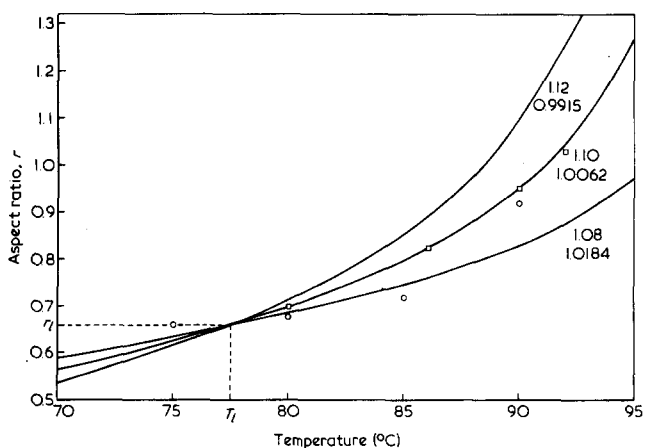

Figure 6 Fit regime I, $\phi = 1$ to the data of $\bigcirc$, Blundell and Keller[12]; and $\square$, Valenti and Pedemonte[14] for crystals grown from 0.01 g/100 ml solutions in xylene, and for the case where both γ and ρ are treated as adjustable parameters and σ_e^{110} is temperature dependent. The upper numbers assigned to the curves are ρ and the lower are γ. The calculated values of r below r_1 are not observable. The values of ρ and γ indicate the high dependence of r on these parameters and, hence, the high sensitivity with which they can be determined. The sensitivity of the fit to the data is similar for regime II and other applicable values of ϕ
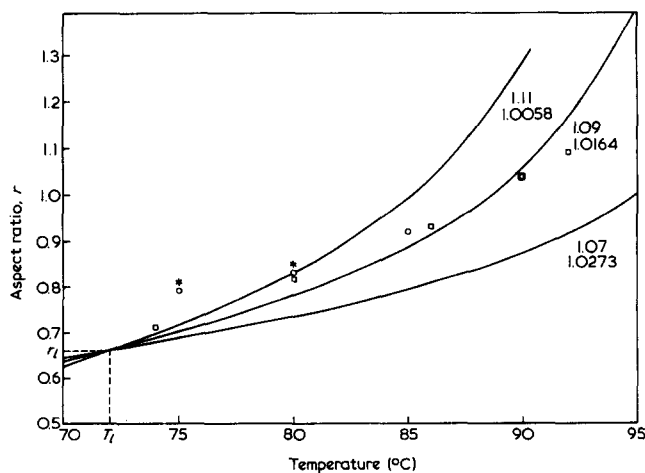

Figure 7 The same calculations as in *Figure 6*, but for the data on crystals grown from 0.1 g/100 ml solutions in xylene[12,14]. For significance of asterisks, see text

Table 3 Values of γ and ρ needed to fit the experimental data

ϕ		Regime I				Regime II			
		σ_e^{110} constant		σ_e^{110} temperature dependent		σ_e^{110} constant		σ_e^{110} temperature dependent	
		$C=0.01$	$C=0.1$	$C=0.01$	$C=0.1$	$C=0.01$	$C=0.1$	$C=0.01$	$C=0.1$
1	ρ	1.15	1.15	1.10	1.09	1.31	1.31	1.20	1.18
	γ	0.968	0.972	1.006	1.016	0.869	0.878	0.933	0.950
1/2	ρ	1.31	1.31	1.20	1.18	fit not possible		fit not possible	
	γ	0.851	0.855	0.922	0.939				
0	ρ	fit not possible		fit not possible		0.69	0.69	0.80	0.82
	γ					1.651	1.667	1.400	1.368

C = concentration (gm polymer/100 ml solvent)

It is also evident from these Figures that the fit is better for the 0.01 g/100 ml solution data than for the 0.1 g/100 ml. For the latter, the lower temperature experimental points are generally above the calculated curve. For the two points marked with an asterisk, the authors[12] remark that these solutions may have crystallized or started to crystallize during cooling to the crystallization temperature, in which case these points would have to be plotted at higher temperatures. Even so, the curve for 0.1 g/100 ml data seems to exhibit a lower temperature dependence than the calculated curves. This seems to be the case for all the calculations for the 0.1 g/100 ml solution data, and may result from the choice for the value of T_l being too high. However, as indicated previously, the only aim here is to show general trends and to illustrate the value of this method of analysis rather than provide specific numbers and it is believed that searching for a better fit (if possible) would not change the general nature of the conclusions.

The results for regimes I and II and applicable values of ϕ are given in *Table 3*. The results for $\phi = 0$, regime II, are markedly different from the other results and are discussed separately later. Some important points can be made about the other results. First, ρ is always greater than unity, as expected from the previous discussions, and it varies from ≈ 1.09 to 1.3 depending on the actual values of the other parameters used in the analysis. This result is not consistent with early calculations of the energies of isolated {110} and (200) folds[42], but it is consistent with recent calculations of Mazur *et al*.[43]* for laterally-stacked folds lying in (001) surfaces. It is also consistent with the observation that (200) sectors in crystals grown from xylene apparently melt or transform at a lower temperature than {110} sectors[44]. The value of ρ in all cases with otherwise similar parameters is lower when σ_e^{110} is taken as temperature dependent than when it is not. This follows directly from the increased temperature dependence of r provided by the temperature dependence of σ_e^{110}, i.e. the temperature dependence of r does not have to be provided by a large value of ρ.

Similarly, ρ increases on changing from $\phi = 1$ to $\phi = \frac{1}{2}$ in regime I, and from regime I to regime II for $\phi = 1$. In each of these cases, the argument of the first exponential in equation (9) decreases by a factor of two. Indeed, the values of ρ for regime I, $\phi = \frac{1}{2}$, are the same as those for

regime II, $\phi = 1$. In these two situations, the arguments of the first exponential are the same, and this shows the important effects of this term in establishing the location of the r *versus* T curve. The small changes in γ then fix the temperature dependence. However, while the mathematical basis for this behaviour is clear, the physical basis is not.

Of considerable interest are the values of γ. In all cases except regime I, $\phi = 1$ with a temperature dependent σ_e^{110}, the value is less than unity, which indicates that the lateral surface energy associated with the deposition of a stem on a (200) face is less than that for deposition on a {110} face. The implication is that the net free energy change in going from the solution phase to an isolated stem on the (200) face is larger than for a {110} face. In an analysis of aspects of the energetics of polyethylene crystallization, Patel and Farmer[41] have calculated the interaction energy of an all-*trans* polyethylene stem eight methylene units long, deposited on otherwise smooth (200) and {110} crystal faces, with the neighbouring substrate stems of the same length. The lateral packing of the chains was assumed to be as in the orthorhombic unit cell of straight-chain paraffins. The energies were -9.0 and -7.5 kcal mol^{-1}, respectively. As these calculations correspond to the energy change resulting from taking an all-*trans* stem from infinity and depositing it in crystallographic registry on each of the two faces, their results, and those here concerning the ratio of the lateral surface free energies, γ, are consistent with one another except for the case of regime I, $\phi = 1$, with σ_e^{110} dependent on temperature. In the absence of knowledge of the corresponding entropy changes involved in depositing a stem on the two different faces, however, it is not possible at this stage to compare the results of Farmer and Patel's interaction energy calculations quantitatively with the values of γ derived from the analysis here of the experimental data on r.

The determination by Patel and Farmer[41] that the interaction energy of a single stem deposited on a (200) face is greater than for one on a {110} face of an orthorhombic straight-chain alkane crystal is confirmed by calculations by Mazur for the case of the orthorhombic straight-chain alkane $C_{21}H_{44}$ (ref. 45). Interstem interactions in straight-chain alkanes have been considered previously by Boistelle and Aquilano[46]. They illustrate in their paper an interstem interaction energy map (Figure 2, ref. 46) which appears to indicate that there is no difference in interaction energy for a stem deposited on a (200) face and one deposited on a {110} face. Discussion of the apparent difference in the results of Boistelle and

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* More pertinent calculations, i.e. on the energies of staggered {110} and (200) folds corresponding more closely to the packing of folds in hollow pyramidal crystals grown from xylene, are currently being carried out

Aquilano[46], and the results of Patel and Farmer[41] and Mazur[45] is beyond the scope of the present paper. However, the foregoing comments indicate that in future the resolution of the origins of the differences in habit exhibited by polyethylene crystals should involve, *inter alia*, a further examination of the matter of interstem interaction energies, coupled with a consideration of the question of the entropy changes corresponding to the deposition of a stem on the different crystal faces. Currently, the result (see *Table 3*) that $\gamma > 1$ for regime I, $\phi = 1$, σ_e^{110} temperature dependent, which contrasts with $\gamma < 1$ for the other cases with $\phi = 1$ in both regimes, and $\phi = \frac{1}{2}$ for regime I, remains unexplained.

In considering the results for regime I, $\phi = 1$ in *Table 3*, it is evident that the values of γ obtained are close to unity. The question of whether the data could be fitted assuming $\gamma = 1$ was examined, therefore. It was possible to fit the data reasonably closely for the 0.01 g/100 ml, but not for the 0.1 g/100 ml preparation. In both cases a different value of ρ was obtained than shown in *Table 3*, and the temperature dependence of r exhibited by the calculated curves was more pronounced than in the experimental ones. The difference in the case of the 0.01 g/100 ml preparation data, although distinct, was, however, relatively small. Considering the limited amount of data available the possibility that $\gamma = 1$ in that case cannot be excluded. For the 0.1 g/100 ml preparation data, however, the difference between the calculated curves with $\gamma = 1$ and the experimental data was beyond what would be considered reasonable, experimental error.

An interesting result which emerges from a consideration of *Table 3* is that, except for the case of regime II, $\phi = 0$ (which is considered later), the behaviour of γ and ρ with concentration in all the other cases is independent of the regime and ϕ. Three features are noteworthy in this connection. First, in all these cases the value of γ is lower for the 0.01 g/100 ml preparation than for the 0.1 g/100 ml preparation. This implies that in addition to being different from one another, the lateral surface free energies and, hence, the interfacial tensions between the solution and the {110} and (200) faces in the crystals, vary differently with concentration. Second, it is possible to obtain a good fit of the experimental data with the same value of ρ for both the 0.01 g/100 ml and 0.1 g/100 ml preparations when σ_e^{110} is assumed to be independent of temperature. Whether this would have been possible with a more extensive set of experimental data to fit is not known. Third, with σ_e^{110} taken as temperature dependent, the data for the preparations of different concentrations cannot be fitted with the same value of ρ. In all cases ρ is lower for the 0.1 g/100 ml than the 0.01 g/100 ml preparation, which implies that the end surface free energies and, hence, the interfacial tensions between the solution and the {hkl} and {h0l} fold surfaces of the {110} and (200) sectors, respectively, are not only different but also change differently with concentration. The changes in γ and ρ and, hence, the interfacial tensions associated with changes in solution concentration are small. The crystal habit is evidently very susceptible to such small changes, the determination of which is an important capability of this method of analysis.

Finally, it is necessary to discuss the case of regime II, $\phi = 0$. For this case, ρ is less than unity, and γ is significantly greater than unity, varying from ≈ 1.37 to 1.67. The origin of these changes in behaviour from the

other results is easy to ascertain. As ϕ passes through the value $\frac{1}{2}$ in regime II, the sign of the argument of the first exponential in equation (9b) changes sign. Hence, the roles of ρ and γ are reversed. As, to obtain a lozenge, the argument of the first exponential must be negative, it follows that $\rho > 1$ for $\phi > \frac{1}{2}$, and $\rho < 1$ for $\phi < \frac{1}{2}$. This is considered more fully later, where it is proposed that analysis with ϕ close to or below $\frac{1}{2}$ for regime II is not applicable.

Effect of ϕ. That ϕ has an important influence on the results has been shown previously, but the clearest effects are evident in an investigation of the regions around $\phi = \frac{1}{2}$, for regime II, and $\phi = 0$ for regime I in the attempt to fit the results with γ and ρ as adjustable parameters, both being temperature independent. *Figure 8* shows the values of γ and ρ necessary to fit the results as a function of ϕ for the regime II case. Starting at $\phi = 1$, ρ increases as ϕ approaches $\frac{1}{2}$, and approaches $+\infty$ at that point. Passing through $\phi = \frac{1}{2}$, ρ decreases discontinuously to $-\infty$, and then increases, passing through zero at $\phi \approx 0.4$ for the values of the parameters used in this paper. It then continues to increase with further decreases in ϕ,
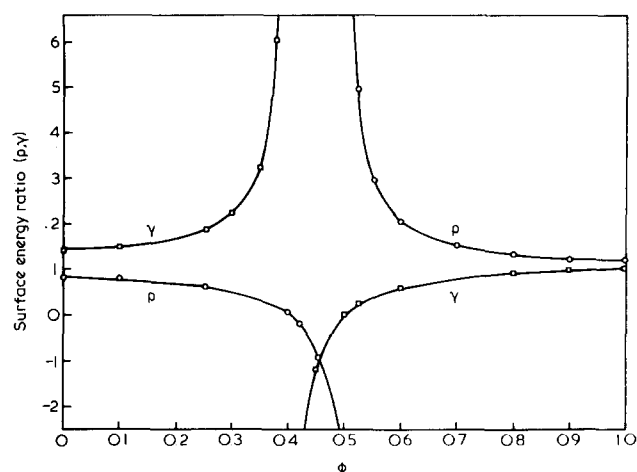

Figure 8 The dependence on ϕ of the values of ρ and γ rneeded to fit the data for the crystals grown from 0.01 g/100 ml solutions for the case of regime II growth. Infinities and negative values for ρ and γ are obtained at $\phi = \frac{1}{2}$. These aphysical results are not obtained if three adjustable parameters are used (see text). O, ρ; □, γ
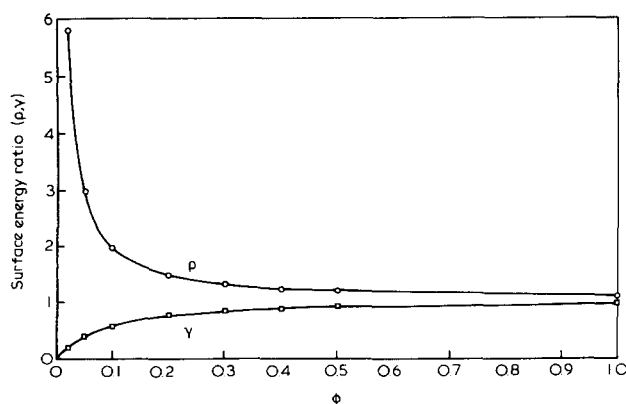

Figure 9 Same as *Figure 8* for the case of regime I growth. Here, as ϕ approaches zero, ρ approaches ∞, and γ approaches zero. These aphysical results are not obtained if three adjustable parameters are used (see text). O, ρ; □, γ

approaching the value shown in *Table 3* as ϕ approaches zero. The other parameter, γ, follows a reciprocal course. Starting from $\phi = 1$, it decreases, passes through zero at $\phi = \frac{1}{2}$, approaches $-\infty$ at the point where $\rho = 0$, at which it increases discontinuously to $+\infty$, and then decreases smoothly to the value at $\phi = 0$ given in *Table 3*.

In the case of regime I, as ϕ approaches zero, ρ approaches infinity and γ approaches zero. This is shown in *Figure 9*.

The reason for the behaviour shown in *Figures 8* and *9* is clear from equation (9) and does not have any physical significance. Negative values of surface energies cannot, of course, occur, and values of the ratios, γ and ρ significantly different from unity would appear to be physically unrealistic from calculations of interaction energies. Thus, it is necessary to conclude that this two-parameter (γ and ρ) fit of the data is inapplicable for ϕ at $\approx \frac{1}{2}$ for regime II and $\phi \approx 0$ for regime I.

This problem does *not* arise if three parameters are used to fit the data. For example, with $\gamma = 1$ and ρ temperature dependent, it is possible to fit the data for all values of ϕ in both regimes. Indeed, at $\phi = \frac{1}{2}$ in regime II, σ_e^{110} temperature dependent, and setting the temperature coefficient of ρ as $0.00231°C^{-1}$, then $r = 1.069$ at $85°C$, and similarly reasonable values at all the other crystallization temperatures. Thus, it appears that if reasonable behaviour is required at approximately $\phi = \frac{1}{2}$ for regime II and $\phi = 0$ for regime I, then either a three-parameter fit is necessary, or the physically unacceptable results for these values of ϕ for the two-parameter fit arise from an incomplete treatment of the kinetics problem. This is discussed more fully in the Discussion.

DISCUSSION

Two clear conclusions can be drawn from the results obtained. These arise from the calculations shown in *Figures 4* and *5*, and are the following:

(1) $\gamma\rho \equiv (\sigma\sigma_e)^{200}/(\sigma\sigma_e)^{110} > 2d_{110}/a \approx 1.09$ at the dissolution temperature T_d^0.

(2) The experimental results of Blundell and Keller[12] and Valenti and Pedemonte[14] shown in *Figure 3* cannot be fitted with a single adjustable parameter. For example, if γ is stipulated to be equal to unity, and ρ is taken as the single adjustable parameter, the data cannot be fitted.

Both of these conclusions are independent of the other parameters of the problem: σ_e^{110}; ϕ; and the regime. Treating γ and ρ as adjustable parameters, their values have been determined where possible from the analysis. However, at approximately $\phi = \frac{1}{2}$ in regime II, and $\phi = 0$ in regime I, the calculated values diverge unreasonably (*Figures 8* and *9*) and negative values are encountered (*Figure 8*). Such behaviour does not arise if γ is fixed and ρ is taken to be linearly dependent on temperature, the two adjustable parameters then being its value at a specified temperature and its temperature coefficient, but this procedure is equivalent to a three-parameter fit.

From these results, several arguments can be made. First, the most marked effects of ϕ arise for regime II at $\phi = \frac{1}{2}$ and below. It might be argued that the unreasonable results shown in *Figure 8* might arise because regime II growth is inapplicable to these crystals, but no such argument could be made for the similar behaviour at $\phi = 0$

for regime I. Moreover, the argument about the inapplicability of regime II would oppose the results of the Lauritzen z test[25] and at least some experimental results[23] which indicate that at least at relatively high undercoolings crystals grow in a mixed mode, and possibly in regime II, as the crystals attain a sufficient size. The effect of ϕ must arise, therefore, from some other cause.

The second argument that could be advanced concerning the effects of ϕ is that either or both of the surface energy ratios are temperature dependent. As discussed previously, choosing $\gamma = 1$ and allowing ρ to have a linear temperature dependence permits a good fit of the data for all values of ϕ and for both regimes. Unfortunately, there is no basis for choosing $\gamma = 1$, and any other reasonable value could have been chosen. Even so, such a data fitting procedure effectively involves three undetermined parameters, and there are not enough relevant data and knowledge in the literature to permit their determination. It is believed that the surface energy ratios may indeed be temperature dependent. This could explain the general trend in the temperature dependence of r shown in *Figure 2*; but this cannot be demonstrated with the data available.

Finally, with regards to the value of ϕ, it is necessary to discuss how this parameter is used in the kinetic theory[1]. ϕ is a parameter that apportions the free energy of crystallization to the forward and backward steps in the stem deposition process. For $\phi = 1$, all of that free energy is assigned to the forward step (i.e. stem deposition at the end or beginning of the growing strip) while for $\phi = 0$, all of it is assigned to the backward step (i.e. removal of a stem from the end of the growing strip). Frank and Tosi[47] were the first to address the problem of the apportionment of the free energy to the forward and backward steps. They concluded that the free energy change is 'associated in large measure with the "upward" step'. As the deposition of the first stem from the liquid phase is by far the largest 'upward' step, this would imply $\phi = 1$ is the most reasonable value of ϕ, at least for regime I, where the deposition of the first stem is the rate controlling process. It could also be argued that perhaps the most reasonable apportionment would be $\phi = 1$ for the first stem, and $\phi = 0$ for all subsequent stems because for them the forward step is 'downward' and the backward step is 'upward'. As carried out previously by Lauritzen and Passaglia[26] such a 'mixed' problem has not been solved in closed form because the rate equations are not integrable. In the present version of the theory[1,2] ϕ is apportioned in the same way for all steps. This appears to be the only formulation that is integrable in closed form[1]. This 'mixed ϕ' formulation could, of course, be applied to this analysis by numerical computation, but this has not been attempted. With the present formulation, and considering that in regime I the first stem deposition is the rate controlling step, it is tentatively concluded that the most reasonable analysis is that for regime I, with $\phi = 1$ or close to it. Fortunately, application of the z-test[25] and analysis of experimental growth rate data[1] both indicate that the crystals grow by regime I over most of the temperature range. However, a dichotomy concerning the relative magnitudes of the lateral surface free energies arises. From the results for the regime I, $\phi = 1$ case given in *Table 3*, $\gamma < 1$ when σ_e^{110} is assumed to be independent of temperature, where $\gamma > 1$ when σ_e^{110} is taken as temperature dependent. Clearly, both results cannot be correct although γ is very

close to unity in both cases. This dichotomy remains unresolved, and is not considered here further except to note that $\gamma < 1$ would be more consistent with the interstem interaction energy calculations of Patel and Farmer[41] mentioned previously.

It is now necessary to discuss the effect of concentration on r and its implications. It was noted previously, with reference to the data in *Figure 3* and other observations[9,14], that the manifestation of increases in r with increasing concentration at a given temperature opposes the predictions of the kinetic theory. Given that T_d^0 for a given polymer molecular weight and solvent system increases with concentration (*Table 1*) and, hence, that ΔT at a particular crystallization temperature is correspondingly larger when the concentration is higher, then it would be expected from equation (9) that r should decrease with increasing concentration (provided, of course, that all the other terms in the equations are independent of concentration). In view of the experimental results which exhibit a contrary effect of concentration on r, it was deduced that the surface energies must be dependent on concentration. Calculations here have shown that small relative changes of the order of 1% in surface energy ratios are sufficient to affect r significantly and, hence, the fit to the data in *Figure 3*. The results in *Table 3* show that such small changes in the values of γ, and in some cases both γ and ρ, are necessary to account for the observed changes in r with concentration. As noted previously, the implication of the changes in γ with concentration in the range 0.01–0.1 g/100 ml is that the interfacial tensions between the {110} and (200) crystal faces and the solution are not only different and dependent on concentration, but also that they change differently with concentration. The same implications apply to the {khl} and {h0l} surfaces of the {110} and (200) sectors, respectively, in the case of changes in ρ with concentration.

These indications that the surface energies are dependent on concentration are consistent with results reported by Cooper and Manley[23]. Their analysis of the effect of temperature, concentration, and molecular weight, on the growth rate of the {110} faces of crystals formed in xylene indicated that the product $(\sigma\sigma_e)^{110}$ changes significantly with concentration and molecular weight, although the direction of the change depended on the method of analysis of the growth rate data. Whichever the direction, it would seem reasonable on the basis of their results to expect that $(\sigma\sigma_e)^{200}$ would also change with concentration. The results in *Table 3* simply require that the changes in surface energies (and, hence, interfacial tensions) with concentration be slightly different for growth at the {110} and (200) faces. Alfonso *et al.*[27] have analysed the effects of temperature, concentration and molecular weight on the habits of polyethylene crystals in terms of the kinetic theory assuming regime I growth and that $\sigma^{110} = \sigma^{200}$. In addition to concluding, as here (*Table 3*), that for a given concentration and molecular weight $\sigma_e^{200} > \sigma_e^{110}$ they also report that the term $[a/2\sigma^{200}\sigma_e^{200} - d_{110}\sigma^{110}\sigma_e^{100}]$ decreases with increasing concentration. An examination of *Table 3* shows that the product $\gamma\rho$ increases very slightly with concentration in all cases. It is easily shown from this result that here the term $[a/2\sigma^{200}\sigma_e^{220} - d_{110}\sigma^{110}\sigma_e^{110}]$ increases slightly with concentration. The origin of this difference in the two sets of results has not been investigated, but may result from the

more simplified treatment of Alfonso *et al.*[27].

From the results and discussion of the analysis of the effects of temperature and concentration on the aspect ratio, it is now possible to consider the effects of molecular weight (MW) on r which apparently differ depending on the solvent. As discussed previously the terms T_d^0 and ΔT in equation (9) are dependent on MW. As T_d^0 increases with MW then for the same solvent, polymer concentration, and crystallization temperature, r would be expected to be smaller the higher the MW, assuming of course that all the other parameters in equation (9) are independent of MW. This expected trend has been confirmed by Khoury and Bolz[15] in a study of the effect of temperature and molecular weight on the aspect ratio of crystals grown from 0.01 g/100 ml solutions of polyethylene fractions in heptyl acetate and in dodecanol which are relatively poorer solvents for polyethylene as compared with xylene.

Here, two examples are used to illustrate the significant effects which MW can have on r. Thus, crystals of two polyethylene fractions, I ($M_n = 11\,400$, $M_w = 13\,600$) and II ($M_n = 28\,900$, $M_w = 32\,100$) grown from 0.01 g/100 ml solutions of the fractions in heptyl acetate at 105°C had aspect ratios of 3.5 and 2, respectively. The aspect ratios of crystals of grown from 0.01 g/100 ml solutions of the same fractions in dodecanol at 115°C were 6 and 2.4, respectively. A tendency for r to decrease with increase in molecular weight at constant temperature is also shown by some data due to Keith[9] for crystals grown from solutions of relatively high concentrations (> 0.5 g/100 ml) in dotriacontane. Similar behaviour has been observed by Labaig[48] in lamellar crystals grown in very thin films of polyethylene fractions crystallized from the melt; these crystals exhibited a broad range of aspect ratios (up to 15 for some fractions) and curved lateral profiles. These observations which, for the reasons given previously, are at least qualitatively consistent with the predictions of the kinetic theory (note that in the case of crystallization from the melt T_m^0 increases with MW), differ from the results reported for crystals grown from xylene. Thus, contrary to an earlier observation reported by Takamizawa *et al.*[13], Keller and Willmouth[11] found that the aspect ratio of crystals grown from 0.01 g/100 ml solutions in xylene at 80°C, increased with increasing molecular weight*. Evidence has been cited by Valenti and Pedemonte[14] which is consistent with this latter effect in the case of crystals grown from xylene. As discussed previously, in the case of the effect of concentration on r, such behaviour suggests that for crystals grown from xylene the surface free energies change with increasing molecular weight such that the effect on r is opposite to, and overrides, that due to the increase in T_d^0 with MW. This is evidently not the case for the crystals grown from heptyl acetate, dodecanol and dotriacontane. The manifestation of decrease in r with increasing molecular weight at constant temperature indicates that the effect of changes in T_d^0 with MW dominates in the latter cases. The possible occurrence of changes in surface energies with MW, which are such that they reinforce rather than oppose the effects of increases in T_d^0 with MW, cannot, of course, be ignored in these cases.

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* It is noteworthy that the effect of changing molecular weight was studied by Keller and Willmouth[11] by examining crystals of Marlex 6009 polyethylene to which increasing amounts of high-molecular-weight fractions precipitated from stirred solutions were added

Rigorous analysis of the effects of MW, concentration and temperature on the habits of crystals grown from various solvents will require more data on T_d^0 and its dependence on MW and concentration for various solvents, as well as corresponding data on the effect of MW, concentration and temperature on r. Only then will it be possible to isolate and determine the origins of the respective and/or interrelated influences which temperature (*per se*), ΔT, MW, concentration, and solvent, have on the lateral growth habits of polyethylene crystals. The method of analysis described in this paper clearly is appropriate. A complicating aspect, however, in this connection is the need for accounting for the tendency for the longer edges of crystals with large aspect ratios (r approximately larger than 2–3) to have curved profiles (see previously).

CONCLUSIONS AND SUMMARY

(1) A method has been described for analysing of the change of aspect ratio with temperature of polyethylene crystals grown from solution, provided that the aspect ratio represents steady-state growth. The method is based on the kinetic theory of polymer crystal growth, and it can in principle be used to determine the relative values of the surface free energies associated with growth at the {110} and (200) crystal faces with great sensitivity. However, it cannot give the actual values of the surface energies.

(2) To obtain the proper temperature dependence of the aspect ratio, the ratio of surface energies $(\sigma\sigma_e)^{200}/(\sigma\sigma_e)^{110}$ at the equilibrium dissolution temperature T_d^0 must be greater than ≈ 1.09. If $\sigma^{200}/\sigma^{110}$ is further required to be equal to unity or some other constant value, the experimental data (Figure 3 from refs. 12 and 14) on aspect ratio *versus* temperature for polyethylene crystals grown from xylene cannot be fitted using the ratio $\sigma_e^{200}/\sigma_e^{110}$ as a single adjustable parameter.

(3) Using both $\sigma^{200}/\sigma^{110}$ and $\sigma_e^{200}/\sigma_e^{110}$ as adjustable parameters, their values can be determined with high sensitivity by fitting the data. The actual values obtained for these ratios depend upon the crystallization regime (I and II), and the values chosen for the other parameters used in the analysis, i.e.: σ_e^{110} and its temperature dependence, and particularly the value of ϕ, the parameter that apportions the free energy of crystallization to the forward and backward steps during the stem deposition process. Where this analysis is believed to be unambiguous with respect to the values of ϕ, $\sigma_e^{200}/\sigma_e^{110}$ is greater than unity, and the value of $\sigma^{200}/\sigma^{100}$ is close to or slightly less than unity.

(4) Infinities and negative values of the surface free energy ratios arise from the analysis at $\phi = \frac{1}{2}$ for regime II. For regime I, $\sigma_e^{200}/\sigma_e^{110}$ tends towards infinity and $\sigma^{200}/\sigma^{110}$ tends towards zero at $\phi = 0$. These physically impossible results can be avoided by using a three-parameter fit using the ratio $\sigma_e^{200}/\sigma_e^{110}$ and its linear temperature dependence as adjustable parameters and assigning a fixed constant value (taken as unity in this analysis) to the ratio $\sigma^{200}/\sigma^{110}$. The limited data and knowledge available do not permit such an analysis; the fit to the data is excellent using only two parameters. Hence, the greatest obstacle to using this method for obtaining values of the surface energy ratios are the lack of data and/or the correct value to assign to the parameter ϕ

in the kinetic theory. A possible way of avoiding the latter difficulty, i.e. making $\phi = 1$ for the first stem deposition and $\phi = 0$ for all subsequent stems, is suggested. In this case, the rate equations are not integrable and numerical methods are required.

(5) With this present knowledge concerning the value of ϕ, and based on the results of the application of the Lauritzen z test[25], regime I growth and $\phi = 1$ appear to be the most reasonable conditions for analysing the experimental data examined.

(6) The effect of concentration on the aspect ratio was also examined. The experimental data analysed cannot be explained by the effect of concentration on the dissolution temperature T_d^0. On the basis of the theoretical framework used here, its effect on the aspect ratio can only be explained in terms of a difference in the change of the lateral surface free energies σ^{110} and σ^{200}, and/or the end surface free energies σ_e^{110} and σ_e^{200}, with concentration. Only small relative changes of the order of 1% are necessary. Changes in these surface energies imply that the interfacial tensions at the {110} and (200) growth faces and/or the corresponding sector surfaces change differently with concentration.

(7) The effects of molecular weight on the aspect ratio of polyethylene crystals grown from xylene and other solvents is briefly discussed.

ACKNOWLEDGEMENT

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