

A different approach to morphological diversity and surface nucleation in linear polyethylene

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Abstract

The classical Kossel–Stranski crystal model is adapted to a critical re-examination of surface nucleation in polyethylene. Several aspects of the diverse morphologies displayed by this polymer are well accounted for. The suggestion is made that curved {200} faces in lenticular crystals arise as a consequence of normal growth rather than nucleated growth on these faces. Processes generally involved in surface nucleation and subsequent layer spreading are discussed with emphasis upon entropic considerations. This leads to the view that, although nucleation kinetics are followed, molecular conformations can become more tightly clumped than is commonly thought to follow inevitably from layer spreading.

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1. Introduction

From one standpoint, that of simplicity of molecular structure, linear polyethylene is undoubtedly the prototypical chain polymer. However, in terms of morphological diversity (including occurrence in some circumstances of seemingly stable curved surfaces in crystals whose principal growth kinetics are unmistakably controlled by surface nucleation and layer spreading) and of its readiness to undergo structural changes in the solid state (such as rapid isothermal thickening) it is a veritable chameleon, at times seeming to play the role of protoatypical polymer. Some aspects of its unusual behavior can, I believe, be freshly illuminated by an analytical approach that, to my knowledge, has not previously been explored in this context. It is in principle the same approach as that adopted (ca. 1925–30) by Kossel [1] and Stranski [2] (KS) in their pioneering physical studies of crystal growth in simple monatomic and ionic crystals. Their simple models are well suited for adaptation to crystals comprised of units bound by very short-ranged van der Waals forces, such as encountered in

chainfolded (CF) lamellae of linear polyethylene or in extended chain (EC) crystals of paraffinic oligomers.

By applying the classical KS model to polyethylene I shall develop a rationale that may account for several puzzling aspects of crystalline morphology in CF lamellae of that polymer. Of particular interest will be the elusive (200) facets which appear only at higher crystallization temperatures and in turn become anomalous by developing remarkably smooth curved profiles that conventional theory fails to handle in a convincing fashion; the explanation may lie at a more fundamental level than restricted layer spreading alone. Reminding myself of some often-overlooked aspects of classical nucleation theory and applying the KS model to surface nucleation in polyethylene has also suggested some revisions to current theory. Although modifying only a few predictions of that theory, these revisions nevertheless seem to open a route to understanding finer points where conclusions based upon rigid application of existing formalism have in recent years appeared inconsistent with experience.

In an effort to avoid confusions of purpose it seems desirable that I should first resurrect and establish some basic tenets that later figure prominently in my arguments. In this I ask the reader's indulgence, which I trust will eventually appear adequately justified by clearer exposition.

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2. The classical Kossel–Stranski model and other preliminaries

2.1. Binding energies and the ‘half-energy’ or growth site

In its simplest form the KS model is that of a monatomic solid in the form of a crystal of simple cubic structure, atoms being represented as cubes with interaction energy V_1 between nearest neighbors (cubes sharing a common face) and V_2 between next-nearest neighbors (cubes sharing a common edge). Although an idealization in that no monatomic solid has such a simple structure, the model nevertheless illustrates realistically the relative binding energies of atoms in various situations on a crystal surface having incomplete layers and/or incomplete rows, situations varying from atoms buried within the surface to isolated adatoms dotted here and there upon it. In the particular case of an atom such as that lightly shadowed in Fig. 1 (at a position called in solid state physics a kink site and being the analogue of a niche site in a CF polymer lamella (see later)), even this simplest of models reveals a most important feature of such sites that holds true not only for more sophisticated models but also for real crystals as well. These are sites in which atoms inevitably possess exactly one half as many nearest neighbors, to any reasonable order of nearness, as do atoms deeply buried within the lattice. Remembering that interaction energies V_1 , V_2 , etc. are always shared between two neighbors, we see that the binding energy at a half-energy site is exactly the total binding energy of the crystal divided by the total number (assumed large) of atoms or other units. It is then evident that growth or dispersal of the crystal can in effect be considered as repetitive addition or removal of units at half-energy sites. The corresponding binding energy can therefore be identified as the enthalpy of formation or the latent heat of solidification when the crystal is formed from vapor, liquid or solution. We shall later find this a useful reference level when assessing relative activation energies involved in different modes of surface nucleation.

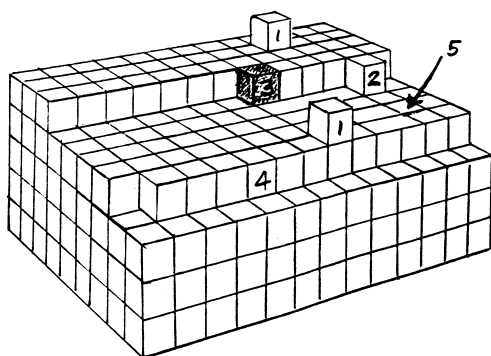


Fig. 1. A Kossel–Stranski model crystal. Numerals indicate the number of next-nearest neighbors adjoining various units. Of particular interest is the shaded ‘half-energy’ site with three nearest neighbors.

2.2. Surface energies: origins and subtleties

The origin of surface tension in liquids, and its numerical equivalence in a given system of units with surface energy, is a concept presenting little difficulty to beginning students of physics. As clearly recognized by Gibbs, however, corresponding concepts in solids are considerably more complex. That crystals may have polyhedral equilibrium forms argues at once that phase boundaries involving crystals have anisotropic surface energies related to the natures and structures of both adjoining phases. Appreciation of the underlying physics in the case of a crystal in contact with its melt we owe, I believe, largely to the perceptiveness of Spaepen [3]. Consider a plane interface between a crystal of pure material and its melt at equilibrium; that is, when free energy G per unit mass is the same throughout the bulk of either phase. How then does G vary as we pass through the interphase region where structure is unlikely to change *abruptly* on an atomic scale (and, indeed, probably cannot do so)? It is evident that enthalpy, being dependent primarily upon interatomic distances can change relatively quickly on passing from solid to liquid although, as we shall see later, there may be some increase on passing through the last few atomic layers of crystal. Compensating increase in entropy, on the other hand, being largely dependent upon disorder, can develop only upon passing far enough into the liquid for there to be no residual ordering enforced by surface structure or proximity. (In polymers, clearly, this can require distances comparable to random coil dimensions.) In the transition region, therefore, there is excess free energy owing to what Spaepen termed ‘negentropy’—a local deficit of entropy otherwise necessary to compensate for increased enthalpy. From this perception, it is evident that surface free energy at a crystal face will have a unique value only if assessed within the broad expanse of that surface, and not immediately contiguous to edges where structure and binding are inevitably different.

It might appear that one could calculate surface energy of a principal facet of a crystal in contact with its vapor merely by supposing the crystal to be cleaved cleanly at such a facet and then assessing resulting change in enthalpy. In practice this is unreliable and may result in values that are considerably overestimated, largely because relaxation of interplanar spacings within newly created surface layers is difficult to assess or has been ignored. We shall have occasion to remember this later.

2.3. Theories of surface nucleation

First, let us remind ourselves of the traditional formalism followed in the case of monatomic substances or small molecular compounds. We imagine a smooth close-packed (low energy) facet of a crystal, doubtless with mobile crystallizable units (adatoms or molecules) dotted here and

there in short-term residency on the surface (adsorbing and, being weakly bound, desorbing again). We imagine some of these to aggregate in small surface patches, and consider how large such a patch has to become in order to reach metastability with potential for nucleation and ongoing growth, and how likely such a patch is to form. We estimate the free energy of formation of a patch (consisting of a sizable number N of units) which we suppose to have a shape determined by symmetry of the crystal (square patch on a cubic crystal, say). We recognize a negative contribution ($\propto N$) from enthalpy accompanying condensation of the N units and a positive contribution ($\propto N$) associated with the outer *edge* of the patch where (a) units are less tightly bound (by an appreciable fraction of latent heat) and (b) where there is *edge surface energy* (also $\propto N$). (Of these two factors, the former is often ignored and the latter regarded, perhaps erroneously, as the more significant.) There is also a positive contribution associated with reduction in entropy accompanying ordering of initially randomly dispersed adsorbed units during formation of the patch. This latter contribution was clearly acknowledged by most early workers in the field [4–7]; it has important consequences when thermodynamic driving force for crystallization is small but, regrettably, it came to be ignored, and ultimately forgotten, in much subsequent work. More attention has been focused upon dimensionality, that is, upon opposing contributions depending upon different powers of N . From this one can predict appropriately small critical sizes for nuclei (whose accuracies cannot be closely checked); but as a shortcut it cannot be relied upon for accurate calculation of activation energies of formation.

Another unfortunate trend has been to identify the edge surface energy of a surface patch with the surface energy of a corresponding extended side face of the crystal. This is clearly an incautious and unwarranted assumption.

It may seem paradoxical, when each new layer is added to a facet of a crystal and expands its lateral faces, that it would not add commensurate surface energy to these faces as well. The point is that the edge of the new layer is not yet so tightly bound as it will be when covered by a number of successive layers. We must remember reversible relaxation processes near free surfaces; the ultimate energy balances are obvious but are arrived at incrementally. The mistake is in charging the entire bill to the initial act of nucleation before the full series of subsequent events have been considered and associated charges have been laid off elsewhere.

2.4. Accessibility and entropic activation barriers

The remaining preliminary we need to consider is this. When dealing with monatomics or small molecular compounds the entropic considerations already referred to are generally expressed (using Boltzmann's relation $S = k \ln W$) as ratios of large numbers of sites

available for occupation and smaller but significant numbers actually occupied. With polymers the corresponding concepts have to be expressed in a different, and less familiar, manner. For example, we might be faced with the following question. What are the relative probabilities of a given stem site on a growing polymer lamella being filled (a) by a mobile chain length of a molecule that remains in close proximity by virtue of already being 'anchored' nearby by partial crystallization or adsorption or (b) by a completely different free molecule finding its way to the stem site by chance? In the spirit of statistical mechanics we instinctively think of relative frequencies with which candidate molecules present themselves for possible attachment. But how do we express this in thermodynamic terms? Are there circumstances when it is vital that we do so or, at least, follow out the logic of doing so?

Let us compare two competing mechanisms for which frequency factors are ν_1 and ν_2 ($\nu_1 > \nu_2$). The ratio of their probabilities is then $W_1/W_2 = \nu_1/\nu_2$ and, since $W = \exp(S/k)$, we can write $W_1/W_2 = \exp\{(S_1 - S_2)/k\} = \exp(T\Delta S/kT)$ where $T\Delta S = (S_1 - S_2) = \ln(\nu_1/\nu_2)$ in *units* of kT . If the competing mechanisms arise straightforwardly as part of a rate process (growth, say) then we may either say that, relative to mechanism 2, mechanism 1 has been accelerated by a factor (ν_1/ν_2) or that, relative to mechanism 1, mechanism 2 has been retarded by an entropic activation barrier of magnitude $\Delta S = (S_1 - S_2)$, that is by a factor $\exp(-T\Delta S/kT) = \nu_2/\nu_1$. These are equivalent statements, of which the former is far the simpler; in the context of rate of a growth process the factor will in all likelihood be subsumed anyway into an arbitrary front factor often written G_0 . *However, when a frequency ratio such as ν_1/ν_2 arises in circumstances that directly affect formation of a nucleus, we must use the ΔS representation and incorporate this additional entropy with the entropy term already present in the expression for ΔG^* , the free energy of activation energy for formation of the nucleus in question. The effect of doing so is then much more consequential.* We recall that a nucleation term in a growth rate ultimately takes the form $\exp(-B/T\Delta T)$, B being an assembly of constants and ΔT the supercooling, and that it therefore dominates in controlling rapidly varying rates of nucleation and growth at smaller supercoolings. It is easily seen that if a nucleation process, for which the activation energy by conventional calculation is ΔG^* in *units* of kT , is assisted mechanistically by a favorable frequency factor, f say, then ΔG^* will be reduced by $(\ln f)$ *units* of kT and rate of nucleation will be increased by $\exp(\ln f)$, that is, by f times. Such possibilities can be of enormous consequence as we shall see later. In rate processes, by comparison, frequency factors usually influence Arrhenius terms only; these are relatively insensitive to changes in supercooling and their magnitudes are often of less than pressing interest.

3. The Kossel–Stranski model adapted for lamellae in linear polyethylene

Fig. 2 shows in c -axis projection part of the polyethylene lattice. Since molecular stems in all-*trans* conformations are well rounded in cross-section (discussed later, Fig. 3) and pack with setting angles approximately $\pm 45^\circ$ to a and b axes, we may for present purposes regard them as cylinders. Moreover, most electron in these molecules being concentrated near central axes we may, to good approximation, assess interaction energies from inter-axial distances using $V \propto r^{-6}$, as appropriate for van der Waals forces. Further, since these interactions are reduced to $\approx 1.5\%$ with each doubling of interatomic distance it will suffice, again to good approximation, to limit consideration to interactions within (ab) planes of CH_2 groups at the same level and multiply by the number of such planes involved in a lamella. (Integration that would effectively weaken reduction of interaction energy with distance could be required with longer ranged forces, but not in present circumstances as we shall shortly confirm.) Interactions between nearest neighbors of ascending order (first, second, etc.) we denote by V_1, V_2, V_3 , etc. Corresponding inter-axial distances, between a corner $[a, b] = [0, 0]$ of a unit cell and successive nearest neighbors are r_1 to $[1/2, 1/2] = 4.56 \text{ \AA}$, r_2 to $[0, 1] = 5.00 \text{ \AA}$, r_3 to $[1, 0] = 7.63 \text{ \AA}$, r_4 to $[1/2, 3/2] = 8.42 \text{ \AA}$ and r_5 to $[1, 1] = 9.12 \text{ \AA}$. It would be quite sufficient to confine ourselves to V_1, V_2 and V_3 but it is no inconvenience to include interactions at all inter-axial distances up to 10 \AA . Since I shall later be concerned mostly with behavior at crystallization temperatures ca. 125°C I have included, as a further (probably inconsequential) refinement, correction of unit cell dimensions to allow for thermal expansion.

On the basis of $V \propto r^{-6}$ we find interaction energies normalized to $V_1 = 1$ to be $V_2 = 0.576$, $V_3 = 0.046$, $V_4 = 0.025$, and $V_5 = 0.016$. It is easily seen that a stem site deep within the lamella has a full complement of nearest neighbors providing interaction energy $4V_1 + 2V_2 + 2V_3 + 4V_4 + 4V_5 = 5.408$ normalized units. It follows that a half-

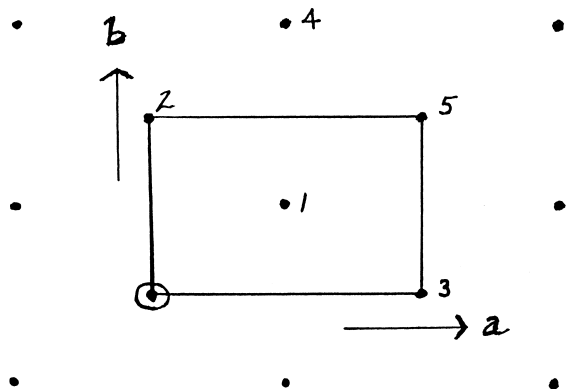


Fig. 2. c -Axis projection of polyethylene lattice. Relative to the molecule at the lower left-hand corner of the unit cell we denote examples of neighboring sites in order of nearness (see text).

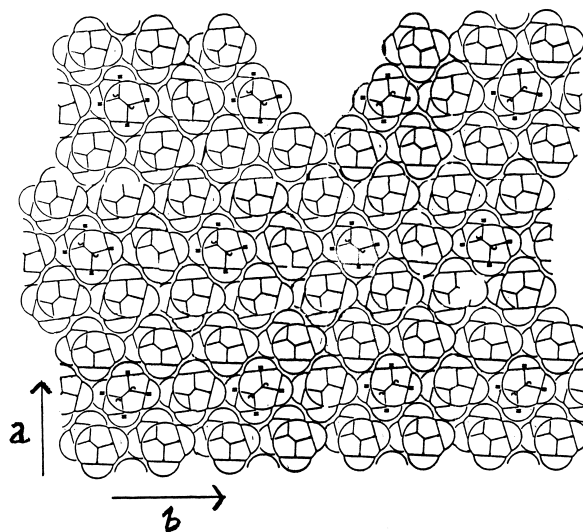


Fig. 3. Portion of polyethylene lattice (a -axis vertical and (200) planes horizontal). Note that at the tip of the reentrant in the (200) surface the lattice to the right is undistorted whereas, to the left, molecules in the upper three rows are rotated in a 'faulted structure' such that continuity of rows in (200) planes cannot be maintained.

energy niche site at the end of an incomplete row of stems on any of the closer packed planes [$\{110\}$, $\{200\}$, or $\{020\}$] in three dimensions} has a binding energy of 2.704 normalized units. As compared with this norm we are ultimately interested in the deficit of binding energy experienced by an isolated stem attached to one of the closer packed planes (especially ($\{110\}$); this will prove to be a measure of the major component of the activation energy for nucleation on that plane. For the moment I shall concentrate on this component and omit consideration of surface energy at lateral surfaces of the nucleating stem, upon which too much emphasis may hitherto have been placed in other studies; I am not ignoring the latter surface energy but temporarily postponing any assessment of its magnitude while pursuing a new approach. Here I must emphasize that I do not differ from the Lauritzen–Hoffman approach [8,9] in considering the addition of a first stem (first stem plus first fold for CF lamellae) as the critical step in surface nucleation; I merely wish to estimate activation energies differently and, despite approximations involved, according to other, possibly stricter, physical precepts.

It is evident upon inspection that, relative to the binding energy ($W/2$) at a niche site, the cost of a nucleating stem on (110) is $1V_1 + 1V_5$, on (200) it is $1V_2$, and on (020) it would be $1V_3$ (in each case, including the niche site, free energy Q associated with a fold would be included, if appropriate). Neglecting Q for the moment, the relative costs of nucleating stems on (110), (200), and (020), expressed as decimal fractions of ($W/2$) are 0.393, 0.213, and 0.017, respectively. These ratios are surprisingly insensitive to whether they are calculated using an inverse sixth, fifth or fourth power law for interactions (for the latter two cases they become 0.360, 0.220, 0.027 and 0.341, 0.222, 0.041,

respectively); I take this as justification for earlier neglect of integration over sheets of molecules. The ratios are also very revealing.

3.1. Morphological implications

It is no surprise that the most costly nucleus would form on the closest packed planes $\{110\}$ which should be the slowest growing, and dominant, facets seen in crystals grown without major influence from diffusion fields near interfaces. This is certainly the case in crystallization from dilute solutions at lower temperatures when the habit is rhombic. (In the following I shall ignore some dependence of habit upon the natures of solvents used in crystallizations from solution and concentrate more upon the influence of crystallization temperature which carries over more or less continuously from solution to melt.) With increase in temperature, rhombs become slightly and then more pronouncedly truncated by the appearance of $\{200\}$ facets which, as the trend continues, become weakly but unmistakably curved though remarkably free from apparent micro-faceting. Ultimately, crystals become elongated and distinctly lenticular in shape, often with narrow $\{110\}$ facets meeting at fast growing $\pm b$ axes and with extensive faces (nominally $\{200\}$) smoothly arced with modest curvature around the ends of $\pm a$ axes. We shall return to this anomalous and intriguing behavior presently.

A notable feature of the ratios previously cited is the considerable disparity between relative costs of surface nucleation on $\{200\}$ and $\{020\}$ facets. The cost on $\{020\}$ is so cheap that such faces should grow very rapidly out of existence and, in fact, we *never* see them exposed. Moreover, growth along b axes ought to be relatively fast under all conditions and $\{110\}$ faces should always appear to meet on b axes in sharp protuberant corners. This is indeed the case over the entire range of temperatures studied. On the other hand, the absence of $\{200\}$ facets in rhombs grown rapidly (usually dendritically) at lower temperatures, despite a somewhat lower activation energy for nucleation, is largely attributable to the angle at which $\{110\}$ facets meet along a axes (67.4°) being much smaller than the corresponding angle for facets meeting along b axes (112.6°). This has a marked effect on relative supplies of solute diffusing to the two locales [10]. A further obvious factor is that, once a given facet becomes short, the probability of chance nucleation upon it is reduced accordingly. As growth rate decreases with increase in temperature a more equitable balance seems to be established so that small $\{200\}$ facets begin to appear. I am going to plead ignorance of the nature of molecular folding along such short straight facets; the evidence is conflicting and inconclusive. That there may be *regular* $\{200\}$ folding along these facets, inevitably with what is likely to be considerable strain in the folds, seemed to be supported by infra-red spectroscopic studies by Krimm and his associates [11], although in retrospect the *regularity* of

such folding in a given plane may not have been assured. Supporting the supposition of strained $\{200\}$ folds, it is true that $\{200\}$ sectors are slightly less stable than $\{110\}$ sectors but the difference in ‘melting’ temperature seems inordinately small and might be explicable on several other grounds. What concerns me is that cooling solutions containing crystals with straight $\{200\}$ facets causes spiky a -oriented overgrowths bounded by $\{100\}$ facets to sprout normally from them; just how these might nucleate on $\{200\}$ fold planes seems to me quite mysterious.

Building upon an (almost) space-filling representation of the polyethylene lattice due to Bunn [12] and having produced a drawing as in Fig. 3, later backed up by calculations of interatomic distances, I began to realize that the (200) face of this particular lattice is quite unusual in several respects. First, successive molecules in the same (200) plane are loosely bound and, even at closest contact, barely capable of touching one another. Except insofar as prevented by folding, they could easily undergo essentially free rotation (scarcely surprising perhaps in that rotator phases of higher paraffins are well known). Secondly, and likely more important, there are abundant opportunities for ‘mistakes’ to occur in depositing sequences of stems on existing (200) planes. One such mistake has been incorporated deliberately in Fig. 3, as explained in the legend, and I note that it takes a keen eye to spot it without having attention drawn to it. (Corresponding ‘mistakes’ are most unlikely on $\{020\}$ and impossible on $\{110\}$ planes.) In short, the (200) surface plane is loosely packed and likely quite disordered, and would have associated with it a *very small* entropy of fusion. In other words, it would be a prime candidate for ‘normal’ growth, a technical term implying growth normal to itself governed kinetically by attachment kinetics and, on a local scale at least, having nothing whatever to do with nucleation kinetics (which govern growth by layer spreading). If true, this would signify that a lenticular crystal in polyethylene is the first example I have encountered in any material that exhibits ‘mixed kinetics’, that is, nucleation-controlled growth along one major axis and normal growth along another. Other examples, whether in polymers or not, must be exceptionally rare or, at least, seem to have passed unnoticed.

3.2. Curved $\{200\}$ faces: do they represent normal growth?

Relative to growth rates on $\{110\}$ faces, established phenomenology makes it clear that there is a significant difference between corresponding growth rates on (secondary) $\{200\}$ facets in truncated rhombs at lower temperatures and on extensive $\{200\}$ faces in lenticular crystals grown from solution or melt at high temperatures. In conventional theory, such growth rates are proportional to $\sqrt{(ig)}$ where i is nucleation rate per unit length of lateral surface and g is a relatively temperature-insensitive rate of layer spreading. Within the formalism, therefore, attention becomes focused on g , which on curved $\{200\}$ faces seems to behave

anomalously. If so, the explanation must in some manner reflect structural considerations at molecular level. I propose for consideration the novel view that curved $\{200\}$ faces represent normal growth and not mysteriously frustrated layer spreading as commonly supposed. I would perhaps be less daring were it not for the fact that Barnes and Khoury [13] in 1974 reported growth of extraordinary *circular* single crystals of poly-(chlorotrifluoroethylene) that in retrospect clearly seem to suggest normal growth in chain-folded lamellae of at least one polymer (not that anyone at the time suspected such a connection, myself included).

Normal growth is common for metal crystals grown from melt, transitions for which entropic changes are small (though when crystallization occurs from the vapor phase entropic changes are considerably larger and thermal etching at elevated temperatures then affirms occurrence of faceted interfaces). Surface layers in normal growth are so disordered as to be almost liquid-like and interfacial surface energies are close to being isotropic. Addition of fresh material at such an interface is essentially diffused in the disordered surface with minimal effect on surface profile. The contrast with additions to close-packed facets that then remain exposed as well-defined adsorbed atoms or surface patches could not be more pronounced. Going deeper within liquid-like surface layers, however, there must be progressive development of the crystalline order that persists throughout the bulk phase.

From Fig. 3 we sense that disorder could arise in several ways at $\{200\}$ faces in lenticular crystals. It would not be unexpected for subsequent progressive ordering to be slow when stems are joined by folds. It is even possible that short sequences of loosely bound stems in (200) planes at the surface could associate with their inter-axis spacings determined more by ease of folding than by maintenance of the nominal lattice spacing. Further ordering could take considerable time to develop despite appreciable molecular mobility in the initially disordered state, and it would make for slow growth of a stable structure without a melting point anomaly. I offer this proposal that normal growth is involved in formation of curved $\{200\}$ faces in polyethylene, not in certainty of its validity, but as something to be thought about and, in particular, as a stimulus for renewed experimental research.

4. Surface nucleation and layer spreading

The kinetic theory of Lauritzen and Hoffman (LH) [8,9] was conceived more than four decades ago, initially in the limited context of endeavoring to account for chain folding in lamellae grown from dilute solution. It was soon adapted with little fundamental change to dealing (somewhat more controversially) with chain folding in the considerably more complicated situation of crystallization from melt (for a review see Ref. [14]). It has deservedly assumed an honored central role in polymer crystal physics by virtue of mostly

focusing correctly upon relevant physical principles. That is not to say, however, that interpretation of how these principles operate interactively has yet reached a wholly satisfactory state. The inherent problem can be stated very simply: one is dealing with cooperative phenomena on the scale of hundreds of atoms, some bonded strongly, some more weakly—much too large a scale for incisive analysis as many body problems, yet too small for reliable guidance in specific circumstances from statistical methods as have proved so valuable, for example, in rubber elasticity or rheology. There are other difficulties as well. The number of basic parameters that can be measured with fair accuracy (no better) is strictly limited to enthalpy ΔH_f of fusion (or solidification), melting points of crystals (in metastable states only), thicknesses of lamellae and, by inference from ΔH_f and melting points as functions of lamellar thickness, the surface free energy σ_e associated with fold surfaces. Another very important parameter, free energy of lateral surfaces σ is not directly measurable but was assessed from temperature dependence of growth rates at small supercooling (with respect to an extrapolated equilibrium melting point T_m^0). Accurate quantification of the many other parameters that arise in theoretical models, or testing of these models (often from calculated growth rates) is then fraught with risk of appreciable error or circular (tautological) argument. Relatively slow progress over four decades of intense study has not been without valid reason.

The LH conception of nucleation and layer spreading on the lateral surface of a lamella was closely patterned on classical models of the time, that is to say, classical models in a then conventional simplified form that, as noted earlier, was somewhat lacking in rigor. (Dimensionality could not be invoked profitably since the principal contributions to free energy of a nucleus were *both* proportional to area added to the lamella. However, good use was made of the marginal stability of lamellae as just grown to relate thickness (l) of crystal and nucleus to σ_e and to Δf , the change in free energy per unit volume of crystal upon solidification.) The cost of nucleation was attributed entirely to the surface energy σ associated with the *end faces* of a new strip of stems on a (110) surface, written $2b_0l\sigma$, where $b_0 = 4.15 \text{ \AA}$ is the depth of the strip and, since this cost is as great for one added stem as for several in a row, the critical sized nucleus was identified as the first stem (whether or not a fold is included does not change the cost markedly). In other words, the activation energy for forming the critical nucleus was assessed from a rather rudimentary geometrical and physical abstraction supposedly representing a short length of a single rounded molecule that has straightened and come to rest in a slight trough (stem site) on a surface. Of course, in practice, this activation energy is measured by analyzing kinetic data in an unobjectionable manner; it is the identification of σ so obtained with lateral free energy of a lamella, and presumption that the *same* activation energy for nucleation of a new layer is operative under all

circumstances, that appear to be questionable features of the LH formalism.

4.1. Surface nucleation approached on the KS model

Using the KS model the same situation can be addressed by comparing the free energies associated with addition of a stem plus fold to a half-energy site on (110) and similar addition to a nucleating site on the same face. Let the thickness of the crystal involved be l and let T_0 be the temperature at which the crystal would melt without thickening. At this temperature we suppose that the addition of a stem to a half energy site results (per unit volume of crystal) in a decrease in enthalpy ΔH and an increase in entropy of ΔS . Then at T_0 the thermodynamic driving force for crystallization, reckoned as a decrease in free energy, is

$$(-)\Delta G_1 = a_0 b_0 l \{ -\Delta H + T_0 \Delta S \} + Q = 0 \quad (1)$$

where $a_0 b_0$ is the cross-sectional area of the molecule and Q is the free energy associated with a single fold. We shall assume, as is commonly done, that ΔH and ΔS do not change significantly with small changes in temperature. Then at a moderately lower temperature T we have for addition to a half-energy site the driving force

$$-\Delta G_2 = a_0 b_0 l \{ -\Delta H + T \Delta S \} + Q \quad (2)$$

and at the same temperature for adding a nucleating stem plus fold to the surface the driving force would be

$$-\Delta G_3 = a_0 b_0 l \{ -(1 - \alpha)\Delta H + T \Delta S(1) \} + Q \quad (3)$$

where $\alpha \approx 0.39$ is the correction to ΔH for loss of nearest neighbors ($1V_1 + 1V_5$) and $\Delta S(1)$ is the change in entropy associated with addition of the *very first* stem from the nucleating molecule. The cost of nucleation then becomes Eq. (2) minus Eq. (3), that is

$$\Delta G^* = a_0 b_0 l \{ \alpha \Delta H + T(\Delta S(1) - \Delta S) \} \quad (4)$$

(It should be noted that we have not as yet included in Eqs (3) or (4) any attempted assessment of surface energy attributed to the nucleating stem. Rather we would prefer to compare the activation energy predicted by Eq. (4) with an empirical value and see what might be learned in consequence.)

A troubling concern in evaluating expression (4) is uncertainty regarding contributions of individual stems to ΔS depending upon how long a molecule they are part of and how much of its overall length has already crystallized. The fact that both ΔH and melting point for a crystal of given thickness vary only slightly with molecular weight of polymer (except perhaps for quite short chains or oligomers) may suggest in general that on a per stem basis there is little variation in ΔS throughout such a crystal. On that basis, that is, ignoring the second bracketed term on the right of equation (4), as would be appropriate for EC crystals, we find $\Delta G^* \approx a_0 b_0 l \alpha \Delta H$. Hoffman's analysis of kinetic data [14] has shown $\Delta G^* = 2b_0 l \sigma$ with σ taking a value close to

12 ergs cm^{-2} . Equating the two expressions suggests that our estimate of (an effective value for) σ would be $\sigma_{\text{eff}} \approx (a_0 \alpha \Delta H)/2$. Since from Ref. [14] $a_0 = 4.55 \times 10^{-8}$ cm, $\Delta H = 2.8 \times 10^9$ ergs and $\alpha \approx 0.4$ (see earlier, Section 3) we find $\sigma_{\text{eff}} \approx 25$ ergs cm^{-2} . All in all, this is a satisfactory result. There may be some overestimation for reasons mentioned in Section 2.2. Apart from that, we shall see in Section 4.2 that empirical values for activation energies derived from kinetics are likely to be significantly reduced, relative to calculated values for a first isolated stem, because of averaging with ongoing assisted nucleation as growth proceeds. Unfortunately, there is no clear indication of how much of ΔG^* should be associated directly with surface energy. Note that inclusion of the thickness l in Eq. (4) ensures that our estimated ΔG^* is inversely proportional to ΔT , as is required.

Estimation from first principles of contributions ΔS in calculations such as the above is beyond my competence, yet I would hope it will be attempted by others. I would hope, in particular, that there may be found a dependence of ΔG^* upon molecular weight of a nucleating molecule, one that might finally provide a cogent explanation for the well-known fractionation of lower molecular weight species during crystallization from melt.

4.2. Layer spreading or clumped molecules?

Layer spreading is commonly a uniform process in crystals composed of small neatly fitting units is often shown by geometrically regular growth and appearance of shallow spiral steps surrounding screw dislocations. Lauritzen and Hoffman initially imagined layer spreading on a growing polymer crystal to follow a similarly regular progression of adding new stems as a molecule underwent folding, incurring a 'work of chain folding, Q ' at each reversal of direction. As a description of what happens *on a local scale* during slow crystallization of a highly mobile coiled chain in dilute solution, or during *very slow* crystallization of a molecule in a viscous melt, this may be reasonably accurate, although the folds may well represent a redistribution of gauche bonds more than a net creation of new ones. Beyond that, complications multiply rapidly. For example, continued growth of a freshly nucleated layer depends upon further molecules adding (without cost of nucleation) to stem sites immediately adjacent to the last ones filled. In general, they will neither do this without delay (entropic considerations again) nor beginning neatly at a chain end rather than somewhere in mid-chain. We may end up with two long cilia issuing from the new layer, one at each end of the original nucleating molecule. And so on. In terms of accessibility there may before long arise fairly frequent instances of such cilia able to undergo appreciably cheapened (assisted) nucleation on the layer above that in which initial attachment began. In fairly short order, growth processes on a local scale may depart considerably from the idealized model and growth

rates may well become significantly enhanced, thereby mimicking ‘idealized’ circumstances but with reduced ΔG^* . Frequent instances of superfolding, and dependence of growth rate upon concentration of solute considerably slower than linear, are common even in crystallization from dilute solution; these are doubtless attributable to ‘real’ behavior of this kind.

A further complication arises as nucleation rate increases. Quite apart from superfolding a redundancy is bound to develop when layers become multiply nucleated and, growth rate, while still increasing, begins to lag behind more rapidly increasing nucleation rate. This brings about the onset of Regime II. It is important to recognize the complications attending such processes, yet it is to be borne in mind that so long as nucleation kinetics are followed ($\ln G \sim -1/T\Delta T$) the dominant mechanism in stem addition is still layer spreading, however irregular it may be or broken up into bursts. Inevitably, theoretical treatments of such behavior, even when sophisticated [15], are considerably oversimplified but undoubtedly aided by averaging over many contributing processes. Nevertheless, with rapid crystallization there will be a tendency for individual molecules to occupy several adjacent layers in what might be described as somewhat clumped conformations rather than extended single layers. Indeed, in such crystallization from the melt it would be difficult to conceive of a probability of non-adjacent reentry $\approx 1/3$ [14] arising otherwise, and I need hardly stress the significance of Section 2.4 above in supporting such a view.

I may also mention that it is a view that was brought home to Chen and me quite pointedly in the course of a recent study of how giant screw dislocations are formed in dendritic crystals of polyethylene [10]. Had it not been for

this strong evidence that nucleation can in some circumstances be so markedly assisted by ‘accessibility’ as to produce morphological anomalies of consequence, the present paper would probably not have been attempted, even though most of the thoughts and viewpoints expressed have been in my mind for some time.

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