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Morphology of crystals: Internal and external controlling factors

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Internal and external factors that influence the morphology of crystals are studied based on an inhomogeneous cell model. After discussing the reason of the failure of two basic assumptions, the equivalent wetting condition and the proportionality condition, the influence of the ambient phase is explicitly taken into account in terms of the surface characteristic scaling factor C_l^*. In connection with the solid-fluid interfacial structure, which is commonly determined by the crystal and the ambient phase, C_l^* will provide the essential information concerning how the morphology of the crystals is affected. Within the framework of our formalism, internal and external factors controlling both equilibrium forms and growth forms of crystals are described separately. This offers a guideline for the modification of the habit of crystals. To describe the morphology of crystals, the periodic bond chain analysis can be used to determine the internal controlling factors, and the interfacial structure analysis, which is developed in this paper, can be used to determine the external controlling factors. These analyses are applied to predict the growth forms of *n*-paraffin crystals.

I. INTRODUCTION

As a historical subject, the morphology of crystals has drawn attention for centuries. Initial problems were related to why a particular crystal possesses a certain shape when it grows from a certain environment. With the development of theories in crystal growth mechanisms and in the structure of the solid-fluid interface,[1,2] knowledge of this subject has been improving. Recently, research on the influence of tailormade additives on the morphology of crystals has been carried out for various practical reasons. It is known that the morphology of crystals is controlled both by the structure of crystals and the growth parameters.[1,2] As was realized nearly 300 years ago,[3] the anisotropy of the growth rates determines the morphology of crystals. This anisotropy is partly determined by the crystal structure, but can be drastically influenced by the growth parameters. Therefore, as a key step for the molecular design of tailormade additives, understanding the internal and external factors affecting the morphology of crystals is necessary.

To predict the growth morphology of crystals, theories like the Hartman-Perdok theory[4-8] have been developed. According to the principles of the Hartman-Perdok theory, the relative growth rate of faces $\{hkl\}$ on crystals is assumed to be proportional to the attachment energy of faces $\{hkl\}E_{hkl}^{att}$. This is the energy released per structural unit when a slice of a crystal (with the thickness d_{hkl}) is attached to the crystal surface.[8] This relationship between the relative growth rate and E_{hkl}^{att} has been justified by Hartman and Bennema,[7] based on the theories of growth kinetics and certain conditions. This theory is successful to some extent, especially in the case that crystals are grown from the vapor phase. However, in many cases discrepancies between the theoretical morphology and the observed morphology occur especially when crystals are grown from solutions or the melt. To remove this difficulty, some prescriptions based on statistical mechanical Ising models have been developed.[2,9,10] In the context of these prescriptions, the concept of the roughening phase transition is introduced. This implies that the influence of the ambient phase is to some extent taken into account. Indeed, compared with other theories, the results obtained from the approach of roughening transition theories are much closer to reality.[9,10] Nevertheless, some deviations still remain.

We notice that the crystal surfaces are boundaries between the crystal phase and the ambient phase (including solute, solvents, and impurities). Therefore, under the equilibrium condition or in the growth process, the structure of both the crystal and the ambient phase will influence the shape and the size of the surfaces of the crystals, and the morphology of the crystals. Since the growth of crystals is also determined by thermodynamic conditions, parameters, such as temperature and supersaturation, will also affect the morphology of crystals. For the aforementioned theories, although the influence of the mother phase can be taken into account in a limited way, they are still based on the assumption that the structure and molecular behavior of solid and solute molecules is similar. (This is one of the basic assumptions of cell models. The proportionality condition results from this similarity.) This is the main cause of the discrepancies between predicted and observed growth forms.

Contrary to growth forms, the equilibrium form of a crystal can be described unambiguously using the surface free energy of the faces $\{hkl\}$.[11] However, calculations of the surface free energy for crystallographic orientations $\{hkl\}$ remain problematic due to lack of knowledge of the structure of the solid-fluid interface.

This paper describes a study on the morphology of crystals from both points of view of the internal structure of crystals and the external effects of the ambient phase. We will start from the interfacial region to analyze the mutual influence of both the solid and the ambient phase

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on the morphology of crystals. The basic idea is that we first analyze the influence of the solid structure [this can be done by the conventional periodic bond chain (PBC) analysis or the network analysis[1,2,8]]. The results of the PBC analysis are coupled with the influence of the ambient phase (or fluid phase). Since the interactions between the solid and the fluid phase occur at the solid-fluid interface, this coupling is related to the interfacial structure. In order to characterize this coupling, a so-called surface characteristic scaling factor C_l^* is introduced. The following discussions will be primarily devoted to investigating this factor.

II. TWO BASIC ASSUMPTIONS AND THE RELATION TO AN INHOMOGENEOUS CELL MODEL

In the world of crystal growth, cell models or Ising models are commonly used explicitly or implicitly. In cells models, both the crystal and the ambient phase are divided into cells of the same shape and size. When each cell has m bonds connecting neighboring cells, the dissolution enthalpy (per structural unit) for a solution system consisting of the solute A and the solvent B is given by

$$\Delta\tilde{H}_{\text{diss}} = \sum_{j=1}^{m} \Phi_j \; . \tag{1}$$

Here Φ_j is the exchange bond energy between cells in the two bulk phases in the jth direction, and is expressed as[12-14]

$$\Phi_j \simeq \tfrac{1}{2}(\Phi_j^{AA} - \Phi_j^{SS}) + (1 - X_A)^2 \Phi_j^{\sigma} \tag{2a}$$

and

$$\Phi_j^{\sigma} = \Phi_j^{AB} - \tfrac{1}{2}(\Phi_j^{AA} - \Phi_j^{BB}) \; , \tag{2b}$$

where X_A is the mole faction of solute A, the superscripts AA, BB, AB, SS represent the interaction of solute-solute units, solvent-solvent units, solute-solvent units, and solid-solid units, respectively.

Note that we still cannot use expressions (1) and (2a) to calculate Φ_j directly from experimental data. The values of Φ_j^{SS} in Eqs. (2a) and (2b) may often be calculated from general physical chemical considerations or quantum chemical considerations. However, the values of Φ_j^{AA}, Φ_j^{BB}, and Φ_j^{AB} are normally unknown. In order to overcome this difficulty *the proportionality condition* was introduced.[1,2] This condition implies that in any case the bond energies Φ_j^{AA}, Φ_j^{BB}, and Φ_j^{AB} are supposed to be proportional to Φ_j^{SS} as

$$\Phi_1 : \Phi_2 : \ldots : \Phi_j : \ldots : \Phi_m = \Phi_1^{AA} : \Phi_2^{AA} : \ldots : \Phi_j^{AA} : \ldots : \Phi_m^{AA} = \ldots = \Phi_1^{AB} : \Phi_2^{AB} : \ldots : \Phi_j^{AA} : \ldots : \Phi_m^{AB} = \Phi_1^{SS} : \Phi_2^{SS} : \ldots : \Phi_j^{SS} : \ldots : \Phi_m \; . \tag{3}$$

From Eqs. (2a) and (3) we find

$$\Phi_j \Big/ \sum_{k=1}^{m} \Phi_k = \Phi_j^{SS} \Big/ \sum_{k=1}^{m} \Phi_k^{SS} \; . \tag{4}$$

It then follows from Eq. (4) that, after substituting Eq. (1),

$$\Phi_j = (\Phi_k^{SS} / 2E_{SS}^{\text{cr}}) \Delta H_{\text{diss}} \; , \tag{5}$$

$$E_{SS}^{\text{cr}} = \tfrac{1}{2} \sum_{k=1}^{m} \Phi_k^{SS} \tag{6}$$

(E_{SS}^{cr} is approximately equal to the sublimation energy of crystals). It has to be noted that normally the proportionality condition introduced in (3) is associated with the equivalent wetting condition when morphological issues are discussed. According to this assumption, Eq. (3) is equally applicable to different faces on a crystal. The implications of the proportionality condition is that the anisotropy of the interaction energies of a solid-fluid system is the same as that of the crystal structure. In other words, the morphology referenced to vacuum is supposed to be the same as that referenced to the fluid phase.

The exchange bond energy between the first interfacial fluid layer adjacent to the solid phase and the first interfacial solid layer adjacent to the fluid phase, is expressed by[12,14]

$$\phi_j = \tfrac{1}{2}(\phi_j^{AA} - \phi_j^{SS}) + [1 - X_A(0)]^2 \phi_j^{\sigma} + X_A(0)(\phi_j^{SA} - \phi_j^{AA}) + [1 - X_A(0)](\phi_j^{SB} - \phi_j^{AB}) \; , \tag{7}$$

$X_A(0)$ is the concentration of the solute in the first fluid layer, the expression for ϕ_j^{σ} is similar to (2b). The value of ϕ_j is directly related to physical processes occurring at the solid-fluid interface, such as the roughening transition, two-dimensional nucleation, etc.[1,2,12,14] The bond energies and the structure of the interface determine the growth kinetics and the growth rate of a crystal surface.

To estimate the bond energy at the surface, *the so-called equivalent wetting condition* was introduced by Jackson.[15] Although there are various expressions for this condition, in general it can be written as

$$\phi_j \simeq \Phi_j \; . \tag{8}$$

As a consequence of Eq. (8), various bond energies in the bulk phase (such as Φ_j^{SS}, Φ_j^{AA}, Φ_j^{AB}, etc.) are equal to the corresponding bond energies at the interface (such as ϕ_j^{SS}, ϕ_j^{AA}, ϕ_j^{AB}, etc.). It thus follows that the concentration of solute (or solvent) in the bulk phase X_A (or X_B) is equal to that at the interface. This condition implies that both the fluid and the solid are completely homogeneous throughout the bulk up to the dividing surface.[12,14] This is the so-called homogeneous phase approximation or the first approximation of the equivalent wetting. Apart from this, it can be seen from Eq. (7) that to fulfill Eq. (8), we must have $\phi_j^{SA} \simeq \phi_j^{AA}$ and $\phi_j^{SB} \simeq \phi_j^{AB}$.[12] We call this the second approximation of the equivalent wetting condition.

It follows from experimental evidence[1] that the equivalent wetting condition leading to (8) has turned out to be invalid in most cases. For crystals grown from systems consisting of simple structural units, the use of the equivalent wetting condition underestimates ϕ_j, while for systems consisting of chainlike molecules, the equivalent wetting condition overestimates ϕ_j. The main reason for the failure of the equivalent wetting is the application of the homogeneous phase approximation.[14] Investigations concerning the structure of crystal-fluid interfaces by computer simulations and density-functional theories[16–20] show that due to the ordering of fluid layers and the relaxation or reconstruction of solid layers in the interfacial regions, the structure of the solid-fluid interface is different from that of the bulk. This indicates explicitly that the homogeneous phase approximation and hence the equivalent wetting condition are invalid. (Note that the second approximation of the equivalent wetting condition is considered to be somehow reasonable if the homogeneous phase approximation is modified.) In addition, the interfacial structure in one crystallographic orientation is different from the others. Therefore, the proportionality condition is also questionable.

To describe the solid-fluid interface of a crystal-solution system, the so-called inhomogeneous cell model has recently been developed.[12,14,21] According to this model, the surface characteristic scaling factor is defined in the following way:

$$C_l^* = \sum_{j=1}^{m} \phi_j \Big/ \sum_{j=1}^{m} \Phi_j = \Delta\tilde{H}_{\text{diss}}^I / \Delta\tilde{H}_{\text{diss}} \,, \tag{9a}$$

$$\Delta\tilde{H}_{\text{diss}}^I = \sum_{j=1}^{m} \phi_j \,. \tag{9b}$$

This factor is orientation dependent.[21] In terms of the concentration or the density of the structural units, this factor can be written as[14]

$$C_l^* \simeq \ln X_A(0)/\ln X_A \tag{10a}$$

or in the case of crystals in contact with the melt, as

$$C_l^* \simeq \ln(\rho_f^I/\rho_s^I)/\ln(\rho_f/\rho_s) \,, \tag{10b}$$

where ρ_f and ρ_s denote the density of structural units in the fluid and in the solid phase, respectively, and the superscript “I” indicates the corresponding properties in the regions adjacent to the dividing plane between the solid and the fluid. Note that the equivalent wetting condition implies that $C_l^* = 1$ or $X_A(0) = X_A$.

For an interfacial system consisting of isotropic structural units, profiles of the concentration of fluid units at the interface can be described by an exponential law[21] as

$$X_A(z) = X_A[1 + (X_A^{\zeta} - 1)\exp(-z/n^*)] \,, \tag{11}$$

where z is the distance away from the solid surface (normalized by the interplanar distance of the crystal face d_{nhnknl}), the exponent $\zeta = C_l^* - 1$, n^* is the normalized characteristic thickness of the interface, and defined in such a way that at $z = n^*$, $[X_A(n^*) - X_A]/[X_A(0) - X_A] = e^{-1}$. Using Eqs. (9a) and (11), the surface free energy may, in principle, be calculated for interfacial systems of isotropic units if the factors C_l^* and n^* are known.[22]

We notice that within the framework of cell models the proportionality condition given by Eq. (3) is, in principle, valid for the bulk phase, However, directly extrapolating Eq. (3) to all crystallographic orientations will evidently lead to a wrong conclusion. Here we assume that the principle of the constancy of the ratio in Eq. (3) can be independently applied to different crystallographic orientations. This means for crystal face $(h_i k_i l_i)$

$$\begin{aligned} \phi_1^{(i)}:\phi_2^{(i)}:\ldots:\phi_j^{(i)}:\ldots:\phi_m^{(i)} &= \Phi_1:\Phi_2:\ldots:\Phi_j:\ldots:\Phi_m \\ &= \Phi_1^{SS}:\Phi_2^{SS}:\ldots:\Phi_m^{SS} \,. \end{aligned} \tag{12}$$

It follows from Eq. (9a) that for a particular orientation,

$$\begin{gathered} \phi_1^{(i)}/\Phi_1 \simeq \phi_2^{(i)}/\Phi_2 \simeq \ldots \simeq \phi_j^{(i)}/\Phi_j \simeq \ldots \simeq \phi_m^{(i)}/\Phi_m \simeq \Delta\tilde{H}_{\text{diss}}^{I(i)}/\Delta\tilde{H}_{\text{diss}} = C_{l(i)}^* \\ \text{or} \\ \phi_1^{(i)}/\Phi_1^{SS} \simeq \phi_2^{(i)}/\Phi_2^{SS} \simeq \ldots \simeq \phi_j^{(i)}/\Phi_j^{SS} \simeq \ldots \simeq \phi_m^{(i)}/\Phi_m^{SS} \simeq C_{l(i)}^* \Delta\tilde{H}_{\text{diss}}/2E_{ss}^{\text{cr}} \,. \end{gathered} \tag{13}$$

Equation (12) therefore holds for each crystallographic orientation i, provided the ratio C_l^* depends on i. The surface characteristic scaling factor is explicitly used to scale the bond energy difference between the bulk phase and the interfacial phase in a certain crystallographic orientation. Therefore, it is necessary to apply both (12) and (13). In distinction with the condition given by (3), Eqs. (12) and (13) are called *the generalized proportionality condition.* They form the basis for the following treatment. It can be seen that the proportionality condition is a special case of the generalized proportionality condition. In case that C_l^* is independent of the surface orientation, Eqs. (12) and (13) reduce to Eq. (3). Note that if Eq. (3) expresses to a large extent the crystal structure factor determining the morphology, Eq. (13) shows the modification in the morphology of crystals due to specific influence of the fluid phase at equilibrium.

III. EQUILIBRIUM FORMS AND GROWTH FORMS OF CRYSTALS

A. Equilibrium forms

As mentioned in Sec. I, equilibrium forms of crystals can be described on the basis of the Gibbs-Wulff theorem. Within the framework of this theorem, equilibrium forms of crystals depend on the surface free energy in different orientations and can be constructed by Wulff plots. In Wulff plots, sharp cusps occur corresponding to all orientations of flat (or F) faces. In case the temperature is relatively low,[1,11,24] the equilibrium form has a polygonal shape according to these sharp cusps in different directions, and is bounded by F faces. In this case, the equilibrium form can be determined by a complete set of F faces and their radius vectors.[11] On the other hand, according to Herring,[23] the surface free energies of rough faces, such as stepped (S) or kinked (K) faces, are linearly related to the surface free energies of flat (or F) faces. Therefore, F faces play an essential role in the determination of the equilibrium forms of crystals. In the following the equilibrium form will be discussed from this point of view.

Suppose that in total n F faces are identified from a given crystal structure under certain conditions[1] (in this case, $n \geq 3$). The radius vector $\mathbf{D}_i$ indicates the orientation of F face $(h_i h_i k_i)$ $(i=1,2,\ldots,n)$, and the distance from the face to the origin ($|\mathbf{D}_i|$). The set of mutual ratios of the radius vectors is well defined and represent the main characters of the Wulff plot.[1,10,24] This implies that the equilibrium form of crystals EF can be described by a set of radius vectors

$$\mathrm{EF}=D=\{D_1,D_2,\ldots,D_n\} \;. \tag{14}$$

Presume that the crystallographic orientations of these F faces are set in a certain order from 1 to n. Then the equilibrium form of crystals EF can be simply expressed as an ordered set of elements by

$$\mathrm{EF}=D=\{D_1,D_2,\ldots,D_n\} \;. \tag{15}$$

(We will define the order of the crystallographic orientations $1,2,\ldots,n$ later.) Here D_i denotes the length of $\mathbf{D}_i$, and is proportional to a certain physical property (such as the surface free energy). From a physical point of view, the values for different orientations are not linearly correlated.

We note that only the orientation-dependent factors will determine the shape of crystals. Henceforth, each element of D should be reduced by $D_{\min}$, the minimum element is set D. The set D is rewritten as

$$D=\{\tilde{D}_1,\tilde{D}_2,\ldots,\tilde{D}_n\} \;, \tag{16}$$

$$\tilde{D}_i=D_i/D_{\min} \;. \tag{17}$$

This reduction guarantees that all face-independent factors are deleted. Based on this convention, it can be stated that if two ordered sets are equal to each other, the same morphology of crystals is defined.

According to the Gibbs-Wulff theorem, the following proportionality relation holds:

$$D_i=K\sigma_i \quad (K\text{:const}) \;, \tag{18}$$

where σ_i denotes the surface free energy of face $(h_i k_i l_i)$. It follows from Eqs. (16) and (17) that

$$D=\tilde{\sigma} \;, \tag{19}$$

$$\tilde{\sigma}=\{\tilde{\sigma}_i\} \;,$$

and (20)

$$\tilde{\sigma}_i=\sigma_i/\sigma_{\min} \;.$$

(Here the subscript $i=1,2,\ldots,n$.) In this sense, the ordered set $\tilde{\sigma}$ i the key factor to determine the equilibrium shaped of crystals.

It follows from our previous results[22] that for a crystal in contact with two-component solutions, the surface free energy can be expressed for crystal surface $(h_i k_i l_i)$ as

$$\sigma_i M_i=\sigma_i^0 C_{l(i)}^* + \sigma_i' \;, \tag{21}$$

where M_i is the mesh area of the face,

$$\sigma_i^0=\eta_i \Delta h_d^A \tag{22}$$

and

$$\begin{aligned}\sigma_i' = n_i^* X_A W_i\{ & -kT_s \ln(X_A/X_B)+[W_i/(2\ln X_A)+1] \\ & +\Delta h_d^B[(X_A W_i/2-X_B)/(X_B \ln X_B)-1]\}\end{aligned} \tag{23}$$

$(W_i=X_A^{\zeta}-1)$. Δh_d^q ($q=A$ or B) corresponds to the (bulk) exchange energy due to bringing a structural unit q from an environment of the pure solid state into the solution state. For the solute units $(q=A)$, it can be seen that $\Delta h_d^A \simeq \Delta\tilde{H}_{\mathrm{diss}}$. η_i is the orientation factor of crystal face $(h_i k_i l_i)$. In the case that only the first- or somewhat the second-nearest-neighbor interactions need to be taken into account, this factor can be defined according to the Hartman-Perdok theory[8] as

$$\eta_i=E_{SS(i)}^{\mathrm{att}}/(2E_{ss}^{\mathrm{cr}}) \simeq E_{(i)}^{\mathrm{att}}/\Delta\tilde{H}_{\mathrm{diss}} \;, \tag{24}$$

where $E_{(i)}^{\mathrm{att}}$ is the attachment energy of crystal face i in the environment of solutions, $E_{SS(i)}^{\mathrm{att}}$ is the attachment energy in reference to the vacuum.

From Eqs. (21)–(24), it is clear that each element σ_i in the set $\tilde{\sigma}$ is a function of the parameters M_i, $C_{l(i)}^*$, η_i, and σ_i'. This implies that in relation to $\tilde{\sigma}$, the other four ordered sets of parameters can be defined in the following way:

$$M=\{M_i\} \;, \tag{25}$$

$$\eta=\{\eta_i\} \;, \tag{26}$$

$$C_l^*=\{C_{l(i)}^*\} \;, \tag{27}$$

and

$$\sigma'=\{\sigma'_i\} \tag{28}$$

$(i=1,2,\ldots,n)$. The relation between $\tilde{\sigma}$ and these parameter sets is defined by Eqs. (21) and (22).

Obviously, η and M are determined by the bond structure of crystals. Therefore, they represent the influence of the internal structural factor on $\tilde{\sigma}$ (or the morphology of crystals).

On the other hand, C_l^* and σ' are determined by the structure of the solid-fluid interface and thermodynamic properties of both the solid and the fluid bulk phase. Therefore, in spite of the crystal structure, various spatial conformations of fluid units (including the solvent and impurities), and interactions between those units and the solid surface will affect the parameter sets C_l^* and σ'. In this sense, both sets incorporate the symmetry and properties which the crystal and the mother phase have in common.

Let us now define the crystallographic order of elements in D. In the description of the morphology of crystals, the ordering of the face orientations which follows from the structure should be invariant with respect to the mother phase and independent of the external factors. The elements of η possess that character. Therefore, we define that the order of crystallographic orientations i is set in such a way to be $\eta_1<\eta_2<\cdots<\eta_n$. This order of crystallographic orientations from 1 to n is maintained in the elements of D and other parameter sets, disregarding the magnitude of each element in those sets.

B. Growth forms

In analogy with equilibrium forms, growth forms of crystals may also be constructed by the Wulff plot. Instead of D_i, we use R_i, the reduced growth rate of the face i, to describe growth form of crystals. Then, analogous to (15), the growth form of a crystal GF can be described in the following way:

$$GF=R=\{R_1,R_2,\ldots,R_n\}\ , \tag{29}$$

where R_i is the growth rate of face $(h_ik_il_i)$ reduced by the minimum growth $R_{\min}$, and the crystallographic order of elements in R is follows according to the aforementioned convention. Similar to the equilibrium form, the growth forms of crystals having a given structure are determined by set R. EAch element of set R included only orientation-dependent factors. (All orientation-independence factors are deleted in the reduction process.) Obviously, R_i will be influenced by the structure of different crystal surfaces, kinetic factors, and conformations and configurations of fluid molecules. Again, these factors can be classified as internal and external factors, i.e., can be attributed to the structure and properties of the crystal, and of the ambient phase, respectively.

Since so many factors determine the growth rate of crystal surfaces, up to now there is no unambiguous theory to describe growth forms of crystals. Nevertheless, *ad hoc* recipes exist, which to some extent work reasonably well. These recipes are based on the Hartman-Perdok theory and the roughening transition theory. Similar to the former theory,[7] these recipes may also be qualitatively justified.[25]

According to the approach of the roughening transition theory,[2,9,25] the growth rate of flat faces $(h_ik_il_i)$ may be expressed as

$$R_i=\tilde{K}_{\rm RT}/\Delta\theta_i^r \quad (\tilde{K}_{\rm RT}\ \text{, the reduction constant})\ , \tag{30a}$$

where $\Delta\theta_i^r=\theta_i^r-\theta$,

$$\theta_i^r=2kT_i^r/\phi_i^{\rm str}\ ,\quad \theta=2kT/\phi^{\rm str}\ . \tag{31}$$

[Equation (30a) is valid in the domain $\Delta\theta_i^r>0$.] Here θ_i^r is the dimensionless roughening temperature of face $(h_ik_il_i)$, T_i^r is the actual roughening temperature, $\phi_i^{\rm str}$ is the strongest bond energy in the structure, and θ is the dimensionless temperature. Expression (30a) is inspired by the fact that the larger the difference between θ and θ_i^r (for a flat face, $\theta<\theta_i^r$) the higher the resistance against growth (or surface integration), and hence the lower the growth rate. In this approach, if a surface has $\Delta\theta^c\leq 0$, it is a rough face. Rough faces grow faster than flat faces, and ultimately disappear from the growth form. Therefore, these rough faces $(\Delta\theta^c\leq 0)$ are crystallographically irrelevant,and are not taken into account.

There are various versions of the principle of the Hartman-Perdok theory.[1,8] Here we would express this approach in the following way:

$$R_i=\tilde{K}_{\rm HP}(E_i^{\rm att}/\Delta\tilde{H}_{\rm diss}) \quad (\tilde{K}_{\rm HP}\ \text{, the reduction constant})\ . \tag{32a}$$

We note that Eqs. (30a) and (32a) are introduced on the basis of the proportionality condition and the equivalent wetting condition. Since the growth of crystals is directly correlated to the interfacial structure and interfacial bond energies, Eqs. (30a) and (32a) should be modified within the framework of the inhomogeneous cell model. According to the definition of the surface characteristic scaling factor C_l^* given by (9a), (30a) can be rewritten as

$$R_i=\tilde{K}_{\rm RT}(C^*_{l(i)}\Theta_i^r-\Theta)^{-1}\ , \tag{30b}$$

$$\Theta_i^r=2kT_i^r/\Phi^{\rm str}\ ,\quad \Theta=2kT/\Phi^{\rm str}\ . \tag{33}$$

When $C^*_{l(i)}\Theta_i^r>>\Theta$, Eq. (30b) can be simplified as

$$R_i\simeq\tilde{K}_{\rm RT}(C^*_{l(i)}\Theta_i^r)^{-1}\ . \tag{30c}$$

In Eq. (32a), the proportionality condition given by (3) is applied. If it is assumed that in a certain direction, interfacial solid units have bond energies close to those of bulk solid units, then it follows that $E_i^{\rm att}$ in Eq. (32a) is independent of the interfacial fluid structure, and this value remains unchanged. However, $\Delta\tilde{H}_{\rm diss}$ in Eq. (32a) is correlated to the exchange energy at the surface. For this reason, it must be replaced by its value at the interface, $\Delta\tilde{H}^I_{\rm diss}$. Then Eq. (32a) upon substitution of (9a) becomes

$$R_i=\tilde{K}_{\rm HP}\eta_i/C^*_{l(i)}\ . \tag{32b}$$

Following (30b) and (30c), a new ordered parameter set is defined as

$$\Theta^r=\{\Theta_i^r\} \quad (i=1,2,\ldots,n)\ . \tag{34}$$

Similar to D, the set R is also dependent on the parameter sets η, Θ^r, and $\mathbf{C}_l^*$. These parameters will influence R in such a way as expressed in Eqs. (30b) and (32b). It is clear that η and Θ^r represent internal factors which influence growth forms, while $\mathbf{C}_l^*$ represents the influence of the ambient phase on the morphology of crystals.

It has to be noted that for complicated molecular systems, conformations and configurations of growth units are very relevant in considering the structure and properties at the surface. In relation to the solid surface structure, configurations and conformations of interfacial fluid units vary for different crystallographic orientations. Some of these growth units adjacent to the solid surface are in such favorable conformations that they can be directly in equilibrium with solid units at the surface. (We call them the "effective growth units" in what follows.) Others may be in unfavorable conformations, which cannot come directly in equilibrium with the solid units at the surface. Therefore, in the calculation of C_l^* mainly the effective growth units are taken into account. Concerning the effect of molecular conformations, it can, in principle, be estimated by means of C_l^*. We will come back to this issue in Sec. IV.

C. Principles of prediction and modification of the morphology of crystals

It can be seen from the foregoing discussion that the internal and external factors controlling the morphology of crystals are considered separately within the framework of our formalisms as η, Θ^r, $\mathbf{C}_l^*$, and σ'. It can be seen that factors expressed in terms of η and Θ^r are subjected to the bond structure of crystals (or the internal controlling factors), and cannot be changed. As mentioned earlier, these factors can be determined by the network analysis or PBC analysis.[1,2,9,10]

On the other hand, changes in the external factors affect $\mathbf{C}_l^*$ and σ' and consequently the shape of crystals. In this sense, $\mathbf{C}_l^*$ and σ' represent the external controlling factors. Since $\mathbf{C}_l^*$ and σ' are directly related to the interfacial structure of crystals, they can, in principle, be determined by an interfacial structure (IS) analysis. (We will practically describe this analysis in Sec. IV.) As soon as η, Θ^r, $\mathbf{C}_l^*$, and σ' are available, the morphology of crystals can finally be predicted on the basis of Eqs. (21), (30a), and (30b).

We notice that the habit of crystals with a given structure can be modified by changing $\mathbf{C}_l^*$ (as well as σ'). This can, in principle, be done by introducing tailormade additives to the system, or changing the concentration and other growth conditions. Using tailormade additives is obviously one of the most efficient ways, because $\mathbf{C}_l^*$ can be directly affected in the way as shown in (10a) or (10b). Suppose that impurity or solvent molecules are preferentially adsorbed on crystal faces $\{h_ik_il_i\}$. Then, in competition with those impurity or solvent molecules, growth units are repelled from the surfaces. According to Eq. (10a), the value of $C_{l(i)}^*$ will be enhanced resulting in the modification of $\mathbf{C}_l^*$. From the point of view of growth kinetics, it follows that the roughening temperature of those faces will increase, and the growth of the faces becomes relatively slower. Therefore, the growth habit of crystals is modified.

Based on this principle, the molecular design of tailormade additives becomes possible. As we know one of the easiest ways to modify the shape of crystals is to inhibit the growth of crystals in some directions. We may design additives which can preferentially adsorb onto the surface, leaving other important surfaces unaffected. Then, for the aforementioned reasons, the growth habit of crystals will be changed. The efficiency of specific tailormade additives and the influence on the morphology of crystals can be estimated by calculating C_l^* for different crystal faces.[26-29] In the near future, we expect that significant progress can be made in the field of molecular design for tailormade additives.

IV. THE MORPHOLOGY OF *N*-PARAFFIN CRYSTALS

As mentioned in Sec. III C, the morphology of crystal can be predicted by carrying out the PBC analysis and the IS analysis. In this section, we will apply this principle to predict growth forms of *n*-paraffin crystals. More attention will be paid to the IS analysis since the concept is put forward in this paper.

Normal paraffins crystallize in four modifications: triclinic, monoclinic, orthorhombic, and hexagonal, depending on the number and parity of the number of carbon atoms in paraffin molecules, and on the temperature, impurities, and other factors.[30] Recently the morphology of *n*-paraffin crystals with different structure has been investigated in great detail by the PBC analysis.[9,10,34] In the following, the growth forms of crystals with the orthorhombic and the triclinic structure are described independently according to Eq. (32a) (only the PBC analysis is performed) and the modified approach given by (32b) (both the PBC analysis and the IS analysis need to be carried out). The theoretic growth forms will be compared with the observed growth forms.

A. The morphology of orthorhombic *n*-paraffin crystals

In the following, our concentration will be focused on normal paraffin crystals having orthorhombic structure, in the space group P_{bcm} for odd-numbered paraffins[31,32] and P_{ca2_1} for even-numbered paraffins.[31,33] We take *n*-$C_{21}H_{44}$ and *n*-$C_{36}H_{74}$ crystals as an example. According to (32a), the elements of η must be calculated. This can be done on the basis of the Hartman-Perdok (or PBC) theory.[1,2,8] First, important bonds in a given crystal structure should be calculated. It follows that PBC's can then be identified from the crystal structure. A PBC is defined as an uninterrupted chain of bonds which has the periodicity $[uvw]$ of the lattice. From the obtained PBC's, F faces (or flat faces) can be found. For those faces we can carry out further calculations. (An F face is a crystallographic face having two nonparallel sets of PBC's, both parallel to the surface.) For more details concerning the PBC analysis of paraffin crystals, see Refs.

9 and 10. Note that under certain conditions, some roughened F faces roughening temperatures are much lower than the actual temperature. In most cases, such faces are very unlikely to occur on crystals. Therefore, they can be excluded from our considerations. In the following discussions, only those faces whose roughening temperatures are above or slightly below the actual temperature under current growth conditions are relevant and are taken into account. Following the ordering convention mentioned above, the elements of those sets are ordered as the faces $\{001\}$ and $\{110\}$ for n-$C_{21}H_{44}$ crystals, the faces $\{001\}$, $\{00\bar{1}\}$, $\{110\}$, $\{111\}$, and $\{11\bar{1}\}$ for n-$C_{36}H_{74}$ crystals. According to our results,[9,10] the growth forms of n-$C_{21}H_{44}$ and n-$C_{36}H_{74}$ are defined according to (32a) in the following sets:

$$R=\eta=\{1,12.6\} \quad (\text{for } n\text{-}C_{21}H_{48}) \tag{35}$$

and

$$R=\eta=\{1,1,23.8,23.9,23.9\} \quad (\text{for } n\text{-}C_{36}H_{74})\ . \tag{36}$$

Constructed according to the Wulff plot, n-$C_{21}H_{44}$ and n-$C_{36}H_{74}$ crystals have a lozenge shape, bounded by the large $\{001\}$ faces and the narrow $\{110\}$ side faces. The growth forms of crystals of n-$C_{21}H_{44}$ and n-$C_{36}H_{74}$ according to (35) and (36) are shown in Figs. 1(a) and 1(b), respectively.

For the purpose of comparison, the theoretical and observed growth forms of n-$C_{21}H_{44}$ crystals (grown from an n-hexane solution) and of n-$C_{36}H_{74}$ crystals (grown from an m-xylene solution) are shown in Fig. 2. It can be seen that orthorhombic paraffin crystals indeed have a lozenge shape. Nevertheless, some discrepancies between predicted growth forms and observed growth forms remain. The predicted growth forms show a too thick growth habit for the n-paraffin crystals. From the discussions given in Sec. III, we can see that these contradictions result from the application of the proportionality condition given by Eq. (3). This means that $C^{*}_{l(i)}$ was implicitly considered to be orientation independent of crystallographic orientations and the carbon number of n-paraffin molecules. According to our recent studies,[21,29] $C^{*}_{l(i)}$ depends not only on the orientation of surface i, but also on the chain length of paraffin molecules and the properties of the solvent and impurities. Undoubtedly, to improve our predictions, Eq. (32b) is a better alternative.

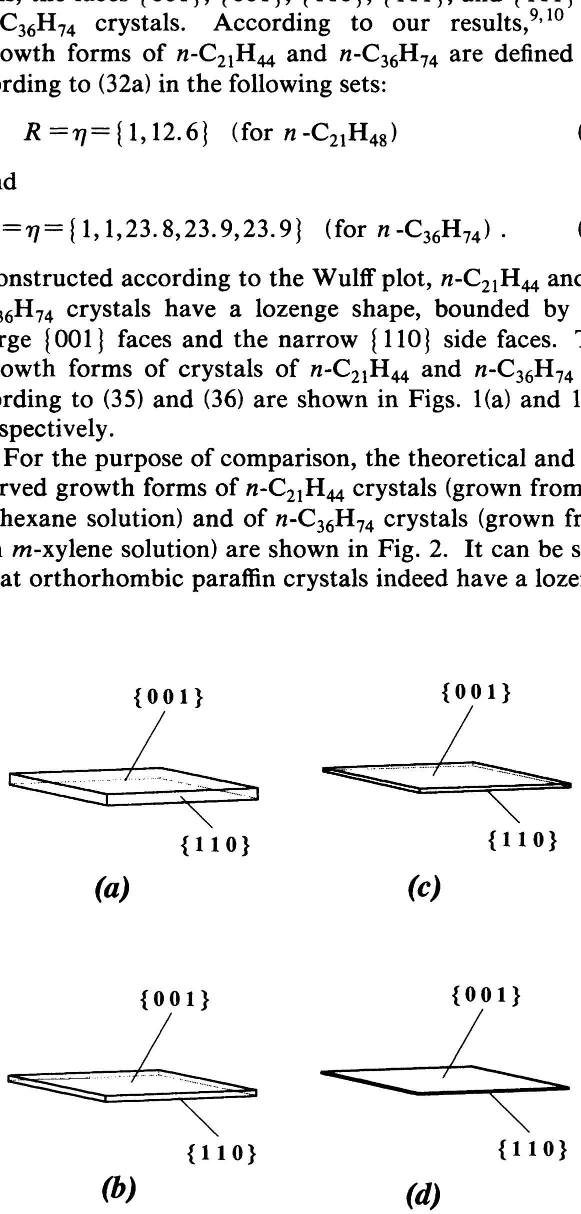

FIG. 1. (a) and (c), theoretical growth forms of n-$C_{21}H_{44}$ crystals; (b) and (d), theoretical growth forms of n-$C_{36}H_{74}$ crystals. The growth forms of (a) and (b) correspond to (32a) and (c) and (d) to (32b). The growth forms of n-paraffin crystals are platy, bounded by the large $\{001\}$ faces (and the $\{00\bar{1}\}$ faces for n-$C_{36}H_{74}$ crystals) and the narrow side faces $\{110\}$. After considering the influence of the ambient phase, the growth habits given by (c) and (b) are much thinner.

Now the problem is how to calculate C_l^{*} for different surfaces. This is the question of the IS analysis. The calculation is carried out using Eq. (10a) or (10b). In the equations, the term $X_A(0)$ (or ρ_f^I) can be evaluated according to various theories. Here a self-consistent field theory[26–28] is used to calculate $X_A(0)$ (or ρ_f^I). (This formalism was first developed by Scheutjens and Fleer to investigate solid-fluid interfacial systems of polymers. Now a computer program has been developed to calculate profiles of density at the interface according to this theory. For more details, see Refs. 26–29.) As discussed in Secs. III B and III C, we notice that the fraction of effective growth units at the surface is in a subtle way related to the interfacial structure, and hence influences the morphology of crystals.

According to the results obtained form self-consistent field calculations,[29] at equilibrium, most fluid paraffin molecules in the first fluid layer adjacent to the solid phase are preferentially lying parallel to the solid surface, while only a very small number of fluid n-paraffin molecules are transverse. As regards the surface structure of n-paraffin crystals, at the side faces (including the $\{110\}$ faces) solid paraffin molecules are packed lying parallel to the surface having a similar alignment as molecules in the crystal structure [see Fig. 3(a)]. Note that among those parallel fluid paraffin molecules, different orientations of molecular chains within the XY plane and different chain conformations of molecules still occur. However, they can easily be converted from one state to another by thermal fluctuations, and for that reason, we will not distinguish between them. Nonparallel fluid paraffin molecules have higher-energy levels than molecules lying parallel to the surface. They tend to transfer spontaneously to parallel conformations, provided the available space is sufficient. Therefore, all fluid paraffin molecules are considered to be effective with respect to the solid surface structure of the $\{110\}$ faces. For the $\{001\}$ faces, the surface structure of the crystal phase is different. Solid n-paraffin molecules are positional with their chain axis transverse to the surface. Therefore, for fluid n-paraffin molecules to be incorporated in the structure, their molecular chains must also be aligned transversely to the surface; thus, only those molecules which "stand" on the surface will become effective. [See Fig. 3(b).] Because this transverse orientation of the fluid molecular chain axis does not correspond to the ground state, an extra driving force is necessary to activate the parallel-lying

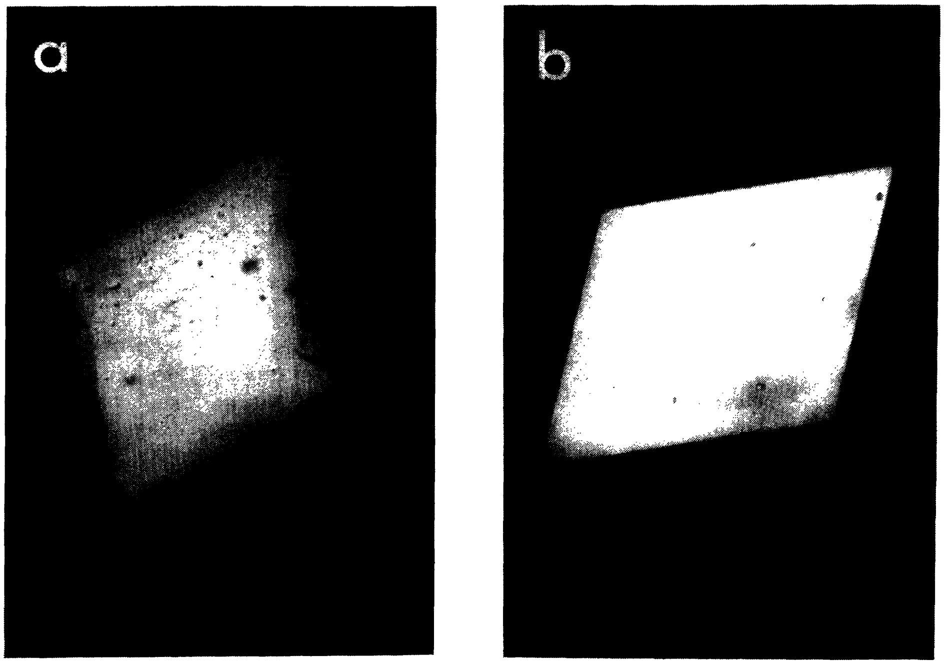

FIG. 2. (a) A crystal of n-$C_{21}H_4$ grown from an n-hexane solution; the equilibrium temperature $T_s \simeq -3.23\,^{\circ}C$ and the supercooling $\Delta T \simeq 0.03\,^{\circ}C$. (b) A crystal of n-$C_{36}H_{74}$ grown from an m-xylene solution; $T_s = 33.08\,^{\circ}C$, $\Delta T = 0.16\,^{\circ}C$.

molecules causing them to "stand" on the surface; the longer the molecular chains, the larger the driving force. Ultimately, the "standing" molecules are effective, the parallel-lying molecules are ineffective. In the calculation of $X_A(0)$ at the $\{001\}$ faces, only the portion of "standing" n-paraffin molecules is taken into account.

In addition to the effect of molecular conformations, the excess energy (per structural unit), has a direct influence on $C^*_{l(i)}$. In this case, the excess energy is proportional to $E_i^{\rm att}$. This implies that $C^*_{l(i)}$ depends monotonically on $E_i^{\rm att}$. Figure 4 shows the value of $C^*_{l(i)}$, calculated by the self-consistent field theory, as a function of $E_i^{\rm att}/E_0^{\rm att}$ (here $E_0^{\rm att} = E_{110}^{\rm att}$). It is clearly indicated in this figure that as the relative attachment energy $E_i^{\rm att}/E_0^{\rm att}$ decreases, $C^*_{l(i)}$ increases almost linearly.

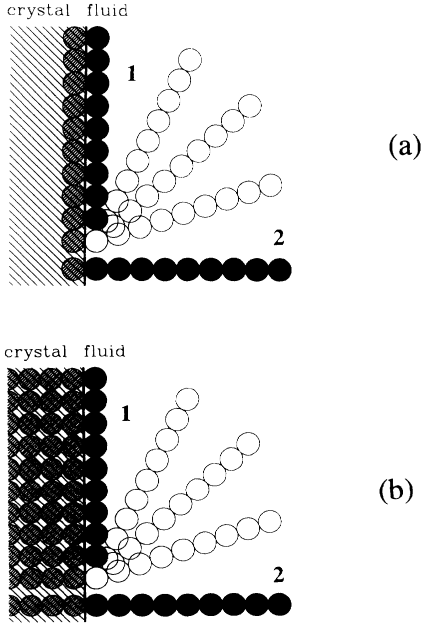

FIG. 3. Illustration of the structure of the crystal surfaces and the conformations of n-paraffin molecules at the interface. (a) The $\{110\}$ faces of orthorhombic n-paraffin crystals. (b) the $\{001\}$ faces of n-paraffin crystals. Conformation "1" indicating the molecules lying parallel to the surface; conformation "2" indicating the molecules "standing" on the surface.

From the results of the calculations, the values of the elements of C_l^* for both n-$C_{21}H_4$ and n-$C_{36}H_{74}$ crystals are now given by

$$C_l^* = \{3.1, 1\} \quad (\text{for } n\text{-}C_{21}H_{44}) \tag{37}$$

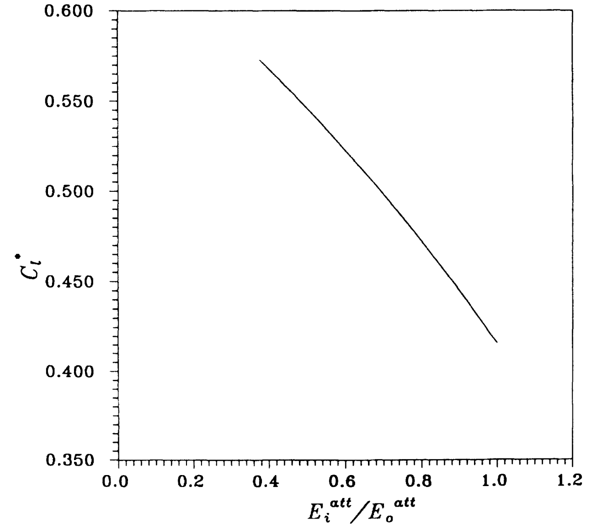

FIG. 4. The surface characteristic factor C_l^* plotted vs the relative attachment energy $E_i^{\rm att}/E_0^{\rm att}$ for n-$C_{21}H_{44}$ crystals. Here the influence of chain conformations is not taken into account. $E_0^{\rm att} = E_{110}^{\rm att}$.

and

$$C_l^* = \{3.32, 3.32, 1.003, 1, 1\} \quad (\text{for } n\text{-C}_{36}\text{H}_{74}) \ . \tag{38}$$

According to (32b), (35), and (36) should be modified according to

$$R = \{1, 39.6\} \quad (\text{for } n\text{-C}_{21}\text{H}_{44}) \ , \tag{39}$$

$$R = \{1, 1, 78.6, 79.1, 79.1\} \quad (\text{for } n\text{-C}_{36}\text{H}_{44}) \ . \tag{40}$$

Based on (39) and (40), the modified growth forms of n-$C_{21}H_{44}$ and n-$C_{36}H_{74}$ crystals are constructed by the Wulff plot, and shown in Figs. 1(c) and 1(d). It can be seen that the modified theoretical growth forms are now much closer to the observed growth forms.

B. The morphology of triclinic *n*-paraffin crystals

Triclinic n-paraffin crystals have the space group symmetry $P_{\bar{1}}$.[31,35] In this section the morphology of n-$C_{24}H_{50}$ crystals is treated. According to the results of PBC analysis,[34] the important F forms for the crystals are ordered in the sets as {001}, {010}, {011}, {100}, {101}, {111}, and {110}. It is obtained from our calculations based on Eq. (32a) that the growth form of n-$C_{24}H_{50}$ crystals is defined according to the internal structure in the set:

$$R = \eta = \{1, 9.27, 9.62, 12.5, 12.6, 14.1, 14.7\} \ . \tag{41}$$

Constructed by the Wulff plot, n-$C_{24}H_{50}$ crystals have a platy shape, confined by the large {001} faces and the narrow side faces {010}, {101},and {111} [see Fig. 5(a)].

Applying the same principles of the IS analysis described in the last section, the growth form defined by Eq. (41) can be modified by considering the influence of the ambient phase. In the case n-$C_{24}H_{50}$ crystals growing from iso-octane solutions, (41) is modified according to (32b) as

$$R = \{1, 27.9, 29.7, 57, 57.8, 77.2, 88.1\} \ . \tag{42}$$

Correspondingly, the modified growth form of n-$C_{24}H_{50}$ crystals, is given in Fig. 5(b). It can be seen that the shape of crystals is very thin, flat needlelike shape, which is different from that shown in Fig. 5(a). In spite of this, the small side faces {100} instead of the side faces {111} and {101}, occur on the top of the needle. In comparison, it is found that this predicted morphology is very close to the observed morphology of n-$C_{24}H_{50}$ crystals grown from iso-octane solutions (see Fig. 6).

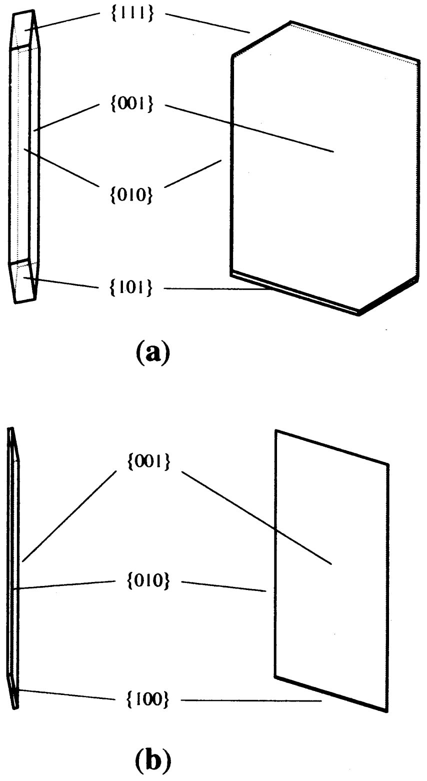

FIG. 5. The theoretic growth forms of triclinic even n-paraffin crystals. (a) The growth form of n-$C_{24}H_{50}$ crystals according to Eq. (32a). In this case, only the factor corresponding to the bond structure of crystals are considered and the shape of the crystal is platy. (b) The growth form of the crystals according to Eq. (32b). In this case, the influence of the fluid phase (an n-$C_{24}H_{50}$-iso-octane solution) is taken into account. The crystal becomes a flat needlelike shape.

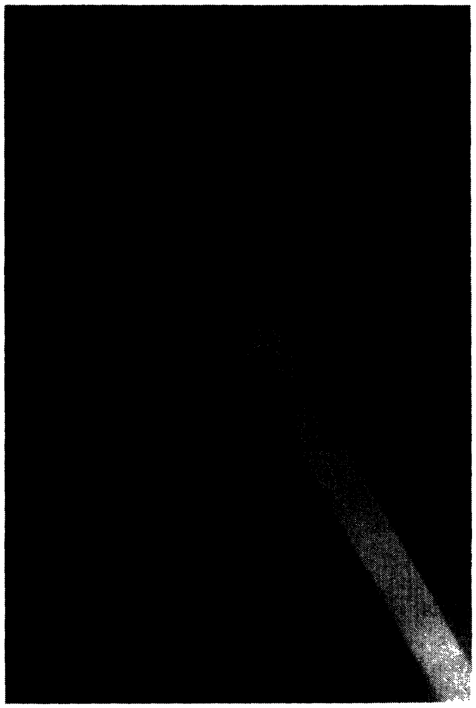

FIG. 6. A crystal of n-$C_{25}H_{50}$ growing from an iso-octane solution ($T_s = -6.87\,^{\circ}\text{C}$, supersaturation $\sigma = 1.5\%$). The crystal has a flat needlelike shape, bounded by the large {001} faces the narrow side faces {010} and the small faces {100} on the tip.

C. Discussion

The simple examples discussed in Secs. IV A and IV B demonstrate the relevant formalisms presented in Sec. III. It has been shown that by taking the influence of the ambient phase into account, the predicted growth forms of crystals look very similar to the observed ones. In the case of orthorhombic *n*-paraffin crystals, only a small number of different crystal faces are in competition. The influence of the ambient phase only causes the change in the thickness of the crystals. If the influence of the ambient phase is very strong, the shape of the crystals can change drastically. For example, when some tailormade additives are added to the system for that purpose, the paraffin crystal shape is modified from platelike to needlelike.[9] On the other hand, for triclinic *n*-paraffin crystals, several different crystal faces are in competition, changes in R, brought about by the influence of the ambient phase, cause the disappearance of some crystal faces (see Fig. 5). Then a considerable change in the crystal shape can be observed.

It can be seen from the foregoing discussions that may be influenced by the external factors controlling the growth morphology of crystals may include the effect of solvent and impurity and that of supersaturation and kinematic factors (surface integration kinetics, mass and heat transfer, etc.). Under certain conditions, these factors are explicitly or implicitly taken into account within the framework of our formalisms. As shown in Eq. (10a), $\mathbf{C}_l^*$ is directly related to the molecular structure, properties, and concentrations of the solute and the solvent. Therefore, in the calculation of $C_{l(i)}^*$, these parameters of the solute and the solvent should be very well defined. It follows that the influence of the solvent or impurities on the morphology of crystals can be directly seen from the change in $C_{l(i)}^*$. This guarantees that the effect of solvent and impurity can be appropriately taken into account within the framework of our formalisms.

The effect of supersaturation on the morphology of crystals is quite mixing. For simple molecule systems, at very low supersaturations, the reduced growth rate R_i is independent of the supersaturation, while on increasing the supersaturation R_i changes and ultimately adopts the value 1, all faces having the same growth rate.[7] This behavior implies that at low supersaturations the habit is more extreme, at high supersaturations more isometric. In the case of complex molecule systems, this effect and the effect of the solvent will be coupled with each other at a relatively high supersaturation.[10] Then this can, in principle, be discussed in the IS analysis. In general, we assume that our formalisms can only be appropriately applied within the low supersaturation range. Thus, the supersaturation becomes a face-independent factor and does not appear in Eqs. (30a), (30b), (32a), and (32b).

We notice that according to Harman and Bennema,[7] at low supersaturations, the relation between R_i and the kinematic factors can be approximately replaced by the relation between R_i and E_i^{att}. This implies that the kinematic factors are considered properly within our formalisms.

On the other hand, the growth forms of crystals are determined by so many factors that our formalisms can only give a statistical average of the morphology of crystals. In this sense, it is almost impossible and also unnecessary to include all factors into a generalized model.

V. CONCLUSIONS

Internal and external factors controlling the morphology of crystals are given by $\mathbf{M}$, η, Θ^r, $\mathbf{C}_l^*$, σ', etc. If we define the behavior of fluid units and other external factors as the "symmetry" of the ambient phase, it follows from Eqs. (21), (30b), and (32b) that the shape and external symmetry of crystals is a composite result brought about by the macroscopic symmetry of crystals and the "symmetry" of the ambient phase. In the case of crystals in contact with a microscopically isotropic medium, the highest external symmetry of crystals, which is determined by the internal symmetry of crystals, occurs. (In fact, that crystals consist of isotropic building units growing from vapor comes very close to this situation.) Otherwise, the actual external symmetry of crystals may be lower than the higher external symmetry. We may, in principle, influence the shape and external symmetry of crystals by changing the "symmetry" of the ambient phase.

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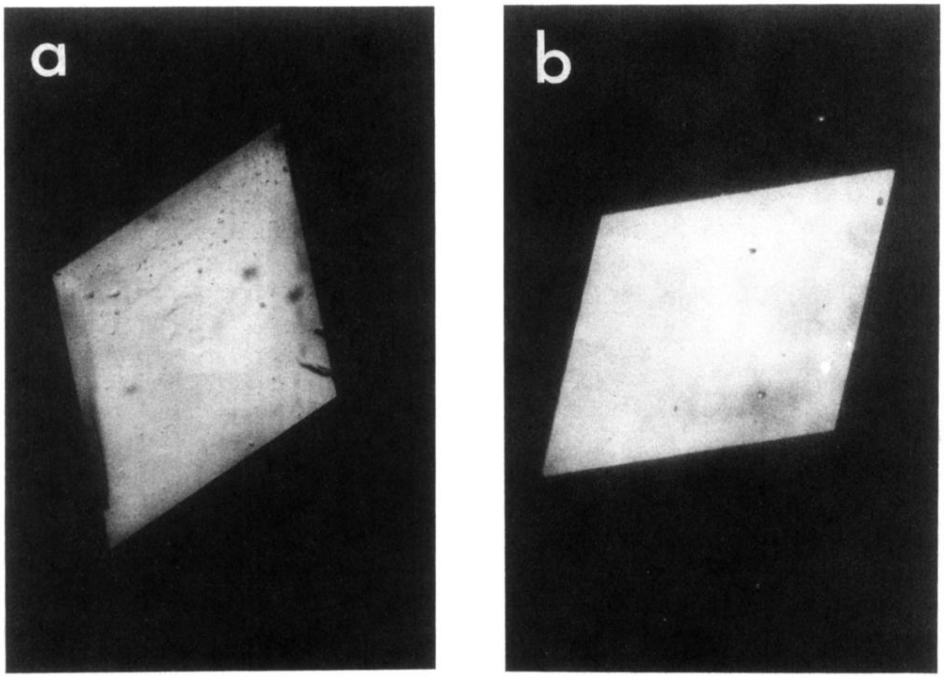

FIG. 2. (a) A crystal of n-$C_{21}H_4$ grown from an n-hexane solution; the equilibrium temperature $T_s \simeq -3.23\,^\circ C$ and the supercooling $\Delta T \simeq 0.03\,^\circ C$. (b) A crystal of n-$C_{36}H_{74}$ grown from an m-xylene solution; $T_s = 33.08\,^\circ C$, $\Delta T = 0.16\,^\circ C$.

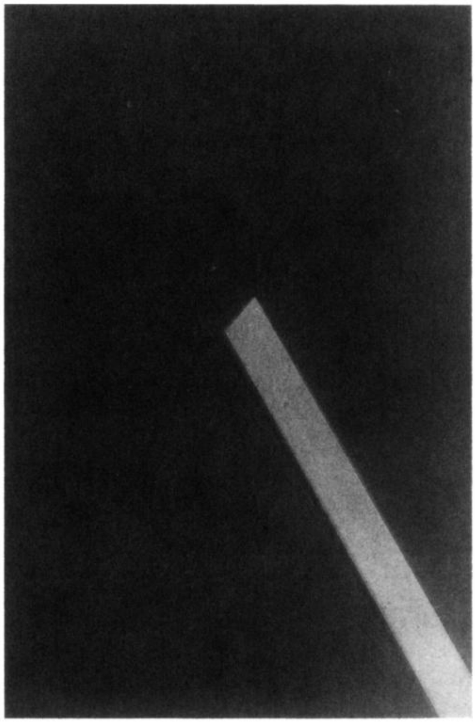

FIG. 6. A crystal of n-$C_{25}H_{50}$ growing from an iso-octane solution ($T_s = -6.87\,^\circ$C, supersaturation $\sigma = 1.5\%$). The crystal has a flat needlelike shape, bounded by the large $\{001\}$ faces the narrow side faces $\{010\}$ and the small faces $\{100\}$ on the tip.