Growth Forms of Crystals: Possible Implications for Powder Technology

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Abstract

In this paper, a one-layer regular solution model for the interface crystal mother phase is treated from first principles. From this model, the concepts of thermal roughening and kinetic roughening are derived. These concepts correspond to a roughening transition under the influence of the temperature and a driving force for crystallization, respectively. The results of the simple theory are compared with recent advanced theories inspired by computer-simulation studies leading to the theory of roughening transition and kinetic roughening. It is shown how these theories can be integrated with the crystallographic morphological theory of Hartman and Perdok. Examples of mainly organic crystals are reviewed. Observed growth forms are interpreted by means of the theories discussed above.

1. Introduction

1.1 Concepts to describe shapes of crystals

In this paper, an introduction will be given on statistical-mechanical surface theories which are integrated with crystallographic-morphological theories. It will be shown how, in principle, growth forms of crystals can be predicted from these integrated theories. Growth forms of crystals result from a crystal growth process, caused by a non-equilibrium driving force. This may be a supersaturation for growth from solution or an undercooling for growth from the melt.

In most cases, crystal growth forms of single crystals are bounded by flat faces. The orientation of these faces is described with three integers (hkl). Crystal growth forms of a particular compound and crystal structure are in most cases characterized by combinations of forms of faces {hkl}. Such characteristic combinations of forms of different sizes are called habits of crystals. A form of faces indicated as \{hkl\} is a combination of faces such as \{hkl\}, \{hkl\}, \{hkl\}, which can be transformed into each other by the symmetry operations of the point group (in this case two mutual perpendicular mirror planes. Note that h means -h). Apart from the concept of habit, we will also use the concept of shape of a crystal or the concept of morphology of a crystal. Morphology implies first of all a theoretically predicted growth form. This is compared with the observed morphology or habit of single crystals. The shape of a crystal may correspond to a given form of a crystal. In this paper the concepts: morphology, habit, crystal growth from, and shape will be freely used without further definition. The meanings of these concepts will become clear from the context.

1.2 Aim and contents of the paper

Using the simplest possible statistical-mechanical, regular solution models of the interface crystal-mother phase as a heuristic and didactic tool, basic concepts like roughening transition and kinetic roughening of the interface will be introduced. Implications for crystal growth mechanisms will then be discussed. The results will be compared with results of recent theories on crystal surfaces and crystal growth.

Next, principles of classic crystallographic-morphological theories will be discussed and followed by a discussion of the crystallographic-morphological theory of Hartman and Perdok.
It will be shown how the statistical-mechanical models for the interface and the Hartman Perdok theory can be integrated. Next, a variety of successful predictions of the morphology of crystals will be reviewed. Recent research on shapes of organic crystals will be reviewed.

1.3 Practical implications of the morphology of crystals for powder technology

Separation processes of mother liquid from the crystallized mass of crystals using, among others, filtration processes may depend strongly on shapes of resulting crystals. The following example from the oil industry can be given. During temperature lowering of about 10°C of gasoline, the high fraction of paraffins crystallizes as lozenge-shaped flat, platy crystals. The precipitate of these crystals blocks filters and pumps of storage tanks, trucks and cars. Adding specific tailor-made additives, platy paraffin crystals are changed into needle-like crystals, which no longer block filters.

Shapes of crystals which result from all kinds of crystallization production processes may play a crucial role in resulting properties of powders. So powders consisting of crystals with needle-like shapes, platy shapes, shapes of flat needles or blocks etc. will behave differently. One of the hot subjects of research in the field of (industrial) crystallization is currently: (i) to understand habits of crystals, and on this basis, (ii) finding ways to change crystal habits by varying solvents and designing specific tailor-made additives (for a survey see ref. 21).

2. Jackson's one-layer regular solution model for the crystal-mother phase interface

2.1 Principles of the model

In the original lattice-gas or regular-solution-like model of Jackson for the interface, the interface crystal-mother phase is partitioned into equal cells (for surveys and references see ref. 24-30, for regular solution see ref. 31). In order to simplify our case we will use a tetragonal or square lattice with a fourfold axis perpendicular to the interface with the orientation (001). This gives square cells which are equal in size and shape. Following the tradition of so-called lattice gas or Ising models, the cells can have only two properties: solid or fluid. In original Ising models used in theories of magnetism, these properties are spin up or spin down. In the simplest possible regular solution version of Jackson's solid-fluid interface model, the interface consists of only one mixed solid-fluid layer on top of a completely solid crystal (see also Fig. 2 below). This first layer on top of the solid body can be considered as a square, mixed solid-fluid crystal. In the following, we will apply the usual formalism of regular solutions to this model (see also Fig. 2).

2.2 Regular solution model

The mixed solid-fluid one-layer model can now be singled out and we will give the simplest possible statistical mechanical-thermodynamic treatment for this model (equation 15).

As an artificial thermodynamic reference state, we start with a two-dimensional 100-percent-pure solid crystal and a 100-percent-pure fluid.
These pure reference crystals are mixed. We will calculate the change of free energy due to the mixing process. The pure solid crystal consists of $N_s$ solid cells or blocks and the pure fluid crystal of $N_f$ fluid blocks. Therefore, the original joint reference, free energy $F^*$ of the two crystals, is given by

$$F^* = N_s \mu_s^* + N_f \mu_f^*$$  \tag{1}$$

$\mu_s^*$ and $\mu_f^*$ are the chemical potentials of one solid and one fluid cell. It is essential for lattice gas or Ising models that the internal rotational and vibrational degrees of freedom of solid and fluid cells do not change due to mixing. This implies that although solid-fluid bonds are formed which replace solid-solid and fluid-fluid bonds, the chemical potentials of solid and fluid cells do not change.

According to thermodynamics, the change in free energy is given by

$$\Delta F_{mix} = \Delta U_{mix} - T \Delta S_{mix}$$  \tag{2}$$

because $F^*$ (equation (1)) remains unchanged. Here $\Delta U_{mix}$ and $\Delta S_{mix}$ are the energy of mixing and the entropy of mixing, respectively, resulting from mixing of the two pure reference crystals. According to the principles of regular solution theory, it is assumed that the entropy of mixing can be given in good approximation by the expression resulting from an ideal mixing process. According to Boltzmann, the statistical-mechanical expression for the entropy $S$ is given by

$$S = k \ln g$$  \tag{3}$$

Here, $k$ is the Boltzmann constant and $g$ the number of configurations of the system under consideration. For the reference state of the pure crystals $g = 1$ and hence

$$S^* = 0$$  \tag{4}$$

After mixing the entropy becomes

$$S = k \ln \frac{N!}{N_s! N_f!}$$  \tag{5}$$

Using the well known Stirling approximation which is valid for large numbers $N$

$$\ln N! \simeq N \ln N - N$$  \tag{6}$$

equation (5) becomes

$$\Delta S_{mix} = S - S^* = -kTN(x_s n_s x_f n_f + x_f n_f x_s n_s)$$  \tag{7}$$

Here, $N$ is the total number of cells in the two-dimensional mixed solid-fluid crystal or

$$N = N_s + N_f$$  \tag{8}$$

and $x_s$ and $x_f$ are the fractions of solid and fluid cells in the mixed solid-fluid crystal

$$x_s = \frac{N_s}{N}, \quad x_f = \frac{N_f}{N}$$  \tag{9}$$

and

$$x_s + x_f = 1$$  \tag{10}$$

Equation (10) expresses that cells are either in a solid or a fluid state. We have now an expression for $\Delta S_{mix}$ given by equation (7).

In order to calculate $\Delta U_{mix}$, the zeroth order mean field or Bragg Williams approximation is introduced, which is typical for regular solution models.

This zeroth order approximation implies that in the mixed solid-fluid crystal, a solid cell is generally surrounded by the same number of fluid and solid cells as the average composition of the mixed crystal. This implies that possible preferential clusterings of solid cells around a solid cell or fluid cells around a solid cell, and likewise for clusterings of fluid cells, are ruled out. Now, the average number of fluid cells surrounding one solid cell $n_{sf}$ is given by

$$n_{sf} = 2x_f$$  \tag{11}$$

Here, $z$ is the coordination number of a solid cell. This is the number of the closest neighbouring cells. For our square lattice, $z = 4$. The total average number of fluid cells $N_{sf}$ surrounding the $N_s$ solid cells is given by

$$N_{sf} = 2N_s x_f$$  \tag{12}$$

$N_{sf}$ corresponds to the total average number of solid-fluid closest-neighbouring contacts between cells or bonds. In the pure solid and pure fluid crystal, only the closest neighbouring bond energies $ss$ (solid-solid) and $ff$ (fluid-fluid) occur. It can be said when using the zeroth order approach that due to the mixing process, normally $N_{sf}$ ss bonds and ff bonds are replaced by $N_{sf}$ sf bonds. For the formation of one sf bond, one half ss and one half ff bond energy
must be broken. This can be demonstrated by
the following. We start with a pure solid and a
pure fluid crystal and exchange a solid and a
fluid cell. Then in our square, two-dimensional
crystals, 4 ss bonds are broken in 4 ff bonds.
These are replaced by 8 sf bonds. So for the
formation of one sf bond, 1/2 ss and 1/2 ff bond
must be broken. It thus follows that the formation
energy of one solid-fluid bond energy \( \Phi \)
referenced to a pure solid and a pure fluid
crystal is given by

\[
\Phi = \Phi^{ss} - \frac{1}{2} (\Phi^{ss} + \Phi^{ff})
\]

Here, \( \Phi^{ss} \) and \( \Phi^{ff} \) are negative energies and
the generalised energy, \( \Phi \), which plays a key
role in the formalism to be developed is sup­
posed to be positive. Substituting equation (13)
into equation (12), writing according to equa­
tion (10) \( x_r = 1 - x_s \), and dropping the index s in
\( x_s \), we obtain for \( \Delta U_{mix} \) the expression

\[
\Delta U_{mix} = NkT x(x - 1)
\]

Here, \( x \) is the fraction of solid cells in the mixed
solid-fluid crystal and

\[
a = \frac{\Phi}{kT}
\]

We recall that for our square lattice, \( z = 4 \). \( \Phi \) is
for a square lattice with one type of closest
neighbouring bond given by equation (13). Sub­
tituting the expressions for mixing entropy
(equation (7)) and energy of mixing (equations
(14, 15) in equation (2)), the following expres­sion
for the free energy change due to the mixing
process is obtained

\[
F = F_f + \Delta F_{mix}
\]
\[
= NkT x(x - 1) + NkT (xlnx + (1-x)ln(1-x)) - N\Delta \mu^* + N\mu_f^*
\]

Here

\[
\Delta \mu^* = \mu_f^* - \mu_s^*
\]

The two last terms of equation (16) follow from
equation (1) and equation (10).

In the case of thermodynamic equilibrium, the
chemical potential of a solid cell has to be equal
to the chemical potential of a fluid cell. Other­
wise, growth or dissolution would occur. So

\[
\mu_f = \mu_s^*
\]

and equation (16) changes in

\[
F = kT x(x - 1) + NkT (xlnx + (1-x)ln(1-x)) + N\mu_f^*
\]

2.3 Implications of the model
If equation (19) is divided by \( NkT \) we get

\[
f(x) = ax (1-x) + xlnx + (1-x)ln(1-x)
\]

In equation (20) we have omitted the term \( \mu \gamma \)
which is a constant for constant \( T \). \( f(x) \) is given by

\[
f(x) = \frac{F(x)}{NkT}
\]

and has the meaning of the average free energy
per solid and fluid cell in the mixed solid-fluid
crystal divided by \( kT \).
In Fig. 1 we have plotted the function \( f(x) \) given
by equation (20) in dependence of \( x \) for different
\( a \) values. For values of \( a > 2 \) two minima occur
separated by a maximum for \( x = 0.5 \). For values of \( a \leq 2 \) only one minimum occurs for \( x = 0.5 \).

The function \( f(x) \) results from adding the two
functions: \( \Delta u_{mix} \) and \( -T\Delta s_{mix} \). The dimensionless
energy of mixing term \( \Delta u_{mix} \) is given by

\[
\Delta u_{mix} = \frac{\Delta U_{mix}}{NkT} = -ax^2 + ax
\]

Since \( a \) is supposed to be positive, this is a
mountain parabola, with a maximum at \( x = 0.5 \).
The dimensionless entropy term \( T\Delta s_{mix} \) is given by

\[
-T\Delta s_{mix} = \frac{T\Delta S_{mix}}{NkT} = xlnx + (1-x)ln(1-x)
\]

Taking the first derivative of equation (23)
yields the following expression

\[
\frac{dT\Delta s_{mix}}{dx} = lnx - ln(1-x)
\]

It can be seen that this first derivative goes
to \(-\infty\) if \( x \rightarrow 0 \) and to \(+\infty\) if \( y \rightarrow 1 \). Since
the expressions \( xlnx \) and \((1-x)ln(1-x)\) are nega­tive, because \( x \) and \( 1-x \) are smaller than unity,
the function \(-T\Delta s_{mix}\) has the shape of a basin
with infinite steep slopes for \( x \rightarrow 0 \) and \( x \rightarrow 1 \).
By adding the basin function \(-T\Delta s_{mix}\) and the
mountain parabola function $\Delta u_{\text{mix}}$, two minima close to $x=0$ and $x=1$ occur separated by a maximum. This only holds if $\alpha$ is large enough. If $\alpha$ becomes smaller and smaller due to, for example, an increase in temperature (see equations (13,15)), the mountain parabola equation (22) shrinks. This implies that the maximum of the $f(x)$ function decreases and that the minima shift towards the middle (Fig. 1). If $\alpha$ continues to decrease, a critical point is reached where the basin entropy function becomes dominant, which results in only one minimum for $x=0.5$. It will be shown below that the critical value for $\alpha$ is $\alpha^c=2$.

### 2.4 Physical interpretation of the model

#### Here Figure 2

In Fig. 2, a sketch is given of an interpretation of the two-dimensional regular solution model developed so far. It can be seen from Fig. 1 that if $\alpha>2$, the two-dimensional mixed solid-fluid crystal will reach a minimum in the free energy by separating itself in a solid phase or solid domains with some fluid cells, and in a fluid phase or fluid domains with some solid cells. Then, two-dimensional domains will be separated by edges of steps with an edge-free energy larger than zero. If $\alpha$ decreases (or, keeping the bond energy $\Phi$ constant, by increasing the temperature), more and more solid cells will appear in the fluid domains as ad atoms on the surface, and more and more fluid cells will appear in the solid domains as surface vacancies. For $\alpha\approx2$, one phase or one domain occurs consisting of 50% solid cells and 50% fluid cells (see again Fig. 1).

The results of the two-dimensional regular solution model can now be given the following physical interpretation. If $\alpha>2$, a crystal face will be essentially flat because the surface will consist of large solid domains separated by steps with an edge free energy larger than zero. That surfaces which are flat over very large distances do occur can be demonstrated with the following argument. Assume that we have a very large surface consisting of one solid domain. Due to statistical fluctuations, only surface vacancies of fluid cells and ad atoms of solid cells can be formed. Large islands on top of the solid domains or large basins in the solid domains cannot be formed by statistical fluctuations, because the edge free energy of a step separating solid and fluid domains is larger than zero. If, however, $\alpha<2$, the possible edge free energies between (metastable) solid and fluid domains vanish and a surface may freely roughen up by statistical fluctuations. Then there is no need to maintain an overall flatness.

It follows from the considerations presented in this section that if $\alpha$ is larger than a critical value, a crystal surface is in essence flat, but if $\alpha$ is smaller than a certain critical value it is in essence rough. It can be seen from equations (13,15) that $\alpha$ is inversely proportional to the absolute temperature. We can therefore rephrase the statement given above in the following way: there exists for a crystal face a characteristic temperature $T^*$, to be called the roughening temperature, which is inversely proportional to $\alpha^c$ so that if

$$\alpha>\alpha^c \text{ or } T<T^*, \quad \gamma>0$$

and if

$$\alpha<\alpha^c \text{ or } T\geq T^*, \quad \gamma=0$$

(25)

$\gamma$ is defined as the edge free energy per unit of length of a step. If $\alpha>\alpha^c$ or $T<T^*$, solid and fluid domains are separated by well-defined boundaries which correspond to steps with an edge free energy larger than zero. If $\alpha\leq\alpha^c$ or $T\geq T^*$, solid and fluid domains become one phase and edge free energies between (artificial) boundaries vanish. It thus follows that the change in the $f(x)$ function from a function characterized by two minima corresponding to the solid and the fluid phases separated by a maximum, to one minimum corresponding to one mixed solid-fluid phase (see Fig. 1), can be given the preliminary interpretation of the roughening transition.

### 2.5 Kinetic roughening

In this section, the influence of a driving force for crystallization on the roughening transition will be studied. It was discussed above that in the case of thermodynamic equilibrium, $\Delta \mu^* = 0$ (see equations (17,18)). It is, however, possible that the mother phase and the crystal surface under consideration are not in thermodynamic equilibrium and that, for example, $\mu$, the chemical potential of a fluid cell is larger than the
chemical potential of a solid cell. In this case, a
driving force for crystallization occurs. In case
of growth from solution, the chemical potential
of a fluid cell may be given by

\[ \mu = \mu^0 + kT \ln x \]  

(26)

here, \( \mu^0 \) is the standard chemical potential and
\( x \) is the fraction of solute. In the case of ther-
modynamic equilibrium, the chemical potential
of a solid cell is in principle equal to the chemi-
cal potential of a fluid cell, so that we can write

\[ \mu_s = \mu^0 + kT \ln x_{eq} \]  

(27)

where now \( x_{eq} \) is the fraction of solute for a
saturated solution in equilibrium with the solid
phase. The driving force of crystallization is for
relatively low supersaturations \( \Delta \mu \) given by

\[ \Delta \mu = \mu_s - \mu = kT \ln x_{eq} = kT \ln (1 + \sigma) \approx kT \sigma \]  

(28)

The dimensionless driving force \( \beta' \) is defined as:

\[ \beta' = \frac{\Delta \mu}{kT} (\approx \sigma) \]  

(28a)

It may also be interpreted as relative overpres-
sure for growth from the vapour, relative under-
cooling for growth from the melt etc.. The
general term \( \Delta \mu \) can now be introduced in
equation (16) in the following way:

\[ F = NkTa \times (1 - x) + NkT(\ln x + (1 - x) \ln (1 - x)) \]
\[ - Nk \Delta \mu - \beta'x \]  

(29)

Dividing equation (29) again by \( NkT \) we get

\[ f'(x) = ax(1 - x) + xlnx + (1 - x)ln(1 - x) - \beta'x \]  

(30)

In equation (30), we distinguish between an \( f'(x) \)
curve due to a driving force for crystallization
and an \( f(x) \) curve corresponding to ther-
modynamic equilibrium (equation (29)).

In Fig. 3, relative free energy curves \( f(x) \) are
plotted for \( a = 3 \) and \( \beta' = 0.1 \) and 0.5, respective-
ly. Due to the non-equilibrium positive driving
force \( \beta' \), a linear curve \( -x \beta' \) with a negative
slope \( - \beta' \) is added to the equilibrium curves
\( f(x) \). It can be seen from Fig. 3 that if \( \beta' \) is larger
than a certain value we get the situation that
only one minimum survives. This corresponds to
the fact that the thermodynamically stable
phase is the solid phase. This obviously occurs
for an \( f'(x) \) curve with \( a = 3 \) if \( \beta' = 0.5 \). For the
case that \( \beta' = 0.1 \), the solid phase is also the
stable phase, but the fluid phase is metastable.
This means that still two domains occur: the ther-
modynamically-stable solid phase and the
metastable fluid phase. Following the discus-
sion of section 2.4 it can be said that the flat-
ness is maintained. This is no longer the case
when there is only one minimum, due to the
(positive) driving force. In this case the surface
will be roughened. The effect is the same as for
roughening above the roughening temperature.
The reason is, however, quite different. Roughen-
ing is now caused by a driving force for
crystallization. This type of roughening is
called kinetic roughening.

2.6 Boundary between a flat surface and
a kinetically roughened surface

It can be shown (see ref.8) that the boundary
\( \beta'_{max} \) between the three extremes and the one
extreme case is given by

\[ \beta'_{max} = \pm \frac{a}{\sqrt{1 - \frac{2}{a}} + \ln \left( \frac{1 - \frac{2}{a}}{1 + \sqrt{1 + \frac{2}{a}}} \right)} \]  

(31)

Summarizing the discussion on kinetic roughen-
ing and the concept of (thermal) roughening, it
can be stated that equation (25) implies that
roughening transition or thermal roughening is
defined as
and kinetic roughening implies
\[ |\beta'| > |\beta_{\text{max}}| \quad \text{and} \quad a > a^k \rightarrow \text{kinetic roughening} \]  
(33)

Note that for the one-layer mean field model \( a^k = 2 \). Due to the ad hoc mean field approximations and to a lesser extent the one-layer approach, this value differs by 60% from the proper value \( a^k = 3.2 \) which follows from computer simulations.

In Fig. 4 the \( \beta'_{\text{max}} \) versus \( \alpha \) curve is presented (curve 2). In region A, layer growth must occur, but region B corresponds to kinetic roughening. Curve 1 corresponds to the \( \beta'_{\text{max}} \) curve for a multilayer interface model introduced by Temkin (see for survey ref.9 and included references). It can be seen that the one-layer Jackson model and the multilayer Temkin model give essentially the same results.

3. Thermal roughening; integration with Hartman Perdok theory and kinetic roughening

3.1 Monte Carlo Simulations

The one-layer regular solution model of Jackson\(^9\) has the advantage that it yields, in principle, essential concepts for the science of crystal growth such as thermal roughening and...
kinetic roughening. In addition, the regular solution model is easy to understand. The model, however, has its serious limitations. These are amongst others: (i) the limitation of the interface to one layer, and (ii) the application of mean field approximations. The last ad hoc approximation rules out preferential clusterings, which are essential for crystal growth.

Monte Carlo simulations have been carried out by Gilmer et al11) and de Haan et al12) for a multilayer so-called solid-on-solid model. Such a model is defined as a (001) interface of a tetragonal crystal, as discussed above, where overhangs are ruled out. (See Fig. 5). As shown in refs11,12), it is possible to simulate growth for different \( \alpha \) (equation (15)), and \( \beta' \) (equations (28, 28a)) factors. In Fig. (6), dimensionless rates of growth of the (001) surface in dependence of the dimensionless driving force \( \beta' \) are presented. These data result from Monte Carlo simulations obtained from a general and a special-purpose computer, respectively. It can be seen that at low \( \alpha \) values a linear \( R(\beta') \) curve occurs, but at higher supersaturations a curved \( R(\beta') \) curve. For values of \( \alpha \geq 4 \) the curved curve could be fitted with a so-called two-dimensional nucleation curve, using the birth and spread version. This implies that two-dimensional nuclei are formed on the surface, which spread. On top of these spreading layers other two-dimensional nuclei are formed, etc. etc.

The change from a linear to a non-linear curve at a value of \( \alpha \approx 3.2 \) marks the roughening transition. If \( \alpha < 3.2 \), the edge free energy is zero, hence no two-dimensional nucleation barrier occurs and the crystal face will grow with a linear growth rate. Also, the crystallographic orientation (001) (or in general (hkl)) will not be maintained. If \( \alpha > 3.2 \), the edge free energy is larger than zero (equation (25)), and growth progresses with a two-dimensional nucleation mechanism leading to the non-linear curves \( R(\beta') \) of Fig. 6. For sufficiently high \( \alpha \) values the growth rate is extremely slow, since the chance to form large critical nuclei is very low. In this case, growth may proceed via a spiral growth mechanism, induced by a screw dislocation. (We note that two conventions are used to define dimensionless energies or dimensionless temperatures which are expressed as xxx or kTxxx, respectively).

Inspired by the results of Monte Carlo simulations more than ten years ago, the concept of roughening transition on an SOS surface was clarified by experts on statistical-mechanical Ising models (see refs4,5,6,8) for other references). It can be defined in the way carried out above, (see equations (25,32)), but the foundation of this concept is now much stronger compared to the ad hoc and loose intuitive arguments used above. As already mentioned, numerically the value of \( \alpha^2=2 \) is 60% wrong. It follows from simulations that \( \alpha^2=3.6 \).

![Fig. 7 \( \beta_{\text{max}} \) versus \( \alpha \) curves. Upper curve Temkin multilayer model, middle curve ; curve calculated van Leeuwen using a pair approximation [15]. Lowest band boundary of two-dimensional nucleation and kinetic roughening.](image)
much too large. One can say that nature always finds clever fluctuations to reduce the resistance of growth on flat faces. In general, it can be said that the barriers such as those presented in Fig. 1 resulting from mean field models are artificially high. The minima seem to be real. Notwithstanding the criticism on mean field models, these models retain their heuristic and didactic value.

3.2 Spiral growth

In order to explain how crystals can grow on flat faces (below the roughening temperature) at low driving forces ($\beta'$), Sir Charles Frank developed the brilliant theory of spiral growth. The mathematical theory was worked out in the famous paper of Burton, Cabrera, and Frank in 1951. The idea of a growth spiral is demonstrated in Fig. 8 a, b, c, d. Thanks to the fact that almost all crystals are not perfect, screw dislocations are present which are a source of steps. It can be proven from statistical mechanical SOS step models (one dimension lower than the SOS surface model) that steps are always rough up to the absolute zero temperature. So steps grow without a thermodynamic nucleation barrier. This is analogous to the advance velocity of a surface growing above its roughening temperature (see Fig. 6). The centre of the step source does not change, and the curvature at the centre also remains constant. This curvature is the same as the radius of the two-dimensional nucleus $r^*$, which is given by

$$r^* = \frac{\gamma \Omega}{kT \beta'}$$

(34)

Here, $\gamma$ is the edge free energy of a step expressed in energy per surface area and $\Omega$ is the molecular volume of an atom, molecule, etc. in the solid state. Thanks to the interaction of the step source, created by the screw dislocation, the edge free energy, which below the roughening temperature is larger than zero (equations (25, 32)), and the driving force, which gives a curved step, a very special dissipative structure occurs: the growth spiral. Note that growth spirals are very flat hills. So the deviation of the orientations (hkl) is extremely small.

The concept of dissipative structure was introduced by Prigogine$^{\text{[4]}}$. It is a structured pattern which develops due to non-linear effects under the influence of a thermodynamic driving force. A dissipative structure produces entropy.

3.2 Hartman Perdok theory and connected nets

So far, very simple lattice gas models were used leading to concepts of roughening transition, kinetic roughening and spiral growth. Real crystals may have very rich crystallographic structures, and it has been shown that the world of statistical mechanical Ising models and the world of rich crystal structures, in principle at least, can be integrated.

The principles of the application of the integrated theory can be summarized as follows:

(i) First the bonds and bond energies between molecules must be determined. To determine the overall bond energies between molecules, the best available crystallographic data concerning mutual distances between molecules and their atoms are used and the best interatomic (for example, Buckingham) interaction potentials available.

(ii) Next, the molecules are reduced to points or centres of gravity and the so-called crystal graph is determined$^{\text{[4, 5, 6, 8]}}$. A crystal graph consists of a (infinite) set of points corresponding to the centres of gravity of molecules or growth units (or complexes) from which the crystal grows, and the relations or bonds between the centres of gravity. The relevant bonds of the crystal graph are the bonds correspond to closest neighbouring bonds. The crystal graph fulfills the symmetry of the space group of the crystal structure.

(iii) In order to predict the slowest growing
faces, which will dominate the crystal growth form, from the crystal graph, the so-called connected nets have to be determined. A connected net is defined as a two-dimensional graph where all points are connected to each other. This means that one can go from any point in the connected net to any other point by an arbitrary uninterrupted path of bonds. In order to determine genuine connected nets, it must be possible to partition the whole crystal graph unambiguously in equal parallel stacks of connected nets with an overall thickness of the interplanar distance $d_{hk0}$ corrected for the extinction conditions of the space group.

In the concept of connected nets, the world of crystallography and the statistical-mechanical Ising models meet. Since in all crystallographic directions the edge energy of a connected net is larger than zero, connected nets show a roughening transition. So faces parallel to a connected net will have a high resistance against growth if they can grow below their roughening temperature with a layer mechanism. (This means spiral growth is in most cases dominant. Two-dimensional nucleation will occur rarely, if no screw dislocation emerges at the surface). Therefore, faces parallel to connected nets will dominate crystal habits.

Apart from connected nets, non-connected nets also occur. It is then not possible to connect within the thickness $d_{hk0}$ the points of the crystal graph to each other, using bonds of the set of bonds of the crystal graph. For such a net, the edge energy in at least one direction is zero. A face parallel to such a net has a roughening temperature $T^*=0K$. The concept used here was first developed by Hartman and Perdok more than 35 years ago. A face parallel to a connected net was called an F (flat) face. Connected nets consist of at least two sets of parallel-connected uninterrupted chains of bonds of the crystal graph with a periodicity of the lattice of the crystal graph [uvw]. Such chains are called PBCs (Periodic Bond Chains).

A net containing at least two sets of connected PBCs is a connected net, and as already mentioned is parallel to an F face. A face parallel to an unconnected net consisting of only one set of parallel PBCs is called an S (stepped) face. A face parallel to an unconnected net without any PBCs is called a K (kined) face.

### 3.3 Order-disorder phase transition in two-dimensional connected net

Let us rephrase the theory of roughening transition summarized by equations (25, 39) in the following way:

\[
\begin{align*}
\text{if } \theta < \theta^R & \quad \gamma > 0 \\
\text{if } \theta \geq \theta^R & \quad \gamma = 0
\end{align*}
\]

(32)

Here, $\theta$ and $\theta^R$ are defined as dimensionless temperatures.

\[
\theta = \frac{2kT}{\Phi_{str}} \quad \theta^R = \left(\frac{2kT}{\Phi_{str}}\right)^R
\]

(35)

$\Phi_{str}$ is the strongest bond energy of a crystal graph. So, $\theta$ and $\theta^R$ are referenced to this bond energy. $\Phi_{str}$ has the shape as equation (13).

Onsager showed in 1944 that for a two-dimensional crystal or a connected net, an order-disorder phase transition occurs. Onsager was also able to calculate exactly the order-disorder phase transition temperature for simple nets with a given ratio of bond energies. This temperature is also known as the Ising temperature. So, using Onsager’s approach and contrary to the regular solution theory, $\theta^c$ can be calculated exactly. Recently, a method was developed to apply this theory to real complex-connected nets. Onsager’s results and the new method can be summarized as follows:

\[
\begin{align*}
\text{if } \theta < \theta^c & \quad \gamma > 0 \\
\text{if } \theta \geq \theta^c & \quad \gamma = 0
\end{align*}
\]

(36)

Here, $\theta^c$ is the dimensionless Ising temperature using the same convention as eq (35). We note that equation (36) has the same meaning as equation (25,32a,b).

In the formalism developed in ref., a probe step is introduced into the one-layer mixed solid-fluid crystal by forcing two screw dislocations of opposite sign, connected by a step, into this layer. (Note that when applied to magnetism the Ising temperature corresponds to the Curie temperature).

It was proposed to use the dimensionless Ising
temperature $\theta^c$, as a criterion for the relative morphological importance (MI) for a form of faces \( \{hkl\} \) on the crystal growth form. It is then assumed that the higher the $\theta^c$, the higher the MI. MI is defined as a (qualitative) statistical measure for the relative size and the relative frequency of occurrence of the faces of this form on the crystal growth form. The higher these quantities, the higher the MI.

We note that the reasons for using the Ising temperature of a two-dimensional connected net, instead of the more relevant roughening transition temperature in a multilayer interface as a criterion for the MI are the following:
(i) notwithstanding that the character of the roughening phase transition flat-rough is quite different from the character of an order-disorder phase transition in a connected net, it turns out that for simple models:
\[ \theta^R \approx \theta^C \]  
So it is reasonable to assume that it also holds true for more complex models.
(ii) For more complex crystal structures, $\theta^c$ contrary to $\theta^R$, $\theta^C$ can be calculated, provided the connected nets are real planar nets (i.e. no crossing bonds and nets with more floors occur). However, in this latter case, good approximations are often possible.

3.4 Roughening and kinetic roughening
Assume that we have a sequence of Ising or roughening temperatures of the connected nets of a crystal graph:
\[ \theta^R_1 > \theta^R_2 > \cdots > \theta^R_n > \theta^C \]  
If, at low supersaturations all faces grow below their roughening temperature as flat faces, it can be predicted that as the supersaturation increases, first face m will grow as a kinetically rough face and will become rounded, next faces m-1, etc. Or in other words: first the weakest faces with the lowest $\theta^c$ and, consequently lowest edge free energy, will grow as a kinetical rough face, next the next-weakest face, etc.

3.5 Proportionality condition
We recall that generalized bond energies $\Phi_i$ as used, for example, in eqs. (35) have the shape as given by equation (13). Since $sf$ and $ff$ bond energies are generally unknown, the following ad hoc approximations are usually introduced to calculate bond energies $\Phi_i$.
(i) the proportionality condition, implying that for two arbitrary bond energies $\Phi_i$ and $\Phi_j$ of the crystal graph, the following relation holds:
\[ \Phi_j : \Phi_i = \theta^R_j : \theta^R_i \]  
(ii) in order to calculate the actual bond energies, one other expression is needed, and the following approach has proved to be possible. Assume that the relative Ising or roughening temperatures are calculated for the connected nets or F faces of the faces 1, 2, ..., q, and that an order of decreasing $\theta^c$ values is obtained:
\[ \theta^C_1 > \theta^C_2 > \cdots > \theta^C_n > \theta^C_S > \cdots \]  
If it is observed that faces of the form p are flat, but faces of the form q are rough (or absent), then one may conclude that for the actual dimensionless temperature:
\[ \theta = \frac{2kT}{\Phi_{str}} \]  
according to the theory of roughening transition the following relation holds:
\[ \theta^C_q > \theta > \theta^C_p \]
We note that in all expressions for $\theta^C$, $\theta^R$, $\theta^C$, these values are referenced to the strongest bond energy $\Phi_{str}$. Since the actual temperature $T$ of the mother phase from which the crystal grows can be measured, $\Phi_{str}$ can be estimated from equations (41, 42), and using eq. (39), all $\theta^C$’s can be calculated. In the following, some results of research on growth and morphology of organic and anorganic crystals will be mentioned.

5. Morphology of organic crystals
5.1 Cyclohexane
Cyclohexane, $C_6H_{12}$, forms plastic crystals with a cubic, closely-packed structure in which the $C_6H_{12}$ molecules rotate almost freely and switch continuously from a chair to a boat configuration. The crystal graph can be considered as a cubic FCC lattice. Taking the closest neighbouring bonds, two types of connected nets, (111) and (100), can be identified.
This will lead to crystals having the shape of an octahedron. The corners may be cut off by cube faces. However, since the mobility of the cyclohexane molecules within the lattice close to the melting point of 6°C is very high, the enthalpy of melting $\Delta H^m$ is only 2.68 kJ mol$^{-1}$. This suggests that faces of cyclohexane crystals grow above their roughening temperatures with rounded-off rough faces from the melt, even at very low undercooling. This is indeed the case. It is interesting to see that the bond structure of the crystal graph still shows up in the anisotropy of the surface or growth rates. If the size of a growing crystal increases, the crystal form becomes unstable and dendritic growth starts with six branches, which are emitted from the rounded-off corners of the rounded-off pseudo-octahedron. (See Fig. 9d.) Instable crystal growth leading to dendritic or cellular growth will always occur if crystals grow above their roughening temperature.

5.2 Crystal of buckyball $C_{60}$ molecules

Very recently, crystals of $C_{60}$ were grown from the vapour phase. Now, $\Phi = -\frac{1}{\mu}$ (equation (13)), since $\Phi^{ss}$ and $\Phi^{ff}$ are zero. The faces $\{111\}$ and $\{100\}$ are now growing below their roughening temperature and crystals in the shape of cube octahedrons are grown from the vapour phase (see schematic drawing Fig. 10 and ref.19). Very recently, $C_{70}$ crystals were also grown from the vapour phase. These show an HCP and FCC structure. Expected and observed morphologies for both crystal structures were in agreement with each other (work in progress).

5.3 Naphthalene and biphenyl

Very recently, crystals of $C_{60}$ were grown from the vapour phase. Now, $\Phi = -\frac{1}{\mu}$ (equation (13)), since $\Phi^{ss}$ and $\Phi^{ff}$ are zero. The faces $\{111\}$ and $\{100\}$ are now growing below their roughening temperature and crystals in the shape of cube octahedrons are grown from the vapour phase (see schematic drawing Fig. 10 and ref.19). Very recently, $C_{70}$ crystals were also grown from the vapour phase. These show an HCP and FCC structure. Expected and observed morphologies for both crystal structures were in agreement with each other (work in progress).
Biphenyl in toluene observed with polarising microscopy.
(a) relative supersaturation $\sigma=0.20\%$.
(b) $\sigma=27\%$ obviously {110} faces are flat. But for this value of $\sigma$ {201} faces are kinetically roughened.
(c) for $\sigma=99\%$ {110} faces are also kinetically roughened.

Extensive work has been done on naphthalene and biphenyl growing from different solvents and the melt. It can be predicted that naphthalene crystals will be dominated by two strong (001) F faces of the form {001} and also four F faces of the form {110} forming a parallelogram, and two F faces of the form {201} which will truncate the parallelogram (see Fig. 11).

Looking at the experimental growth forms of napht biphenyl Crgsbh growing from the organic solvent toluene, it can be seen that a crystal is indeed limited by the strongly dominant {001} faces and the four faces of the form {110}. Often faces of the form {201} occur. In Fig. 12 a and b, these are kinetically roughened (see further refs 4-6).

5.4 Orthorhombic paraffin
It can be derived from the crystallograph of paraffin of the odd orthohombic structure that paraffin crystals will be limited by two large (001) faces, four faces of the form {110}, and sometimes faces of the form {010}. (See Fig. 13 a,b.) In Fig. 13 c, a paraffin crystal with a number of 23 C atoms growing from a slightly supersaturated hexane solution is presented growing below the roughening temperature of the {110} faces. In Fig. 13 d, a C23 paraffin crystal is presented also growing from a hexane solution, but now above the roughening temperature. The roughening temperature turned out to be 10, 65 °C ± 0.5 °C and is low. This must be attributed to a strong interaction between solute and solvent molecules with the solid molecules. This makes the $\Phi'$ energies extra
negative, and as can be seen from equation (13), \( \Phi_i \) low\(^1\). Very recently, a very special kind of kinetic roughening was observed; a so-called rough-flat-rough transition\(^2\).

5.5 Morphology of \( \beta \)-lactose

Fig. 14a Projection of crystal structure of monoclinic lactose crystals, down to the c axis of the \( \alpha \)-lactose hydrate lattice. The O atoms are shown as larger and the C atoms as smaller circles; H atoms are omitted. GLU = glucose part; GAL = galactose part of lactose molecule. W = water; \( \cdots \cdots \) = screw axis; \( a \sin \beta = 0.7470 \) nm.

Fig. 14b Crystal graph of lactose obtained after reducing lactose molecules to centres of gravity. Overall bonds are p, q, r, s, t, u, v.

Fig. 14c Constructed hypothetical crystal based on the criterion: rate of growth of a face (hkl) is inversely proportional to the Ising temperature \( \beta \).

Fig. 14d Observed tomahawk lactose crystals seen from different angles. Crystals seen enlarged about 25 times.

Fig. 14e Schematic drawing of observed lactose crystal.

Fig. 14f Where "wrong" \( \beta \) lactose molecules are absorbed blocking occurs. Where they are rejected no blocking occurs.
In Fig. 14 a, a projection is presented seen in the direction of the shortest b axis. The sugar-lactose molecules consist of a lactose and galactose moiety. Taking closest neighbouring hydrogen bonds, the complex sugar-lactose molecules are reduced to centres of gravity. In Fig. 14 b, the crystal graph is presented. This looks like a pseudo-body-centred structure. In Fig. 14 c, a crystal growth form is presented based on the principle that the rate of growth of faces parallel to connected nets is inversely proportional to \((\theta)^{-1}\). This predicted morphology is in absolute conflict with the observed morphology (Fig. 14 d, e), and the schematized habit (Fig. 14 e), which is also called “tomahawk habit”. The reason is that due to a meta-rotation equilibrium in the solution, 80% of the lactose molecules have a “wrong” glucose part. The lactose part in solution and crystal has the same configuration. In Fig. 14 f, a scheme is given of the reason for the anormal tomahawk morphology. On the left hand side, wrong molecules enter and block the growth. On the right hand side, these blocking molecules cannot enter and do not block the growth. In Figs. 14 d, e, f, the dramatic blocking effect is demonstrated. The (O10) face does not grow at all. Adjacent faces grow very slowly.

Using a systematic-logical recipe to describe the blocking effect on different crystallographic faces, it was possible to explain the deviation from the ideal morphology in a satisfactory way (see refs.22-23). This drastic change in morphology is an example of how specific tailor-made additives can change the ideal morphology in a systematic and drastic way. This is an example of an unplanned naturally-induced tailor-made additive. Pioneer work on mannmade tailor-made additives giving planned changes in morphology has been carried out by Dr. Ziva Berkovitch-Yellin. (See reference 2)

6. Conclusions

From the examples given above it can be concluded that an integrated Hartman-Perdok roughening temperature theory based on Ising models, where the whole interface is partitioned into equal cells which can have two properties, namely either solid or fluid, leads to relevant results for a wide variety of totally different crystal structures. Most important is the interpretation of observed roughening transition and kinetic roughening phenomena. Specific subtle interactions between solvent or additives with a special orientation \{hkl\} may change the crystal habit drastically. Crystals growing above the roughening temperature or which are kinetically roughened will soon show dendritic or cellular growth. Crystals growing below the roughening temperature are not kinetically roughened-up and have a much higher resistance against instabilities.

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