Heterogeneous two-dimensional nucleation and growth kinetics

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A kinetic model is developed to describe the growth of crystals under the influence of foreign particles in terms of heterogeneous two-dimensional nucleation. In the context of this model, the free energy barrier of two-dimensional nucleation in the presence of foreign particles and the kinetics for the nucleation and growth are examined theoretically. It follows that the contact angle, size and density of adsorbed foreign particles play a crucial role in controlling the 2D nucleation barrier and growth kinetics. Based on our model, many crucial experimental findings, such as dust-induced surface roughening and the various kinetics of dislocation-free growth, are properly interpreted. The promotion effect of foreign particles on crystal growth is also analyzed from the view of designing additives. To our knowledge, this is the first systematic consideration of effects of foreign particles on the 2D nucleation process and growth kinetics, and the model generally covers both heterogeneous and conventional homogeneous 2D nucleation growth.

I. INTRODUCTION

The growth of crystals is actually a process of delivering crystallizing substances from the mother phase to the crystal surface and incorporating them into the crystal structure at kink sites. For the growth of crystals bounded by flat faces, surface integration is the rate-limiting step. In this case, due to the existence of two-dimensional nucleation barrier $\Delta G_{2D}^{*}$, the growth of crystals occurs in a flat mode or layer-by-layer fashion at relatively low supersaturations $\sigma$ ($\sigma = \Delta \mu / kT$; $\Delta \mu$ is the difference in chemical potential between solute and solid units).\(^1\,^2\) This implies that the growth occurred in the normal direction is caused by the sweeping of advancing steps over the crystal surface layer by layer. Note that a step where many kinks exist will serve as a sink, where growth units are incorporated into the crystal structure. The way that step sources are generated in the layer-by-layer growth turns out to be one of the crucial issues for the smooth growth.\(^1\,^2\) It is suggested\(^1\,^3\) that one of the following two mechanisms may normally control the growth. If growing crystals are imperfect, the growth is controlled by the spiral growth mechanism or the BCF mechanism.\(^1\,^2\) This implies that the growth occurs in a spiral fashion, whereby one or more screw dislocations on the crystal surface give rise to spiral steps.

For dislocation-free (or perfect) crystals, the growth is controlled by two-dimensional nucleation mechanisms.\(^1\,^3\)

(In distinct from the mechanism, discussed in the following sections, this mechanism will be referred to as the homogeneous 2D nucleation mechanism in this paper.) In this case, the growth of a new layer or the occurrence of steps on a perfect crystal surface will start via the two-dimensional nucleation. After formation of 2D islands on the surface, the growth of the new layer occurs along the crystal surface until the whole surface is completely covered.

We notice that influences of foreign particles were never taken into account by the above-mentioned mechanisms. In other words, the system under consideration is supposed to be a dust-free system. In reality, the presence of foreign particles in crystallization systems is almost unavoidable. These foreign particles are ranging from solid dust particles, gas or liquid bubbles, macro or polymer molecules, secondary nuclei occurring during the growth of host crystals even to impurity molecules. Under normal conditions, they can be transported via flow or convection to interfacial regions and adsorbed at the crystal surface. These adsorbed foreign particles can be served either as “substrates” for two-dimensional nucleation (called hereafter heterogeneous 2D nucleation) or as “obstacles” for the movement of advancing steps, therefore will affect the kinetics and morphology of crystals grown from supercooled or supersaturated solutions.\(^4\,^5\) Moreover, the occurrence of foreign particles on the surface is directly associated with purification, modification of crystallization habit etc. Henceforth, it is of great interest for industrial crystallization, separation, etc.

In this paper, our concentration will be focused on the promoting effect of particles for the growth, caused by heterogeneous 2D nucleation. The so-called heterogeneous 2D nucleation implies that adsorbed foreign particles will serve as nucleation centers for 2D nucleation. Doubtless, a systematic study on this effect on the growth and morphology of crystals and the mechanism will not only allow us to gain a
better understanding of many relevant crystal growth related phenomena happened under normal crystal growth conditions, but will also provide us with new ideas on how to control and modify the crystallization and crystal habits.

In distinct from conventional heterogeneous 3D nucleation, which mainly controls the nucleation and the initial stage of epitaxial growth, heterogeneous 2D nucleation helps to generate 2D steps at a flat and perfect crystal surface, therefore is affecting only the growth kinetics. We notice that although the phenomena of 2D heterogeneous nucleation have been examined both theoretically and experimentally before by different authors, a detailed analysis for the kinetics of this process has not carried out yet. The main arguments behind the previous models are that the promoting effect caused the 2D nucleation is manifested by a change in “surface energy” (defined as step free energy in our terminology), which is evidently over simplified and fails to capture some major characters of the kinetics of this kind of growth.

In this paper, a general model will be developed to describe the kinetics of the heterogeneous two-dimensional (2D) nucleation growth. The paper will be arranged as follows: We first analyze the mechanism and kinetics of heterogeneous 2D nucleation, then apply the theoretical means from the model to interpret an extraordinary finding, the so-called dust-induced roughening occurring in naphthalene crystal-solution systems, and the dislocation-free growth of barium nitrate crystals and ADP (NH4HPO4) crystals from aqueous solutions. In addition, a comparison between our model and traditional theories of crystal growth will be made.

II. FREE ENERGY BARRIER OF 2D NUCLEATION

The heterogeneous 2D nucleation model is based on the following assumptions: (1) the crystal surface is essentially flat and perfect; (2) foreign solid particles adsorbed on the crystals surface have cylindrical shape with an average radius of $R^f$ and an average density of $N^f$, $R^s$ and $N^0$ which remain constant during the growth (cf. Fig. 1).

As mentioned in the previous section, 2D nucleation is one of important events in the layer-by-layer growth. Similar to the 3D nucleation, the 2D nucleation will occur by surpassing the 2D nucleation barrier. Obviously, foreign particles presented at the crystal surface will serve as substrates for the 2D nucleation (cf. Fig. 2), which may lower the nucleation barrier. Therefore, we will first analyze the influence of adsorbed foreign particles on the 2D free energy barrier.

As shown in Fig. 2, we denote the mother phase by subscript $f$, the embryo by $c$, and the nucleating particle by $s$. If we denote volume by $V$ and surface area of the edge by $S$, then the free energy of formation of an embryo of radius $r$ on a nucleating particle of radius $R^f$ is given by

$$
\Delta G = -\Delta \mu V_s/\Omega + \gamma_{sf}S_{cf} + (\gamma_{sf} - \gamma_{sc})S_{sc},
$$

where $\Delta \mu = \mu_f - \mu_c$ ($\mu_f$ and $\mu_c$ are the chemical potential of crystal structural units and of fluid growth units, respectively; $\gamma_{ij}$ is the step free energy of the edge between phases $i$ and $j$ and $\Omega$ is the volume per structural unit. If we write,

$$
m = \cos \theta = (\gamma_{sc} - \gamma_{sf})/\gamma_{cf},
$$

then this is the usual definition of the contact angle $\theta$, provided $-1 \leq m \leq 1$.

Referring again to Fig. 2, we have,

$$
S_{sc} = 2hR^s \phi, \quad S_{cf} = 2hr\psi, \quad V_s = h[r^2(\psi - \sin \phi \cos \phi) - (R^s)^2(\phi - \sin \phi \cos \phi)],
$$

with

$$
\cos \phi = (R^s - r \cos \theta)/l = (R^s - rm)/l,
$$

$$
\sin \phi = [l^2 - (R^s - rm)^2]^{1/2}/l, \quad \cos \psi = -(r - R^s \cos \theta)/l = -(r - R^s r m)/l,
$$

$$
\sin \psi = [l^2 - (r - R^s r m)^2]^{1/2}/l.
$$

and

$$
l = [(R^s)^2 + r^2 - 2R^s rm]^{1/2}.
$$

FIG. 1. Adsorbed solid particles on the crystal surface.

FIG. 2. Schematic illustration of the heterogeneous 2D nucleation. Embryo "c" on nucleating particle "s" in mother phase "f".
To evaluate the critical free energy $\Delta G_c$ for 2D nucleation, we can substitute the expression (3) into Eq. (1) and require that

$$\left( \frac{\partial \Delta G}{\partial r} \right)_c = 0.$$  

(7)

This involves a great amount of work. However, we note that independently of the occurrence of nucleating particles, the radius $r_c$ of critical size embryos is only determined by $\gamma_{ct}$ and the driving force $\Delta \mu$.\textsuperscript{16,17} This implies that $r_c$ must generally satisfy the nucleation equation

$$r_c = \Omega \gamma_{ct} / (\Delta \mu = \Omega \gamma_{ct} / kT \ln(1 + \sigma)).$$  

(8)

Here $\sigma$ is the supersaturation, and defined as $\sigma = (X_A - X_A^0) / X_A^0$; $X_A$ and $X_A^0$ represent the actual concentration and the equilibrium concentration of the solute, respectively. $\sigma$ can be related to $\Delta \mu$ as $\Delta \mu = kT \ln(1 + \sigma)$.\textsuperscript{1-3} This is necessarily true since all parts of the embryo surface must be in equilibrium with the metastable phase $f$. This can be verified by substitution in Eq. (7).

Now substituting the expressions (2)–(8) into Eq. (1) and writing,

$$x = R_s r_c = R_s \Delta \mu / \Omega \gamma_{ct} = R_s kT \ln(1 + \sigma) / \Omega \gamma_{ct},$$  

(9)

the free energy of formation of critical embryo is

$$\Delta G_c = \Delta G_{c\text{ homo}}(m, x),$$  

(10)

with

$$\Delta G_{c\text{ homo}} = \frac{\Omega \gamma_{ct} \pi h}{kT \ln(1 + \sigma)},$$  

(10a)

$$f(m, x) = \frac{1}{\pi} \left\{ \arccos[(x m - 1)/w] + (x^2 - 2 x m) \right\}$$

$$\times \arccos[(x - m)/w] - (1 - x m)$$

$$\times \left[ (w^2 - (1 - x m)^2)^{1/2}/w^2 - x^2(x - m) \right]$$

$$\times \left[ (w^2 - (x - m)^2)^{1/2}/w^2 \right],$$  

(11)

and

$$w = (1 + x^2 - 2 x m)^{1/2}.$$  

(12)

Here $\Delta G_{c\text{ homo}}$ corresponds to the free energy barrier of homogeneous 2D nucleation.\textsuperscript{1}

Substituting appropriate values of $R_s$, $m$, $\gamma_{ct}$, and $\Delta \mu$ into Eqs. 8–12, one can calculate $f(m, x)$ and $\Delta G_c$. For any nucleation process. Note that the factor $f(m, x)$ varies from 1 to 0. Apparently, this factor plays an important role in the determination of the heterogeneous 2D nucleation barrier $\Delta G_c$. One can see from Eq. (10) that the influence of foreign particles on 2D nucleation can be fully characterized by this factor.

In Fig. 3 is shown $f(m, x)$ as a function of $x$ for various values of the parameter $m$. We notice that when $x = 0$ or $m = -1$, $f(m, x) = 1$. $x \rightarrow 0$ implies that solid particles as the nucleating substrate vanish completely. $m = -1$ corresponds to the case where solid particles and embryo’s can not be wetted by the crystal, implying that foreign particles do not catalyze the 2D nucleation any more. Both limits correspond to the case of homogeneous 2D nucleation, and expression (10) agrees exactly with the expression of homogeneous 2D nucleation.\textsuperscript{1} With increasing $x (x \geq 0.01)$ and decreasing $m (-1 \leq m \leq 1)$, $f(m, x)$ decreases from 1 to 0. Referring to Eq. (10), this implies that the nucleation barrier $\Delta G_c$ is ranging from $\Delta G_{c\text{ homo}}$ to 0 ($0 \leq \Delta G_c \leq \Delta G_{c\text{ homo}}$). In this regime, foreign particles play a very crucial role in the 2D nucleation. In the case of $m \rightarrow 1$, foreign particles reduce to embryos of the crystallizing phase. It can be seen from Fig. 3 that when $x \geq 1$, $f(m, x)$ or $\Delta G_c$ becomes completely. This means that 2D embryos with the size equal to or larger than the critical nucleus size have already surpassed the 2D nucleation barrier and, the further deposit of growth units on these embryos lead then to the growth. This is identical to the physical picture of 2D nucleation.\textsuperscript{1} In the case of $x \rightarrow \infty$, a round nucleating particle reduces to a plane. Then the expression (10) describes the nucleation on a plane surface.

III. KINETICS OF 2D NUCLEATION GROWTH

A. Rate of nuclei formation

Let us repeat the picture of the heterogeneous 2D nucleation model. First, a flat crystal surface is presumed. On that surface, some molecular processes occur due to transient visiting molecules which adsorb, form short lived unions, breakup, desorb etc. An instantaneous census would show some distributions of subcritical nuclei (or embryos) with 1, 2, 3,... molecules per embryo. In any one with $g$ molecules, the free energy changes for the $g$ molecules to adsorb and form the $g$mer with the size of $r$ is given by Eq. (1). Nucleation begins with the formation of an embryo of size $r_c$ with $g_c$ molecules. $r_c$ is given by Eq. (8).

We will first discuss the distribution function describing the concentrations of embryos of various sizes. Let us further restrict ourselves to the limiting case where an equilibrium
state exists on the surface between the monomers and gmers. Note that this state does not actually exist in any real process, but this approximation allows us to employ the tools of thermodynamics in our analysis.

Take a basis of a unit area and define the number of monomers, dimers, ..., and gmers on this area to be \( n_1, n_2, \ldots, n_g \). These equilibrium surface concentrations are time invariant. Regarding the ensemble of monomers and gmers on the surface and approximating the equilibrium with the following quasichemical reaction equilibrium,\(^{17}\)

\[ g \text{ Monomer} \rightleftharpoons \cdots \rightleftharpoons g \text{mer} \]

one can easily obtain

\[ (n_g/Z) = (n_1/Z) \exp(-\Delta G_g/kT), \]

(13)

(for all \( g; \ g = 2, 3, 4, \ldots \)) with the effective total number of "molecules" per unit area

\[ Z = n_1 + \sum_{g=2}^g n_g. \]

(14)

Here \( \Delta G_g \) denotes the free energy barrier to form a gmer. Since usually \( n_1 \gg \sum n_g \ (g > 1) \), then \( Z \sim n_1 \), thus

\[ n_g \approx n_1 \exp(-\Delta G_g/kT). \]

(15)

Equation (15) is the expression usually quoted for the distribution of embryo sizes in supersaturated media.

We notice that embryos are not static entities in the microsense. Each particular one is growing larger or smaller as molecules are added or leave the embryo, respectively. In order to obtain the rate of formation of critical size embryos, we need to derive a general expression of the growth rate of a single embryo. For this purpose, we will apply the approach of the three-dimensional nucleation to a two-dimensional case.\(^ {18} \)

Let \( \alpha \) be the rate of molecule addition. That is,

\[ \alpha = \beta' \nu^* a, \]

(16)

where \( \nu^* \) is the collision rate of monomers with an embryo, and \( \beta' \) the sticking probability which is defined as

\[ \beta' = \frac{a}{\lambda_0} \exp(-\Delta G_{\text{step}}/kT) \]

(17)

\( (a \) is the dimension of structural units in the direction parallel to the crystal surface, \( \lambda_0 \) is the distance between two kinks at a step, and \( \Delta G_{\text{step}} \) is the activation free energy for step integration). Also let \( \alpha' \) be the rate at which embryos lose molecules. Rates \( \alpha \) and \( \alpha' \) should be equal if the system were in equilibrium since no embryo would then experience a net growth or disintegration. For an embryo of radius \( r \), the value of \( \alpha \) is determined by the surface concentration of monomers, \( n_1 \). Thus, at equilibrium,

\[ \alpha n_g - \alpha' n_{g+1} = 0. \]

(18)

On the other hand, if there is growth, then the equilibrium distribution is perturbed. Let \( f_g \) be this perturbed surface concentration of gmers \((f_g \leq n_g)\). Assuming a steady state growth process, \( J \), the formation rate of critical nuclei per unit area-time, is equal to the steady state growth of embryos at the surface. This can then be expressed

\[ J = \text{critical sized nuclei formed/unit area-time} = \cdots = 2\lambda' N^0 \pi R^2 (\alpha g f_g - \alpha'_{g+1} f_{g+1}) = \cdots = \text{constant}, \]

(19)

or

\[ J' = \cdots = \alpha g f_g - \alpha'_{g+1} f_{g+1} = \text{constant}. \]

(19a)

Introducing the term \( 2\lambda' N^0 \pi R^2 \) is based on the fact that the rate of heterogeneous 2D nucleation is proportional to the density and perimeter of foreign particles adsorbed at the surface. Here \( \lambda' \) is a reduced constant. For homogeneous 2D nucleation, \( 2\lambda' N^0 \pi R^2 \) should become unity. In this case, \( R^2 \rightarrow a/\sqrt{2} \) and \( N^0 \rightarrow 1/a^2 \). Therefore, \( \lambda' = a/2 \).

Before further analyzing Eqs. (19) or (19a), we introduce the following two boundary conditions

\[ f_g = 0; \]

(20)

\[ \lim_{g \to 1} (f_g/n_g) = 1. \]

(21)

The first is because whenever a \((g-1)\)mer becomes a \( g \)mer, it disappears from our population to begin a new stage—growth. But this event does not disturb the distribution of other embryos (mainly monomers). The second is because both \( n_g \) and \( f_g \) are large numbers when \( g \) is small. It follows that the perturbed concentration of monomers is almost equal to the equilibrium concentration.

Proceeding, rearranging Eq. (19)

\[ J' = \alpha g n_g [(f_g/n_g) - (\alpha_g + 1/\alpha_g) (f_{g+1}/n_{g+1})], \]

(22)

and then using Eq. (18) we obtain

\[ J' = \alpha g n_g (f_g/n_g - (f_g + 1/n_g + 1)). \]

(23)

From Eq. (23) a set of equations can be written:

\[ \begin{array}{l}
J'/\alpha_g n_g = (f_1/n_1) - (f_2/n_2) \\
J'/\alpha_g n_2 = (f_2/n_2) - (f_3/n_3) \\
\vdots \quad \vdots \quad \vdots \\
J'/\alpha_g n_{g-1} = (f_{g-1}/n_{g-1}) - (f_g/n_g - 1/n_{g-1}) - 0
\end{array} \]

(24)

Adding Eq. (24), and taking Eq. (21) into account

\[ \sum_{g=1}^{g-1} (J'/\alpha_g n_g) = f_1/n_1 = 1 \]

(25)

and the growth rate \( J' \) is then given by

\[ J' = \left( \sum_{g=1}^{g-1} (\alpha_g n_g)^{-1} \right)^{-1}. \]

(26)

To obtain \( J' \), the sum must be evaluated numerically. Nevertheless, the sum can be replaced by the integral and Eq. (26) can approximately be rewritten as

\[ J' = \int_1^{g-1} (\alpha_g n_g)^{-1} \, dg \left[ \right]^{-1}. \]

(27)
The evaluation of the integral in Eq. (27) is somewhat difficult. But it can be simplified by determining the dominant terms within the range from \( g = 1 \) to \( g_c \), on which we can focus our attention. Certainly \( n_g \) decreases exponentially with \( g \) so that for large values of \( g \) the inverse \( n_g \) term is large. Therefore, the key issue is to find the variation of \( \alpha_g \) with \( g \).

According to Eq. (16), to find \( \alpha_g \), we need to derive the expression of \( v^* \).

The number of monomers on the surface with speeds between \( v \) and \( v + dv \) and directions between \( \theta \) and \( \theta + d\theta \) is given \( f_v \) \( d_v \) \( f_\theta \) \( d_\theta \), where \( f_v \) is the speed distribution function and \( f_\theta \) the angular distribution function. If all angles are equally probable, \( f_\theta = (1/2\pi) \).

For an embryo, the projected length visible to an external molecule is \((\cos \theta)(dL)\) where \( dL \) is a differential element measured in on the periphery of the embryo.

The number of molecules colliding the unit length of this embryo from all external surface adsorbed molecules, \( \nu^* \), is then,

\[
\nu^* = 2n_1 \int_0^{\pi/2} (\cos \theta/2\pi) d\theta \int_0^{\infty} v f_v \, dv.
\]

Note that \( \int v f_v \, dv \) is just the average speed, \( \bar{v} \). Integrating Eq. (28), multiplying by the arc length of the embryo, \( 2\pi \bar{v}/\pi \) yields

\[
\nu^* = \bar{v} 2\pi r \frac{\psi}{\pi} = 2\pi n_1 \bar{v} \frac{\psi}{\pi}.
\]

Here \( \psi \) can be written, according to Fig. 2 and Sec. II, as

\[
\psi = \arccos[-(1-xm)/w].
\]

Obviously, \( \nu^* \) (or \( \alpha_g \)) increases as the square root of \( g \). For large values of \( g, \alpha_g \) is then only a weak function of \( g \).

Returning to Eq. (27), if regions of high \( g \) contribute most and, in these regions, \( \alpha_g \) is not a strong function of \( g \), one may remove \( \alpha_g \) from under the integral sign and, to approximate it as a constant equal to its value when \( r = r_c \), i.e.,

\[
\alpha_g \approx \alpha_g = 2\beta'_s r_c n_1 \bar{v} \frac{\psi}{\pi}.
\]

As long as we have concluded that the important region for \( g \) in the integral of Eq. (27) is where \( g \approx g_c \), we can simplify the evaluation by rewriting it as

\[
(J')^{-1} = (\alpha_g n_1)^{-1} \int_{g_c}^{\infty} (n_g)^{-1} \, dg.
\]

and with Eq. (15)

\[
(J')^{-1} = (\alpha_g n_1)^{-1} \int_{g_c}^{\infty} \exp(\Delta G/kT) \, dg.
\]

Expanding \( \Delta G \) about \( g_c \), in a Taylor series, we find

\[
\Delta G = \Delta G_c + (\partial \Delta G/\partial g)_c (g-g_c) + (1/2) \times (\partial^2 \Delta G/\partial g^2)_c (g-g_c)^2 + \cdots.
\]

Define

\[
y = g-g_c.
\]

then

\[
J^{-1} = (\alpha_g n_1)^{-1} \left\{ \exp(\Delta G_c/kT) \right\} \times \int_{1-g_c}^{\infty} \exp[(\Delta G'_c(y)/kT] + (\Delta G''_c(y)/2kT + \cdots) \, dy.
\]

But \( \Delta G'_c \) at \( g = g_c \) is zero, and truncating after the second term. Approximating the lower limit as \(-\infty \), then

\[
J' = 2F_g n_g \left( 2\pi kT/Q \right)^{1/2},
\]

\[
Q = -\left( \partial^2 \Delta G/\partial g^2 \right)_{g=g_c},
\]

where \( Q \) is positive so that the integral is an error function.

Henceforth the last remaining step is to evaluate \( Q \). For the heterogeneous 2D nucleation the second derivative of \( \Delta G \) is very complex. Note that the derivatives are evaluated at \( g = g_c \) so are not a function of \( g \). In most cases \( x \) is small or is large, \( f(m,x) \) turns out to be constant. We can approximate the value of \( (\partial^2 \Delta G/\partial g^2)_{g=g_c} \) by \( f(m,x) (\partial^2 \Delta G_{homo})/\partial g^2 \) \( g=g_c \), therefore \( Q \) can be expressed as

\[
Q \approx \gamma_c \left( \pi \alpha \Omega \right)^{1/2} f(m,x)/2g_c^{3/2},
\]

or, with Eq. (7),

\[
Q \approx \gamma_c \Delta \Omega^2 f(m,x)/2\pi h r_c^3.
\]

By combining Eqs. (31), (32), (33), and (38), an expression for \( J' \) is obtained. Thus, based on Eqs. (19) and (19a),

\[
J = \left[ \beta'_s (2r_c n_1) (2n_g)/(2\pi kT)^{1/2} \right] \times \left[ \gamma_c \Delta \Omega^2 / 2\pi h r_c^3 \right]^{1/2} \left[ \psi / \pi \right] \left[ N^0 (\pi a R)^{1/2} \right].
\]

Eliminating \( r_c \) with Eq. (7),

\[
J = \left[ 2\bar{v} n_1 \bar{v} \left[ \Omega \ln(1+\alpha) / h \right]^{1/2} \right] \left( \Delta G_c / kT \right) \left( \beta'_s \right) \left( \psi / \pi \right) \left[ N^0 (\pi a R)^{1/2} \right],
\]

where \( \lambda' \) is the effective distance around a nucleating particle where the heterogeneous 2D nucleation may occur. In case of homogeneous 2D nucleation \( \lambda' \to r_{str} \) (\( r_{str} \) is the radius of structural units.) We notice that at the crystal surface,

\[
\bar{v} \equiv D_s = a v_h \exp(-\Delta G_{ad-at}/kT),
\]

where \( \Delta G_{ad-at} \) and \( v_h \) are the potential barrier of desorption and the frequency of thermal vibration parallel for ad-atoms, respectively. Let

\[
\delta(m,x,R',N^0) \equiv \left[ \psi / \pi \right] \left[ N^0 (\pi a R)^{1/2} \right].
\]

Eq. (39) is then rewritten as
\[ J = \left( \frac{2Dn_1^2}{\pi} \right) \left( \frac{\Omega \ln(1 + \sigma)}{h} \right)^{1/2} \times \exp \left[ -\frac{\Omega \nu_1^2 \pi h}{(kT)^2 \ln(1 + \sigma)} f(m,x) \right] \beta_m' \delta(m,x,R^*,N^0). \]  

(42)

Note that Eq. (42) includes also homogeneous 2D nucleation as a limited case. In the case of homogeneous 2D nucleation, \( \phi = \pi, R^* = a/\sqrt{2} \) and \( N^0 = 1/a^2 \). Therefore, \( \delta(m,x,R^*,N^0) = f(m,x) = 1 \), and Eq. (42) describes the nucleation rate of homogeneous nucleation.

Evidently, \( f(m,x) \) and \( \delta(m,x,R^*,N^0) \) characterize the difference in the nucleation rate between homogeneous 2D nucleation and heterogeneous 2D nucleation. It can be visualized from Eq. (41) that in the case of heterogeneous 2D nucleation, \( 0 < \delta(m,x,R^*,N^0) < 1 \). This is mainly attributed to the fact that the proportion of the surface which can effectively cause the heterogeneous 2D nucleation, \( N^0 \pi a R^* \), is much less than unity (for homogeneous 2D nucleation, this is equal to unity), and the edge of embryos which can “feel” the collision of incoming growth units is only a part of the circumference of embryos (\( \phi \pi \)).

We notice that in the case of heterogeneous 2D nucleation, \( f(m,x) \) included in the exponential term of Eq. (42) lowers the nucleation free energy barrier, resulting in the increase in the nucleation rate, while \( \delta(m,x,R^*,N^0) \) occurring in the pre-exponential term reduces the nucleation rate. These two factors have significant impact on the growth kinetics. We will discuss this in Sec. IV.

### B. Heterogeneous birth and spread model

In this section we will derive the relation between the growth rate and growth controlling factors. Assume that the chance to have critical size embryos per unit length around an adsorbed nucleating particle is roughly the same for each particle. The best model to describe the growth kinetics of 2D nucleation is the birth and spread model.\(^{16}\) According to this model, the nucleation of critical size nuclei first occurs at a flat crystal surface, then follow simultaneously the growth of these nuclei and the formation of other critical nuclei. This model allows for both nucleation of critical size embryos and subsequent growth at a finite rate. Therefore we adapt the following three assumptions regarding the growth or spreading of the growing nuclei:\(^{16}\) (a) There is no intergrowth between nuclei; (b) The lateral spreading velocity \( V^* \) is a constant, independent of the island size; (c) Nuclei can be born anywhere, around nucleating particles, which can occur on incomplete layers as well as on islands.

Consider a flat crystal surface of area \( A \) without nuclei at the time \( t_1 = 0 \). At the time \( t_2 = \tau \), the total area covered by all the circular growing nuclei is \( A_\tau \). Obviously, nuclei with the critical size generated at different moments between \( t_1 \) and \( t_2 \) have different contributions to \( A_\tau \). During the period from \( t \) to \( t + dt \) (\( 0 \leq t \leq \tau \)), one may expect the birth of \( JA dt \) critical size nuclei on the surface. The area covered by these nuclei at the time \( t = \tau \) is then given as

\[
(JA dt) \pi [r(t)]^2 \left[ \frac{\phi(t)}{\pi} - \sin \psi(t) \cos \psi(t) \right] - \left( \frac{R^*}{r(t)} \right)^2 \left[ \frac{\phi(t)}{\pi} - \sin \phi(t) \cos \phi(t) \right].
\]

(43) with

\[
\cos \psi(t) = -[r(t) - R^* m]/l',
\]

\[
\sin \psi(t) = (l'^2 - [r(t) - R^* m]^2)^{1/2}/l',
\]

\[
\cos \phi(t) = [R^* - r(t)m]/l',
\]

\[
\sin \phi(t) = (l'^2 - [R^* - r(t)m]^2)^{1/2}/l',
\]

\[
l' = [(r(t))^2 + (r(t))^2 - 2R^* r(t)m]^1/2,
\]

and

\[
r(t) = [V^* (\tau - t) + r_c].
\]

(47)

The angles \( \psi(t) \) and \( \phi(t) \) and the radius \( r(t) \) of growing nuclei are indicated in Fig. 2 (c.f. Eqs. 4–6). Here the radius \( r(t) \) of growing nuclei is larger than or equal to \( r_c \) [c.f. Eq. (47)]. Therefore,

\[
A_\tau = \int_0^\tau JA \pi [r(t)]^2 q(t) dt,
\]

(48)

\[
q(t) = \left[ \frac{\phi(t)}{\pi} - \sin \psi(t) \cos \psi(t) \right] - \left( \frac{R^*}{r(t)} \right)^2 \left[ \frac{\phi(t)}{\pi} - \sin \phi(t) \cos \phi(t) \right].
\]

(49)

Assume that \( \tau' \) is the time required to cover the entire area of the surface, i.e., \( A_\tau = A [1 - N^0 \pi (R^*)^2] \). \( AN^0 \pi (R^*)^2 \) is the area occupied by adsorbed foreign particles, and \( N^0 \pi (R^*)^2 \ll 1 \). It then follows that

\[
A = \int_0^{\tau'} JA \pi [r(t)]^2 q(t) dt + AN^0 \pi (R^*)^2.
\]

(50)

We notice that the 2D islands formed at the earlier stage of the growth contribute mostly to the integral in Eq. (50). For these 2D islands, one has \( r(t) \gg R^* \), and \( \psi(t) \to \pi, \phi(t) \to \pi \). It follows then that \( q(t) \to 1 \). For the critical size nuclei formed at the time very close to \( t = \tau' \), their \( r(t) \) is relatively small and \( q(t) < 1 \) [c.f. Eqs. (47) and (49)]. However, they have trivial contributions to the integral. Based on these facts and noting that small deviations in the integral due to \( q(t) < 1 \) at \( t = \tau' \) can be to a large extent compensated by \( AN^0 \pi (R^*)^2 \), we can approximately take \( q(t) = 1 \) in the evaluation of the integral in Eq. (50). It follows from Eq. (50) that

\[
A = \pi JA (V^*)^2 [\frac{1}{2} (r_c/V^*)^3 + \frac{1}{2} (\tau' + r_c/V^*)^3]
\]

(51)

or

\[
\tau' = \{3[\pi J (V^*)^2] + (r_c/V^*)^3\}^{1/3} - (r_c/V^*).
\]

(52)

Since \( (3/\pi)^{1/3} \approx 1 \), Eq. (52), for small \( r_c \), may be simplified to

\[
\tau' \approx (J)^{-1/3} (V^*)^{2/3}
\]

(53)
we assume hereafter \( V \) small important at any reasonable value of \( r \) independent of \( s \).

Regarding the mediate from which the crystal is grown,

\[ \sim \]  

From Eqs. (58), (61), (63), and (63a) describe the growth kinetics of birth and spread models for both heterogeneous and homogeneous 2D nucleation. As discussed before, by taking \( f(m,x) = \delta(m,x,R^+,N^0) = 1 \) these equations also describe homogeneous 2D nucleation. In this sense, our model covers both heterogeneous and homogeneous 2D nucleation growth. In other words, homogeneous 2D nucleation can be treated as a limited case in our heterogeneous 2D nucleation model.

**IV. DISCUSSIONS**

We have shown in the foregoing sections that the occurrence of foreign particles in a crystal growth system may lower the 2D nucleation barrier and change the growth kinetics. In this section, we will analyze the consequence and confront theoretical results with experiments. Implications of our models for the control of crystallization will also be discussed.

**A. Kinetic roughening induced by solid particles**

According to modern statistical physics of roughening transition theories, a flat crystal surface will undergo a roughening transition at a critical temperature, the so-called roughening temperature \( T_R \). If the temperature is below the roughening temperature \( T_R \), the surface remains essentially flat due to the existence of the step free energy, and the overall crystallographic orientation will be maintained. If the temperature is equal to or above the roughening temperature \( T_R \), the step free energy vanishes. Then the flatness and overall crystallographic orientation of the crystal surface is lost, and the crystal surface becomes rough at molecular scale.

In spite of the roughening transition, a flat crystal surface may kinetically roughen at the temperature below \( T_R \) if the supersaturation \( \sigma \) exceeds a certain critical value \( \sigma_c \). This type of roughening is known as kinetic roughening. It is subject to the vanishing of 2D nucleation barrier at relatively high supersaturations. Recent kinetic roughening induced by dust particles was observed by van der Berg et al. It was found from the experiments that for the growth of naphthalene crystals from the melt, the flat \{110\} faces will locally become rounded off due to the contact with dust particles at relatively low supersaturations, whereas for the area where no dust contact occurs, the surface remains perfectly flat.

This “dust-induced kinetic roughening” can be interpreted with the framework of our heterogeneous 2D nucleation.
critical supersaturation for kinetic roughening can induce kinetic roughening, especially when foreign particles or dust particles and consequently the critical supersaturation of kinetic growth rate of the crystal surface. Looking at Eqs. (58) and (61) at

$$\sigma < \sigma^2 = 3[f(m, x) - 1]C_2 / [T^2 \ln(\delta(m, x, R^s, N^0)],$$

the growth rate of heterogeneous 2D nucleation growth will be higher than that of homogeneous 2D nucleation growth, and at $\sigma > \sigma^2$, the growth rate of homogeneous 2D nucleation growth will be higher than that of heterogeneous 2D nucleation growth. This explains the above-mentioned observations. We notice that the inclusion of foreign particles has also been observed by the experiments. This can be regarded as a direct consequence of the heterogeneous 2D nucleation.

It can be visualized from Eqs. (9) and (10) that $f(m, x)$ (or $x$) is a function of supersaturation $\sigma$. Therefore, in case of heterogeneous 2D nucleation, $\ln(R/\sigma^{5/6})$ is in principle not linearly dependent on $1/\sigma$ unless $x$ is very large (cf. Fig. 3). (In our case, a slight nonlinearity can be visualized from curve 2.) Under normal experimental conditions, $f(m, x)$ can be approximately treated as a constant within a certain range of $\sigma$ if $x$ is not small. According to Eq. (61), the slope of curve 1 gives the step free energy per structure unit $\gamma_{ct} = 0.371kT$. Based on the
ratio between the slope of curve 1 and curve 2, we obtain the average \( \langle f(m,x) \rangle \approx 0.101 \). Assuming \( x \approx 1 \), one can obtain from Eqs. (9) and (30) \( \langle m \rangle \approx 0.65 \), and \( \psi \approx 0.86 \). Subtracting the y interception of curve 2 by that of curve 1 yields the average of \( \langle \delta(m,x,R^4,N^0) \rangle \approx 4.39 \times 10^{-5} \) [cf. Eq. (31)]. From this, one may estimate \( N^0 \approx 3 \times 10^8 \) cm\(^{-2} \) (\( a = 5.74 \) Å, \( R^2 = 0.1 \times 10^{-6} \) m).

In spite of 2D nucleation growth mechanism, the screw dislocation growth also occurs frequently. For the growth of crystals from solution, the growth rate is expressed, according to Chernov,\(^1\) as

\[
R = C_d \sigma^2,
\]

with

\[
C_d = h \pi X_{hkl}^0 k T^* / 19 \gamma_c,
\]

and

\[
\zeta^* = [1 + \beta_d (\pi D)^{-1} \ln(\lambda / h) \sinh(\pi \delta^* / \lambda)]^{-1}.
\]

Here \( \delta^* \) is the thickness of diffusion boundary layer, \( D \) is the diffusivity, \( \lambda \) is the distance between two parallel steps. This implies that the relation between the growth rate and the supersaturation follows the parabolic relation. In comparison with the results of the aforementioned two cases, we also plot in Fig. 4 the data measured from dislocation controlling growth experiments (curve 3 is the regression curve). According to Eq. (69), a nonlinear relation should be obtained. This is in agreement with our results (cf. Fig. 4).

It is interesting to notice that a dislocation-free Ba(NO\(_3\))\(_2\) crystal was recently grown in microgravity, in which no convection and no flows exist and thus no transport of foreign particles towards the surface occurs. Since the source of foreign particles promoting the heterogeneous 2D nucleation at the surface was eliminated and the particles originally occurring at the surface were soon embedded into the crystal structure at the initial stage of the growth, we have then the particle-free surface in the later stage of the growth. In this case, the heterogeneous 2D nucleation growth will not occur. It was indeed found by advanced in situ observation employing real-time phase-shift interferometry\(^2\) that there was no growth at \( 0 < \sigma < 3 \%) \) and that homogeneous 2D nucleation started at \( \sigma = 3 \%) \), which agrees well from the above-mentioned experiment on the ground.

It is interesting to see that similar experiments have also been carried out by Malkin et al.\(^1\) for the growth of the dislocation-free \{101\} faces of ADP [\( (NH_4)_2H_2PO_4\)] crystals from aqueous solutions. A result very similar to Fig. 4 was also obtained. However, the interpretation on the data is not precise enough. Here we will re-interpret their data. According to the authors, the step free energy \( \gamma_c = 11.8 \) erg/cm\(^2\). In the case of heterogeneous 2D nucleation, they obtained \( \gamma_c = 4.2 \) erg/cm\(^2\) for the same orientations. According to our model, \( \langle f(m,x) \rangle \approx 0.127 \) is obtained from these results. Regarding the fact that the curve \( \ln(R / \sigma^{60}) \sim 1 / \sigma \) remains as a straight line for heterogeneous 2D nucleation, \( f(m,x) \) is approximately a constant at different supersaturations. This implies that \( x \) or \( R^4 \) is relatively large, and \( f(m,x) \) is in this case only a function of \( m \). Therefore, \( \langle m \rangle \approx 0.6 \) and \( \Psi = \theta \approx 0.93 \). From the difference between the y intercepts of the two straight lines corresponding to homogeneous and heterogeneous nucleation, we then obtain \( \langle \delta(m,x,R^4,N^0) \rangle \approx 8.1 \times 10^{-12} \). For the \{101\} faces, the distance between the neighboring units in the \{110\} direction is \( a = 1.07 \times 10^{-7} \) cm. If we take their estimation of \( N^0 \approx 1.3 \times 10^3 \) cm\(^{-1} \), \( R^4 \) is then equal to \( 1.8 \times 10^{-7} \) cm, which has the same magnitude as \( a \). This unrealistic result is partly because the size of foreign particles is not taken into account, and \( N^0 \) and \( n_1 \) are not unambiguously distinguished. Based on the fact that \( \langle f(m,x) \rangle \) is a constant, we may conclude that \( x = R^4 / r_c > 10 \) (cf. Fig. 3). This implies that \( R^4 \) should be at least \( 10^2 \) to \( 10^3 \) times larger than \( a \). Presume that \( R^4 \approx 1 \times 10^{-5} \) cm, it follows that \( N^0 \approx 1 \times 10^5 \) cm\(^{-1} \) is a more realistic estimation.

### C. Implications for growth promoters and inhibitors

Nowadays, applying tailor-made additives to control crystallization processes adsorbs a lot of interests. This is because additives or man-made impurities can very strongly affect the nucleation, the growth and morphology of crystals. As mentioned in Sec. I, any foreign particles can inhibit and/or promote the growth of crystals. These two opposite effects can in principle occur simultaneously in the same system. The inhibition effect is attributed to the blocking of advancing steps or the poisoning of kinks at the surface. The promotion effect on which we will in particular focus our attention is obviously subject to the heterogeneous 2D nucleation. For the design of either growth inhibitor or promoters, this effect should be taken into account properly. Apparently, for the design of growth inhibitors, this effect should be avoided while for growth promoters, this effect should be utilized.

As discussed in Secs. II and III, the presence of foreign particles will result in the reduction of 2D nucleation barrier \( \Delta G_c \) in terms of \( f(x,m) \). Looking at Fig. 3, one can find that in order to obtain the maximum effect, \( m \) should be close to \( 1 \). This implies that interactions between adsorbed foreign particles and growth units should be strong. In addition, the size of foreign particles should be similar to or larger than that of the critical nuclei under experimental conditions (\( x \approx 1 \)). Referring to Eq. (8), under the supersaturation at which the growth may occur, \( R^4 \) should at least have the magnitude of \( \Omega \gamma_c kT \ln(1 + \sigma) \). In practice, dust particles and polymer molecules may have a sufficient size to catalyze the growth.

On the other hand, in order to avoid the promotion effect, the following measurements should be taken: Choose foreign particles with \( m \) very close to \( 1 \) and \( R^4 \) as small as possible. The first means that foreign particles and growth units should be repulsive with each other. The latter means that foreign particles should not be too large, if possible, as small as possible. From this point of view very large polymer molecules or macromolecules may not be suitable for the purpose of inhibition.
V. SUMMARY AND CONCLUSIONS

The influence of foreign particles on the 2D nucleation and growth kinetics of crystal faces was systematically examined. The size and contact angle of adsorbed foreign particles exert a very strong effect on the free energy barrier of 2D nucleation. Foreign particles being relatively large in size and having small contact angle can substantially lower the 2D nucleation barrier, therefore have a direct impact on the nucleation rate and the growth kinetics. In comparison with other growth mechanisms, heterogeneous 2D nucleation is a kinetically favorable event at relatively low supersaturations while at relatively high supersaturations homogeneous 2D nucleation becomes more kinetically favorable. Experimentally, foreign particles may induce kinetic roughening and promote the growth at lower supersaturation. This is attributed to the lowering of 2D nucleation barrier. The promotion effect of additives for the growth, subject to the induction of 2D nucleation, can be controlled by changing the size and contact angle of the additives.

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9 I. N. Stranski, Z. ElectroChem. 35, 393 (1929).