A new kinetic model for three-dimensional heterogeneous nucleation

X. Y. Liu

URPS, Quarry Road East, Bebington, Wirral L63 3JW, United Kingdom

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Despite the relevance to most aspects of crystallization, a comprehensive understanding of the kinetics of heterogeneous nucleation has not been well established yet. In this paper, a new kinetic model based on the “steady-state” approach will be put forward to describe both heterogeneous and homogeneous nucleation. As a key point in this model, the effect of foreign particles on both the nucleation barrier, the “chain reaction” process and the transport of structural units is taken into account. Ranging from low to high supersaturations, heterogeneous nucleation plays a more comprehensive role in nucleation than we expected, depending on the size of foreign particles and the interaction and structural matching between foreign particles and the nucleating phase. It follows that genuine homogeneous nucleation may only be possible at very high supersaturations, and can become easier when convection is eliminated. The results have been verified by the CaCO$_3$ nucleation experiments. This general model allows us to describe many unexpected nucleation phenomena for the first time, and will have significant impact on the control of nucleation, understanding of crystallization in microgravity, the measurement of the crystal–fluid interfacial tension, and crystallization in general. © 1999 American Institute of Physics.

I. INTRODUCTION

Nucleation, the creation of a new crystal phase in the body of the mother phase, is one of the most fundamental aspects of phase transition in general and crystal growth in particular. Depending on the role of foreign bodies, nucleation can occur either via homogeneous nucleation or heterogeneous nucleation. In homogeneous nucleation, the potential barrier, which a system must overcome in order to create a (crystalline) nucleus in the ideally homogeneous mother phase and which determines the rate of nucleation, is defined by the interfacial energy between the crystallizing phase and the ambient phase and thermodynamic driving force. One the other hand, the occurrence of foreign bodies may exert an additional factor on the nucleation barrier and rate. The nucleation promoted by the foreign bodies is then regarded as heterogeneous nucleation.

It has been widely accepted that nucleation plays a key role in controlling polymorphism, epitaxial growth, ripening, spherulitic crystallization, size distribution of crystals, crystal network formation, and in the growth of large and high quality single crystals, including protein crystals. In the past thirty years, although many models have been published to describe the kinetics of nucleation, much confusion remains. The major issues associated with this subject are the effect of foreign bodies on the general kinetics for heterogeneous nucleation. In most cases of crystallization, it is almost impossible to remove completely from nucleating systems foreign bodies, ranging from solid or liquid particles, gas bubbles, macromolecules, and the wall of crystallization vessels. Then some simple but crucial questions arise: (1) How do foreign bodies affect the nucleation kinetics, and (2) when can we obtain genuine homogeneous nucleation? Associated with these questions, we note that one of most effective ways to obtain the surface free energy of crystals is via nucleation experiments, based on the assumption of homogeneous nucleation. If the effect of foreign particles can not be avoided, the surface free energy will not be measured accurately. Actually, this has been a standing issue for several decades.

It is generally believed that at low supersaturations, heterogeneous nucleation will be dominant, and at high supersaturations, homogeneous nucleation will occur. Nevertheless, our current results show that nucleation can be controlled by more than two independent processes. In addition, it was found by Tsukamoto et al. that the interfacial tension of CaCO$_3$ obtained from nucleation experiments in microgravity is much higher than that from “homogeneous” nucleation experiments in gravity. These unusual findings indicate that our previous knowledge about nucleation is very much insufficient.

Concerning the models developed so far for heterogeneous nucleation kinetics, most attention was focused solely on the effect of foreign bodies on the nucleation barrier. How foreign particles with different sizes and interactions with the nucleating phase affect the general kinetic process, including the surface process and the transport of structural units, has not been systematically considered yet. This insufficient understanding has significantly restricted our capability in controlling nucleation in general, and proper interpretation of experimental results.

It is my purpose in this paper to develop a new model to describe the kinetics of heterogeneous nucleation, taken into account the effects of foreign bodies on both the nucleation
barrier and the “polymerization reaction sequence” of three-dimensional (3D) nucleation. This will include the exchange of structural units between embryos and the mother phase. This comprehensive treatment is for the first time taken to describe the kinetics of heterogeneous nucleation. In order to obtain a genuine understanding on general nucleation phenomena, we will examine how the effect of the size and structural and energetic properties of the surfaces of foreign particles on the nucleation kinetics. Within the framework of this approach, homogeneous nucleation can be treated as a limited case of heterogeneous nucleation. To check the model, the predicted nucleation behavior is confronted with experiments performed under both gravity and microgravity conditions.

II. KINETICS OF HETEROGENEOUS NUCLEATION

The model to be developed is based on the following assumption of the nucleating particles as a spherical shape with the average radius and density of \( R^s \) and \( N^o \) (see Fig. 1). The assumption of the spherical shape is necessary for mathematical simplicity, but it also physically reasonable, since in the size range where shape effects enter, particles occurring in many processes tend to be spherical. Taking into account the fact that we envisage the crystal is very small, less than 100 molecules across and it is likely to be some kinetically rough at supersaturations where nucleation occurs, this assumption is also reasonable. In the interests of simplicity, we neglect the differences between various crystal faces and use instead average values for the quantities involved. This is unlikely to have more than a small effect in most cases.

A general and simple picture of 3D nucleation can be described as follows. The constituent atoms or molecules in the solution may, on collision, join into groups of two, three, four, or more particles, forming dimers, trimers, tetramers, etc. The kinetics of nucleation is described by the nucleation rate \( J \), which is defined as the number of nuclei created per unit volume-time, and determined by the nucleation barrier, kink integration rate, transport, and other factors.

In this section, we will first briefly discuss the effect of the foreign particles on the nucleation barrier. Our major attention will then be focused on the kinetic process and the implications.

A. Nucleation free energy barrier

In this part, we will derive the critical free energy barrier of heterogeneous nucleation in a similar way as given by Fletcher.\(^6\) As shown in Fig. 1, 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 \( R^s \) is given by

\[
\Delta G = -\Delta \mu V_f / \Omega + \gamma_{cf} S_{cf} + (\gamma_{sj} - \gamma_{sc}) S_{sc},
\]

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; \( \gamma_{sj} \) is the step free energy of the edge between phases \( i \) and \( j \) and \( \Omega \) is the volume per structural unit. If we write,

\[
m = \cos \theta = (\gamma_{sc} - \gamma_{sj}) / \gamma_{cf},
\]

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

Referring again to Fig. 1, we have

\[
S_{sc} = 2 \pi (R^s)^2 (1 - \cos \phi), S_{cf} = 2 \pi r^2 (1 - \cos \phi)
\]

and

\[
V_f = \frac{1}{2} \pi r^3 (2 - 3 \cos \phi + \cos^3 \phi) - \frac{1}{2} \pi (R^s)^3 (2 - 3 \cos \phi + \cos^3 \phi),
\]

with

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

\[
\cos \phi = -(r - R^s \cos \theta) / l = -(r - R'm) / l,
\]

and

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

To evaluate the critical free energy \( \Delta G_c \), we can substitute the expression (3) into (1) and require that

\[
(\partial \Delta G / \partial r)_c = 0.
\]

Regarding the fact that the radius of curvature \( r_c \) of critical size embryos is only determined by \( \gamma_{cf} \) and the driving force \( \Delta \mu \), we then have

\[
r_c = 2 \Omega \gamma_{cf} / \Delta \mu = 2 \Omega \gamma_{cf} / kT \ln(1 + \sigma).
\]

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 solution at the given temperature, respectively. \( \sigma \) can be related to \( \Delta \mu \) as \( \Delta \mu = kT \ln(1 + \sigma) \)\(^{-1/3} \).

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

\[
x = R^s / r_c = R^s \Delta \mu / 2 \Omega \gamma_{cf} = R^s kT / 2 \Omega \gamma_{cf} \ln(1 + \sigma),
\]

the free energy of formation of critical embryo is

\[
\Delta G_c = \Delta G_{c homo} / (m, x),
\]

with

\[
\Delta G_{c homo} = \frac{16 \pi \gamma_{cf}^3 \Omega^2}{3[kT \ln(1 + \sigma)]^2}.
\]
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into Eqs. (8)–(13), 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. Obviously, this factor plays an important role in determination of the heterogeneous nucleation barrier \( \Delta G_c \).

One can see from Eq. (10) that the influence of foreign particles on the nucleation barrier can be fully characterized by this factor.

In Fig. 2, \( f(m,x) \) is shown as a function of \( x \) for various values of the contact angle \( \theta \). We notice that when \( x \to 0 \) or \( \theta = \pi \), \( f(m,x) = 1 \). \( x \to 0 \) implies that solid particles as the nucleating substrate vanish completely. \( \theta = \pi \) corresponds to the case where solid particles and embryos cannot be “wetted” by the crystal, implying that foreign particles do not catalyze the nucleation any more. Both limits correspond to the case of homogeneous nucleation, and expression (10) agrees exactly with the expression of homogeneous nucleation.1 With increasing \( x \) \((x \geq 0.01)\) and decreasing \( \theta \) \((0 \leq \theta \leq 2 \pi)\), \( f(m,x) \) decreases from 1 to 0. Referring to Eq. (10), this implies that the nucleation barrier \( \Delta G_c \) changes 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 nucleation. In the case of \( \theta \to 0 \), foreign particles reduce to embryos of the crystallizing phase. It can be seen from Fig. 2 that when

x \geq 1, \( f(m,x) \) or \( \Delta G_c \) vanishes completely. This means that embryos with the size equal to or larger than the critical nucleus size have already surpassed the 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 nucleation.1 In the case of \( x \to \infty \), a round nucleating particle reduces to a plane. Then the expression (10) describes the nucleation on a plane surface.

B. Rate of nuclei formation

The kinetics of nucleation is virtually characterized by the nucleation rate \( J \). The nucleation rate is defined as the number of nuclei \((r > r_c)\) created per volume-time. In this section, we will analyze in detail the nucleation rate of crystalline phase in the presence of foreign particles.

Let us repeat the picture of the heterogeneous nucleation model. On the substrate surface, some molecular processes occur due to transient visiting molecules which adsorb, form short lived unions, break-up, 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).

Let us first discuss the distribution function describing the concentrations of embryos of various sizes. We will restrict ourselves to the limiting case where an equilibrium state exists on the surface between the monomers and g-mers. 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 volume near the substrate and define the number of monomers, dimers,... and \( g \)-mers on this volume to be \( n_1, n_2, ..., n_g \). These equilibrium surface concentrations are time-invariant. Regarding the ensemble of monomers and \( g \)-mers on the surface and approximating the equilibrium with the following quasi chemical reaction equilibrium17

\[ g \text{ Monomer} \rightleftharpoons \cdot \cdot \cdot \rightleftharpoons g \text{-mer}, \]

one can easily obtain

\[ (n_g/Z) = (n_1/Z)^g \exp(-\Delta G_g/kT) \] (14)

(for all \( g = 2,3,4,... \)) with the effective total number of “molecules” per unit volume

\[ Z = n_1 \sum_{g=2}^{\infty} n_g. \] (15)

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

\[ n_g \equiv n_1 \exp(-\Delta G_g/kT). \] (16)

Equation (16) is the expression usually quoted for the distribution of embryo sizes in supersaturated media.

We notice that embryos are not static entities in the micro-sense. 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 three-dimensional homogeneous nucleation to the heterogeneous nucleation case. 18

Let $\alpha$ be the rate of molecule addition. That is

$$\alpha = \beta'_{c}v^{*},$$

(17)

where $v^{*}$ is the collision rate of monomers with an embryo, and $\beta'_{c}$ the sticking probability which is defined as

$$\beta'_{c} = \frac{v}{\lambda_{0}} \exp(-\Delta G_{\text{step}}^{*}/kT)$$

(18)

($v$ denotes the vibration frequency of structural units in the neighborhood of the surface, $a$ is the dimension of structural units in the direction parallel to the crystal surface, $\lambda_{0}$ is the average distance between two kinks at the surface, 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, $n_{g}$. Thus, at the detailed balance between the growth and disintegration of embryos, one has

$$\alpha_{g}n_{g} - \alpha'_{g+1}n_{g+1} = 0.$$  

(19)

On the other hand, if there is growth, then the equilibrium distribution is perturbed. Let $f_{g}$ be the perturbed surface concentration of $g$-mers ($f_{g} \leq n_{g}$). Assuming a steady-state growth process, $J'$, is equal to the steady-state growth of embryos at the surface. This can then be expressed or

$$J' = \text{critical sized nuclei formed/unit volume-time}$$

$$= \cdots = \frac{\alpha_{g} f_{g} - \alpha'_{g+1}f_{g+1}}{1} = \text{constant}.$$  

(20)

Before further analyzing Eq. (19) or Eq. (20), we introduce the following two boundary conditions:

$$f_{g_{c}} = 0,$$  

(21)

$$\lim_{g \rightarrow 1}(f_{g}/n_{g}) = 1.$$  

(22)

The first is because whenever a $(g_{c} - 1)$-mer becomes a $g_{c}$-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 and rearranging Eq. (20), one has

$$J' = \alpha_{g}n_{g}(f_{g}/n_{g}) - (\alpha_{g} + 1/\alpha_{g}(f_{g} + 1/n_{g})).$$  

(23)

Then using Eq. (19) we obtain

$$J' = \alpha_{g}n_{g}(f_{g}/n_{g}) - (f_{g} + 1/n_{g} + 1).$$  

(24)

From Eq. (24) a set of equations can be written

$$J' / \alpha_{g} n_{g} = \left(\frac{f_{1}/n_{1}}{1} - \frac{f_{2}/n_{2}}{1} - \frac{f_{3}/n_{3}}{1} - \cdots \right)$$  

(25)

Adding Eq. (25), and taking Eq. (21) into account

$$\sum_{g=1}^{g_{c}-1} (J'/\alpha_{g} n_{g}) = f_{1}/n_{1} = 1,$$  

(26)

and the growth rate $J'$ is then given by

$$J' = \left[\sum_{g=1}^{g_{c}-1} (\alpha_{g} n_{g})^{-1}\right]^{-1}.$$  

(27)

To obtain $J'$, the sum must be evaluated numerically. Nevertheless, the sum can be replaced by the integral and Eq. (27) can approximately be rewritten as

$$J' = \left[\int_{1}^{g_{c}} (\alpha_{g} n_{g})^{-1} dg\right]^{-1}.$$  

(28)

The evaluation of the integral in Eq. (28) 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 $v^{*}$. $v^{*}$ can be defined as the frequency of growth units colliding into the surface of an embryo with a radius of $r$. Obviously, this frequency if proportional to the surface area of the embryo. For an embryo created on a spherical substrate as shown in Fig. 3, this area is given by

$$S_{ef} = 4\pi r^{2}f^\prime(m,x),$$  

(29)

with

$$f^\prime(m,x) = \frac{1 + (1 - x)m}{w}.$$  

(30)
It follows then that
\[ \nu^* = \eta n_1 4 \pi r^2 f'(m,x). \] (31)

Obviously, \( \nu^* \) (or \( \alpha_g \)) increases as the cubic root of \( g \) (\( r \sim g^{1/3} \)). For large values of \( g \), \( \alpha_g \) is then only a weak function of \( g \).

Returning to Eq. (28), 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.,
\[ \alpha_g \approx \alpha_{g_c} = 4 \pi a \beta' n_1 (r_c)^2 f'(m,x). \] (32)

As long as we have concluded that the important region for \( g \) in the integral of Eq. (28) is where \( g < g_c \), we can simplify the evaluation by rewriting it as
\[ (J')^{-1} = \alpha_{g_c}^{-1} \int_{g_c}^{s_c} (n_g)^{-1} dg, \] (33)

and with Eq. (15)
\[ (J')^{-1} = (\alpha_{g_c} n_1)^{-1} \int_{g_c}^{s_c} \exp(\Delta G/kT) dg. \] (34)

Expanding \( \Delta G \) about \( g_c \) in a Taylor series, we find
\[ \Delta G = \Delta G_c + (\partial \Delta G / \partial g)(g - g_c) + (1/2)(\partial^2 \Delta G / \partial g^2)(g - g_c)^2 + \cdots. \] (35)

Define
\[ y = g - g_c, \] (36)

then
\[ J^{-1} = (\alpha_{g_c} n_1)^{-1} \left[ \exp(\Delta G_c/kT) \right] \]
\[ \times \int_{1 - \sigma}^{0} \exp((\Delta G')_c(y)/kT + (\Delta G'')_c(y)^2/2kT) dy. \] (37)

But \( \Delta G' \) at \( g = g_c \) is zero, and truncating after the second term. Approximating the lower limit as \( \sim \infty \), then
\[ J' = 2 \alpha_{g_c} X / (2 \pi kT) \] (38)
\[ Q = - (\partial^2 \Delta G / \partial g^2)_{g = g_c}, \] (39)

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

The last remaining step is to evaluate \( Q \). For the heterogeneous 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 where \( x \) is not 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 \( f(m,x) \times (\partial^2 \Delta G_{homo} / \partial g^2)_{g = g_c} \), therefore, \( Q \) can be expressed as
\[ Q \approx \gamma mf \left( \frac{2 \pi \Omega^3}{3} \right)^{1/3} g^{1/3} f(m,x), \] (40)
or, with Eq. (7)
\[ Q \approx \gamma mf \Omega^2 f(m,x)/(2 \pi r^4). \] (41)

By combining Eqs. (31)–(33) and (38), an expression for \( J' \) is obtained, as
\[ J' = 4a \beta' n_1 (r_c)^2 f'(m,x) \frac{\gamma mf}{kT} \left[ \frac{\gamma mf}{kT} f(m,x) \right]^{1/2} \]
\[ \times \exp \left[ - \frac{\Delta G_{homo}}{kT} f(m,x) \right]. \] (42)

The average nucleation rate in the solution depends on the density and size of foreign particles occurring in the system, and is given, according to \( J = 4 \pi a (R^3)^2 N^0 J' \), by
\[ J = 4 \pi a (R^3)^2 N^0 f'(m,x) \left[ f(m,x) \right]^{1/2} B \]
\[ \times \exp \left[ - \frac{16 \pi \Omega^2}{3 kT} \right] \] (43)

with
\[ B = (n_1)^2 4 a \beta' \Omega \left( \frac{\gamma mf}{kT} \right)^{1/2}. \] (44)

In the equations, \( f'(m,x) \), like \( f(m,x) \), is also a function of the “contact angle” \( \theta \) and the substrate and the relative size of particles \( x \). [See Eq. (30).]\( f''(m,x) \) gives a similar plot as Fig. 2(b).

Introducing the term \( 4 \pi a (R^3)^2 N^0 \) is based on the fact that the heterogeneous nucleation takes place only in the liquid layers adjacent to the nucleating particles. Evidently, only for this part of solutions, the nucleation rate will be effectively influenced by the foreign particles. Therefore, the relative effective volume fraction for heterogeneous nucleation is equal to the volume of the liquid is proportional to the density and surface area of nucleating particles occurring in the system, namely \( 4 \pi a (R^3)^2 N^0 \).

In the case of homogeneous nucleation, one has \( f'(m,x) = f(m,x) = 1 \), and \( 4 \pi a (R^3)^2 N^0 \rightarrow 1 \). In this case, Eq. (43) is converted to
\[ J = B \exp \left[ - \frac{16 \pi \Omega^2}{3 kT} \right]. \] (45)

Obviously, this is the expression for the homogeneous nucleation rate. This implies that Eq. (43) is applicable to described both homogenous heterogeneous nucleation.

C. Relation between nucleation rate and foreign particles

As indicated in Eqs. (8) and (10), \( f(m,x) \) and \( f'(m,x) \) characterize the major difference between homogeneous and heterogeneous nucleation kinetics. We have shown above that the occurrence of foreign particles will lower the nucleation barrier, resulting in an increase in nucleation rate. This effect, characterized by \( f(m,x) \), will be escalated by lowering the contact angle between the crystal phase and the substrate and/or increasing the relative size of foreign particles \( x(R^3/r_c^3) \).

On the other hand, foreign particles exert also a negative impact on the nucleation kinetics. As shown in Fig. 3, nucleation on a foreign particles will cause a reduction in the “effective surface of embryos,” where the growth units are
incorporated into the embryos. This tends to slow down the nucleation kinetics, which gives rise to a counter effect against the lowering of the nucleation barrier described by \( f(m,x) \). This effect is captured by \( f'(m,x) \) and \( f''(m,x) \) in the pre-exponential term of \( J \) given by Eq. (10). Therefore, in terms of effective collision, this implies that the lowering of the contact angle \( \theta \) and/or the increase of \( x \) will slow the nucleation kinetics [see Eq. (10)].

In different regimes, these two counter factors will control the nucleation kinetics in very different ways. At low supersaturations, the nucleation barrier is very high [cf. Eq. (2)]. Therefore, the top priority to accelerate the kinetics is to lower the nucleation barrier. Then heterogeneous nucleation will occur preferentially on the particles with a low \( f(m,x) \). Conversely, at higher supersaturations, the exponential term associated with nucleation barrier becomes unimportant. Due to the pre-exponential factors \( f(m,x) \) and \( f''(m,x) \), nucleation on the substrates having a larger \( f(m,x) \) and \( f''(m,x) \) becomes kinetically favorable.

Since \( f(m,x) \) and \( f''(m,x) \) are functions of both \( \theta \) and \( R^* \), the effect of \( f(m,x) \) and \( f''(m,x) \) on nucleation can be expressed in terms of \( \theta \) and \( R^* \), respectively (see Fig. 2). In Fig. 4 the relative nucleation rate \( J/(4\pi a(R^* )^2 N^0 B) \) is plotted via supersaturation \( \sigma \) for different “contact angle” \( \theta \)s and radiuses of foreign particles. As expected, nucleation on foreign particles with lower \( f(m,x) \) and \( f''(m,x) \) (a lower contact angle and/or a large radius) will be dominant at low supersaturations, whereas nucleation on those with higher \( f(m,x) \) and \( f''(m,x) \) (a larger contact angle and/or a small radius) become kinetically favorable at low supersaturations. This implies that for a nucleating system, different foreign particles having distinct surface properties or contact angles with crystalline phase and different sizes will control nucleation at different supersaturation regimes. Homogeneous nucleation can be regarded as an up limited case of heterogeneous nucleation where one has \( f(m,x) = f''(m,x) = 1 \). As shown in Fig. 4, it happens only at very high supersaturations under normal conditions.

### III. DISCUSSIONS

We have in the previous section shown that foreign bodies with different \( f(m,x) \) and \( f''(m,x) \) will control nucleation at different regimes. To examine this, we can measure the incubation time of nucleation \( \tau \) versus supersaturation. Regarding that \( \tau \) is proportional to \( 1/J \), we should obtain a linear relation between \( \ln \tau \) and \( 1/[\ln(1+\sigma)]^2 \) for a given \( f(m,x) \)

\[
\ln \tau = \ln(1/J) = \frac{16\pi \gamma_f \Omega^2}{3kT[kT\ln(1+\sigma)]^2} f(m,x) - \ln\{2\pi a(R^* )^2 N^0 f''(m,x) [f(m,x)]^{1/2} B\}. \tag{46}
\]

According to Eq. (46), the slope of \( \ln \tau - 1/[\ln(1+\sigma)]^2 \), denoted by \( \kappa f(m,x) \), is proportional to \( f(m,x) \) for a given system. \( \kappa = 16\pi \gamma_f \Omega^2/(3kT[kT\ln(1+\sigma)]^2) \) is a constant for a given system. A large slope corresponds to a large \( f(m,x) \). Therefore, the relative \( f(m,x) \) at different supersaturations can be obtained by measuring the change of the slope.

To check above results, the nucleation induction period (\( \tau \) in sec) for precipitation of CaCO\(_3\), measured by Söhnel and Mullin,\(^8\) was plotted as a function of supersaturation \( \sigma \) in Fig. 5. The method employed by Söhnel and Mullin was based on Nielsen’s mixing apparatus.\(^19\) The method is concerned with the measurement of fast changes in the conductivity of a supersaturated solution. If two stable solutions (CaCl\(_2\) and Na\(_2\)CO\(_3\)), which react to form a supersaturated solution of the reactant, are mixed together instantaneously, no detectable changes occur for some time. However, as soon as the reactant starts to precipitate from the solution, the concentration of electrically conductive species begins to decrease and this causes the solution conductivity to diminish.

The length of the period of conductivity “steadiness” decreases with increasing supersaturation and for highly supersaturated solutions it can be less than a millisecond. For more details, see Ref. 8.

As shown by Fig. 5, three straight lines with different slopes.
we denote different regimes. This implies that within the range of super-
growth at one place will suppress nucleation over certain
concentrations so that the occurrence of crystal
rate in general. Apart from this, convection will reduce con-
bulk, which enhances virtually the heterogeneous nucleation
help to bring new seed crystals created on the substrate to the

slopes $[\kappa f(m,x)]$ intercept with each other. This indicates
that three different $f(m,x)$s control nucleation in three dif-
ferent regimes. This implies that within the range of super-
saturations, the nucleation is controlled by three different
types of foreign bodies within regime I–III, respectively. If
we denote $f(m,x)$ and $f''(m,x)$ occurring in these three re-
gions as $f_I(m,x)$, $f''_I(m,x)$, $f''_m(m,x)$, $f''_M(m,x)$,
respectively, according to the slopes of the straight
lines, we have then $f_I(m,x)<f_m(m,x)<f_M(m,x)$ [and
$f''_I(m,x)<f''_m(m,x)<f''_M(m,x)$]. As predicted in Fig. 3 the
particles with a low $f(m,x)$ and $f''(m,x)$ will control the
nucleation at low supersaturations while those with a high
$f(m,x)$ and $f''(m,x)$ will govern the nucleation at high super-
saturations. This completely agrees with our predictions
given in Sec. II C.

In the presence of foreign particles, to achieve genuine
homogeneous nucleation may require substantially high su-
persaturations, in particular when the system contains many
tiny particles, such as macromolecules. These tiny particles
may affect nucleation at high supersaturations. Obviously,
to remove these particles by filtering solutions may be one of
the key steps in achieving homogeneous nucleation. On the
other hand, the effect of the interfaces between crystalliza-
tion systems and their surroundings (such as the wall of crys-
tallization vessels) on nucleation is impossible to be elimi-
nated under gravity.

Under gravity, convection occurs due to the density or con-
centration gradient caused by nucleation and growth. 1,2
Convection will help to transport growth units to the surface
of substrates, which will compensate for the concentration
(or supersaturation) depression during nucleation. It will also
help to bring new seed crystals created on the substrate to the
bulk, which enhances virtually the heterogeneous nucleation
rate in general. Apart from this, convection will reduce con-
centration fluctuations so that the occurrence of crystal
growth at one place will suppress nucleation over certain
distances. In general, convection will substantially promote
the effect of foreign bodies, in particular the foreign bodies
having relatively high $f(m,x)$ [and $f''(m,x)$], such as tiny
particles and the wall of crystallizing vessels, which inevita-
cially occur in all crystallization systems. Once heterogeneous
nucleation occurs at relatively low supersaturation, nucleat-
ing materials are consumed quickly. This leads then to a drop
in the bulk supersaturation. Therefore, the supersaturation
required for genuine homogeneous nucleation is extremely
difficult to reach.

When nucleation occurs under microgravity, the convec-
tion due to the density or concentration gradient is sup-
pressed. This will on one hand eliminate the transport
mechanism which facilitates the heterogamous nucleation,
and on the other hand can easily lead to local high supersatu-
rations. Therefore, in microgravity, heterogeneous nucle-
ation, in particular the heterogeneous nucleation caused by
foreign bodies with relatively high $f(m,x)$, can be sup-
pressed to a larger extent so that homogeneous nucleation
may be achieved more easily.

Recently experiments on the nucleation of CaCO$_3$ in mi-
crogravity carried out by Tsukamoto et al. 7 showed that
the slope of the $\ln(1+\sigma)^2$ plot is four times larger than
that obtained under gravity by Sörenel and Mullin within the
same supersaturation range 8 (see Fig. 5). This strongly indi-
cates that the nucleation occurred in Sörenel and Mullin’s
gravity experiments is heterogeneous nucleation in nature,
while the nucleation occurred in Tsukamoto’s microgravity
experiments is homogeneous nucleation in nature. Based on
Sörenel and Mullin’s result 8 and taking $f(m,x)=1$, the inter-
facial free energy of CaCO$_3$ obtained from the microgravity
experiments [cf. Eq. (1)] is 170 mJ/m$^2$ at 25 °C, almost
the same as that obtained from the contact angle measuremen-
t. 7 This strongly suggests the occurrence of homogeneous
nucleation in microgravity.

IV. SUMMARY AND CONCLUSIONS

The influence of foreign particles on the 3D nucleation
was systematically examined. The size and contact angle of
adsorbed foreign particles exert a very strong effect on the
free energy barrier of 3D nucleation, as well as the transport
of growth units to the surface embryos. At low supersatura-
tions, the top priority to accelerate the nucleation kinetics is
to lower the nucleation barrier. Foreign particles being rela-
tively large in size and/or having a small contact angle can
substantially lower the 3D nucleation barrier, therefore, will
control on the nucleation rate at the low supersaturation re-
gime. At high supersaturations, the nucleation barrier is rela-
tively low. Then the top priority to accelerate the nucleation
kinetics is to improve the transport of growth units to the
embryos surface. Then, foreign particles being relatively
small in size and/or having a large contact angle may control
on the nucleation rate at the high supersaturation regime.
Genuine homogeneous nucleation generally requires a very
high supersaturation, which may not be easy to achieve un-
der gravity condition due to convection. In microgravity, het-
erogeneous 2D nucleation may become difficult due to the
elimination the gravity. Under this condition, genuine homo-
genous nucleation may be much easy to be obtained.
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