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A new kinetic model for three-dimensional heterogeneous nucleation
Heterogeneous nucleation on convex spherical substrate surfaces: A rigorous thermodynamic formulation of Fletcher’s classical model and the new perspectives derived

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Fletcher’s spherical substrate model [J. Chem. Phys. 29, 572 (1958)] is a basic model for understanding the heterogeneous nucleation phenomena in nature. However, a rigorous thermodynamic formulation of the model has been missing due to the significant complexities involved. This has not only left the classical model deficient but also likely obscured its other important features, which would otherwise have helped to better understand and control heterogeneous nucleation on spherical substrates. This work presents a rigorous thermodynamic formulation of Fletcher’s model using a novel analytical approach and discusses the new perspectives derived. In particular, it is shown that the use of an intermediate variable, a selected geometrical angle or pseudocontact angle between the embryo and spherical substrate, revealed extraordinary similarities between the first derivatives of the free energy change with respect to embryo radius for nucleation on spherical and flat substrates. Enlightened by the discovery, it was found that there exists a local maximum in the difference between the equivalent contact angles for nucleation on spherical and flat substrates due to the existence of a local maximum in the difference between the shape factors for nucleation on spherical and flat substrate surfaces. This helps to understand the complexity of the heterogeneous nucleation phenomena in a practical system. Also, it was found that the unfavorable size effect occurs primarily when \( R < 5r^c \) (\( R \): radius of substrate and \( r^c \): critical embryo radius) and diminishes rapidly with increasing value of \( R/r^c \) beyond \( R/r^c = 5 \). This finding provides a baseline for controlling the size effects in heterogeneous nucleation.

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I. INTRODUCTION

A convex spherical surface is one of the most commonly encountered catalyzing surfaces for heterogeneous nucleation in nature. From a geometrical point of view, a spherical contour is one of the basic shapes by which geometry describes nature. From a practical perspective, substrate particles such as dust particles that naturally exist in a gaseous or liquid media or those artificially fabricated by many processes for control of nucleation are typically on a micrometer or submicrometer scale. As a result, it is physically more reasonable to describe them as spherical particles than flat substrates. On the other hand, from a crystallographic perspective, the assumption of a spherical geometry neglects the differences between various crystal faces and therefore allows for use of average values for the quantities involved such as surface free energies. This significantly simplifies the thermodynamic analysis. Such simplifications are necessary for the formulation of a nucleation problem. Hence, the subject of nucleation on a convex spherical surface is one of the basic problems in heterogeneous nucleation.

Fletcher\textsuperscript{4} was the first to thermodynamically describe the nucleation phenomenon on a convex spherical surface following Volmer’s seminal flat substrate model.\textsuperscript{2} Fletcher derived a shape factor for nucleation on a spherical substrate and revealed the overall size effect of a spherical substrate on the energy barrier to nucleation. Prior to Fletcher, Turnbull’s transformation nucleus model\textsuperscript{3} discussed the size effect of a small flat substrate on heterogeneous nucleation in supercooled liquid metals. Turnbull pointed out that for a metal nucleus to grow into a grain, the linear dimension of the flat substrate must be greater than the critical embryo size \( 2r^c \). This criterion defines a minimum substrate size or a minimum undercooling for the formation of a grain on a flat substrate.\textsuperscript{3} However, Turnbull’s model was not appreciated until recently.\textsuperscript{4} Fletcher’s spherical substrate model provides new insights and extends perspectives on heterogeneous nucleation and its control. So, it constitutes another classical model for heterogeneous nucleation.

Because of its generic nature, Fletcher’s model has been used extensively on a regular basis by researchers across various disciplines despite the controversy concerning the validity of the spherical-cap assumption and the use of the bulk thermodynamic properties to describe a nucleus.\textsuperscript{5} Some recent examples where Fletcher’s model has shown an important impact can be found in the work referenced.\textsuperscript{6–16} The
reason is straightforward: Fletcher’s model helps understand and control the nucleation phenomena occurring in various processes and systems.

However, a rigorous thermodynamic formulation of the model has been missing due to the analytical difficulties involved in the thermodynamic formulation. In fact, Fletcher’s shape factor, the core part of his model, was derived using an indirect approach, where Fletcher omitted to meet two essential requirements for defining the energy barrier to nucleation, as will be shown subsequently, because of the challenges embedded in the thermodynamic analyses. This has not only left the model fundamentally deficient but also likely obscured its other important features, which would otherwise have helped to better understand and control the heterogeneous nucleation phenomena on a spherical substrate.

This work presents a rigorous thermodynamic formulation of the nucleation phenomena on a convex spherical substrate using a novel analytical approach. It starts with a critical review of Fletcher’s approach and then proceeds to the development of a rigorous formulation of the problem. The formulation leads to a number of new perspectives on nucleation on spherical substrates whose significance is discussed in comparison with nucleation on a flat substrate.

II. FLETCHER’S APPROACH

Fletcher\(^1\) considered vapor condensation on a convex spherical substrate of radius \(R\) (Fig. 1), where following Volmer’s classical model,\(^2\) the embryo was assumed to be a spherical cap of radius \(r\). The free energy of formation of such an embryo is

\[
\Delta G = \Delta G_V V_2 + \sigma_{21} S_{21} + (\sigma_{23} - \sigma_{13}) S_{23},
\]

where \(\Delta G_V\) is the free energy difference per unit volume of the embryo between phase 1 and phase 2, \(V_2\) is the volume of the embryo, and \(\sigma_{ij}\) is the interfacial free energy per unit area of the interface \(S_{ij}\) between phases \(i\) and \(j\). According to Fig. 1,

\[
V_2 = \frac{1}{2} \pi r^2 (2 - 3 \cos \psi + \cos^3 \psi) - \frac{1}{2} \pi R^2 (2 - 3 \cos \phi + \cos^3 \phi),
\]

\[
S_{21} = 2 \pi r^2 (1 - \cos \psi),
\]

\[
S_{23} = 2 \pi R^2 (1 - \cos \phi).
\]

The two geometrical angles \(\psi\) and \(\phi\) are defined by

\[
\cos \psi = \frac{r - R \cos \theta}{d} = \frac{mR - r}{d},
\]

\[
\cos \phi = \frac{R - r \cos \theta}{d} = \frac{R - mr}{d},
\]

where

\[m = \cos \theta = \frac{\sigma_{13} - \sigma_{23}}{\sigma_{21}}\]

and

\[d = \sqrt{R^2 + r^2 - 2Rrm}.\]

Fletcher pointed out that the critical embryo radius \(r^*\) should be the same as that for homogeneous nucleation, namely,

\[r^* = -\frac{2\sigma_{21}}{\Delta G_V} \frac{1}{3} f(m, x),
\]

also, as a means of verification, it should satisfy

\[
\left(\frac{\partial \Delta G}{\partial r}\right)_{r=r^*} = 0.
\]

Substituting Eqs. (2)–(6) and (9) into Eq. (1) and rearranging respective terms, the free energy of formation of a critical embryo of radius \(r^*\) can be written as

\[
\Delta G^* = \frac{16\pi\sigma_{21}^3}{3(\Delta G_V)^2} f(m, x),
\]

where \(x = R/r^*\) and \(f(m, x)\), the Fletcher shape factor, is given by

\[
f(m, x) = \frac{1}{2} \left[ 1 - \left( \frac{mx - 1}{g} \right)^3 \right] + x \left[ 2 - 3 \left( \frac{x - m}{g} \right) \right. \\
+ \left. \left( \frac{x - m}{g} \right)^3 \right] + 3mx^2 \left( \frac{x - m}{g} - 1 \right),
\]

where

\[g = \sqrt{1 + x^2 - 2mx}.\]

The approach used above by Fletcher is simple, where Fletcher justified the inference described by Eq. (9).\(^1\) However, Fletcher’s formulation left two critical questions unanswered. First, because the anticipated expression of \(\partial \Delta G/\partial r\) will clearly involve terms containing \(r^n\), where \(n > 1\), as will be shown below by Eq. (14), it is unknown if \(r^* = -2\sigma_{21}/\Delta G_V\) is the only solution existing to Eq. (10) or not. Second, for \(\Delta G(r^*)\) to be the energy barrier to nucleation,
\( \partial^2 \Delta G / \partial r^2 < 0 \) must be met at \( r = r^* \). However, it is unknown if \( \Delta G(r^*) \) achieves a local maximum at \( r = r^* \) or not, namely, if \( \partial^2 \Delta G / \partial r^2 < 0 \) occurs at \( r = r^* \), or if \( \partial^2 \Delta G / \partial r^2 \) ever exists at \( r = r^* \) because of the unidentified nature of \( \partial^2 \Delta G / \partial r^2 \). In fact, it has proved difficult to verify Eq. (9) by substituting it into Eq. (10) because of the lack of an analytical expression of \( \partial \Delta G / \partial r \).

In an attempt to address these concerns, efforts were made to formulate an explicit expression for \( \partial \Delta G / \partial r \) by substituting Eqs. (2)–(8) into Eq. (1) and then differentiating it with respect to the embryo radius \( r \). The differentiation resulted in a lengthy complex expression without a clear indication for a meaningful structure. However, if \( r^* = -2 \sigma_{21} / \Delta G_V \) were a solution to \( \partial \Delta G / \partial r = 0 \), the expression should contain a term \( (\Delta G_V r + 2 \sigma_{21}) \). Following this clue, we obtain, after a great amount of labor as warned by Fletcher, 1

\[
\frac{\partial \Delta G}{\partial r} = \pi r (\Delta G_V r + 2 \sigma_{21}) \left[ 2 + \frac{m \left( \frac{R}{r} \right) - 1}{1 + \left( \frac{R}{r} \right)^2} \right],
\]

(14)

where the variable \( R/r \) was introduced to help simplify the expression; it differs from \( R/r^* \). The validity of Eq. (14) can be readily substantiated using Eq. (29) to be formulated later.

Equation (14) revealed that \( r^* = -2 \sigma_{21} / \Delta G_V \) is indeed a stationary point for \( \Delta G \) at which \( \partial \Delta G / \partial r = 0 \). However, the expression in the pair of square brackets in Eq. (14) suggests that there likely exist other stationary points, which would make \( \partial \Delta G / \partial r = 0 \) as well. Unfortunately, it has proved impossible to exclude such possibilities from Eq. (14). In addition, it has proved impossible to verify by using Eq. (14) that \( \partial^2 \Delta G / \partial r^2 < 0 \) is satisfied at \( r = r^* \) because of the analytical complexities involved as well as the fact that \( m \) and \( R/r \) are two independent variables. Apparently, a different approach is needed to define all possible stationary points for heterogeneous nucleation on a convex substrate surface and to determine if \( \partial^2 \Delta G / \partial r^2 < 0 \) occurs at any of these stationary points. Nevertheless, it should be pointed out that it is natural and logical to have derived an expression such as Eq. (14) for \( \partial \Delta G / \partial r \) because \( m \), \( R \), and \( r \) are the three most direct variables that affect \( \Delta G \).

### III. A NOVEL AND RIGOROUS ANALYTICAL APPROACH TO THE FORMULATION OF FLETCHER’S MODEL

Subsequent to many attempts, we have come across an analytical approach that would allow for a rigorous thermodynamic formulation of the nucleation problem on a spherical substrate surface. The key point of the approach is to use the cosines of the two geometrical angles \( \psi \) and \( \phi \), \( \cos \psi \) or \( \cos \phi \), illustrated in Fig. 1, to describe both \( \Delta G \) and \( \partial \Delta G / \partial r \). At first glance, neither \( \cos \psi \) nor \( \cos \phi \) is a direct variable for the nucleation problem considered, but it is remarkable that they hold the key to solving the problem and to revealing the interesting features of heterogeneous nucleation on a convex spherical substrate.

Define according to Eqs. (5) and (6)

\[
A = \cos \psi = (mR - r)d^{-1},
\]

(15)

and

\[
B = \cos \phi = (R - mr)d^{-1}.
\]

(16)

Then

\[
\frac{\partial A}{\partial r} = d^{-3} R^2 (m^2 - 1) = d^{-1} (A^2 - 1)
\]

(17)

and

\[
\frac{\partial B}{\partial r} = d^{-3} R (m^2 - 1) = \frac{r}{R} \frac{\partial A}{\partial r}.
\]

(18)

Substituting Eqs. (2)–(4) into Eq. (1) and then using Eqs. (15) and (16) give

\[
\Delta G = \frac{\pi}{3} \Delta G_V \left[ r^3 (2 - 3A + A^3) - R^3 (2 - 3B + B^3) \right] + 2 \pi \sigma_{21} [r^2 (1 - A) - mR^2 (1 - B)].
\]

(19)

For ease of analysis, define

\[
\Theta_1 = r^3 (2 - 3A + A^3) - R^3 (2 - 3B + B^3)
\]

(20)

and

\[
\Theta_2 = r^2 (1 - A) - mR^2 (1 - B).
\]

(21)

Note that \( R \) and \( r \) are two independent variables, i.e., \( \partial R / \partial r = 0 \). Differentiating Eq. (20) with respect to \( r \) yields

\[
\frac{\partial \Theta_1}{\partial r} = 3r^2 (2 - 3A + A^3) + 3r \frac{\partial A}{\partial r} [r^2 (A^2 - 1) + R^2 (1 - B^2)],
\]

(22)

where Eq. (18) was used to eliminate \( \partial B / \partial r \) from the expression. It was realized by using Eqs. (15) and (16) that

\[
r^2 (A^2 - 1) + R^2 (1 - B^2) = 0.
\]

(23)

This is another critical step of the analysis. As a result
Similarly, using Eq. (18) and noting that \( \partial R/\partial r = 0 \) and \( \partial m/\partial r = 0 \), we obtain

\[
\frac{\partial \Theta_1}{\partial r} = 3r^2(2 - 3A + A^3).
\] (24)

Then, using Eqs. (15) and (17)

\[
\frac{\partial \Theta_2}{\partial r} = 2r(1 - A) + r(mR - r) \frac{\partial A}{\partial r}.
\] (25)

On the other hand, according to Eqs. (19)–(21)

\[
\frac{\partial G}{\partial r} = \frac{\pi}{3} \Delta G_v \frac{\partial \Theta_1}{\partial r} + 2\pi\sigma_2 \frac{\partial \Theta_2}{\partial r}.
\] (27)

Substituting Eqs. (24) and (26) into Eq. (27) eventually leads to

\[
\frac{\partial \Delta G}{\partial r} = (\Delta G_v \pi r^2 + 2\sigma_2 \pi r)(2 + A)(1 - A)^2
\] (28)

or

\[
\frac{\partial \Delta G}{\partial r} = (\Delta G_v \pi r^2 + 2\sigma_2 \pi r)(2 + \cos \psi)(1 - \cos \psi)^2.
\] (29)

As will be shown below, the formulation of Eq. (29) is crucial to the thermodynamic formulation of the nucleation problem considered. Note that \( \cos \psi = [m(R/r) - 1]/\sqrt{1 + (R/r)^2 - 2m(R/r)} \) according to Eqs. (5) and (8). Using this relationship, it is easy to find that Eqs. (14) and (29) can readily reduce to each other. In other words, the two different expressions, which were attained from different approaches, provide a means of validation for each other. However, as pointed out previously, Eq. (14) will lead nowhere.

Because \( A = \cos \psi \) and \( \psi \neq 0 \) (Fig. 1), it is obvious from Eq. (28) or Eq. (29) that \( r^* = -2\sigma_2 / \Delta G_v \) is the only solution that satisfies \( \partial \Delta G/\partial r = 0 \), namely, \( \Delta G(r) \) has only one stationary point for heterogeneous nucleation on a convex spherical substrate. Recall the expression of \( \partial \Delta G/\partial r \) for heterogeneous nucleation on a flat substrate surface,

\[
\frac{\partial \Delta G}{\partial r} = (\Delta G_v \pi r^2 + 2\sigma_2 \pi r)(2 + \cos \theta)(1 - \cos \theta)^2.
\] (30)

where \( \theta \) is the contact angle between the embryo and substrate. The only difference between Eqs. (29) and (30) lies in that existing between \( \theta \), the contact angle between the embryo and flat substrate, and \( \psi \), a geometrical angle for nucleation on a spherical substrate with a contact angle \( \theta \) (Fig. 1). It follows that if \( \psi \) were regarded as a pseudocontact angle, Eqs. (29) and (30) would be identical to each other. Enlightened by these new insights, a detailed comparison of \( f(m,x) \) with the shape factor for nucleation on a flat substrate surface, \( S(\theta) \), will be presented in Sec. IV.

Because of the formulation of Eq. (28), it is now straightforward to determine if \( \Delta G \) achieves a local maximum or not at \( r = r^* \). According to Eq. (28)

\[
\frac{\partial^2 \Delta G}{\partial r^2} = (2\pi \Delta G_v r + 2\pi \sigma_2)(2 + A)(1 - A)^2
\]

\[
+ r(\pi \Delta G_v r + 2\pi \sigma_2) \frac{\partial [(2 + A)(1 - A)^2]}{\partial r}.
\] (31)

Substituting \( r = r^* = -2\sigma_2 / \Delta G_v \) yields

\[
\frac{\partial^2 \Delta G}{\partial r^2} \bigg|_{r=r^*} = -2\sigma_2 (2 + A)(1 - A)^2.
\] (32)

Note that \( |A| < 1 \), where \( A = \cos \psi \) and \( \psi \neq 0; 180^\circ \) (Fig. 1),

\[
\frac{\partial^2 \Delta G}{\partial r^2} \bigg|_{r=r^*} = -2\sigma_2 (2 + A)(1 - A)^2 < 0.
\] (33)

Therefore, \( \Delta G(r^*) \) is a local maximum.

It has now been established that \( r^* = -2\sigma_2 / \Delta G_v \) is the only stationary point at which both \( \partial \Delta G/\partial r = 0 \) and \( \partial^2 \Delta G/\partial r^2 < 0 \) are satisfied for heterogeneous nucleation on a spherical substrate. Accordingly, \( \Delta G(r^*) \) defines the energy barrier to nucleation. Substituting \( r^* = -2\sigma_2 / \Delta G_v \) into Eq. (1) and rearranging the expression confirmed Fletcher’s shape factor \( f(m,x) \) given by Eq. (12).

IV. DISCUSSION

The preceding analyses provide a rigorous thermodynamic basis, within the framework of the classical theory of nucleation, for understanding heterogeneous nucleation on a spherical substrate. In addition, it furnishes unique perspectives for a comparative study between heterogeneous nucleation on spherical and flat substrates.

In analyzing the nucleation phenomena on a spherical substrate, Fletcher\(^1\) plotted the shape factor \( f(m,x) \) as a function of \( x = R/r^* \) and \( m \), which is reproduced in Fig. 2, to discuss the combined effects of the substrate size \( 2K \) in relation to the critical embryo size \( 2r^* \) and the contact angle \( \theta \) in the form of \( m = \cos \theta \). Fletcher’s analyses revealed that for a
given contact angle, nucleation is always easier on a flat surface than on a convex spherical surface, and the smaller the spherical substrate in relation to the critical embryo, the higher the energy barrier to nucleation.

The similarities revealed between Eqs. (29) and (30) suggest that the shape factor for heterogeneous nucleation on a spherical substrate, \( f(m, x) \), is likely to be similar to its counterpart for nucleation on a flat substrate, \( S(\theta) \), where \( S(\theta) = (\cos^3 \theta - 3 \cos \theta + 2)/4 \). In Fletcher’s Fig. 2, the connection between \( f(m, x) \) and \( S(\theta) \) is missing. Figure 3(a) plots \( f(m, x) \), designated \( f(\theta, x) \), as a function of \( \theta \) and \( x \), where \( \theta \) was varied from 0° to 180° and \( x \) from 1 to 1000 and beyond. In comparison, Fig. 3(b) plots \( S(\theta) \) versus \( \theta \). As can be seen, despite its deceptively complex expression, \( f(\theta, x) \) varies in an analogous fashion as \( S(\theta) \), irrespective of the relative substrate size \( (x = R/r^*) \). In fact, \( \lim_{x \to \infty} f(\theta, x) = S(\theta) \), which was confirmed numerically by comparing \( f(\theta, x) \) with \( S(\theta) \) for large values of \( R/r^* \), although \( f(\theta, x) \) or \( f(m, x) \) does not analytically reduce to \( S(\theta) \) when \( x = R/r^* \to \infty \). So, the \( f(\theta, x) \) curve that corresponds to \( x = R/r^* \to \infty \) in Fig. 3(a) is identical to \( S(\theta) \). As a result, the size effect is seen in Fig. 3(a) as though the \( S(\theta) \) curve were shifted leftward when the relative substrate size \( (R/r^*) \) decreases from \( x = R/r^* \to \infty \) to \( x = 1 \). The S-shaped plot of \( f(\theta, x) \) shown in Fig. 3(a) in conjunction with Fletcher’s original Fig. 2 gives a complete description of the size and contact angle effects for heterogeneous nucleation on a convex spherical surface.

The intriguing relationship between \( \psi \) and \( \theta \) suggested by Eqs. (29) and (30) inspired efforts to determine the equivalent contact angles for heterogeneous nucleation on spherical and flat substrate surfaces. This was done by solving Eq. (34) below with respect to different values of \( x \) in the range \( x \in [1, \infty) \): \[ f(\theta_F, x) = S(\theta_F), \] (34)

where \( \theta_F \) and \( \theta_F \) are the equivalent contact angles for nucleation on spherical and flat substrate surfaces, respectively, subject to the same critical embryo radius \( r^* \). Figure 4 plots the difference between \( \theta_F \) and \( \theta_5 \), \( (\theta_F - \theta_5) \), versus \( \theta_5 \), with respect to different values of \( x \).

Because nucleation is easier on a flat substrate than on a spherical substrate, \( \theta_5 \) is expected to be constantly smaller than \( \theta_F \) in order for a spherical substrate to be as potent as a flat substrate. This was verified by Fig. 4. It is, however, interesting to note from Fig. 4 that there exists a local maximum difference between \( \theta_F \) and \( \theta_5 \), \( (\theta_F - \theta_5)_{\text{max}} \), for each specified value of \( x \). Also, this local maximum difference decreases with increasing \( x \) and approximately vanishes when \( x \) \to 100, beyond which spherical substrates are effectively flat in relation to the critical embryo as can be inferred from Fig. 3(a). The characteristic contact angle at which
characteristic contact angle at which $x=R/r^*$ and increases with increasing value of $x=R/r^*$.

To further elucidate the observation of $(\theta_f-\theta_S)_{\text{max}}$, the difference between the two shape factors $f(\theta,x)$ and $S(\theta)$, $[f(\theta,x)-S(\theta)]$, was investigated with respect to different contact angles and substrate sizes. Figure 5 summarizes the results by plotting $[f(\theta,x)-S(\theta)]$ as a function of $\theta$ and $x$. Because of the observation of $(\theta_f-\theta_S)_{\text{max}}$, it is not surprising that there exists a local maximum in the difference between the two shape factors $f(\theta,x)$ and $S(\theta)$, $[f(\theta,x)-S(\theta)]_{\text{max}}$ for each specified value of $x$. Similarly, $[f(\theta,x)-S(\theta)]$ decreases as $x$ increases and vanishes when $x>100$. The characteristic contact angle at which $[f(\theta,x)-S(\theta)]_{\text{max}}$ occurs also increases with increasing $x=R/r^*$. Clearly, the existence of $(\theta_f-\theta_S)_{\text{max}}$ is determined by the dependence of $[f(\theta,x)-S(\theta)]$ on $\theta$ and $x$.

In general, heterogeneous nucleation in a metastable parent phase occurs on the most potent nucleating substrates first and proceeds progressively to the less potent ones. A practical nucleation system contains background nucleating substrates with different contact angles and morphologies. The existence of $(\theta_f-\theta_S)_{\text{max}}$ helps to understand the complexity of heterogeneous nucleation in a practical system.

Another important feature to note from Fig. 3(a) is that the size effect is most noticeable when $x=R/r^*<5$ and diminishes quickly with increasing $x$ beyond five, where the shape factor curves have practically overlapped each other when $x>5$ or $R>5r^*$. This finding is readily applicable to practical problems including the optimization of the size of particle additions for inoculation of alloy melts or seeding practices.

To better understand this size effect feature, an analysis was made of the composition of $f(\theta,x)$. Following the organization of Eqs. (2)–(4), Eq. (12) can be rearranged using the two intermediate variables $A$ and $B$ defined previously as follows:

$$f(m,x) = f(\theta,x) = \frac{1}{2} \left[ -2 - 3A + A^3 + x^3(2 - 3B + B^3) \right] + \frac{1}{2} \left[ 3(1-A) - 3m^2(1-B) \right].$$

Consequently, Eq. (35) can be divided into the volume component $f^V(\theta,x)$ and the surface component $f^S(\theta,x)$, where

$$f^V(\theta,x) = \frac{1}{2} \left[ -2 - 3A + A^3 + x^3(2 - 3B + B^3) \right]$$

and

$$f^S(\theta,x) = \frac{1}{2} \left[ 3(1-A) - 3m^2(1-B) \right].$$

Figures 6 and 7 plot $f^V(\theta,x)$ and $f^S(\theta,x)$ as a function of $\theta$ and $x$. Both $f^V(\theta,x)$ and $f^S(\theta,x)$ exhibit a similar sigmoid profile but in a reverse fashion. As can be seen from comparing Fig. 3(a) with Figs. 6 and 7, $f(\theta,x)$ is dictated mainly by $f^S(\theta,x)$. This is reasonable as the surface component comprises the barrier to nucleation. In addition, it is interesting to note that the dependence of both $f^S(\theta,x)$ and $f^F(\theta,x)$ on $x$ occurs principally when $x=R/r^*<5$ as well. This means that neither the volume component nor the surface component will change appreciably once the relative substrate size $R/r^*$ is greater than five because the spherical substrate is quickly approaching a flat substrate when $R/r^*>5$.

The critical embryo radius $r^*$ is typically of the order of magnitude of $10^{-1} \mu$m in many cases. This means that the unfavorable size effect observed when $x=R/r^*<5$ can be effectively precluded by using substrate particles of larger than $1 \mu$m in diameter ($2R>10r^*$). This provides a baseline for controlling the size effect in seeding or inoculation practices.
A rigorous thermodynamic formulation has been realized of Fletcher’s spherical substrate model using a novel analytical approach, where a geometrical angle $\psi$ between the embryo and spherical substrate was used as an intermediate variable to formulate the first derivative of the free energy change $\Delta G$ with respect to the embryo radius $r$, $\partial \Delta G / \partial r$. If $\psi$ were regarded as a pseudocontact angle, the thermodynamic descriptions of $\partial \Delta G / \partial r$ for nucleation on spherical and flat substrates would be identical. The use of $\psi$ to describe $\partial \Delta G / \partial r$ facilitates the establishment of a rigorous thermodynamic basis for understanding the nucleation phenomena on a spherical substrate. In addition, it inspired the discovery of a number of interesting features for nucleation on a spherical substrate compared to nucleation on a flat substrate. It was found that despite its deceptively complex expression, the shape factor for nucleation on a spherical substrate, $f(\theta, x)$, varies in an analogous fashion as the shape factor for nucleation on a flat substrate, $S(\theta)$. However, a local maximum difference occurs at a characteristic contact angle between the two shape factors. Accordingly, this leads to a local maximum difference between the equivalent contact angles for nucleation on spherical and flat substrate surfaces. This helps to understand the complexity of heterogeneous nucleation in a practical system. The unfavorable size effect occurs primarily when $R < 5r^*$ and diminishes rapidly when $R > 5r^*$, determined by both the surface component and the volume component of the shape factor but the surface component plays the major role. To enhance heterogeneous nucleation, the substrate radius needs to be at least five times the critical embryo radius.

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