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Nucleation and growth of a core-shell composite nucleus by diffusion

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The critical radius of a core-shell-type nucleus grown by diffusion in a phase-separated solution is studied. A *kinetic* critical radius rather than the *thermodynamic* critical radius of standard classical nucleation theory can be defined from the diffusional growth equations. It is shown that there exist two kinetic critical radii for the core-shell-type nucleus, for which both the inner-core radius and the outer-shell radius will be stationary. Therefore, these two critical radii correspond to a single critical point of the nucleation path with a single energy barrier even though the nucleation looks like a two-step process. The two radii are given by formulas similar to that of classical nucleation theory if the Ostwald-Freundlich boundary condition is imposed at the surface of the inner nucleus and that of the outer shell. The subsequent growth of a core-shell-type postcritical nucleus follows the classical picture of Ostwald's step rule. Our result is consistent with some of the experimental and numerical results which suggest the core-shell-type critical nucleus.

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I. INTRODUCTION

Nucleation and growth are basic phenomena that play vital roles in the processing of various materials across many industries and in various natural phenomena [1]. In particular, the growth of fine particles in solution, such as semiconductor quantum dots [2], biominerals [3], and other molecular crystals [4,5], has attracted considerable interest recently since such materials have many potential applications spanning the electronics to the biomedical industries. In nucleation and growth, material transport by diffusion and its effect on the size (radius) of the critical nucleus often plays a fundamental role in controlling the size of the products [6–11].

In particular, growth by diffusion has been studied as it applies to various problems such as precipitation from solution [6], liquid droplet nucleation from a supersaturated vapor [7], vapor bubble nucleation from a supersaturated solution [8], and colloidal particle formation [9] from solution. However, the nucleation and growth processes were studied separately in many cases [12,13]. Furthermore, nucleation by diffusion has not attracted much attention, except for a recent attempt to bridge diffusion and thermodynamic evolution [14–16]. Indeed, it is well recognized [10] that the evolution equation known as the Zeldovich relation [17,18] from classical nucleation theory (CNT) and the diffusional growth equation are formally the same for the postcritical nucleus.

In our previous paper [16], we pointed out that the two evolution equations based on the thermodynamic CNT and the kinetic diffusional growth equation lead to two different definitions of critical radii (i.e., *thermodynamic* and *kinetic*). However, except for the growth of bubbles in solution, the nucleation and growth of condensed matter proceeds via complex processes. For example, various biomaterials such as protein crystals are not formed directly from the bulk mother solution, but rather from within a phase-separated solution of an intermediate phase [5,19–21] to form a core-shell composite nucleus [22,23]. In fact, such a core-shell-type nucleus has bee observed by experiments [24] and by computer simulations [19,25–28]. Various model calculations [22,29–32] also suggest the existence of core-shell structure.

In this paper, we consider the problem of nucleation and growth of the core-shell-type nucleus in solution by diffusion. Therefore, we consider the two-step nucleation in a three-phase system [20] according to the Ostwald's step rule [31,33], as shown in Fig. 1. Initially, the precritical nucleus (embryo) of the intermediate metastable phase (metastable dense solution L_1) nucleates within the metastable mother solution L_2. Next, the stable crystal C nucleates from the intermediate metastable solution L_1. However, there will be a single composite core-shell critical nucleus with a single energy barrier [19,22,28,30,31]. In such a case, the core-shell critical nucleus forms through the diffusion of materials, which must occur in two steps: bulk diffusion in the original mother solution L_2 and the diffusion in the surrounding shell of the intermediate metastable solution L_1.

This work is complementary to our previous work [23], in which the same problem was considered from the standpoint of dynamics governed by the Fokker-Planck equation within the framework of CNT. Here, we consider the same problem by diffusion in real space. In Sec. II, we show that the evolution equations for the nucleus and shell will afford two distinct critical radii for the core nucleus and the shell. Furthermore, *both* the nuclear radius and the shell radius become stationary simultaneously at a single critical point, as if there were a single activation process. This is consistent with previous thermodynamic arguments [19,22], in which only a single saddle point that corresponded to the core-shell-type nucleus was identified. In Sec. III, we further show that by imposing the Ostwald-Freundlich boundary condition [15,16] for this core-shell system, these two critical radii are given by formulas similar to those of CNT. Finally, in Sec. IV, we discuss the results of our model and conclude by pointing out that the scenario given by this model would explain, qualitatively, some experimental and numerical observations of the core-shell-type nucleus.

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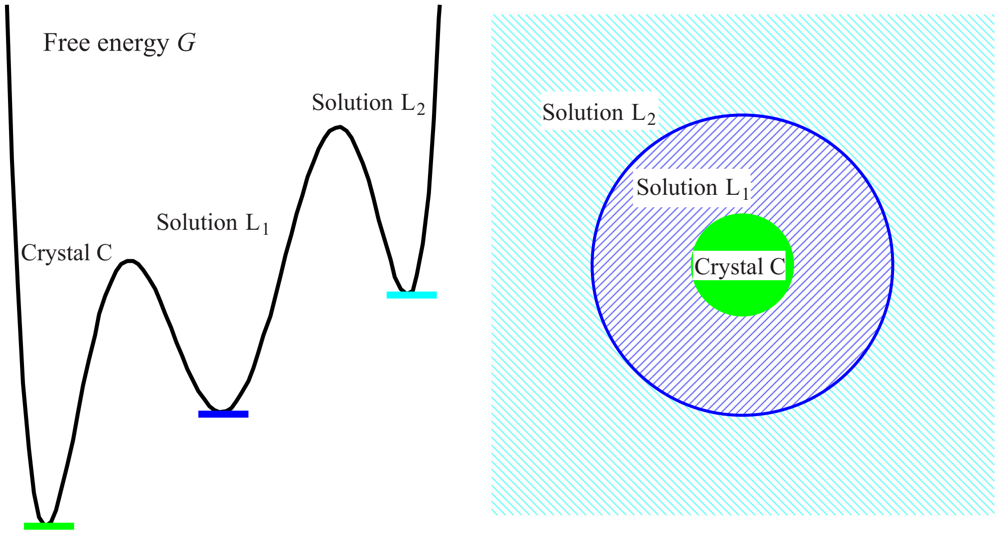

FIG. 1. A model of a core-shell-type composite nucleus in a three-phase system. The phase transition occurs from metastable solution L_2 to stable crystal C via the intermediate metastable solution L_1 ($L_2 \rightarrow L_1 \rightarrow C$) according to the Ostwald's step rule (left). The spherical crystal nucleus C is grown from the solution L_1, which is phase separated from the original mother solution L_2 to form a spherical shell around the crystal C. Therefore, the critical nucleus is the composite nucleus of core-shell structure (right).

II. NUCLEATION AND GROWTH OF A CORE-SHELL NUCLEUS FROM A TWO-PHASE SOLUTION BY DIFFUSION

We consider a spherical core-shell-type composite nucleus composed of a stable crystal phase (C) surrounded by an intermediate metastable liquid solution (L_1) nucleated in the original metastable mother liquid solution (L_2), shown in Fig. 1. Of course, the formation of such a core-shell-type embryo (precritical nuclear) needs additional thermodynamic discussion [19,22,30,31]. Here, we pay most attention to the critical and postcritical nucleus after forming such a core-shell-type embryo. We consider a two-step nucleation and growth process $L_2 \rightarrow L_1 \rightarrow C$ instead of one-step direct nucleation $L_2 \rightarrow C$. The crystal nucleus C with radius R_C is surrounded by an intermediate metastable solution L_1, which is separated at a radius R_L by a boundary from the original metastable solution L_2 (Fig. 1). The two liquid phases L_1 and L_2 are assumed to be phase separated.

When the crystal nucleus C is grown by diffusion, as shown in Fig. 2, the diffusional growth equation can be written as

$$\frac{dR_C}{dt} = -v_m j_{R_C}, \tag{1}$$

where v_m is the molecular volume in the nucleus C, and

$$j_{R_C} = -D_1 \left(\frac{\partial c_1}{\partial r}\right)\bigg|_{r=R_C} \tag{2}$$

is the diffusion flux (j_{R_C}) at the surface of the growing crystal nucleus, where c_1 is the concentration of solute (monomer), D_1 is the solute diffusivity in the solution L_1, and r is the radial coordinate from the center of the nucleus. Note that the incoming diffusional flux must be negative ($j_{R_C} < 0$) in order to feed the nucleus to grow. In Eq. (1), we have neglected the transport term due to the hydrodynamic flow [8,13] because we are mainly interested in the problem near the critical point where the growth of the nucleus becomes stationary ($dR_C/dt = 0$).

Now, the radius R_C of the crystal nucleus grows according to the incoming diffusion flux j_{R_C}. The concentration field $c_i(r,t)$, where $i = 1,2$ correspond to the solution L_1 and L_2, obeys the three-dimensional (3D) diffusion equation [6,10,34]

$$\frac{\partial c_i(r,t)}{\partial t} = \frac{D_i}{r}\frac{\partial^2}{\partial r^2}[rc_i(r,t)] \tag{3}$$

for spherical symmetry, where t denotes the time and D_i denotes the solute diffusivity of the two surrounding phases, L_1 and L_2. The steady state ($\partial c_2/\partial t = 0$) solution for the mother solution L_2 is given by

$$c_2(r) = c_{2,\infty} - [c_{2,\infty} - c_2(R_L)]\frac{R_L}{r}, \quad R_L < r, \tag{4}$$

where $c_2(R_L)$ is the concentration at the boundary of the two solutions L_1 and L_2 at R_L, and $c_{2,\infty} = c_2(r \rightarrow \infty)$ is the bulk

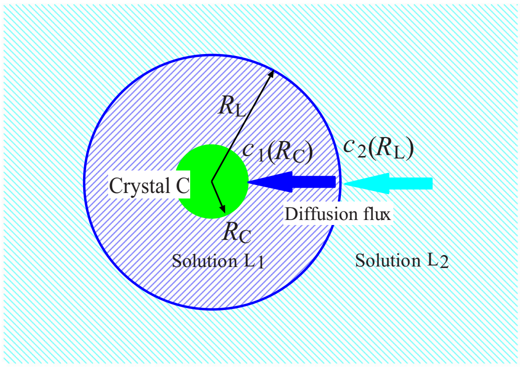

FIG. 2. A diffusion flux into the core-shell composite nucleus. A diffusion flux in the solution L_2 is absorbed into the shell of the solution L_1 and continues to diffuse in the solution L_1 into the stable crystal C. Two fluxes in solution L_2 and L_1 must connect continuously at the boundary of radius R_L.

(oversaturated) concentration of the metastable mother phase L_2. Similarly, the concentration profile of the monomers in the surrounding solution L_1 is given by

$$c_1(r) = \frac{R_L R_C[c_1(R_C) - c_1(R_L)]}{R_L - R_C}\frac{1}{r} + \frac{R_L c_1(R_L) - R_C c_1(R_C)}{R_L - R_C},$$
$$R_C < r < R_L, \tag{5}$$

where $c_1(R_C)$ is the concentration at the surface of the growing core nucleus at R_C, and $c_1(R_L)$ is the concentration at the (inner) boundary of the two solutions L_1 and L_2 at R_L. Note that these steady state concentrations do not depend on the diffusion coefficients D_1 and D_2.

Then, the diffusion flux in the surrounding solution L_1 is given by

$$\begin{aligned} j &= -D_1\left(\frac{\partial c_1}{\partial r}\right) \\ &= D_1\frac{R_L R_C[c_1(R_C) - c_1(R_L)]}{R_L - R_C}\frac{1}{r^2}, \quad R_C \leqslant r \leqslant R_L. \end{aligned} \tag{6}$$

Similarly, the diffusion flux in the surrounding solution L_2, outside the surrounding shell of the solution L_1, is given by

$$\begin{aligned} j &= -D_2\left(\frac{\partial c_2}{\partial r}\right) \\ &= -D_2[c_{2,\infty} - c_2(R_L)]\frac{R_L}{r^2}, \quad R_L \leqslant r. \end{aligned} \tag{7}$$

Since the two fluxes in Eqs. (6) and (7) must be continuous at $r = R_L$, two alternative forms for the flux j_{R_L} at R_L are obtained:

$$\begin{aligned} j_{R_L} &= D_1\frac{R_C[c_1(R_C) - c_1(R_L)]}{R_L(R_L - R_C)} \\ &= -D_2\frac{c_{2,\infty} - c_2(R_L)}{R_L}. \end{aligned} \tag{8}$$

Therefore, the fluxes j_{R_C}, at the inner radius $r = R_C$, are also given by two alternative forms, using either $c_1(r)$ or $c_2(r)$:

$$\begin{aligned} j_{R_C} &= D_1\frac{R_L[c_1(R_C) - c_1(R_L)]}{R_C(R_L - R_C)} \\ &= -D_2\left(\frac{R_L}{R_C}\right)\frac{c_{2,\infty} - c_2(R_L)}{R_C}. \end{aligned} \tag{9}$$

These two fluxes naturally satisfy the continuity of total flux:

$$4\pi R_C^2 j_{R_C} = 4\pi R_L^2 j_{R_L}. \tag{10}$$

Since these fluxes j_{R_C} and j_{R_L} must be negative for the post-critical nucleus, two inequalities $c_{2,\infty} > c_2(R_L)$ and $c_1(R_L) > c_1(R_C)$ hold from Eqs. (8) and (9).

Since the diffusion flux j_{R_C} at the crystal nuclear surface is incorporated into the growing nucleus, the radius R_C of the nucleus grows according to Eq. (1). On the other hand, the diffusion flux j_{R_L} at the surface of the L_1-L_2 boundary at R_L will be incorporated into both the surrounding solution L_1 and the nucleus C, so we must consider the conservation of material given by

$$\frac{dn_1}{dt} + \frac{dn_c}{dt} = -4\pi R_L^2 j_{R_L}, \tag{11}$$

where

$$n_c = \frac{4\pi}{3v_m}R_C^3 \tag{12}$$

is the number of monomers in the nucleus C, and

$$n_1 = \int_{R_C}^{R_L} 4\pi r^2 c_1(r)dr \tag{13}$$

is the number of monomers in the surrounding solution L_1. Then, Eq. (11), combined with Eqs. (12) and (13), leads to the evolution equation for R_L,

$$\frac{dR_L}{dt} = -\frac{1}{c_1(R_L)}j_{R_L} + \frac{R_C^2[1 - c_1(R_C)v_m]}{R_L^2 c_1(R_L)}j_{R_C}, \tag{14}$$

where we have replaced dR_C/dt with Eq. (1). The first term on the right-hand side denotes the increase in the number of monomers in solution L_1 due to the incoming flux j_{R_L}, and the second term denotes the decrease in the number of monomers in L_1 which are incorporated into nucleus C. Note that $c_1(R_C)v_m \ll 1$, as the molecular volume $1/c_1(R_C)$ in solution L_1 at the surface of the nucleus at R_C is much larger than the molecular volume v_m in the nucleus C.

Using Eq. (10), Eqs. (1) and (14) can be written as

$$\frac{dR_C}{dt} = -v_m j_{R_C} = -v_m\left(\frac{R_L^2}{R_C^2}\right)j_{R_L}, \tag{15}$$

$$\begin{aligned} \frac{dR_L}{dt} &= -v_m\left[\frac{c_1(R_C)}{c_1(R_L)}\right]j_{R_L} \\ &= -v_m\left(\frac{R_C^2}{R_L^2}\right)\left[\frac{c_1(R_C)}{c_1(R_L)}\right]j_{R_C}. \end{aligned} \tag{16}$$

Therefore, the stationary conditions $dR_C/dt = 0$ and $dR_L/dt = 0$ for the critical radius R_C^* and R_L^* will be satisfied simultaneously when $j_{R_C} = j_{R_L} = 0$, which leads to

$$c_2(R_L^*) = c_{2,\infty}, \tag{17a}$$

$$c_1(R_L^*) = c_1(R_C^*) = c_{1,\infty}, \tag{17b}$$

where $c_{1,\infty}$ is a fictitious concentration when the crystal nucleus C is surrounded only by the solution L_1 and the solute concentration $c_1(r)$ is given by a formula similar to Eq. (4). These simultaneous equations define the *kinetic critical radius* R_C^* and R_L^*. Therefore, there is a single core-shell-type critical nucleus which corresponds to a single saddle point [19,22]. The critical nucleus having the radii R_C^* and R_L^* is surrounded by a wetting layer of uniform solution L_1 with the concentration $c_1(r) = c_{1,\infty}$ from Eq. (5), which is surrounded further by a uniform solutions L_2 with the concentrations $c_2(r) = c_{2,\infty}$ of the metastable mother solution from Eq. (4).

We will not consider another solution $R_L^* \to \infty$ derived from Eq. (17a) because this solution corresponds to the direct nucleation from the metastable intermediate solution L_1 rather than the indirect nucleation from the mother solution L_2. Note that the stationary condition $dR_C/dt = 0$ or $j_{R_C} = 0$ inevitably leads to the stationarity of another radius $dR_L/dt = 0$ or $j_{R_L} = 0$ because of the conservation of material in Eq. (10). When the inner radius R_C becomes stationary, the outer radius R_L must also become stationary. Therefore, the critical nucleus is always a composite nucleus of core-shell structure.

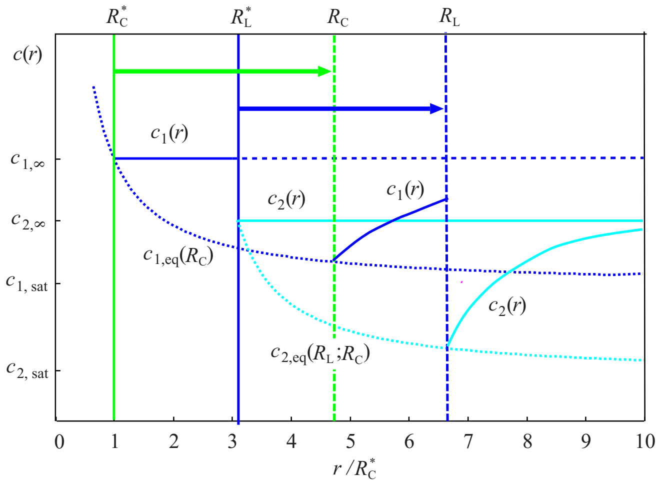

FIG. 3. Concentrations $c_1(r)$ and $c_2(r)$ of monomers around the growing nucleus as a function of distance r from the center of the nucleus. The critical nucleus having the radii R_C^* and R_L^* is surrounded by a wetting layer of uniform concentration $c_1(r) = c_1(R_C^*) = c_1(R_L^*) = c_{1,\infty}$, which is surrounded further by a uniform solution with the concentrations $c_2(r) = c_{2,\infty}$ of the metastable mother solution to form a core-shell critical nucleus. As the postcritical nucleus begins to grow ($R_C^* \to R_C$, $R_L^* \to R_L$), the concentrations $c_{1,\text{eq}}(R_C)$ and $c_{2,\text{eq}}(R_L;R_C)$ at the surface of both the core nucleus at R_C and outer boundary at R_L given by the Ostwald-Freundlich boundary condition in Eqs. (30) and (32) start to decrease. Then, the concentrations $c_1(r)$ of the solution L_1 and $c_2(r)$ of the solution L_2 are no longer uniform and concentration gradients appear around the nucleus, according to Eqs. (6) and (7), and diffusional flux ensures that the growing nucleus is fed.

In Fig. 3, we show a schematic concentration profile $c_1(r) = c_{1,\infty} = \text{const}$ and $c_2(r) = c_{2,\infty} = \text{const}$ for the core-shell critical nucleus with critical radii R_C^* and R_L^*. We also show a schematic concentration profile $c_1(r)$ and $c_2(r)$, which are not uniform, for a postcritical nucleus with $R_C > R_C^*$ and $R_L > R_L^*$. The concentration profile of the postcritical nucleus will be discussed in the next section using the thermodynamic argument.

III. OSTWALD-FREUNDLICH BOUNDARY CONDITION IN A TWO-PHASE SOLUTION

In order to find the boundary values $c_1(R_C)$ and $c_2(R_L)$, we will consider the chemical equilibrium of this composite core-shell nucleus. Within the capillarity approximation, the Gibbs free energy of the composite nucleus in Fig. 2 is given by

$$G(n_c,n_1) = -n_C\Delta\mu_1 - n_1\Delta\mu_2 + 4\pi R_C^2\gamma_{c,1} + 4\pi R_L^2\gamma_{1,2}, \tag{18}$$

where $\gamma_{c,1}$ and $\gamma_{1,2}$ are the surface tensions of the C-L_1 interface at R_C and of L_1-L_2 at R_L, respectively. The number of monomers n_C in the core and n_1 in the shell are given by Eqs. (12) and (13), respectively. The chemical potential differences $\Delta\mu_1$ and $\Delta\mu_2$ of the two solutions L_1 and L_2 relative to that of the stable core nucleus C are related to the bulk solute (oversaturated) concentrations $c_{1,\infty}$ and $c_{2,\infty}$ of the two solutions L_1 and L_2 through

$$\Delta\mu_1 = \beta^{-1}\ln(c_{1,\infty}/c_{1,\text{sat}}), \tag{19}$$

$$\Delta\mu_2 = \beta^{-1}\ln(c_{2,\infty}/c_{2,\text{sat}}), \tag{20}$$

with $\beta^{-1} = k_BT$ and $c_{i,\text{sat}}$ $(i = 1,2)$ being the saturation concentration of the two solutions which are equilibrium at the C-L_1 and L_1-L_2 flat interfaces. Note that $c_{2,\infty} = c_2(r \to \infty)$ [Eq. (4)] is the concentration of the oversaturated solution, which is larger than the saturation concentration $c_2(R_L \to \infty) = c_{2,\text{sat}}$. However, $c_{1,\infty}$ does not correspond to $c_1(r \to \infty)$ [Eq. (5)], but is larger than $c_1(R_C \to \infty) = c_{1,\text{sat}}$.

From Eq. (18) together with Eqs. (12) and (13), the chemical potential μ_C of the core nucleus C with radius R_C is given by

$$\begin{aligned}\mu_C(R_C) &= \frac{\partial \Delta G}{\partial n_C}\\ &= -v_m\Delta\mu_2[c_1(R_C^*) - c_1(R_C)]\\ &\quad -2v_m\gamma_{c,1}\left(\frac{1}{R_C^*} - \frac{1}{R_C}\right),\end{aligned} \tag{21}$$

where the critical radius R_C^* is given by an implicit equation,

$$\Delta\mu_1 - c_1(R_C^*)v_m\Delta\mu_2 = \frac{2\gamma_{c,1}v_m}{R_C^*}, \tag{22}$$

and is written formally as the classical CNT critical radius for the core nucleus,

$$R_C^* = \frac{2\gamma_{c,1}v_m}{\Delta\mu_{1,\text{eff}}}, \tag{23}$$

with

$$\Delta\mu_{1,\text{eff}} = \Delta\mu_1 - c_{1,\infty}v_m\Delta\mu_2, \tag{24}$$

where we have used $c_{1,\infty} = c_1(R_C^*)$, is the effective supersaturation of the solution phase L_1 for the critical nucleus. Note that $c_{1,\infty}v_m \ll 1$ so that $\Delta\mu_{1,\text{eff}} \simeq \Delta\mu_1$. Then, Eq. (23) becomes exactly the CNT critical radius when the crystal C is directly nucleated from the intermediate metastable solution L_1.

Similarly, the chemical potential μ_1 of the spherical shell of the surrounding solution L_1 with the outer radius R_L and the inner radius R_C is given by

$$\begin{aligned}&\mu_1(R_L;R_C)\\ &\quad = \frac{\partial \Delta G(n_C,n_1)}{\partial n_1}\\ &\quad = \frac{\Delta\mu_2}{c_1(R_L)}[c_1(R_L^*) - c_1(R_L)] - \frac{2\gamma_{1,2}}{c_1(R_L)}\left(\frac{1}{R_L^*} - \frac{1}{R_L}\right)\\ &\qquad + \frac{\Delta\mu_2}{c_1(R_C)}[c_1(R_C^*) - c_1(R_C)] + \frac{2\gamma_{c,1}}{c_1(R_C)}\left(\frac{1}{R_C^*} - \frac{1}{R_C}\right),\end{aligned} \tag{25}$$

where, again, the critical radius R_L^* is given by

$$R_L^* = \frac{2\gamma_{1,2}}{c_{1,\infty}\Delta\mu_2}, \tag{26}$$

where we have used $c_1(R_L^*) = c_{1,\infty}$ from Eq. (17b). The critical radius in Eq. (26) is given exactly by the CNT formula when a solution L_1 is nucleated from the mother solution L_2. Note that the chemical potential μ_1 in Eq. (25) depends indirectly on the core radius R_{C}. Then Eq. (21) is written as

$$\mu_{\mathrm{C}}(R_{\mathrm{C}}) = -\frac{2v_{\mathrm{m}}\gamma_{1,2}}{R_{\mathrm{L}}^{*}c_{1,\infty}}[c_{1,\infty} - c_1(R_{\mathrm{C}})] - 2v_{\mathrm{m}}\gamma_{\mathrm{c},1}\left(\frac{1}{R_{\mathrm{C}}^{*}} - \frac{1}{R_{\mathrm{C}}}\right), \tag{27}$$

and Eq. (25) is written as

$$\begin{aligned}\mu_1(R_{\mathrm{L}};R_{\mathrm{C}}) &= \frac{2\gamma_{1,2}}{R_{\mathrm{L}}^{*}}\left[\frac{1}{c_1(R_{\mathrm{L}})} - \frac{1}{c_{1,\infty}}\right] - \frac{2\gamma_{1,2}}{c_1(R_{\mathrm{L}})}\left(\frac{1}{R_{\mathrm{L}}^{*}} - \frac{1}{R_{\mathrm{L}}}\right)\\ &\quad + \frac{2\gamma_{1,2}}{R_{\mathrm{L}}^{*}}\left[\frac{1}{c_1(R_{\mathrm{C}})} - \frac{1}{c_{1,\infty}}\right] + \frac{2\gamma_{\mathrm{c},1}}{c_1(R_{\mathrm{C}})}\left(\frac{1}{R_{\mathrm{C}}^{*}} - \frac{1}{R_{\mathrm{C}}}\right),\end{aligned} \tag{28}$$

where we have used Eq. (17b). Equations (27) and (28) are the thermodynamic driving force of the growing nucleus.

Therefore, if the surrounding solution L_1 is always in chemical equilibrium with the core nucleus at the C-L_1 interface at R_{C}, the concentration at the interface $c_1(R_{\mathrm{C}})$ is given by the equilibrium concentration $c_{1,\mathrm{eq}}(R_{\mathrm{C}})$, which is related to the chemical potential μ_{C} of the core nucleus C given by Eq. (27) through

$$\mu_{\mathrm{C}}(R_{\mathrm{C}}) = \beta^{-1}\ln[c_{1,\mathrm{eq}}(R_{\mathrm{C}})/c_{1,\infty}], \tag{29}$$

which leads to the Ostwald-Freundlich (OF) or Gibbs-Thomson equation given by

$$c_{1,\mathrm{eq}}(R_{\mathrm{C}}) = c_{1,\infty}\exp[\beta\mu_{\mathrm{C}}(R_{\mathrm{C}})]. \tag{30}$$

Then, $c_{1,\mathrm{eq}}(R_{\mathrm{C}}^{*}) = c_{1,\infty}$ at the critical point of nucleation from Eq. (17b) because $\mu_{\mathrm{C}}(R_{\mathrm{C}}^{*}) = 0$. The concentration $c_{1,\mathrm{eq}}(R_{\mathrm{C}})$ is expected to decrease monotonically as a function of R_{C} from Eq. (27).

Similarly, if the solution L_2 is in chemical equilibrium with a droplet shell of the solution L_1 with the outer radius R_{L} and inner radius R_{C}, the concentration at the interface $c_2(R_{\mathrm{L}})$ is given by the equilibrium concentration $c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})$, which is related to the chemical potential $\mu_1(R_{\mathrm{L}};R_{\mathrm{C}})$ of the shell given by Eq. (28) through

$$\mu_1(R_{\mathrm{L}};R_{\mathrm{C}}) = \beta^{-1}\ln[c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})/c_{2,\infty}], \tag{31}$$

which leads to the OF equation given by

$$c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}}) = c_{2,\infty}\exp[\beta\mu_1(R_{\mathrm{L}};R_{\mathrm{C}})]. \tag{32}$$

Note that the concentration $c_2(R_{\mathrm{L}}) = c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})$ at the boundary R_{L} depends on the radius R_{C}. The equilibrium concentration $c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})$ is also expected to decrease monotonically as a function of R_{L} for a fixed R_{C} from Eq. (28). At the critical point with R_{L}^{*} and R_{C}^{*}, $c_{2,\mathrm{eq}}(R_{\mathrm{L}}^{*};R_{\mathrm{C}}^{*}) = c_{2,\infty}$ because $\mu_1(R_{\mathrm{L}}^{*};R_{\mathrm{C}}^{*}) = 0$ from Eq. (28).

When the core nucleus C and the surrounding solution L_1 are always in chemical equilibrium, $c_1(R_{\mathrm{C}}) = c_{1,\mathrm{eq}}(R_{\mathrm{C}})$. Similarly, when the surrounding spherical shell of solution L_1 and the mother solution L_2 are always in chemical equilibrium, $c_2(R_{\mathrm{L}}) = c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})$. The concentration $c_1(R_{\mathrm{L}}) \neq c_{1,\mathrm{eq}}(R_{\mathrm{L}})$ is determined from the continuity condition of Eqs. (8) and (9). Two equilibrium concentrations $c_{1,\mathrm{eq}}(R_{\mathrm{C}})$ and $c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})$ are determined from the implicit equations (27), (30), (28), and (32) by replacing $c_1(R_{\mathrm{C}})$ by $c_{1,\mathrm{eq}}(R_{\mathrm{C}})$ and $c_2(R_{\mathrm{L}})$ by $c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})$

In Fig. 3, we show a schematic concentration profile $c_1(r)$ and $c_2(r)$ given by Eqs. (5) and (4) as well as $c_{1,\mathrm{eq}}(R_{\mathrm{C}})$ and $c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})$ (for a fixed R_{C}) at the boundaries for the postcritical core-shell critical nucleus with $R_{\mathrm{C}} > R_{\mathrm{C}}^{*}$ and $R_{\mathrm{L}} > R_{\mathrm{L}}^{*}$.

For the postcritical nucleus, the concentration profiles $c_1(r)$ and $c_2(r)$ given by Eqs. (5) and (4) are no longer uniform and the depletion zone increases. Since the two interfaces at R_{C} and R_{L} become flat as $R_{\mathrm{C}} \to \infty$ and $R_{\mathrm{L}} \to \infty$, two concentrations $c_{1,\mathrm{eq}}(R_{\mathrm{C}})$ and $c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})$ at the boundaries must approach their saturation concentration at the flat interface $c_{1,\mathrm{sat}}$ and $c_{2,\mathrm{sat}}$. Therefore, we have

$$c_{1,\mathrm{eq}}(R_{\mathrm{C}}) \to c_{1,\mathrm{sat}}, \tag{33}$$

$$c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}}) \to c_{2,\mathrm{sat}}, \tag{34}$$

as shown in Fig. 3

When the radii R_{C} and R_{L} are close to the critical radii R_{C}^{*} and R_{L}^{*}, we can replace $c_2(R_{\mathrm{L}})$ with $c_{2,\mathrm{eq}}(R_{\mathrm{L}};R_{\mathrm{C}})$ in Eqs. (8) and (9), and expand the exponential in Eq. (32). Then the driving forces $j_{R_{\mathrm{C}}}$ and $j_{R_{\mathrm{L}}}$ of growing nucleus radii are given by

$$j_{R_{\mathrm{C}}} = D_2\left(\frac{R_{\mathrm{L}}}{R_{\mathrm{C}}}\right)\frac{\beta c_{2,\infty}\mu_1(R_{\mathrm{L}};R_{\mathrm{C}})}{R_{\mathrm{C}}}, \tag{35}$$

$$j_{R_{\mathrm{L}}} = D_2\frac{\beta c_{2,\infty}\mu_1(R_{\mathrm{L}};R_{\mathrm{C}})}{R_{\mathrm{L}}}. \tag{36}$$

Not only the growth velocity dR_{C}/dt but also dR_{L}/dt vanish at the critical point when $R_{\mathrm{C}} = R_{\mathrm{C}}^{*}$ and $R_{\mathrm{L}} = R_{\mathrm{L}}^{*}$ because $\mu_1(R_{\mathrm{C}}^{*},R_{\mathrm{L}}^{*}) = 0$ from Eq. (28).

Equations (15) and (16) combined with Eqs. (35) and (36) are similar in form to the Zeldovich relation [16,18] derived from the thermodynamic evolution equation [10,16,18]. Therefore, the Zeldovich relation can be equivalent to the diffusional growth equation in our core-shell nucleus as well. However, this is valid only near the thermodynamic critical point with critical radii R_{C}^{*} and R_{L}^{*}, as it is recognized that the expansion of the exponential in Eq. (32) is valid only near the critical radius, and the full expression in Eqs. (30) and (32) will be necessary to describe the subsequent growth of the nucleus [35].

Now, we can discuss the evolution of this composite core-shell nucleus from Eqs. (35) and (36). When the concentration is uniform and oversaturated [$c_1(r) = c_{1,\infty} > c_{1,\mathrm{sat}}$ and $c_2(r) = c_{2,\infty} > c_{2,\mathrm{sat}}$], the core radius R_{C} and the outer-shell radius R_{L} reach the critical radius R_{C}^{*} and R_{L}^{*} simultaneously. Therefore, there is only a *single critical point* which corresponds to a *single critical nucleus* characterized by *two critical radii* R_{C}^{*} and R_{L}^{*}. After passing through this single critical point characterized by *a single energy barrier*, two radii R_{C} and R_{L} of the core-shell nucleus start to increase. The growth of the nucleus exactly follows exactly the same scenario given by CNT, by regarding the R_{C} and R_{L} as the radius of nucleus.

In the limit of $R_{\mathrm{C}} \to \infty$ and $R_{\mathrm{L}} \to \infty$, we have

$$j_{R_{\mathrm{C}}} \to -D_2 \frac{c_{2,\infty} - c_{2,\mathrm{sat}}}{R_{\mathrm{C}}}, \tag{37}$$

$$j_{R_{\mathrm{L}}} \to -D_2 \frac{c_{2,\infty} - c_{2,\mathrm{sat}}}{R_{\mathrm{L}}}, \tag{38}$$

from Eqs. (8), (9), and (34). Then the evolution equations (15) and (16) are written as

$$R_{\mathrm{C}} \frac{dR_{\mathrm{C}}}{dt} = v_{\mathrm{m}} D_2 (c_{2,\infty} - c_{2,\mathrm{sat}}), \tag{39}$$

$$R_{\mathrm{L}} \frac{dR_{\mathrm{L}}}{dt} = v_{\mathrm{m}} D_2 (c_{2,\infty} - c_{2,\mathrm{sat}}). \tag{40}$$

Therefore, two radii grow according to the classical law [6,34] $R_{\mathrm{C}} \propto \sqrt{t}$ and $R_{\mathrm{L}} \propto \sqrt{t}$. Furthermore, $R_{\mathrm{L}}^2 - R_{\mathrm{C}}^2 \to \mathrm{const.}$ Then, the radius R_{C} eventually catches up to R_{L} as $R_{\mathrm{C}} \to \infty$ and the surrounding shell of solution L_1 disappears, as the Ostwald's step rule predicted [31,33].

IV. DISCUSSION AND CONCLUSION

In this paper, we considered the evolution of a core-shell-type nucleus. The diffusional growth equations both for the core nucleus and the surrounding shell lead to two evolution equations similar to the Zeldovich equation of classical nucleation theory (CNT). Therefore, the kinetic critical radii for both the core radius and the surrounding shell radius can be defined, and there must be a single core-shell critical nucleus which corresponds to a single critical point and a single energy barrier. When diffusion is so fast that the concentrations at the two surfaces are maintained at the value given by the equilibrium Ostwald-Freundlich boundary condition, simple expressions similar to those for the thermodynamic critical radius of CNT can be derived. Our formulation further predicts a growing postcritical nucleus with a core nucleus surrounded by a metastable intermediate solution, whose thickness will be decreased during the course of evolution in accordance with the Ostwald's step rule.

Although our discussion takes into account the two-step diffusion of a composite nucleus, a more thorough consideration not only of the diffusion processes but also of the reaction and the reorganization processes within the bulk crystal nucleus is required to understand the growth of a near-spherical solid nucleus, since simple diffusional attachment is known to lead to nonspherical fractal structures [36,37]. Numerical simulations such as the kinetic Monte Carlo method [2,38] hold the greatest potential for the study of such reorganization processes. Finally, since we considered only the material diffusion and neglected the heat flow, the instability and fractal growth [39] of the nucleus caused by thermal diffusion cannot be discussed within our present formalism.

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APPENDIX

Here, we have provided the results for the two-dimensional (2D) circular core-shell nucleus. The main differences from the three-dimensional (3D) spherical nucleus of the main text are the mathematical forms of the solution of diffusion equation and the thermodynamic Ostwald-Freundlich condition.

The solution of the 2D diffusion equation (3) is written as [40]

$$\begin{aligned} c_1(r) = {} & \frac{c_1(R_{\mathrm{L}}) - c_1(R_{\mathrm{C}})}{\ln R_{\mathrm{L}} - \ln R_{\mathrm{C}}} \ln r \\ & + \frac{c_1(R_{\mathrm{C}}) \ln R_{\mathrm{L}} - c_1(R_{\mathrm{L}}) \ln R_{\mathrm{C}}}{\ln R_{\mathrm{L}} - \ln R_{\mathrm{C}}}, \\ & R_{\mathrm{C}} < r < R_{\mathrm{L}}, \end{aligned} \tag{A1}$$

$$\begin{aligned} c_2(r) = {} & \frac{c_{2,\infty} - c_2(R_{\mathrm{L}})}{\ln R_\infty - \ln R_{\mathrm{L}}} \ln r \\ & + \frac{c_2(R_{\mathrm{L}}) \ln R_\infty - c_{2,\infty} \ln R_{\mathrm{L}}}{\ln R_\infty - \ln R_{\mathrm{L}}}, \\ & R_{\mathrm{L}} < r < R_\infty, \end{aligned} \tag{A2}$$

where R_∞ is the large radius from the nucleus and $c_{2,\infty}$ is the concentration at this distance.

The free energy of the core-shell nucleus in the 2D case that corresponds to Eq. (18) is written as

$$G(n_{\mathrm{c}}, n_1) = -n_{\mathrm{C}} \Delta\mu_1 - n_1 \Delta\mu_2 + 2\pi R_{\mathrm{C}} \gamma_{c,1} + 2\pi R_{\mathrm{L}} \gamma_{1,2}, \tag{A3}$$

with

$$n_{\mathrm{C}} = \frac{\pi}{v_{\mathrm{m}}} R_{\mathrm{C}}^2 \tag{A4}$$

and

$$n_1 = \int_{R_{\mathrm{C}}}^{R_{\mathrm{L}}} 2\pi r c_1(r) dr. \tag{A5}$$

Following the same procedure as that of Sec. III, the critical radius R_{C}^* which corresponds to Eq. (23) is given by

$$R_{\mathrm{C}}^* = \frac{\gamma_{\mathrm{c},1} v_{\mathrm{m}}}{\Delta\mu_{1,\mathrm{eff}}}, \tag{A6}$$

where $\Delta\mu_{1,\mathrm{eff}}$ is given by Eq. (24). The critical radius R_{L}^* of the intermediate metastable solution is give by the formula

$$R_{\mathrm{L}}^* = \frac{\gamma_{1,2}}{c_{1,\infty} \Delta\mu_2}, \tag{A7}$$

similar to Eq. (26). Therefore, Eqs. (A6) and (A7) can be derived from Eqs. (23) and (26) by replacing $2\gamma_{c,1}$ with $\gamma_{c,1}$, and $2\gamma_{1,2}$ with $\gamma_{1,2}$. Using the same replacement in Eqs. (27) and (28), we can derive the formula for the chemical potentials $\mu_{\mathrm{C}}(R_{\mathrm{C}})$ and $\mu_{\mathrm{L}}(R_{\mathrm{C}}, R_{\mathrm{L}})$ in the two-dimensional case. The evolution of the nucleus is described by Eqs. (15) and (16) with Eqs. (35) and (36). Therefore, the scenario of nucleation and growth of the two-dimensional core-shell nucleus is the same as that of the three-dimensional nucleus.

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