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Classical nucleation theory for solute precipitation amended with diffusion and reaction processes near the interface

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During the processes of nucleation and growth of a precipitate cluster from a supersaturated solution, the diffusion flux between the cluster and the solution changes the solute concentration near the cluster-solution interface from its average bulk value. This feature affects the rates of attachment and detachment of solute atoms at the interface, and, therefore, the entire nucleation-growth kinetics is altered. Unless quite obvious, this effect has been ignored in classical nucleation theory. To illustrate the results of this approach, for the case of homogeneous nucleation, we calculate the total solubility and the nucleation rate as functions of two parameters of the model (the reduced interface energy and the inverse second Damköhler number), and we compare these results to the classical ones. One can conclude that discrepancies with classical nucleation theory are great in the diffusion-limited regime, when the rate of bulk diffusion is small compared to the rate of interface reactions, while in the opposite interface-limited case they vanish.

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Normally, first-order phase transitions within the binodal-spinodal gap occur along the nucleation-growth-coarsening sequence. If the chemical composition of the initial and final phases is equal, the transition is called polymorphic (e.g., freezing and condensation). In this case, the transition kinetics is controlled entirely by the rate of interface reactions, and the transition occurs in the *interface-limited* regime. On the other hand, the kinetics of precipitation from a solution depends also on the rate of the bulk solute diffusion. A diffusion flux between a precipitate cluster and an ambient solution creates a nonuniform solute concentration profile around the cluster. If the cluster is subcritical, the diffusion flux is directed outside of it and the local solute concentration near the cluster-solution interface exceeds the average one. In the case of the supercritical cluster, the diffusion flux is directed inside it and the local solute concentration near the interface is less than the average one. This perturbation of the solute concentration profile around the clusters has been recently observed in kinetic Monte Carlo simulations [1]. Obviously, this fact has to be taken into account when one calculates the nucleation barrier. Nevertheless, this perturbation is neglected in the classical nucleation theory (CNT), and the solute concentration outside of the clusters is set equal to the average one (see, e.g., Ref. [2] and references therein). To overcome this disadvantage, different two-step nucleation pathways, including intermediate-concentration states between the parent solution and the final precipitate phase, were considered. For example, Lutsko has recently shown that the nucleation scenario including long-range low-amplitude concentration fluctuations is much more probable than the direct classical one [3]. Peters studied the coupling between slow diffusion transport and nucleation using the diffusion equation with the Ostwald-Freundlich boundary condition to show that certain types of concentration profiles can drive a classically precritical nucleus over the nucleation barrier [4]. With a similar approach, Iwamatsu [5] introduced a kinetic critical size different from the thermodynamic one, thus demonstrating the importance of kinetic effects for the choice of a nucleation pathway. For an extended description of the recent progress in nucleation theory and simulations, see, e.g., a review by Agarwal and Peters [6]. Unfortunately, the models mentioned above are restricted to the *diffusion-limited* case, when the rate of diffusion is small compared to the rate of interface reactions. In this case local thermodynamic equilibrium at the cluster interface is assumed. To build a general theory, applicable in the whole diffusion-limited to interface-limited range, a linked-flux model has been introduced by Russell [7] and further developed by Kelton [8]. It considers an intermediate nearest-neighbor shell between the cluster and the solution, which exchanges solute atoms with both adjacent phases. A number (or a concentration) of solute atoms in this shell is an additional characteristic of the cluster, which enters the free-energy functional along with the number of atoms inside the cluster. But again, the solute concentration outside of the shell is set equal to the average one, giving a somewhat artificial "staircase" picture of the solute concentration profile. In this paper, the solute concentration profile is calculated from a diffusion equation with an unusual boundary condition [see Eq. (12) below], derived from the balance equation for solute atoms inside the cluster. Modified expressions for the attachment and detachment rates are then used in the Becker-Döring scheme [9] to consider the kinetics of solute precipitation and to compare the new results to the CNT ones.

The rate of precipitation, being the first-order phase transition, is conventionally described by the value of the flux of clusters in the dimension space [9]:

$$J_{n,n+1} = w^{(+)}_{n,n+1} g(n,t) - w^{(-)}_{n+1,n} g(n+1,t), \tag{1}$$

where $g(n,t)$ is a time-dependent distribution function (a concentration of the clusters consisting of n atoms) and $w^{(+)}_{n,n+1}$ and $w^{(-)}_{n+1,n}$ are, respectively, the rates of attachment and detachment of solute atoms at the cluster-solution interface. The special case when the flux (1) is zero for any n:

$$J_{n,n+1} = 0, \quad \forall\, n, \tag{2}$$

corresponds to the state of detailed balance, when the precipitating phase is in equilibrium with the solution. The

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equilibrium [corresponding to the state of detailed balance (2)] distribution function $g_{\mathrm{eq}}(n)$ can be expressed in Boltzmann form [2]:

$$g_{\mathrm{eq}}(n) = C \exp[-G(n)/k_{\mathrm{B}}T], \tag{3}$$

where C is a normalization constant, k_{B} is Boltzmann's constant, T is the temperature, and $G(n)$ is a value of the thermodynamic potential of a heterogeneous system consisting of the n-atom cluster and the perturbed solution.

One can consider the process of clusterization as a sequence of elementary reversible attachment reactions [see Eq. (8) below], in which a dissolved atom, located at a one-elementary-jump distance from the interface, joins the cluster. From the thermodynamic point of view, the work of attachment of a dissolved atom to the n-atom cluster is equal to the difference of the thermodynamic potentials $G(n+1) - G(n)$. On the other hand, in the continual approximation ($n \gg 1$), the work of attachment is equal to the difference $\Delta\mu(n)$ between the chemical potential of a clusterized atom and that of a dissolved atom, located at a one-elementary-jump distance from the interface. Therefore, supposing that the cluster is a sphere with a radius of

$$r_{\mathrm{n}} = r_0\sqrt[3]{n}, \quad r_0 = \sqrt[3]{3\omega_0/4\pi}, \tag{4}$$

ω_0 being an average volume per atom of the cluster, in the capillarity approximation the work of attachment is as follows (see Appendix A for details):

$$G(n+1) - G(n) \underset{n\gg 1}{=} \Delta\mu(n) = k_{\mathrm{B}}T \ln\left[\frac{c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}})}{c_{\mathrm{s}}(r_{\mathrm{n}})}\right], \tag{5}$$

where $c_{\mathrm{s}}(r_{\mathrm{n}})$ is a quasistationary concentration of dissolved atoms near the interface [see Eq. (14) below] and

$$c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}}) = c_{\mathrm{s}}^{\mathrm{eq}} \exp\left(\frac{\alpha}{\sqrt[3]{n}}\right), \quad \alpha = \frac{8\pi r_0^2\sigma}{3k_{\mathrm{B}}T} \tag{6}$$

is a size-dependent thermodynamic equilibrium solute concentration at the interface, with a reduced interfacial energy α, being a dimensionless thermodynamic parameter of the model. Equation (6) is a form of the Gibbs-Thomson relation, where $c_{\mathrm{s}}^{\mathrm{eq}}$ represents thermodynamic equilibrium solubility, and σ is a coefficient of tension at the cluster interface. Therefore, in the state of detailed balance (2), with the equilibrium distribution function given by Eq. (3) and the work of attachment given by Eq. (5), from Eq. (1) one can derive a ratio of the attachment and detachments rates as follows:

$$\frac{w_{n,n+1}^{(+)}}{w_{n+1,n}^{(-)}} = \exp\left[-\frac{G(n+1)-G(n)}{k_{\mathrm{B}}T}\right] = \frac{c_{\mathrm{s}}(r_{\mathrm{n}})}{c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}})}. \tag{7}$$

Assuming that the solute concentration profile around the cluster remains unperturbed, one can set $c_{\mathrm{s}}(r_{\mathrm{n}}) = \bar{c}_{\mathrm{s}}$ ($\bar{c}_{\mathrm{s}}$ being the average bulk solute concentration) in Eq. (5) to obtain from Eq. (7) the CNT result $w_{n,n+1}^{(+)[\mathrm{CNT}]}/w_{n+1,n}^{(-)[\mathrm{CNT}]} = \bar{c}_{\mathrm{s}}/c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}})$ [see Eqs. (21) and (22) below].

The elementary acts of attachment and detachment of solute atoms at the cluster-solution interface can be considered as a reversible chemical reaction:

$$A_{\mathrm{s}} \rightleftharpoons A_{\mathrm{c}}, \tag{8}$$

where A_{s} and A_{c} denote a solute atom in the dissolved and clusterized states, respectively. The elementary reactions (8) take place within a spherical interface layer with a radius of r_{n} and a thickness equal to the mean elementary jump distance d. Let the direct reaction (attachment) be characterized by a reaction rate constant k. Since the concentration of dissolved atoms A_{s} within the interface layer is $c_{\mathrm{s}}(r_{\mathrm{n}})$, the total rate of attachment within the layer is

$$w_{n,n+1}^{(+)} = 4\pi r_{\mathrm{n}}^2 dk c_{\mathrm{s}}(r_{\mathrm{n}}). \tag{9}$$

Now, using Eq. (7), one can derive the rate of detachment as follows:

$$w_{n+1,n}^{(-)} = 4\pi r_{\mathrm{n}}^2 dk c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}}). \tag{10}$$

The value of solute concentration at the interface $c_{\mathrm{s}}(r_{\mathrm{n}})$ can be obtained as a result of solution of the quasistationary diffusion boundary problem. A discussion of the range of validity of the quasistationary approximation is presented in Appendix B.

The quasistationary spherically symmetric solute concentration profile $c_{\mathrm{s}}(r)$ around the cluster is subject to the diffusion equation:

$$\frac{\partial}{\partial r}[r^2 j(r)] = 0, \quad j(r) = -D\frac{\partial c_{\mathrm{s}}(r)}{\partial r}, \tag{11}$$

where D is a solute diffusion coefficient in the solution.

The normal component [10] of the solute flux across the interface is proportional to the difference of the detachment (10) and attachment (9) rates:

$$j(r_{\mathrm{n}}) = \frac{w_{n+1,n}^{(-)} - w_{n,n+1}^{(+)}}{4\pi r_{\mathrm{n}}^2} = \frac{D}{r_0\lambda}\left[c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}}) - c_{\mathrm{s}}(r_{\mathrm{n}})\right],$$
$$\lambda = \frac{D}{r_0 dk}, \tag{12}$$

where λ is a dimensionless kinetic parameter of the model, proportional to the inverse of the second Damköhler number $\mathrm{Da}_{\mathrm{II}}$ (see, e.g., Ref. [11]).

One can consider the second boundary condition as follows:

$$c_{\mathrm{s}}(\infty) = \bar{c}_{\mathrm{s}}. \tag{13}$$

By solving the diffusion equation (11) with the boundary conditions (12) and (13), and substituting Eq. (4) for the cluster radius, one obtains the following expression for the value of solute concentration at the interface (see, e.g., Ref. [12]):

$$c_{\mathrm{s}}(r_{\mathrm{n}}) = \bar{c}_{\mathrm{s}} + \frac{\sqrt[3]{n}\left[c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}}) - \bar{c}_{\mathrm{s}}\right]}{\sqrt[3]{n} + \lambda}. \tag{14}$$

From Eq. (14) one can see that, for finite values of the parameter λ, the quasistationary value of solute concentration at the interface lies between the values of $\bar{c}_{\mathrm{s}}$ and $c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}})$. In the diffusion-limited regime, when the rate of diffusion is much less than the rate of interfacial reactions, $\lambda \ll \sqrt[3]{n}$ and $c_{\mathrm{s}}(r_{\mathrm{n}}) = c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}})$. In the interface-limited regime, when the rate of interfacial reactions is much less than the rate of diffusion, $\lambda \gg \sqrt[3]{n}$ and the CNT assumption $c_{\mathrm{s}}(r_{\mathrm{n}}) = \bar{c}_{\mathrm{s}}$ holds. However, in a general case, the parameter λ takes finite values (see, e.g., Ref. [11]), so that neither a diffusion-limited nor an interface-limited simplified picture is valid.

Below, as an example, we study the process of homogeneous precipitation from a supersaturated solution in the framework of the Becker-Döring approach [9]. The distribution function $g(n,t)$ of the clusters is subject to the next kinetic (master) equation [9], valid for $n > 1$:

$$dg(n,t)/dt = J_{n-1,n} - J_{n,n+1}. \tag{15}$$

The system of Eqs. (15) must be supplemented with an additional equation for the reduced bulk solute concentration

$$g(1,t) = \bar{c}_{\rm s}(t)/c_{\rm s}^{\rm eq} \tag{16}$$

to satisfy the law of conservation of the total solute concentration q [see Eq. (24) below]:

$$dg(1,t)/dt = -\sum_{n=2}^{\infty} n\, dg(n,t)/dt. \tag{17}$$

From Eqs. (9) and (10), taking into account Eqs. (14) and (6), one finds

$$w_{n,n+1}^{(+)} = \frac{1}{t_{\rm nucl}} \frac{\sqrt[3]{n^2}}{\lambda} \exp\left(\frac{\alpha}{\sqrt[3]{n}}\right) \times \left\{1 + \left[g(1,t)\exp\left(-\frac{\alpha}{\sqrt[3]{n}}\right) - 1\right]\frac{\lambda}{\lambda + \sqrt[3]{n}}\right\}, \tag{18}$$

$$w_{n+1,n}^{(-)} = \frac{1}{t_{\rm nucl}} \frac{\sqrt[3]{n^2}}{\lambda} \exp\left(\frac{\alpha}{\sqrt[3]{n}}\right), \tag{19}$$

where

$$t_{\rm nucl} = \left(4\pi r_0 D c_{\rm s}^{\rm eq}\right)^{-1} \tag{20}$$

is a characteristic nucleation time scale. With a different approach, the same result was recently obtained for a particular case of precipitation from solid solutions [13].

Equations (18) and (19) for the rates of attachment and detachment at the interface need to be compared to the corresponding equations, derived in the framework of the CNT (see, e.g., Ref. [2] and references therein). In the present notations, the CNT expressions for the rates of attachment and detachment are as follows:

$$w_{n,n+1}^{(+)[\rm CNT]} = \frac{1}{t_{\rm nucl}} \frac{\sqrt[3]{n^2}}{\lambda + \sqrt[3]{n}} g(1,t), \tag{21}$$

$$w_{n+1,n}^{(-)[\rm CNT]} = \frac{1}{t_{\rm nucl}} \frac{\sqrt[3]{n^2}}{\lambda + \sqrt[3]{n}} \exp\left(\frac{\alpha}{\sqrt[3]{n}}\right). \tag{22}$$

From Eq. (21) one can see that $w_{n,n+1}^{(+)[\rm CNT]} = 0$ for $\bar{c}_{\rm s} = 0$, while, according to Eq. (14), the quasistationary concentration of solute atoms near the interface remains finite in this case: $c_{\rm s}(r_{\rm n}) = c_{\rm s}^{\rm eq}(r_{\rm n})\sqrt[3]{n}/(\sqrt[3]{n} + \lambda)$. It means that, once a solute atom has been detached from the interface (via one elementary jump), in the framework of the CNT it has to diffuse into the bulk of the solution, with no chance to be attached back on the next step. Therefore, Eq. (21) is inconsistent with the principle of reversibility of the interface reactions (8). On the other hand, from general speculations it follows that the rate of detachment ("evaporation") must be proportional to the area of the interface, i.e., $w_{n+1,n}^{(-)} \propto \sqrt[3]{n^2}$. In the present theory, this condition is satisfied for any n [see Eq. (19)], while in the CNT it is satisfied only for $\sqrt[3]{n} \ll \lambda$ [see Eq. (22)]. Therefore, by neglecting the perturbation of the solute concentration profile near the interface, the CNT underestimates the rates of detachment and attachment of solute atoms. One can note that the pairs of Eqs. (18), (21) and (19), (22) are asymptotically equivalent for $\lambda \gg \sqrt[3]{n}$. Great values of the parameter λ correspond to the interface-limited precipitation regime, when the mobility of dissolved atoms at the interface is small compared to the bulk one. In this case, the solute concentration profile around the cluster is flat and one can get from Eq. (14) $c_{\rm s}(r_{\rm n}) = \bar{c}_{\rm s}$, in agreement with the CNT assumption. Therefore, the present theory contains the CNT in itself as a limiting case. At the same time, the value $dn/dt = w_{n,n+1}^{(+)} - w_{n+1,n}^{(-)}$, which is determined solely by the diffusion solute flux in the solution, is equal in both the CNT and this theory. That is why both theories give the same results in the asymptotic coarsening regime, but they differ in the range of ultrafine clusters (see Fig. 3 below).

Under the condition of detailed balance, when the flux of clusters in the dimension space (1) becomes zero for any n [see Eq. (2)], the equilibrium distribution function (3) can be expressed as follows:

$$g_{\rm eq}(n) = \begin{cases} g_{\rm eq}(1), & n = 1; \\ g_{\rm eq}(1)\prod_{i=2}^{n} w_{i-1,i}^{(+)}\big/ w_{i,i-1}^{(-)}, & n \geqslant 2. \end{cases} \tag{23}$$

For a discussion of the range of validity of Eq. (23), see Appendix C.

In the range of undersaturated and saturated solute concentrations, i.e., for $0 \leqslant g_{\rm eq}(1) \leqslant 1$, the equilibrium distribution function is finite: $\lim_{n\to\infty} g_{\rm eq}(n) = 0$, while in the range of supersaturated concentrations, i.e., for $g_{\rm eq}(1) > 1$, the equilibrium distribution function is divergent: $\lim_{n\to\infty} g_{\rm eq}(n) = \infty$.

A total solute concentration (expressed in units of $c_{\rm s}^{\rm eq}$) can be calculated as follows:

$$q = \sum_{n=1}^{\infty} n g(n,t). \tag{24}$$

In the limiting case $g_{\rm eq}^{*}(1) = 1$, corresponding to the saturated solute concentration, Eq. (24) with $g(n,t) = g_{\rm eq}^{*}(n)$ can be utilized to calculate the total solubility, taking into account both the single dissolved atoms and *heterophase fluctuations* (ultrafine clusters):

$$q^{*} = \sum_{n=1}^{\infty} n g_{\rm eq}^{*}(n). \tag{25}$$

Figure 1 shows the relative total solubility $q^{*}/q^{*[\rm CNT]}$ as a function of two dimensionless model parameters α and λ. The values corresponding to the present theory and the CNT are calculated from Eq. (25) with the attachment and detachment rates given by Eqs. (18), (19) and (21), (22), respectively. From Fig. 1, one can see that the CNT systematically underestimates the total solubility and that this discrepancy decreases with an increase of λ. It should be noted that, within the present model, a contribution from heterophase fluctuations to the total solubility (25), depending on the values of the model parameters, may exceed by several orders of magnitude the solubility of monomers [13].

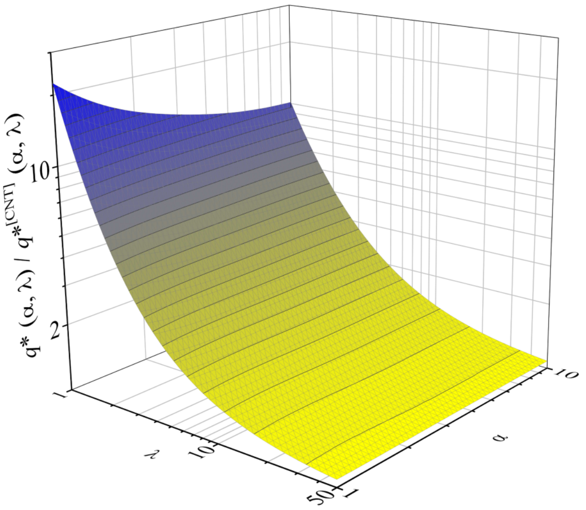

FIG. 1. Relative total solubility $q^*/q^{*[\mathrm{CNT}]}$ vs model parameters α and λ.

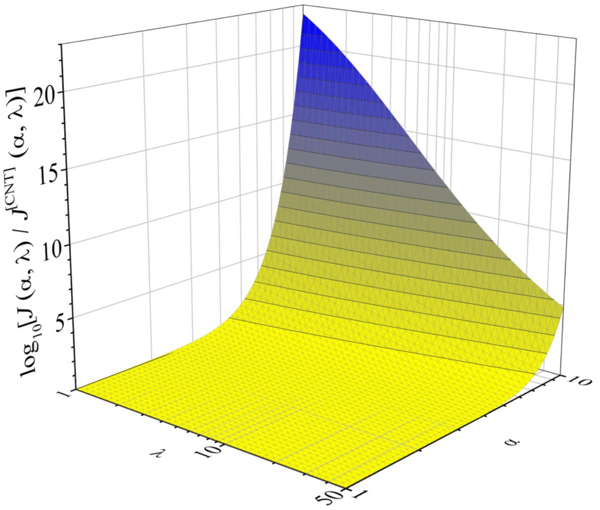

FIG. 2. Decimal logarithm of the relative nucleation rate $J/J^{[\mathrm{CNT}]}$ at a constant supersaturation $g_{\mathrm{eq}}(1) = 15$ vs model parameters α and λ.

In the steady-state nucleation regime, the flux of clusters in the dimension space (1) is constant for any n:

$$J_{n,n+1} = J = \mathrm{const}, \quad \forall\, n. \tag{26}$$

The steady-state distribution function in this case is as follows (see, e.g., Ref. [14]):

$$\frac{g_J(n)}{g_{\mathrm{eq}}(n)} = \frac{g_J(1)}{g_{\mathrm{eq}}(1)} - J\sum_{i=1}^{n}\left[w_{i,i+1}^{(+)} g_{\mathrm{eq}}(i)\right]^{-1}. \tag{27}$$

Following Zeldovich [15], one can set $g_J(1)/g_{\mathrm{eq}}(1) = 1$ and $\lim_{n\to\infty} g_J(n)/g_{\mathrm{eq}}(n) = 0$ to obtain from Eq. (27) an explicit form for the steady-state flux of clusters in the dimension space (the nucleation rate):

$$J = \left\{\sum_{i=1}^{\infty}\left[w_{i,i+1}^{(+)} g_{\mathrm{eq}}(i)\right]^{-1}\right\}^{-1}. \tag{28}$$

Figure 2 shows the decimal logarithm of the relative nucleation rate $J/J^{[\mathrm{CNT}]}$ at the degree of supersaturation $g_{\mathrm{eq}}(1) = 15$ as a function of two dimensionless model parameters α and λ. The values corresponding to the present theory and the CNT are calculated from Eq. (28), with the attachment and detachment rates given by Eqs. (18), (19) and (21), (22), respectively. From Fig. 2, one can see that the CNT systematically underestimates the nucleation rate. While in the range of small values of α this discrepancy is negligibly small, it quickly increases and may achieve many orders of magnitude with an increase of α and a decrease of λ. In the diffusion-limited two-step nucleation model, a qualitatively similar result was recently obtained by Lutsko [3].

Below, we compare the results of the present model for precipitation kinetics with those of the CNT, for the same values of the total solute concentration (24) $q = 10^4$ and the model parameters $\alpha = 3$ and $\lambda = 1$. Details of the numerical method used in these calculations can be found in the paper by Turkin and Bakai [16]. In each calculation, the homogeneous state of the solution (only single atoms, no clusters) is taken as an initial condition. The dashed and solid curves in Fig. 3 show the solutions of the system of Eqs. (15) and (17) at $t/t_{\mathrm{nucl}} = 10^{10}$, with the rates of attachment and detachment, given by this model [Eqs. (18) and (19)] and by the CNT [Eqs. (21) and (22)], respectively. The low-n steep parts of the curves describe heterophase fluctuations and coincide with the corresponding equilibrium distributions (23), shown by symbols. At the same time, the high-n flat parts describe the clusters, which evolve according to the Lifshitz-Slyozov-Wagner (LSW) theory [17,18]. The inset in Fig. 3 shows the numerical data recalculated according to the rule $f(x)dx = g(n)dn$, where $x = \sqrt[3]{n/n_{\mathrm{c}}}$ is a reduced cluster size, and $n_{\mathrm{c}} = [\alpha/\ln g(1,t)]^3$ is the cluster critical size. One can see that the calculated curves approach the Lifshitz-Slyozov (LS) distribution function [17], shown by the dotted curve. One can note that this model gives a much wider range of heterophase fluctuations than the CNT does. This result qualitatively explains why this model gives larger

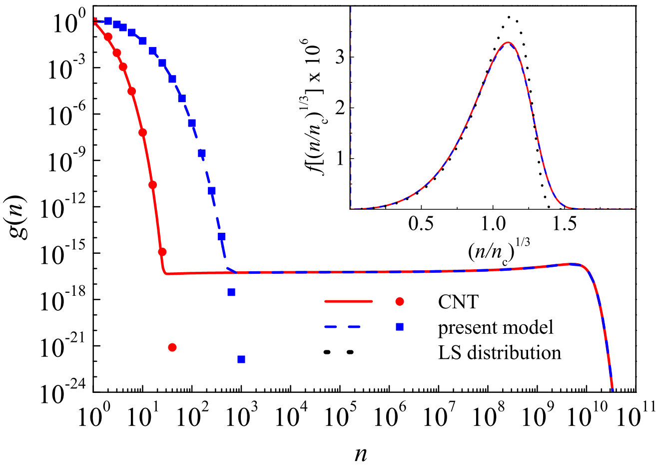

FIG. 3. A distribution of clusters vs number of atoms at $t/t_{\mathrm{nucl}} = 10^{10}$, calculated in the framework of the CNT and this model. Symbols show the corresponding equilibrium distributions of heterophase fluctuations. The inset shows the calculated distributions in reduced coordinates together with the LS distribution function.

values for the total solubility (see Fig. 1) and the nucleation rate (see Fig. 2) compared with the CNT results. At the same time, in the high-n range both models give identical results, in agreement with the LSW theory. This happens because the difference of the attachment and detachment rates (the net solute flux, which solely enters the LSW theory) is equal in both this theory and the CNT.

In summary, the proposed model of precipitation from solutions is grounded on the basic assumptions of the CNT, with an exception of the postulate of a homogeneous distribution of solute atoms around the clusters. Taking into account the diffusion and reaction processes around the clusters allows the correct derivation of the attachment and detachment rates at the interface, which enter the master kinetic equation and govern the process of precipitation. The reduced interface energy and the inverse second Damköhler number are found to be the appropriate model parameters. Numerical calculations of the total solubility and the nucleation rate show that the CNT systematically underestimates both of these values, and that the corresponding discrepancies, depending on the values of the model parameters, may achieve many orders of magnitude. However, the discrepancies vanish in the limit of the interface-limited precipitation, when the solute concentration at the interface approaches its value in the bulk.

The main goal of this study is to consider the effect of the diffusion-defined concentration profile around the clusters on the nucleation kinetics. Further improvements of the CNT, such as allowing the cluster-solution interface to be nonsharp and the cluster shape to be nonspherical, are also expected to be important, as was recently demonstrated for the case of polymorphic transitions [19]. The internal structure of the cluster and its chemical composition can be considered as additional variables, extending the coordinate space in which the nucleation pathway is determined [20].

I am grateful to A. Turkin for sharing his numerical code and for helpful discussions. I wish to thank a referee for revealing the relation between the kinetic parameter λ and the second Damköhler number.

APPENDIX A: DERIVATION OF THE WORK OF ATTACHMENT AT THE INTERFACE

The concentration profile of a heterogeneous system, consisting of the spherical cluster with a radius of $r_{\rm n}$ and the perturbed solution around it, can be written as follows:

$$c(r) = \theta(r_{\rm n} - r)c_{\rm c}(r) + \theta(r - r_{\rm n})c_{\rm s}(r), \tag{A1}$$

where $c_{\rm c}(r)$ is a concentration profile inside the cluster, and $c_{\rm s}(r)$ is a concentration profile in the solution. In Eq. (A1), the Heaviside step function $\theta(x)$ is used to account for a singularity of the concentration profile at the cluster interface at $r = r_{\rm n}$, in agreement with the CNT assumption. Therefore, a number N of solute atoms in a spherical region with a radius of $R \gg r_{\rm n}$ can be computed as follows:

$$N = 4\pi \int_0^R c(r) r^2 dr. \tag{A2}$$

Therefore, using Eqs. (A2) and (A1), one can express the law of conservation of the total number of solute atoms N in the course of the precipitation process in the following form:

$$\frac{dN}{dn} = 4\pi r_{\rm n}^2 \frac{dr_{\rm n}}{dn}[c_{\rm c}(r_{\rm n}) - c_{\rm s}(r_{\rm n})] = 0. \tag{A3}$$

Here and below, we utilize the well-known relations for the singular functions:

$$\frac{d}{dx}\theta(x - b) = \delta(x - b), \qquad \int_a^c \delta(x - b) f(x) dx = f(b),$$

where $\delta(x)$ is the Dirac δ function and $a < b < c$.

From Eq. (A3) one can see that $c_{\rm c}(r_{\rm n}) = c_{\rm s}(r_{\rm n})$, meaning that the concentration profile is continuous across the interface.

On the other hand, a number n of solute atoms inside the cluster is

$$n = 4\pi \int_0^R \theta(r_{\rm n} - r) c_{\rm c}(r) r^2 dr. \tag{A4}$$

In the same way, from Eq. (A4) one finds that the next identity at the interface holds:

$$\frac{dn}{dn} = 4\pi r_{\rm n}^2 \frac{dr_{\rm n}}{dn} c_{\rm c}(r_{\rm n}) \equiv 1. \tag{A5}$$

The volume density of the thermodynamic potential of the heterogeneous cluster-solution system can be written as follows:

$$\begin{aligned} f(r) &= \theta(r_{\rm n} - r)c_{\rm c}(r)\mu_{\rm c} + \sigma\delta(r - r_{\rm n}) \\ &\quad + \theta(r - r_{\rm n})c_{\rm s}(r)\mu_{\rm s}(r), \end{aligned} \tag{A6}$$

where $\mu_{\rm c}$ is the chemical potential of a clusterized atom, σ is a coefficient of tension at the interface, and

$$\mu_{\rm s}(r) = \mu_{\rm c} + k_{\rm B}T \ln\left[c_{\rm s}(r)/c_{\rm s}^{\rm eq}\right] \tag{A7}$$

is the chemical potential of a dissolved atom in the perturbed solution. In Eq. (A7), $k_{\rm B}$ is Boltzmann's constant, T is the temperature, and $c_{\rm s}^{\rm eq}$ is the thermodynamic equilibrium solubility. In Eq. (A6), the Dirac δ function $\delta(x)$ is used to account for a singularity of the density of the thermodynamic potential at the cluster interface, in agreement with the CNT assumption. From Eq. (A7) one can find that, if the solute concentration profile is uniform with $c_{\rm s}(r) = c_{\rm s}^{\rm eq}$, then $\mu_{\rm s} = \mu_{\rm c}$, meaning that in this case the (macroscopic) cluster is in the state of thermodynamic equilibrium with the solution.

Therefore, a value $G(n)$ of the thermodynamic potential of the cluster-solution system can be computed as follows:

$$G(n) = 4\pi \int_0^R f(r) r^2 dr. \tag{A8}$$

Now, from Eq. (A8), the work of attachment in the continual approximation can be derived as follows:

$$\begin{aligned} G(n+1) - G(n) &\underset{n\gg1}{=} \frac{dG(n)}{dn} \\ &= 4\pi r_{\rm n}^2 \frac{dr_{\rm n}}{dn}[c_{\rm c}(r_{\rm n})\mu_{\rm c} - c_{\rm s}(r_{\rm n})\mu_{\rm s}(r_{\rm n})] \\ &\quad + 8\pi\sigma r_{\rm n}\frac{dr_{\rm n}}{dn} \end{aligned}$$

using Eqs. (A3), (A5), and (A7),

$$= k_{\rm B}T \ln\frac{c_{\rm s}^{\rm eq}(r_{\rm n})}{c_{\rm s}(r_{\rm n})}, \tag{A9}$$

where

$$c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}}) = c_{\mathrm{s}}^{\mathrm{eq}} \exp\left(\frac{8\pi\sigma r_{\mathrm{n}}}{k_{\mathrm{B}}T}\frac{dr_{\mathrm{n}}}{dn}\right) \tag{A10}$$

is a size-dependent thermodynamic equilibrium solute concentration at the interface. If the radius of the cluster is taken in the simplified form (4), Eq. (A10) can be reduced to the well-known Gibbs-Thomson relation (6).

APPENDIX B: KINETICS OF SOLUTE CONCENTRATION AT THE INTERFACE

The time-dependent spherically symmetric solute concentration profile $c_{\mathrm{s}}(r,t)$ around the cluster is subject to the next diffusion equation:

$$\frac{\partial c_{\mathrm{s}}(r,t)}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}[r^2 j(r,t)], \quad j(r,t) = -D\frac{\partial c_{\mathrm{s}}(r,t)}{\partial r}. \tag{B1}$$

The time-dependent normal component [10] of the solute flux across the interface is proportional to the difference of the detachment (10) and attachment (9) rates:

$$j(r_{\mathrm{n}},t) = \frac{w_{n+1,n}^{(-)} - w_{n,n+1}^{(+)}}{4\pi r_{\mathrm{n}}^2} = \frac{D}{r_0\lambda}\left[c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}}) - c_{\mathrm{s}}(r_{\mathrm{n}},t)\right],$$
$$\lambda = \frac{D}{r_0 dk}. \tag{B2}$$

One can consider the second boundary condition as follows:

$$c_{\mathrm{s}}(\infty,t) = \bar{c}_{\mathrm{s}}. \tag{B3}$$

Let the initial solute concentration profile be uniform:

$$c_{\mathrm{s}}(r,0) = \bar{c}_{\mathrm{s}}. \tag{B4}$$

By solving the diffusion equation (B1) with the boundary conditions (B2) and (B3) and the initial condition (B4), and substituting Eq. (4) for the cluster radius, one obtains the next expression for the time-dependent solute concentration at the interface (see, e.g., Ref. [12]):

$$c_{\mathrm{s}}(r_{\mathrm{n}},t) = \bar{c}_{\mathrm{s}} + \frac{\sqrt[3]{n}\left[c_{\mathrm{s}}^{\mathrm{eq}}(r_{\mathrm{n}}) - \bar{c}_{\mathrm{s}}\right]}{\sqrt[3]{n}+\lambda} \times \left[1 - \exp\left(\frac{t}{t_{\mathrm{diff}}}\right)\mathrm{erfc}\left(\sqrt{\frac{t}{t_{\mathrm{diff}}}}\right)\right], \tag{B5}$$

where

$$t_{\mathrm{diff}} = \frac{r_0^2}{D}\left(\frac{1}{\sqrt[3]{n}} + \frac{1}{\lambda}\right)^{-2} \tag{B6}$$

is a characteristic time scale of the diffusion process at the interface.

Equation (20) determines the characteristic time scale t_{nucl} of the nucleation process in both the CNT and this theory. Therefore, values such as $\bar{c}_{\mathrm{s}}$ vary on this time scale. To ensure the treatment of $\bar{c}_{\mathrm{s}}$ in the diffusion boundary condition (B3) as a constant, the diffusion time scale (B6) must be much less than the nucleation one (20): $t_{\mathrm{diff}} \ll t_{\mathrm{nucl}}$. From Eqs. (B6) and (20), one finds that this adiabatic approximation holds when the dimensionless kinetic parameter of the model λ is limited as follows:

$$\lambda \ll \left(3\omega_0 c_{\mathrm{s}}^{\mathrm{eq}}\right)^{-1/2}. \tag{B7}$$

In this adiabatic approximation, the solute concentration at the interface approaches its quasistationary value (14), which can be obtained from Eq. (B5) in the limit $t \to \infty$.

APPENDIX C: A "HYBRID" EQUILIBRIUM DISTRIBUTION FUNCTION OF THE CLUSTERS

It is worth noting that the assumption $n \gg 1$, made during derivation of Eq. (A9), makes the present approach (just like the CNT one) inapplicable in practice for small clusters with $n \gtrsim 1$. Instead, one has to obtain the first several points of the distribution function $g_{\mathrm{eq}}(n)$ in the range $1 \leqslant n \leqslant n^*$ from experimental or simulation (see, e.g., Ref. [21]) data and then to proceed recursively to higher n. This "hybrid" distribution function then reads

$$g_{\mathrm{eq}}(n) = \begin{cases} g_{\mathrm{eq}}^{\mathrm{exp}}(n), & 1 \leqslant n \leqslant n^*; \\ g_{\mathrm{eq}}^{\mathrm{exp}}(n^*)\prod_{i=n^*+1}^{n} w_{i-1,i}^{(+)} \big/ w_{i,i-1}^{(-)}, & n > n^*. \end{cases} \tag{C1}$$

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