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Kyoto University
Theoretical and numerical studies of nucleation kinetics

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Reconsideration on the concept of critical nucleus for single component systems leads to the result that the size \( n_k \) of a kinetic critical nucleus for which the probabilities of its decay and growth balance is not equal to the size \( n^* \) of the thermodynamic one for which the reversible work of nucleus formation takes the maximum value, \( n_k \) is in general smaller than \( n^* \), and there exist two values for \( n_k \), the larger is kinetically unstable but the smaller is stable. The difference between \( n^* \) and the larger \( n_k \) increases but the difference between the two values of \( n_k \) decreases with supersaturation and or temperature, and at the critical state two values of \( n_k \) coincide and it diminishes to 8/27 of \( n^* \) for three dimensional homogeneous nucleation and to 1/4 of \( n^* \) for two dimensional disc nucleation on a substrate. Beyond this critical state \( n_k \) does not exist and for a nucleus with any size the probability of growth is higher than that of decay. The height of the nucleation barrier, i.e., the reversible work of critical nucleus formation, is found to be the main parameter quantitatively controlling the distinction between \( n^* \) and \( n_k \). It is shown that when the distinction between the two kinds of the critical nuclei is significant, the attachment and the detachment rates of monomers do not differ appreciably.

1. Definition of the thermodynamic and the kinetic critical nuclei

Kinetic process at early stage of the first order phase transformation is usually treated in terms of exchange of monomers between a parent phase and mutually independent clusters of a nucleating phase called nuclei. We consider single component systems in the present article. In the thermodynamic treatment of nucleation, nuclei are specified by the number of molecules \( n \) contained in the corresponding hypothetical clusters [1,2,3]. A critical nucleus is then defined as a one for which the reversible work of nucleus formation takes a maximum value, which we call the thermodynamic critical nucleus and denote as \( n^* \). On the other hand, in describing nucleation process it is useful to define a critical nucleus as the size for which the probabilities of decay and growth balance, which we call the kinetic critical nucleus and denote as \( n_k \). The size \( n^* \) and \( n_k \) have been presumed to coincide, but it is recently shown that they do not [4,5]. Suppose a system of a parent phase and nuclei in metastable equilibrium. For simplicity we treat \( n \) as a continuous variable. Metastable equilibrium number density \( c_0(n) \) of nuclei with size \( n \) is given by [6-8]

\[
c_0(n) = \Phi_{LP}(1) \exp[-W^{rev}(n)/kT], n > 1,
\]

where \( c(1) \) denotes the monomer number density, \( \Phi_{LP} \) the Lothe-Pound factor [6-8], \( k \) the Boltzmann constant and \( T \) the absolute temperature. \( W^{rev}(n) \) is given by [3]

\[
W^{rev}(n) \approx -\Delta \mu + \gamma^* A,
\]

where \( \Delta \mu \) represents

\[
\Delta \mu = \mu^p - \mu^\alpha(T, p^\alpha),
\]

and the superscripts \( \alpha \) and \( \beta \) denote a parent phase and a nucleating phase, respectively, \( \mu^p \) and \( \mu^\alpha(T, p^\alpha) \) the chemical potential of a molecule in a parent phase and that in the bulk phase under \( (T, p^\alpha) \). In Eq. (2) \( n \) denotes the number of molecules contained within the volume enclosed by the surface of tension in a bulk phase, \( \gamma^* \) the interfacial tension for a thermodynamic critical nucleus and \( A \) an area of the surface of tension. If we can neglect size dependence of interfacial tension, then \( \gamma^* \) may be approximated by the value for the planar interface. We employ this approximation here and denote the value as \( \gamma \). Since \( n \) dependence of \( \Phi_{LP} \) is negligible [6-8], \( W^{rev}(n) \) takes a maximum value at \( n^* \).

The size \( n_k \) of a kinetic critical nucleus satisfies

\[
K^+(n_k) = K^-(n_k),
\]

where \( K^+(n) \) denotes the attachment rate of monomers to a nucleus with size \( n \) and \( K^-(n) \) the detachment rate from a nucleus. It is assumed that growth or decay of a nucleus results from attachment or detachment of monomers and that collision among nuclei or fission of a nucleus may be neglected.

2. Relation between \( n^* \) and \( n_k \)

2.1. Homogeneous nucleation in three-dimensional systems

In a metastable equilibrium state, the following relation holds for any \( n \) due to the principle of detailed balance:

\[
c_0(n - \delta n)K^+(n - \delta n) = c_0(n)K^-(n),
\]

where \( \delta n \) physically represents a monomer. We see from Eqs. (4) and (5) that a kinetic critical nucleus is determined by the extremum condition of \( c_0(n)K^+(n) \).
or equivalently of $W^{rev}(n) - kT\ln[K^+(n)]$, which may be called the kinetic potential $W^{kin}(n)$ [5]. Employing Eq.(1) with an approximation that $n$ dependence of $\Phi_{\perp P}$ is negligible and noting that $K^+(n)$ is proportional to $n^{2/3}$, the size of a kinetic critical nucleus is determined by the following equation [5]:

$$X^2 - X^3 = B,$$

(6)

where $X$ represents $X = (n/n^*)^{1/3}$. A parameter $B$ is defined as

$$B = 2kT/(3n^* \mu),$$

(7)

where $A_0$ denotes $(8\pi v^2)^{1/3}$, $v$ the molecular volume of the bulk of a nucleating phase, and the following equation for $n^*$ has been employed:

$$n^* = [2\gamma A_0/(3 \Delta \mu)]^{3/2}.$$

(8)

2.2. Nucleation on a substrate

Let us consider next a nucleation of monatomic substance on a substrate. We assume that adatoms on a substrate are in equilibrium with the parent phase and nuclei possess their equilibrium shapes even in nonequilibrium nucleation processes. Consider first a nucleus with the shape of a spherical cap having a contact angle $\theta$. $W^{rev}(n)$ is given by [9,10]

$$W^{rev}(n) \approx -n\Delta\mu + \gamma^* \rho A_1 n^{2/3},$$

(10)

where

$$\gamma_{s\theta} = \gamma_{s\beta} + \gamma \cos \theta.$$

(12)

When adition or subtraction of atoms to or from a nucleus is dominated by the process via adatoms, $K^+(n)$ is proportional to $n^{1/3}$ as in the case of homogeneous nucleation. In this case, the relation between $n^*$ and $n_k$ is determined by

$$X^2 - X^3 = B/K(\theta),$$

(13)

where $B$ is given by Eq.(7) and $K(\theta)$ represents

$$K(\theta) = (2 - 3\cos \theta + \cos^2 \theta)/4.$$

(14)

Whereas, when adition or subtraction of atoms to or from a nucleus is dominated by the direct process on the cap shaped surface, $K^+(n)$ is proportional to $n^{2/3}$ as in the case of homogeneous nucleation. In this case, the relation between $n^*$ and $n_k$ is determined by

$$X^2 - X^3 = B/[2K(\theta)].$$

(15)

Since $K(\theta) \leq 1$ and approaches zero as the contact angle $\theta$ approaches zero, we see from Fig.1 that the difference between $n^*$ and $n_k$ may become significant even when they are approximately the same for homogeneous nucleation.

Considering the case of homoepitaxy, $W^{rev}(n)$ for a nucleus with the shape of circular disc on a substrate is given by

$$W^{rev}(n) = -n\Delta\mu + \sigma L_0 n^{1/2},$$

(16)

where $\sigma$ denotes step free energy, $L_0$ represents $2(\pi a)^{1/2}$, and $a$ the area per atom. The equation which determines $n_k$ becomes

$$Y - Y^2 = D,$$

(17)

where $Y$ represents $(n/n^*)^{1/2}$ and $D$ does

$$D = kT/(2n^* \Delta \mu) = 2kT \Delta \mu/(L_0 a)^2,$$

(18)

and the following expression has been employed:

$$n^* = [L_0 a/(2\Delta \mu)]^{2}.$$

(19)

Similarly to the previous cases, there exist two solutions for $n_k$ as
\[ n_k^{(1)} = (n^*/4)[1 + (1 - 4D)^{1/2}]^2, \]  
\[ n_k^{(2)} = (n^*/4)[1 - (1 - 4D)^{1/2}]^2. \]  
\[ \Delta \mu = (L_0 \sigma^2)/(8kT). \]  

Note again that \( n_k^{(1)} \) approaches \( n^* \) as \( \Delta \mu \) diminishes but the difference between \( n_k^{(1)} \) and \( n^* \) increases with \( \Delta \mu \) and it approaches 1/4 of \( n^* \) at the critical value of \( \Delta \mu \) given by
\[ \Delta \mu_c = (L_0 \sigma^2)/(8kT). \]  

Again, for \( \Delta \mu \) beyond this value the runaway instability occurs [6].

3. Numerical simulation of the kinetically stable critical nucleus

Since the cluster with the size \( n_k^{(2)} \) is kinetically stable as discussed above, we may expect a peak in the cluster number densities \( c(n, t) \) at this size during nucleation. Let us consider the time evolution of \( c(n, t) \) by numerically solving the kinetic equation which is given by
\[ \frac{\partial c(n, t)}{\partial t} = K^+(n-1)c(n-1, t) - K^-(n)c(n, t) \]  
\[ -K^+(n)c(n, t) + K^-(n+1)c(n+1, t) \]  
\[ \]  
In the case of liquid droplet nucleation from vapor, \( K^+(n) \) is given by [11]
\[ K^+(n) = \frac{S P_v A_{0v}n^{2/3}}{\sqrt{2\pi nkT}}. \]  

where \( S \) denotes the supersaturation ratio and \( P_v \) the vapor pressure in the bulk equilibrium state. We take water droplet nucleation from vapor as an example. This system was employed in the numerical calculations for the study of the transient nucleation[12,13]. However they employed low temperatures which give small values of \( B \), e.g., \( B=0.006(<B_c) \) at \( T = 263.2 \) K under \( S = 4.91 \). Since the purpose here is to study the effect of the cluster with the size \( n_k^{(2)} \), we employ the condition which gives higher value of \( B \). Let us consider the case at \( T = 620 \) K under \( S = 1.05 \) [14]. In this case \( n^* = 94, n_k^{(1)} = 35 \) and \( n_k^{(2)} = 22 \). Figs. 2 and 3 show the time evolution of \( c(n, t) \). The characteristic feature of the kinetically stable critical nucleus is not appeared in these figures contrary to our expectation. We discuss this reason in the next section. Thus the existence of the kinetically stable critical nucleus does not necessarily imply the dominance in the cluster number densities at \( n = n_k^{(2)} \) during nucleation.

4. Detailed analysis of the kinetic potential

In the thermodynamic treatment of nucleation, \( W_{\text{rev}}(n^*) \) is used as a measure of stability for a mother phase with respect to a nucleating phase [1]. Since \( W_{\text{rev}}(n^*) = kT/3B_1 \), the increase of \( B_1 \) which gives an appreciable difference between \( n^* \) and \( n_k \) corresponds to decrease of the thermodynamic barrier. For example, \( W_{\text{rev}}(n^*) \) becomes \( 2.25kT \) at the runaway nucleation threshold \( B = B_c \) [15].

\[ q = \frac{K^-(n)}{K^+(n)} \approx \exp \left( \frac{2}{3Bn^*X^3}(X^2 - X^3 - B) \right) = S(X^3), \]  

where \( f(X) = (X^2 - X^3 - B)/X^3 \). \( f(X) \) possesses a maximum \( f_{\text{max}} = \sqrt{B_1}/B - 1 \) at \( X = X_m = \sqrt{B} \). Let us estimate the maximum possible value of \( q \) with the requirement that \( n_k^{(2)} = n^*X^2 \geq N_2 \), where \( X_2 \) denotes the solution of Eq.(6) for a given \( B \). It follows that
A can become relatively large if \( c_20 \frac{A}{g} \) gives that \( nk_2 \). In this case, q can exceed unity only by a few percent.

For the nucleation on a substrate, almost the same discussion as above holds when the cluster shape is three dimensional. When the cluster shape is a two dimensional circular disk, requiring \( n_k \geq N \) gives that

\[
q \leq \exp \left( \frac{2X^2}{3BN} \sqrt{\frac{Bc}{B} - 1} \right).
\]  

(26)

In this case again we get the curves similar to Fig.4, and q can exceed unity only by a few percent.

The distinction between \( n^* \) and \( n_k \) is controlled by the value of \( B \) (or the height of the nucleation barrier). When \( B \) is close to \( B_c \) (the case of low nucleation barrier), \( n_k \) differs from \( n^* \) significantly and \( n_k \) takes an appreciable value. Even when \( B \) is small (the case of high nucleation barrier), the numerical difference between \( n^* \) and \( n_k \) can become relatively large if \( n^* \) is large enough. In such a case, \( n_k \) can also be appreciable. The above analysis shows that q can exceed unity only by a few percent in the size range \( n_k^{(2)} \leq n \leq n_k^{(1)} \) irrespective of the height of the nucleation barrier when we require \( n_k \) to take an appreciable value. This is considered to be the reason why the peak in the cluster number densities at \( n = n_k^{(2)} \) does not appear as described in the last section. This probably means that to observe the kinetically stable clusters some subtle measurements or simulations are needed.

For \( X \gtrsim 1 \) (extremely supercritical cluster size range), \( f(X) \sim 1 \) which gives \( K^-(n)/K^+(n) \approx 1/S \) from Eq.(25). Hence extremely supercritical clusters exhibit a tendency to grow monotonously with \( q \leq 1/S \) independently of the value of \( B \). Note that for the kinetic runaway condition (\( B > B_c \)), the ratio \( q \) varies within the range \( 1/S \leq q \leq 1 \).

5. Nucleated size

When nucleation occurs during a transient process, the rate of formation of clusters with the so-called nucleated size \( n_e \) is important. \( n_e \) is defined such that most of the clusters reached this size grow to experimentally detectable clusters. In the high barrier case, this size is taken as that just outside the so-called critical region, which is usually defined as the one satisfying \( W^{res}(n^*) - W^{res}(n) = kT \). Using \( B \), this definition gives

\[
n_e = n^*(1 + 3\sqrt{B}).
\]  

(28)

However since \( K^+(n) \) and \( K^-(n) \) are quite close to each other over a broad size range for the low barrier cases, we must newly derive a formula for \( n_e \). This is left for a future investigation.

Figure 4. B-dependence of the maximum of the ratio q for \( N = 5 \) and \( N = 10 \), respectively, in three dimensional systems.

Figure 5. Percentages of clusters which finally grow to a large size from the initial size and decay to monomers, respectively, at \( T = 273.2 \) K under \( S = 5 \). \( B = 0.007 \), \( n^* = 58.1 \), \( n_k^{(1)} = 56.8 \) and \( n_k^{(2)} = 0.04 \). At \( T = 273.2 \) K under \( S = 5 \), which gives \( B = 0.007 \) (\( \ll B_c \)). In this case, Eq.(28) gives \( n_e = 73 \), which predicts well the simulation result in Fig.5. We also see in Fig.5 that half of the critical nuclei finally grow to a detectable size. Secondly let us consider the case at \( T = 630 \) under \( S = 1.022 \). In this case, \( B \) is close to \( B_c \) hence the distinction between \( n^* \) and \( n_k \) is appreciable. Eq.(28) gives \( n_e = 458 \). Comparing this value with the results in Fig.6, Eq.(28) seems to overestimate \( n_e \) in this case. Note also that either the kinetic or the thermodynamic critical nucleus does not correspond to the size for which 50 percent of clusters grow to a detectable size. Fig.7 shows the case of the runaway nucleation. Since no kinetic critical nucleus exists in this case, even small
6. Discussion

The results obtained above are based on the principle of detailed balance (5), which is valid for a system in equilibrium. However, since we assume that interaction among nuclei is negligible, \( K^+ (n) \) and \( K^- (n) \) are determined only by temperature, size of a nucleus and the state of a parent phase and do not depend on the actual concentration of nuclei in a system. Hence, the results are applicable to nonequilibrium nucleation processes.

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