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 probabilty 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. 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]

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

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

$$W^{rev}(n) \approx -n \Delta \mu + \gamma^* A, \tag{2}$$

where $\Delta\mu$ represents

$$\Delta\mu = \mu^\alpha - \mu^\beta(T, p^\alpha), \tag{3}$$

and the superscripts α and β denote a parent phase and a nucleating phase, respectively, μ^α and $\mu^\beta(T,p^\alpha)$ the chemical potential of a molecule in a parent phase and that in the bulk β phase under (T,p^α). In Eq.(2) n denotes the number of molecules contained within the volume enclosed by the surface of tension in a bulk β phase, γ^* 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 γ^* may be approximated by the value for the planar interface. We employ this approximation here and denote the value as γ. Since n dependence of Φ_{LP} is negligible [6-8], $W^{rev}(n)$ takes a maximum value at n^*.

The size n_k of a kinetic critical nucleus satisfies

$$K^+(n_k) = K^-(n_k), \tag{4}$$

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:

$$c_0(n-\delta n)K^+(n-\delta n) = c_0(n)K^-(n), \tag{5}$$

where δn 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 Φ_{LP} 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]:

$$X^2 - X^3 = B, \tag{6}$$

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

$$B = 2kT/(3n^* \Delta \mu) = 9kT(\Delta\mu)^2/[4(\gamma A_0)^3], \tag{7}$$

where A_0 denotes $(36\pi v^2)^{1/3}$, v the molecular volume of the bulk of a nucleating phase, and the following equation for n^* has been employed:

$$n^* = [2\gamma A_0/(3 \Delta \mu)]^3. \tag{8}$$

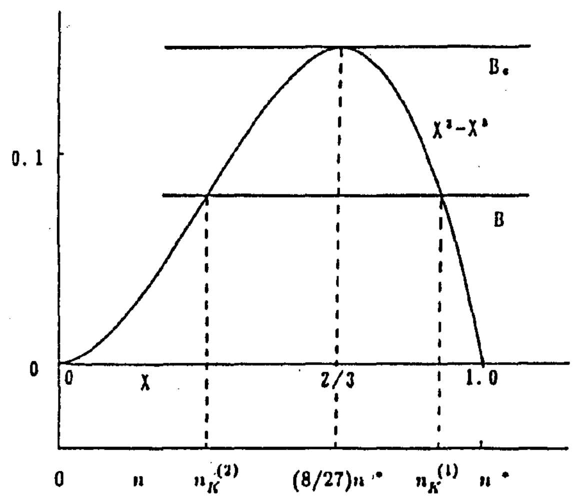

Figure 1. Relation between the kinetic critical nucleus n_k and the thermodynamic one n^* for three dimensional homogeneous nucleation.

Let us study the solution of Eq.(6) graphically in Fig.1 [5]. We see that there exist two solutions in general, $n_k^{(1)}$ and $n_k^{(2)}$. $K^+(n) > K^-(n)$ holds for $n > n_k^{(1)}$ or $n < n_k^{(2)}$, whereas $K^+(n) < K^-(n)$ for $n_k^{(2)} < n < n_k^{(1)}$. As $\Delta\mu$ diminishes, $n_k^{(1)}$ approaches n^* while $n_k^{(2)}$ approaches zero. The difference between $n_k^{(1)}$ and n^* increases with $\Delta\mu$ and $n_k^{(1)}$ approaches 8/27 of n^* at the critical value of $\Delta\mu$ given by

$$\Delta\mu_c = (4/9)[(\gamma A_0)^3/(3kT)]^{1/2}. \tag{9}$$

Two values of n_k approach as $\Delta\mu$ and or T increases and they coincide with each other at $\Delta\mu_c$ for a given T. With $\Delta\mu$ beyond this value, where solution for n_k does not exist, $K^+(n) > K^-(n)$ holds for any n, i.e., nuclei with any size tend to grow and we call it the runaway instability [5].

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 θ. $W^{rev}(n)$ is given by [9,10]

$$W^{rev}(n) \approx -n\Delta\mu + \gamma^* A_1 n^{2/3}, \tag{10}$$

where

$$A_1 = [9\pi v^2(2 - 3\cos\theta + \cos^3\theta)]^{1/3} \tag{11}$$

and the contact angle θ is related to the interfacial free energies γ, $\gamma_{s\alpha}$, $\gamma_{s\beta}$ between a nucleus and the parent phase, substrate and the parent phase, substrate and a nucleus, respectively, by

$$\gamma_{s\alpha} = \gamma_{s\beta} + \gamma\cos\theta. \tag{12}$$

When additon 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

$$X^2 - X^3 = B/K(\theta), \tag{13}$$

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

$$K(\theta) = (2 - 3\cos\theta + \cos^3\theta)/4. \tag{14}$$

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

$$X^2 - X^3 = B/[2K(\theta)]. \tag{15}$$

Since $K(\theta) \leq 1$ and approaches zero as the contact angle θ approaches zero, we see from Fig.1 that the difference between n^* and $n_k^{(1)}$ 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

$$W^{rev}(n) = -n\Delta\mu + \sigma L_0 n^{1/2}, \tag{16}$$

where σ 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

$$Y - Y^2 = D, \tag{17}$$

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

$$D = kT/(2n^*\Delta\mu) = 2kT\Delta\mu/(L_0\sigma)^2, \tag{18}$$

and the following expression has been employed:

$$n^* = [L_0\sigma/(2\Delta\mu)]^2. \tag{19}$$

Similarly to the previous cases, there exist two solutions for n_k as

$$n_k^{(1)} = (n^*/4)[1+(1-4D)^{1/2}]^2, \tag{20}$$

$$n_k^{(2)} = (n^*/4)[1-(1-4D)^{1/2}]^2. \tag{21}$$

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

$$\Delta\mu_c = (L_0\sigma)^2/(8kT). \tag{22}$$

Again, for $\Delta\mu$ beyond this value the runaway instability occurs [5].

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

$$\begin{aligned}\frac{\partial c(n,t)}{\partial t} &= K^+(n-1)c(n-1,t) - K^-(n)c(n,t)\\ &\quad -K^+(n)c(n,t) + K^-(n+1)c(n+1,t)\end{aligned} \tag{23}$$

In the case of liquid droplet nucleation from vapor, $K^+(n)$ is given by [11]

$$K^+(n) = \frac{SP_eA_0n^{2/3}}{\sqrt{2\pi mkT}}, \tag{24}$$

where S denotes the supersaturation ratio and P_e 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., $B \approx 0.006 (\ll B_c)$ at $T = 263.2$ K under $S = 4.91$. Since the purpose here is to study the effect 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 appreared in these figures contrary to our expectation. We discuss this reason in the next section. Thus the existance of the kinetically stable critical nucleus does not necessarily imply the dominance in the cluster number densities at $n = n_k^{(2)}$ during nucleation.

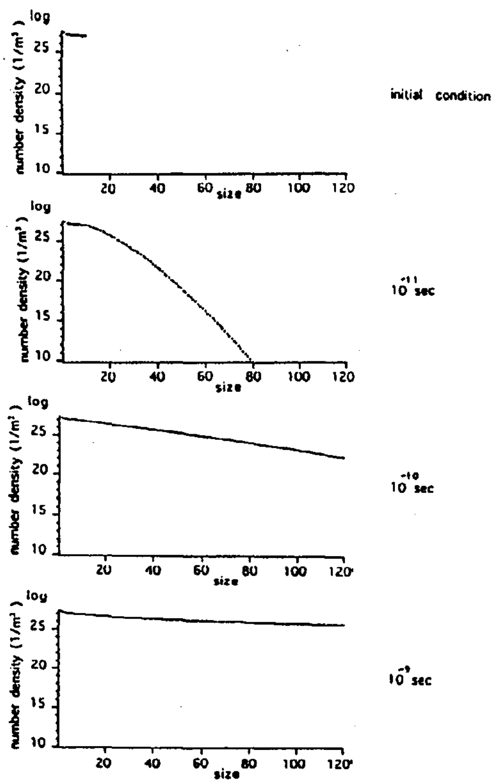

Figure 2. Cluster formation process at $T = 620$K under $S = 1.05$.

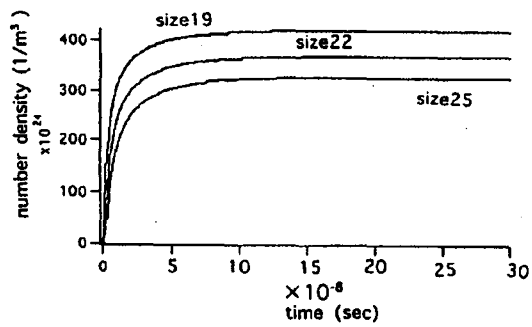

Figure 3. The same result as in Fig.2 but the abscissa is time.

4. Detailed analysis of the kinetic potential

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

Let us analyze the kinetic potential $W^{kin}(n)$ in some detail [15]. The ratio q between $K^-(n)$ and $K^+(n)$ can be expressed in the form

$$q = \frac{K^-(n)}{K^+(n)} \approx \exp\Big(\frac{2}{3Bn^*X^3}(X^2-X^3-B)\Big) = S^{f(X)}, \tag{25}$$

where $f(X) = (X^2 - X^3 - B)/X^3$. $f(X)$ posesses a maximum $f_{max} = \sqrt{B_c/B} - 1$ at $X = X_m = \sqrt{3B}$. Let us estimate the maximum possible value of q with the requirement that $n_k^{(2)} = n^*X_2^3 \geq N$, where X_2 denotes the solution of Eq.(6) for a given B. It follows that

$$q \leq \exp\left(\frac{2X_2^3}{3BN}\left(\sqrt{\frac{B_c}{B}}-1\right)\right). \tag{26}$$

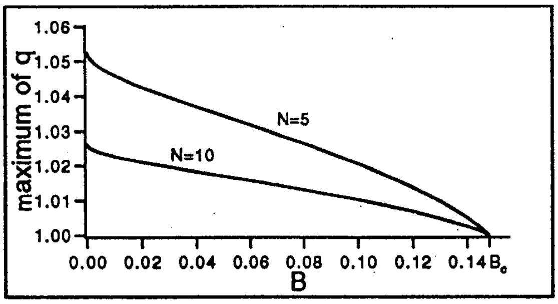

Figure 4. B-dependence of the maximum of the ratio q for $N=5$ and $N=10$, respectively, in three dimensional systems.

Fig.4 shows the B-dependence of the maximum values of q for $N=5$ and 10, respectively. We see that 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 $n_k^{(2)} \geq N$ gives that

$$q \leq \exp\left(\frac{(1-4D)(1-(1-4D)^{1/2})^2}{32ND^2}\right). \tag{27}$$

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), $n_k^{(1)}$ differs from n^* significantly and $n_k^{(2)}$ takes an appreciable value. Even when B is small (the case of high nucleation barrier), the numerical difference between n^* and $n_k^{(1)}$ can become relatively large if n^* is large enough. In such a case, $n_k^{(2)}$ 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 hight of the nucleation barrier when we require $n_k^{(2)}$ 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 cluster some subtle measurements or simulations are needed.

For $X \gg 1$ (extremely supercritical cluster size range), $f(X) \rightarrow -1$ which gives $K^-(n)/K^+(n) \simeq 1/S$ from Eq.(25). Hence extremely supercritical clusters exhibit a tendency to grow monotonously with $q \simeq 1/S$ 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_c is important. n_c 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 $W^{rev}(n^*) - W^{rev}(n) = kT$ [16]. Using B, this definition gives

$$n_c = n^*(1+3\sqrt{B}). \tag{28}$$

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_c. This is left for a future investigation. Here we consider n_c numerically. We solve the kinetic equation (23) under the condition that only the clusters with a given size n_0 exist initially, and obtain the percentages by which the clusters finally grow to the large size and finally decay to monomers, respectively. Monomer density is taken to be a constant corresponding to a given supersaturation. We take the water droplet nucleation from vapor as a numerical example again. We consider three cases, i.e., $B \ll B_c$, $B < B_c$ and $B > B_c$. Fig.5 is the result

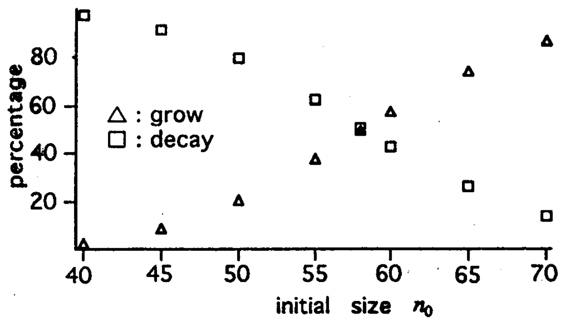

Figure 5. Percentages of clusters which finally grow to a large size from the initial size and decay to monomers, respectively, at $T=273.2$ K under $S=5$. $B=0.007$, $n^*=58.1$, $n_k^{(1)}=56.8$ and $n_k^{(2)}=0.04$.

at $T=273.2$ K under $S=5$, which gives $B=0.007$ ($\ll B_c$). In this case Eq.(28) gives $n_c=73$, 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 $T=630$K 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 $n_c=458$. Comparing this value with the results in Fig.6, Eq.(28) seems to overestimate n_c 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

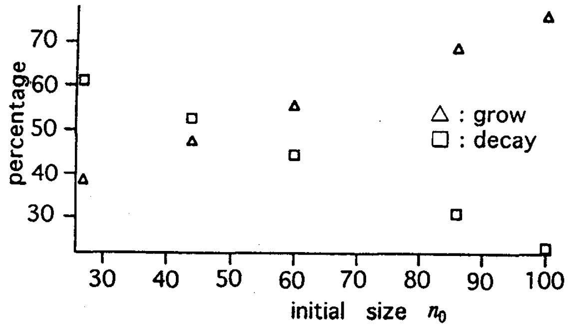

Figure 6. The same calculation as in Fig.5 at $T = 630$ K under $S = 1.022$. $B = 0.143$, $n^* = 214.5$, $n_k^{(1)} = 86.0$ and $n_k^{(2)} = 44.2$.

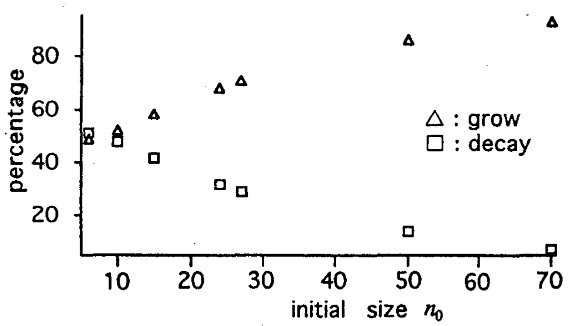

Figure 7. The same calculation as in Fig.5 at $T = 620$ K under $S = 1.08$. $B = 0.362$ and $n^* = 23.9$.

clusters can grow to very large size. Though $n_c = 67$ by Eq.(28) and it seems to predict well the result in Fig.7, the conventional concept of the critical region which is employed in deriving Eq.(28) is no longer valid in this case.

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.

Acknowledgments

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