

## Kinetic and thermodynamic definitions of the critical nucleus in nucleation theory

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The relation between the sizes of the kinetically and the thermodynamically defined critical nucleus in nucleation theory is studied by taking a single-component system as an example, where the former is the size of a cluster for which the probabilities of decay and growth balance and the latter is the one for which the reversible work of cluster formation takes the maximum value. Denoting the former as  $n_K$  and the latter as  $n^*$ ,  $n_K$  is found to be smaller than  $n^*$  when  $n$  is treated as a continuous variable. The formula to relate  $n_K$  to  $n^*$  is derived, which shows that the difference between  $n^*$  and  $n_K$  is about 1% of  $n^*$  in a typical case of water nucleation from the vapor.

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In the thermodynamic treatment of nucleation, clusters are characterized by the number of molecules  $\{n_i^h\}$  contained in the corresponding hypothetical clusters [1,2]. The critical nucleus is usually defined as a cluster for which the reversible work  $W^{\text{rev}}(\{n_i^h\})$  of cluster formation has a saddle point. For simplicity of the following consideration, we take a single-component system as an example and leave out the superscript  $h$  from  $n^h$ . Then  $W^{\text{rev}}(n)$  takes the maximum value for a critical nucleus, which we call a thermodynamically defined critical nucleus and denote as  $n^*$ .

On the other hand, in visualizing the nucleation process, it is useful to define a critical nucleus as the size for which the probabilities of decay and growth balance. Let us call it a kinetically defined critical nucleus and denote it as  $n_K$ . It appears that  $n^*$  and  $n_K$  coincide, because a cluster with the size  $n^*$  is, by definition, in equilibrium with the surrounding mother phase; hence it is tempting to consider the probabilities of its decay and growth balance. The present paper provides a careful study on this point and it is shown that  $n_K$  and  $n^*$  do not coincide.

Consider a single-component system in metastable equilibrium, consisting of a parent phase and clusters of a nucleating phase including those with the size  $n_K$  and larger. Note that the state of metastable equilibrium is just a hypothetical one, because the number densities of larger and larger clusters will increase in reality, and the state of equilibrium cannot be achieved until coexistence of the two macroscopic phases is reached. Hence, to define the state of metastable equilibrium, we introduce a hypothetical barrier which imposes on  $W^{\text{rev}}(n)$  the value infinity for  $n \geq n^\#$  where  $n^\#$  is chosen to be somewhat larger than  $n_K$ . It is supposed that  $n^\#$  is larger than  $n^*$  also.

Take a small portion of the system with volume  $V$  and consider its behavior. The volume  $V$  is chosen to be so small that no clusters exist in it most of the time, yet large enough to allow thermodynamic consideration. If we take numerous snapshot pictures of it, the probability  $P(n)$  to find a cluster with the size  $n$  in it relative to  $P(1)$  [ $\cong 1$ ] with no clusters is given by

$$P(n) \cong P(n)/P(1) = \exp[-W^{\text{rev}}(n)/kT], \quad (1)$$

where  $k$  and  $T$  denote Boltzmann's constant and temperature, respectively. For simplicity in presenting the essential point of the present paper, let us assume that  $n$  may be treated as a continuous variable. Since  $W^{\text{rev}}(n)$  takes its maximum at  $n^*$ , it follows that

$$P(n^* + \delta n) = P(n^* - \delta n) \quad (2)$$

to the order of  $(\delta n)^2$ , i.e., neglecting  $O[(\delta n)^3]$ . It is implicitly assumed above that the interaction among clusters is negligible so that a system with volume  $V$  may be treated as statistically independent from its surroundings. In fact, the concept of the critical nucleus is meaningful only when this assumption holds. Note also that  $P(n)$  represents the probability of fluctuation in equilibrium and the concept of the thermodynamic definition of the critical nucleus is related to the state with the minimum probability of fluctuation, i.e., for  $\delta n > 0$ ,

$$P(n - \delta n) > P(n) \quad \text{for } n < n^*, \quad (3)$$

$$P(n + \delta n) > P(n) \quad \text{for } n > n^* .$$

It may be worthwhile at this point to make a remark on the meaning of  $\delta n$ . Although  $n$  is treated as a continuous variable, physically it can change only by an integer. In this sense  $\delta n$  is an integer; hence  $(\delta n)^2$  is not smaller than the absolute value of  $\delta n$ . This difficulty can be overcome by introducing a new variable which is defined as  $n$  divided, for example, by  $n^*$ . Then the absolute value of  $\delta n/n^*$  is smaller than unity. However, since explicit use of the new variable will result in superfluous complexity, we keep using  $n$  as the variable with this understanding in mind.

Recalling that  $V$  is chosen to be so small that  $P(n) \ll 1$  for  $n \neq 1$ , the metastable equilibrium number density  $c_0(n)$  of clusters with size  $n$  in the system is related to  $P(n)$  by

$$c_0(n) = P(n)/V \quad \text{for } n \neq 1 . \quad (4)$$

Hence,  $W^{\text{rev}}(n)$  and  $c_0(n)$  are related by

$$c_0(n) = \exp[-W^{\text{rev}}(n)/kT]/V, \quad n \neq 1 . \quad (5)$$

Employing the "thermodynamic" reversible work  $W_{\text{th}}^{\text{rev}}(n)$  for cluster formation, Eq. (5) is rewritten as [3-5]

$$c_0(n) = \Phi_{\text{LP}} c(1) \exp[-W_{\text{th}}^{\text{rev}}(n)/kT], \quad n \neq 1, \quad (6)$$

where  $c(1)$  denotes the monomer density,  $\Phi_{\text{LP}}$  the Lothe-Pound factor [3-5], and  $W_{\text{th}}^{\text{rev}}(n)$  is given by [1]

$$W_{\text{th}}^{\text{rev}}(n) = n[\mu^\beta(T, p^\alpha) - \mu^\alpha] + \gamma A + n^{\text{ex}}(\mu^\beta - \mu^\alpha), \quad (7)$$

in which superscripts  $\alpha$  and  $\beta$  denote a parent phase and a nucleating phase, respectively,  $n$  the number of molecules contained in the bulk  $\beta$  phase within the volume enclosed by the surface of tension,  $\mu^\beta$  and  $\mu^\beta(T, p^\alpha)$  the chemical potential of a molecule in a cluster and that in the bulk  $\beta$  phase under  $(T, p^\alpha)$ , respectively,  $\gamma$  the interfacial tension,  $A$  the area of the surface of tension, and  $n^{\text{ex}}$  the interfacial excess molecules. Equation (7) may be approximated as [2]

$$W_{\text{th}}^{\text{rev}}(n) \cong n[\mu^\beta(T, p^\alpha) - \mu^\alpha] + \gamma^* A, \quad (8)$$

where  $\gamma^*$  denotes the interfacial tension for a critical nucleus. Since the  $n$  dependence of  $\Phi_{\text{LP}}$  is negligible [3-5].  $W_{\text{th}}^{\text{rev}}(n)$  takes its maximum value at the size  $n^*$  of the thermodynamically defined critical nucleus.

The size  $n_K$  of a kinetically defined critical nucleus satisfies

$$K^+(n) < K^-(n) \quad \text{for } n < n_K, \quad K^+(n_K) = K^-(n_K), \quad (9)$$

$$K^+(n) > K^-(n) \quad \text{for } n > n_K,$$

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

Let us turn to consideration of the relation between  $n^*$  and  $n_K$ . In the metastable equilibrium state introduced above, the following relation holds for any  $n$  due to the principle of detailed balance:

$$c_0(n)K^+(n) = c_0(n + \delta n)K^-(n + \delta n), \quad (10)$$

where  $\delta n$  physically represents a monomer. It follows from Eq. (10) that

$$c_0(n^* - \delta n)K^+(n^* - \delta n) = c_0(n^*)K^-(n^*). \quad (11)$$

Since  $c_0(n)$  takes its minimum value at  $n^*$ , it follows that

$$c_0(n^*) = c_0(n^* - \delta n) \quad (12)$$

to the order of  $\delta n$ , i.e., neglecting  $O[(\delta n)^2]$ . Hence, we get

$$K^+(n^* - \delta n) = K^-(n^*) \quad (13)$$

to the order of  $\delta n$ . Since  $K^+(n)$  is considered to be proportional to the interfacial area  $A(n)$  of a cluster, it follows that

$$K^+(n - \delta n)/K^+(n) = A(n - \delta n)/A(n) = 1 - 2\delta n/(3n) \quad (14)$$

to the order of  $\delta n$ . Employing Eq. (14) in Eq. (13), we get

$$K^+(n^*)/K^-(n^*) = 1 + 2\delta n/(3n^*). \quad (15)$$

Hence,

$$K^+(n^*) > K^-(n^*), \quad (16)$$

which means that

$$n_K < n^*. \quad (17)$$

Note that the inequality (17) follows from the fact that, to the order of  $\delta n$ ,  $c_0(n^*) = c_0(n^* - \delta n)$  but  $K^+(n^* - \delta n) \neq K^+(n^*)$ . Though this effect may be small as seen in Eq. (14), it is sufficient to result in an appreciable difference between  $n^*$  and  $n_K$  because the  $n$  dependence of  $c_0(n)$  is also weak around  $n^*$ . It is essential to note that Eq. (10) is the clue to find the relation between the attachment and detachment rates, which is needed to find  $n_K$ . We should not rely on the false reasoning that the attachment and detachment rates balance at  $n^*$  due to the equilibrium condition. The equilibrium condition at  $n^*$  implies that appearances of clusters with the sizes  $n^* + \delta n$  and  $n^* - \delta n$  are, to the order of  $(\delta n)^2$ , equally probable, but this does not imply that the transition probabilities from  $n^*$  to  $n^* + \delta n$  and  $n^* - \delta n$  are equal, because many other interconnected quantities are involved in determining the probability of appearance, as implied in Eq. (10) together with Eq. (4).

To see the numerical significance of the difference between  $n^*$  and  $n_K$ , let us derive the formula which relates  $n_K$  to  $n^*$ . Consider the identity

$$K^+(n)/K^-(n) = [K^+(n - \delta n)/K^-(n)][K^+(n)/K^+(n - \delta n)] \quad (18)$$

and rewrite the first factor in the right-hand side (RHS) by using Eq. (10) to get

$$K^+(n)/K^-(n) = [c_0(n)/c_0(n - \delta n)][K^+(n)/K^+(n - \delta n)]. \quad (19)$$

It follows from Eq. (6) that

$$c_0(n)/c_0(n - \delta n) = \exp\{-[W_{\text{th}}^{\text{rev}}(n) - W_{\text{th}}^{\text{rev}}(n - \delta n)]/kT\}, \quad (20)$$

where the  $n$  dependence of  $\Phi_{\text{LP}}$  is neglected. Let us suppose that  $n$  is close to  $n^*$  and expand  $W_{\text{th}}^{\text{rev}}$  in Eq. (20) into the Taylor series about  $n^*$ . It follows that

$$\exp\{-[W_{\text{th}}^{\text{rev}}(n) - W_{\text{th}}^{\text{rev}}(n - \delta n)]/kT\} = 1 + [\partial^2 W_{\text{th}}^{\text{rev}}/\partial n^2](n^* - n)\delta n/kT + o(\delta n), \quad (21)$$

where the differential coefficient is to be evaluated at  $n^*$ . Employing Eq. (8), we get

$$[\partial^2 W_{\text{th}}^{\text{rev}}/\partial n^2] = -\gamma^*(32\pi v^2/81)^{1/3}(n^*)^{-4/3}, \quad (22)$$

where  $v$  denotes the molecular volume for the bulk of a nucleating phase. Employing Eqs. (14), (20), and (21) in Eq. (19), we get

$$\begin{aligned}
& K^+(n)/K^-(n) \\
& = 1 + \{[\partial^2 W_{\text{th}}^{\text{rev}}/\partial n^2](n^* - n)/kT + 2/(3n)\} \delta n \\
& \quad + o(\delta n) . \tag{23}
\end{aligned}$$

The size  $n_K$  of the kinematically defined critical nucleus is given by solving

$$[\partial^2 W_{\text{th}}^{\text{rev}}/\partial n^2](n^* - n)/kT + 2/(3n) = 0 , \tag{24}$$

and we get

$$n_K \cong n^* - 2kT(n^*)^{1/3}/[3\gamma^*(32\pi v^2/81)^{1/3}] , \tag{25}$$

where Eq. (22) has been employed.

Substituting  $T=273$  K,  $\gamma^*=72.8$  erg/cm<sup>2</sup>, and  $v=3 \times 10^{-23}$  cm<sup>3</sup> in Eq. (25) as an example for water droplet nucleation from the vapor, we get

$$n_K \cong n^* - (n^*)^{1/3}/3 . \tag{26}$$

Taking  $n^*$  to be 125, we get  $n_K=123$ . Thus the difference between  $n^*$  and  $n_K$  is about 1% of  $n^*$  for a typical case of water nucleation from the vapor.

The consideration given so far presupposes a system to be in metastable equilibrium. However, since we assume that the interaction among clusters is negligible,  $K^+(n)$  and  $K^-(n)$  are determined only by the temperature, the size of a cluster, and the state of the parent phase and they do not depend on the actual concentration of clusters in the system. Hence the results obtained above may also be applied to nonequilibrium nucleation processes.

The kinetic definition represents more lucidly the role of the critical nucleus in nucleation processes. However, when we evaluate the steady state nucleation rate  $J_s$ , it is the knowledge of  $n^*$  and the values of  $W_{\text{th}}^{\text{rev}}(n)$  and  $K^+(n)$  for the sizes at and around  $n^*$  that are required.  $J_s$  is given by

$$\begin{aligned}
J_s & = c_s(n)K^+(n) - c_s(n+1)K^-(n+1) \\
& = c_0(n)K^+(n)[c_s(n)/c_0(n) \\
& \quad - c_s(n+1)/c_0(n+1)] , \tag{27}
\end{aligned}$$

where  $c_s$  denotes the steady state concentration of clusters and Eq. (10) is employed. It follows from Eq. (27) that

$$\begin{aligned}
& J_s/[c_0(n)K^+(n)] \\
& = c_s(n)/c_0(n) - c_s(n+1)/c_0(n+1) . \tag{28}
\end{aligned}$$

Adding each side of Eq. (28) from  $n=1$  to a size  $n^>$  which is much larger than  $n^*$  and employing the reasonable approximations that  $c_s(1)/c_0(1) \cong 1$  and  $c_s(n^>)/c_0(n^>) \cong 0$ , we get

$$J_s = \{ \sum [c_0(n)K^+(n)]^{-1} \}^{-1} , \tag{29}$$

where  $\sum$  represents the summation from  $n=1$  to  $n^>-1$ , in which the terms at and around  $n^*$  dominate. When nucleation occurs during a transient process, it is  $n_K$  that is relevant and the difference between  $n^*$  and  $n_K$  may become important. This problem is left for future investigation.

In conclusion, it is found that the size  $n_K$  of a cluster for which the probabilities of decay and growth balance is not equal to the size  $n^*$  for which the reversible work of cluster formation takes the maximum value.  $n_K$  is in general smaller than  $n^*$  when  $n$  is treated as a continuous variable. The formula to relate  $n_K$  to  $n^*$  is derived, which shows that the difference between  $n^*$  and  $n_K$  is about 1% of  $n^*$  in a typical case of water nucleation from the vapor.

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