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Effect of immobile impurities on two-dimensional nucleation

Hiroyasu Katsuno,¹ Kiiko Katsuno,² and Masahide Sato³

¹*Computer Centre, Gakushuin University, 1-5-1 Mejiro, Toshima-ku, Tokyo 171-8588, Japan*

²*Seikei University, 3-3-1 Kichijoji-Kitamachi, Musashino, Tokyo 180-8633, Japan*

³*Information Media Center, Kanazawa University, Kakuma-cho, Kanazawa 920-1192, Japan*

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We study the dependence of the critical size of the nucleus on the density of impurity by carrying out a Monte Carlo simulation. We assume that the impurities are fixed on a crystal surface, and neglect restoration of bonds between an impurity atom and an adsorbed atom. We initially prepare one cluster in the system and investigate the change of the cluster size. When the cluster size is the critical value, the frequency of increasing the cluster size is equal to that of decreasing the size. With increasing the impurity density, the critical nucleus becomes large. When the impurity density is sufficiently high, regardless of the initial cluster size, the cluster vanishes after a long time interval, namely, the critical cluster size is diverged.

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I. INTRODUCTION

Foreign substitutional atoms attached on the surface act as trapping centers for adatoms and/or as obstacles preventing growth of an adsorbate [1–4], and affect behaviors of steps and surface morphology [5–13]. When the period between impurities is shorter than the critical nucleus size, the step cannot advance because of the thermodynamic tension, which depends on the step curvature. In their experiment, Nakada and co-workers [14] studied the effect of impurities on a lysozyme crystal using atomic force microscopy. On the (101) surface, many small particles were observed and these act as impurities. The particles are formed by dimers of lysozyme molecules. With increasing the dimer density, the step velocity decreases. When the steps stop advancing, the distance between impurities on a step is as large as the critical nucleus diameter determined by the free energy. Zepeta and co-workers [15] observed adsorption kinetics of antifreeze glycoproteins (AFGPs) attached to an ice interface during solution growth. When the molecules of AFGPs are adsorbed to a specific interface, the growth of the interface is prevented, and the form of the interface becomes a facet. These results [14,15] are explained by pinning with impurities [5]: The impurities halt step advancing when the distance between impurities is comparable with the radius of the critical nucleus.

Recently, Dai and co-workers [16] observed spiral steps on a monoclinic lysozyme crystal. They measured the dependence of step velocities on the distance between adjacent spiral steps and found that the interstep distance is about 50 times larger than the expected value. The interstep distance is proportional to the radius of the critical nucleus, so the experiment suggests that the critical nucleus size is much larger than that expected by the change of free energy in the formation of the nucleus. Since many impurities are contained in commercially purchased protein [14–20], the cause of the unusual interstep distance [16] may be impurities, but previous studies [5–13] cannot explain the enlargement of the critical nucleus size.

In the previous studies [5–13], the effect of impurities attaching on an advancing step is taken into account, but the effect of impurities included in the solid phase is neglected. To explain the enlargement of the critical nucleus size, we need to consider the increase of free energy, which is caused

by the impurities included in the nucleus. Thus, in this paper, taking account of the effect of impurities included in a two-dimensional cluster, we study the possibility of the increase of the critical nucleus radius by immobile impurities. In Sec. II, we introduce our model and estimate the critical nucleus radius and the critical impurity concentration from the thermodynamic point of view. In Sec. III, we carry out a Monte Carlo simulation. In Sec. IV, we summarize results and give brief discussions.

II. MODEL

The critical nucleus radius is thermodynamically determined by the change in free energy ΔG during two-dimensional nucleation. For a pure system, ΔG is expressed as

$$\Delta G = -\frac{S}{\Omega} \Delta\mu + L\beta, \quad (1)$$

where S is the area of a two-dimensional nucleus, $\Delta\mu$ is the chemical potential gain during solidification per unit molecule, Ω is the area occupied by a unit molecule in a nucleus, L is the perimeter of a nucleus, and β is the step free energy. If the step energy is isotropic, the shape of the nucleus is circular. When the radius of the nucleus is r , $S = \pi r^2$ and $L = 2\pi r$. ΔG has the maximum value with the critical nucleus radius. From the condition $d\Delta G/dr = 0$, the critical nucleus radius r^c is given by

$$r^c = \frac{\Omega\beta}{\Delta\mu}. \quad (2)$$

We assume that the density of impurity is c_{imp} and study how the critical nucleus radius changes on the surface with uniform, immobile impurity concentration c_{imp} . When a two-dimensional nucleus with radius r is formed on the surface, the number of impurities in the nucleus is given by $c_{\text{imp}}\pi r^2$. When the area of one impurity is expressed as Ω_{imp} , the total area of impurities is given by $c_{\text{imp}}\pi r^2\Omega_{\text{imp}}$. By taking account of impurities in the nucleus, the chemical potential gain due to solidification is given by

$$-\frac{\pi r^2(1 - \Omega_{\text{imp}}c_{\text{imp}})\Delta\mu}{\Omega}. \quad (3)$$

For simplicity, we assume that recuperation of bonds between an impurity and a molecule in the horizontal direction is neglected. Owing to the formation of the interface between impurities and solid atoms, the increase of the step free energy by nucleation is expressed as

$$2\pi r\beta + c_{\text{imp}}\pi r^2 L_{\text{imp}}\beta, \quad (4)$$

where L_{imp} is the perimeter of an impurity. In Eq. (4), we assumed that the interface energy between impurities and molecules is as large as the step energy. From Eqs. (3) and (4), the total change of the free energy is given by

$$\Delta G = -\frac{\pi r^2}{\Omega} \Delta\mu \left(1 - c_{\text{imp}}\Omega_{\text{imp}} - c_{\text{imp}}\Omega \frac{L_{\text{imp}}\beta}{\Delta\mu} \right) + 2\pi r\beta. \quad (5)$$

The radius of the critical nucleus r_{imp}^c is given by

$$r_{\text{imp}}^c = r^c \left[1 - c_{\text{imp}} \left(\Omega_{\text{imp}} + \frac{\Omega L_{\text{imp}}\beta}{\Delta\mu} \right) \right]^{-1}. \quad (6)$$

From Eq. (6), we find that the critical nucleus size on the surface with impurities is larger than that on a clean surface. When c_{imp} is small, r_{imp}^c increases proportionally to c_{imp} . Then, the increase of r_{imp}^c is accelerated with increasing c_{imp} , and r_{imp}^c is diverged when the impurity density is the critical value c_{imp}^c , defined as

$$c_{\text{imp}}^c = \left(\Omega_{\text{imp}} + \frac{\Omega L_{\text{imp}}\beta}{\Delta\mu} \right)^{-1} = \frac{1}{\Omega_{\text{imp}} + L_{\text{imp}}r^c}. \quad (7)$$

Generally, the radius of impurity is much smaller than the critical nucleus radius in a pure system, so that $c_{\text{imp}}^c \approx (L_{\text{imp}}r^c)^{-1}$.

III. MONTE CARLO SIMULATION

To confirm the relation between the critical nucleus radius and the impurity density, we introduce a Monte Carlo simulation model. The algorithm of our simulation is very simple. We consider a square lattice with the lattice constant $a = 1$. The system size is $L_x \times L_y = L^2$ with the periodic boundary condition. For simplicity, we assume that impurities are immobile: They are prohibited from adsorption, evaporation, and diffusion. Initially, impurities are put on a crystal surface, and there is no impingement of impurities. Impurities act as obstacles for adatoms on the surface. Thus, we can regard the growth of the cluster as that with one component atoms. Then, atoms impinge to one of the sites neighboring on the edge of the cluster with the impingement rate F . The atoms solidify at the edge of the cluster and do not migrate on the surface. Solid atoms forming the edge of the cluster can evaporate. The frequency of the evaporation depends on the number of horizontal bonds n_J , and is expressed as $\omega \exp(-n_J E_J / k_B T)$, where E_J is the bonding energy between nearest-neighboring atoms and ω is the evaporation rate of a lonely adatom. We exclude the number of impurities from n_J , and forbid the evaporation of impurities.

In equilibrium, the infinitely long, straight step could not advance and recede. From the viewpoint of the microscopic process, the evaporation and the impingement of atoms are

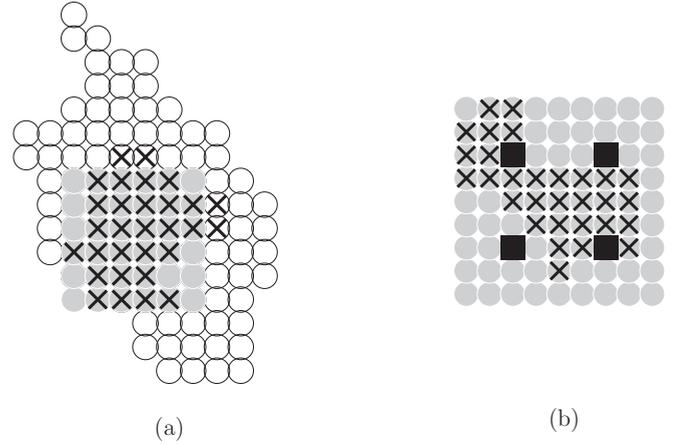


FIG. 1. Changes of cluster size and form for the supersaturation $\sigma = 0.125$ with initial cluster size of (a) 6^2 in a pure system and (b) 9^2 in a system with immobile impurities. The gray circles show an atom forming the initial cluster, and the crosses show a temporal cluster whose size is roughly as large as the critical nucleus size. The open circles in (a) show a form of the cluster at a later stage; note that the cluster vanishes in (b). Filled squares in (b) show immobile impurities.

balanced at kink sites. Since $n_J = 2$ at a kink site, the impingement rate in equilibrium, F^{st} , is expressed as

$$F^{\text{st}} = \omega \exp\left(-\frac{2E_J}{k_B T}\right). \quad (8)$$

When the chemical potential gain by solidification is $\Delta\mu$, the impingement rate F is related to F^{st} as

$$F = F^{\text{st}} \exp\left(\frac{\Delta\mu}{k_B T}\right). \quad (9)$$

Since the supersaturation, $\sigma = (F - F^{\text{st}})/F^{\text{st}}$, is related to $\Delta\mu$ as $\Delta\mu = k_B T \ln(1 + \sigma)$, σ is expressed as

$$\sigma = F \exp\left(\frac{2E_J}{k_B T}\right) - 1. \quad (10)$$

In our simulation, the system size is larger than $L^2 = 60^2$ and the bonding energy satisfies $\exp(-E_J / k_B T) = 0.1$.

Figure 1 shows a typical change of a cluster form during growth [Fig. 1(a)] and shrinking [Fig. 1(b)]. The initial cluster shape is set to square. Since an atom is bound by nearest-neighboring atoms, and we use a square lattice, the initial shape is an equilibrium shape. In Fig. 1(a), the size of the initial cluster, which is expressed by gray circles, is 6^2 and impurities are absent in the system. The cluster expressed by crosses shows a temporal form. During simulation, the desorption and the evaporation of adatoms repeat many times at the cluster edges, so that the form of the cluster is fluctuated and slightly rougher than the initial square. Similarly to a nucleus form in another model [21], the temporal form of the nucleus is not compact. The temporal cluster size is smaller than the initial size because of random fluctuation, but it is as large as the critical nucleus size, which we will mention later. A form of the cluster in the later stage is represented by open circles. After many Monte Carlo trials, the size of the cluster is much larger than the initial size, and the cluster grows steadily.

Figure 1(b) shows the evolution of the shape of the cluster including impurities. The initial cluster size is about 9^2 , which is 2.25 times larger than that in Fig. 1(a), and four impurities are included in the initial cluster. Although the initial size of the cluster is much larger than the critical nucleus size in a pure system, the cluster vanishes. The shape of a temporal cluster, whose size is as large as the critical nucleus size, is rougher than that in Fig. 1(a). Although the initial size is larger than the critical nucleus size in a pure system, the cluster cannot grow large, and vanishes after a long time.

In Fig. 1(b), the cluster shrinks when only a few impurities are included in a cluster, which means that the critical nucleus size becomes larger than that in a pure system owing to impurities. In order to confirm that this observation does not apply only to this one particular case, we determine the critical nucleus size by carrying out many runs, and show that the critical nucleus size increases due to impurities included in the cluster. We initially set immobile impurities at regular intervals and one cluster at random on a surface. To determine the critical nucleus size for various impurity concentrations, we define the probability of irreversible attachment $J(N)$ as

$$J(N) = \frac{P_+(N) - P_-(N)}{P_+(N) + P_-(N)}, \quad (11)$$

where $P_+(N)$ is the frequency of increasing the cluster size from N to $N + 1$, and $P_-(N)$ is the frequency of decreasing the size from N to $N - 1$. With a negative $J(N)$, the probability of the decrease of the cluster size is larger than that of the increase of the size, so that the cluster size decreases on average. With a positive $J(N)$, the cluster size increases on average. The critical nucleus size is determined from the condition that $J(N) = 0$. In our simulation, the separation of a cluster into a few small clusters and the coalescence of clusters occurs. When we count $P_{\pm}(N)$, we except the event of separation and coalescence of clusters, and take account of attachment and detachment between an atom and a cluster. When a cluster size is sufficiently larger than the critical value, shrinking of the cluster hardly occurs and the cluster keeps growing. Thus, in a run, we repeat impingement and evaporation of atoms until the cluster vanishes or is larger than N_{\max}^L , which is larger than the critical value.

First, we determine the critical nucleus size in a pure system. Figure 2 shows the dependence of $J(N)$ on N with $\sigma = 0.125$

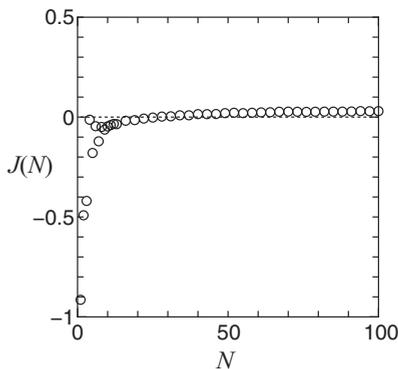


FIG. 2. Dependence of $J(N)$ on N with $\sigma = 0.125$ in a pure system.

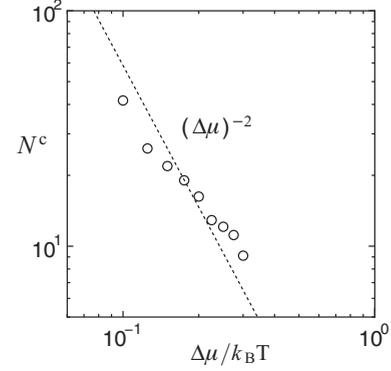


FIG. 3. Dependence of N^c on $\Delta\mu$ in a pure system.

in a pure system. $N_{\max}^L = 150$, and $P_{\pm}(N)$ is summed up for more than 10 000 independent runs. With a small N , the effect of the discreteness of the square lattice is not neglected. When $N = 4$ and 6, owing to the symmetry of the lattice, the compact cluster is stable. Except for these cluster sizes, when $N \leq 10$, $J(N)$ rapidly increases with increasing N . Then, $J(N)$ increases gradually. From Fig. 2, the critical nucleus size N^c is estimated to 26.0. Using various $\Delta\mu$, we investigate the dependence of N^c on $\Delta\mu$ (Fig. 3). Since the side length L^c is equal to $(N^c)^{1/2}$ for the square shape, the dependency of the nucleus size on the chemical potential agrees with the traditional thermodynamic theory given by Eq. (2).

From the above results, we confirm the validity of our model in a pure system. Then, we carry out the simulation and study the effect of impurities included in a cluster on the critical cluster size. From Eq. (6), the dependence of the size of the critical nucleus with impurity N_c^{imp} on c_{imp} is expressed as

$$N_c^{\text{imp}} = N_c \left[1 - c_{\text{imp}} \left(\Omega_{\text{imp}} + \frac{\Omega L_{\text{imp}} \beta}{\Delta\mu} \right) \right]^{-2}. \quad (12)$$

In Fig. 2, the critical nucleus size in a pure system is estimated to be $N^c = 26.0$. Since we use a square lattice with a lattice constant $a = 1$, the circumference of impurity $L_{\text{imp}} = 4$, and $S_{\text{imp}} = s_s = a^2 = 1$ in our model. If we assume that the form

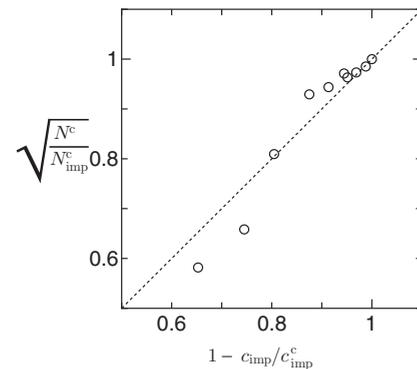


FIG. 4. Dependence of N_c^{imp} on c_{imp} with $\sigma = 0.125$ in the system with impurities. Dotted line represents Eq. (12) with $N^c = 26$ and Eq. (13).

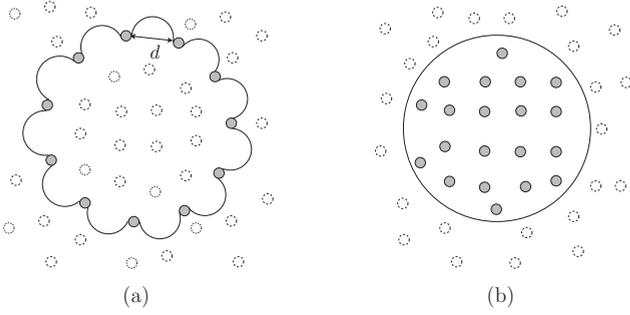


FIG. 5. Schematic picture of (a) Cabrera's model and (b) our model. The solid gray circles represent impurities whose effect is taken into account in the cluster's behavior, and the open dotted-line circles represent impurities that are not assumed to affect the cluster's behavior.

of the nucleus is round, then $\beta/\Delta\mu$ is given by $\sqrt{N^c/\pi}$ from Eq. (2). Thus, the critical impurity density satisfies

$$\frac{1}{c_{\text{imp}}^c} = \left(\Omega_{\text{imp}} + \frac{\Omega L_{\text{imp}} \beta}{\Delta\mu} \right) \approx 12.5. \quad (13)$$

In order to confirm the dependence of the impurity concentration on the critical nucleus size, we perform the simulation with immobile impurities on a surface at regular intervals. Figure 4 shows the dependence of the critical cluster size $N_{\text{imp}}^c(c_{\text{imp}})$ on the impurity density. The supersaturation $\sigma = 0.125$ and the critical nucleus size $N^c \approx 26$, which are obtained from Fig. 2. We count $P_{\pm}(N)$ until the cluster size becomes $N_{\text{max}}^L = 500$ or 0 in a run. The impurity density c_{imp} is defined as $1/n^2$, where n is an integer. The open circles represent the results of the simulation. In Fig. 4, we use c_{imp}^c obtained from Eq. (13), and the dotted line shows the relation given by Eq. (12). In Eq. (13), the estimation is carried out under the assumption of a round cluster, but in our simulation, we use a square lattice and the form of the cluster is not round. Irrespective of the difference, the results of our simulation agree with Eq. (12).

IV. SUMMARY AND DISCUSSIONS

In this paper, we studied the possibility of the increase of the critical nucleus size by impurity. We assumed that immobile impurities were attached on a surface and investigated the change of the free energy by the formation of a cluster. When a cluster is formed in the system with impurities, compared with the nucleation in a pure system, the chemical potential gain decreases and the step energy increases. These effects enlarge the critical cluster size.

To confirm our thermodynamical prediction, we carried out Monte Carlo simulations using a simple model. With a large supersaturation, the dependence of critical cluster size on the

chemical potential gain and the impurity density agrees with theoretical results. From Eq. (7), we found that c_{imp}^c depended on two terms, Ω and $L_{\text{imp}} r^c$. The first term is the effect of the decrease of the solid area by impurities and the second term is that of the increase of the interface by impurities. When the impurity size is smaller than the critical size, c_{imp}^c is mainly determined by the latter effect.

Figure 5 schematically shows the difference between Cabrera's model [5] and our model. In Cabrera's model [5,6] [Fig. 5(a)], once a step passes by impurities and impurities are included in the cluster, the included impurities do not affect the behavior of the cluster shape. Only the impurities attaching a step impede the motion of the step segment. If the distance between impurities d is larger than the critical nucleus size $2r^c$, the step can form the convex curve energetically and advance. As a result, the cluster surrounds impurities. Once the impurities are included in a cluster, they do not affect the motion of the cluster's edge, and the edge moves again. However, if $d < 2r^c$, the edge of the cluster cannot form the curve sufficiently, so that the cluster cannot surround impurities. Thus, the pinning by impurities occurs and the edge stops advancing [Fig. 5(a)] when $c_{\text{imp}} \sim (r^c)^{-2}$.

On the other hand, in our model [Fig. 5(b)], the interface energy between the solid atom and impurities included in a cluster are taken into account. By the interface energy, the chemical potential gain in solidification decreases and the critical nucleus size increases. Our results suggest that the critical cluster size diverges when $c_{\text{imp}} \approx (L_{\text{imp}} r^c)^{-1} \sim (r^c)^{-1}$. In Fig. 1(b), all the impurities were initially put in a cluster and were not on the step edge. The size of the initial cluster was larger than the critical value in a pure system, but the cluster vanished. The simulation result suggests that the shrinking of the cluster is not caused by the Cabrera's scenario, but caused by our scenario.

In our model, the impurities were immobile and the detachment from the surface was neglected. The case that we considered was a very idealized case. To compare the results in real systems, we need to clarify the effect of mobility, namely, the effect of evaporation and surface migration. The investigation of the effect of the mobile impurity on the critical nucleation size is underway.

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