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Applicability of the Fokker-Planck equation to the description of diffusion effects on nucleation

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The nucleation of islands in a supersaturated solution of surface adatoms is considered taking into account the possibility of diffusion profile formation in the island vicinity. It is shown that the treatment of diffusion-controlled cluster growth in terms of the Fokker-Planck equation is justified only provided certain restrictions are satisfied. First of all, the standard requirement that diffusion profiles of adatoms quickly adjust themselves to the actual island sizes (adiabatic principle) can be realized only for sufficiently high island concentration. The adiabatic principle is essential for the probabilities of adatom attachment to and detachment from island edges to be independent of the adatom diffusion profile establishment kinetics, justifying the island nucleation treatment as the Markovian stochastic process. Second, it is shown that the commonly used definition of the "diffusion" coefficient in the Fokker-Planck equation in terms of adatom attachment and detachment rates is justified only provided the attachment and detachment are statistically independent, which is generally not the case for the diffusion-limited growth of islands. We suggest a particular way to define the attachment and detachment rates that allows us to satisfy this requirement as well. When applied to the problem of surface island nucleation, our treatment predicts the steady-state nucleation barrier, which coincides with the conventional thermodynamic expression, even though no thermodynamic equilibrium is assumed and the adatom diffusion is treated explicitly. The effect of adatom diffusional profiles on the nucleation rate preexponential factor is also discussed. Monte Carlo simulation is employed to analyze the applicability domain of the Fokker-Planck equation and the diffusion effect beyond it. It is demonstrated that a diffusional cloud is slowing down the nucleation process for a given monomer interaction with the nucleus edge.

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I. INTRODUCTION

Nucleation is the first stage of new phase formation, which determines the subsequent phase transition kinetics and is broadly studied in basic research and applications [1–6]. The analytical description of steady-state homogeneous nucleation with discrete [7,8] or continuous [9,10] cluster models is commonly referred to as the classical nucleation theory (CNT). Typically, CNT models employ the Fokker-Plank equation (FPE) formalism for the description of cluster kinetics. That is, when volume fraction occupied by nucleating clusters is negligible and the intercluster distances are much larger than their linear dimensions, the cluster ensemble is described by a distribution function $f(n,t)$ defined as the volume [or, in the two-dimensional (2D) case–surface] density of clusters containing n monomers at time t [11–14]. Following the common practice of treating n as a continuous variable, the distribution function evolution is described by the governing Fokker-Planck equation (here–in the Itoh's form):

$$\frac{\partial f}{\partial t} = -\frac{\partial I}{\partial n}, \tag{1}$$

where the flux of nuclei, $I(n,t)$, along the size axis n is defined as

$$I(n,t) = Af - \frac{\partial}{\partial n}(Bf), \tag{2}$$

where A and B are the kinetic coefficients describing the drift and diffusion rates of clusters in the size space. This function is normalized per total volume (or surface in 2D) density of islands, ρ, that is $\int f(n,t)\,dn = \rho$. When the cluster size distribution function is known, many statistical properties of the nucleation process can be deduced. For example, the barrier and the rate of nucleation can be found using the steady-state solution of the FPE.

An important assumption behind the use of the FPE is the Markovian nature of cluster size evolution, where the probabilities of absorption and detachment of monomers at the cluster interfaces are determined by instantaneous monomer concentrations and do not depend on the monomer redistribution history. This requirement is easily satisfied in the case where the monomer capture and emission are rare and the disturbed monomer concentration in the cluster vicinity quickly relaxes to the average concentration in the bulk. However, another frequently met situation, where the cluster growth rate is limited by diffusion transport of monomers, is much less straightforward because one has to consider the deviation of the monomer concentration in the cluster vicinity from the average one. Indeed, the diffusion profiles of monomers in the cluster vicinity include monomers previously emitted by the clusters (Fig. 1), so that the cluster growth has the memory effect. In order to follow the monomer return to the cluster, one has to include a history-dependent term in the Langevin equation for a cluster size [15–17]. Such equation can be reduced to a fractional derivative FPE [18,19], describing abnormal diffusion in the size space. Alternatively, one can include in the model an explicit description of the spatial and temporal kinetics of a monomer concentration field. This restores the Markovian property, but at the cost of an infinite-dimensional FPE [20].

In this paper we discuss some methodological problems met in the application of FPE formalism to the description of diffusion-limited cluster nucleation and suggest a possible

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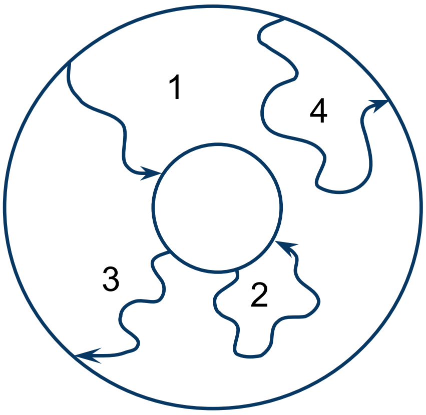

FIG. 1. Different processes contributing to the diffusion transport of monomers in the zone of influence of a selected island. Both currents **1** and **2** contribute to monomer absorption at the island edge, but only the "net" absorption current **1** is used for the evaluation of kinetic coefficients. Similarly, current **3** defines the "net" desorption.

approach to circumvent them. As an example, this approach is applied to the effect of diffusion on surface island nucleation and predicts the kinetic barrier for island nucleation, which is qualitatively different from the earlier predictions (e.g., [21–23]).

II. SOME METHODOLOGICAL ASPECTS OF FOKKER-PLANCK EQUATION DESCRIPTION OF DIFFUSION-CONTROLLED CLUSTER NUCLEATION

A. The validity of adiabatic approximation

The Markovian description of the cluster ensemble implies that the probabilities of monomer absorption and desorption on individual islands are uniquely determined by the island sizes. In the presence of monomer diffusion profiles, this can be achieved only approximately, in a special case where the monomer profiles adjust themselves to any change of a cluster size much faster than the cluster size changes (this condition is usually referred to as the adiabatic principle) [24]. In this case the monomer diffusion profile around a cluster can be treated as being in one-to-one correspondence with the cluster size.

After an absorption or emission of a monomer, the quasi-steady-state diffusion profile in the cluster vicinity reestablishes after a characteristic time $\tau_C \sim R_s^2/D$ [25], where D is the monomer diffusion coefficient and R_s, the characteristic distance from the cluster, where the deviation of the monomer concentration from the average value in the system, C_0, practically vanishes. The fundamental solution of the three-dimensional (3D) steady-state diffusion problem is bounded above at the infinite distance, so the cluster radius R usually can be a good characteristic lengths, and one can safely assume $R_s \sim R$, whereas in 2D case R_s should be of the order of the concentration screening length due to the effect of all sinks in the system. The account of screening or a limited-size influence zone is essential in the two-dimensional case, providing the existence of the steady-state solution itself.

The characteristic time of the island size variation can be estimated as $\tau_R \sim R/(dR/dt)$, where R is the island radius and dR/dt is the growth rate:

$$\frac{dR}{dt} \sim \frac{v}{\lambda} DC_0. \tag{3}$$

Here $v = \exp(-\varepsilon/T)$ is the efficiency of monomer capture at the cluster boundary, where ε is the additional Gibbs energy of the monomer jump between the cluster and its proximity [22] and T is the temperature; λ is the diffusion jump length, which can be also taken as the width of the cluster boundary.

For the validity of the adiabatic principle, condition $\tau_C/\tau_R \ll 1$ must be fulfilled, which is equivalent to

$$\frac{R\lambda}{vR_s^2} \gg C_0. \tag{4}$$

In the three-dimensional case ($R_s \sim R$) this condition limits the allowed monomer concentration, though in practice the limitation is a weak one because CNT is by definition applied to strongly diluted monomer systems. In the 2D case it can be easily verified that, as far as the islands are the only monomer sinks and sources, $R_s^{-2} \sim \rho$, where ρ is the surface island concentration. Then criterion (4) means that for any given average monomer concentration there exists a certain island concentration, below which the adiabatic approximation is inapplicable. In other words, CNT cannot be applied to the description of very early stages of island nucleation, when ρ remains below the critical value.

In view of the latter restriction, it is interesting to discuss in more detail, in which cases Eq. (4) can be satisfied in physical situations. First of all, the nucleation does not always take place at ideally flat surfaces. In the case of alternative sinks for monomers (e.g., steps at vicinal crystal faces) the screening distance R_s remains nonzero even when the surface density of islands vanishes. Second, even in the absence of alternative sinks, the nucleation of islands can occur without any free-energy barrier (e.g., when the monomer emission is strongly energetically unfavorable). In this case, the validity of Eq. (4) becomes a question of time, because the surface density of islands continuously grows, while the average concentration of free monomers decreases. Somewhat more complicated is the nucleation with overcoming of the free-energy barrier. In this case the surface density of the island also quickly becomes nonzero due to fluctuatively formed clusters (dimers, trimers, etc.). Even though these clusters may be subcritical (i.e., on average they emit monomers easier than absorbing them), they contribute to the screening, making R_s finite. However, there is no guarantee that this finite value would become sufficiently large to satisfy Eq. (4) within any reasonable time.

The restrictiveness of Eq. (4) can be weakened in the case in which the efficiency of monomer capture by a cluster is low, $v \ll 1$. This situation can arise, e.g., when the capture of monomers is limited by the availability of places at the cluster periphery that might accommodate a monomer. When clusters are pronouncedly faceted, the rate of cluster growth may be determined by the number of jogs at the cluster edges (a very similar situation of point defect absorption by an edge dislocation is considered in [26]).

B. Cluster diffusion in the size space

Assuming the validity of the adiabatic principle, the kinetic coefficients A and B should be found from the rates of the monomer absorption and desorption by the clusters, which will be referred to below as $P(n)$ and $Q(n)$. The common expression for A is

$$A = P(n) - Q(n), \tag{5}$$

whereas more than one definition of B is possible, though the most often used one is

$$B = \tfrac{1}{2}[P(n) + Q(n)]. \tag{6}$$

A methodological problem that appears in the diffusion-controlled cluster growth case is the correct definition of P and Q.

The requirement of the steady-state diffusion in the vicinity of a cluster imposes a relation between these values, that is [22,23],

$$P(n) - Q(n) = J(C_0, C_{\text{eq}}, n), \tag{7}$$

where J is the diffusional current of monomers to the cluster, which is uniquely determined by the average concentration of free monomers in the system, the equilibrium monomer concentration, C_{eq}, and the cluster size. Being the only restriction on P and Q, relation (7) fixes $P(n)$ and $Q(n)$ only up to an additive constant. This is not a big problem for those applications, where the cluster system behavior is dominated by the drift term in the FPE. However, in the nucleation problems, where both the drift and diffusion terms in the FPE are essential, the uncertainty in the definition of P and Q can strongly influence the predictions, because B is not invariant to P and Q changes by the same value. Evidently, there should exist a certain criterion for the unique selection of P and Q because it is evidently unphysical that the system behavior is affected by the arbitrariness of P and Q selection.

To get a hint as to where the problem comes from and how to deal with it, it is helpful to recall how the FPE (1)–(2) is obtained. A common way of FPE derivation starts with the stochastic Langevin equation for island size [11–14],

$$\frac{dn}{dt} = A + g(n,t), \tag{8}$$

where $g(n,t)$ is the delta-correlated function of time:

$$\langle g(n,t')g(n,t'')\rangle = \langle g^2(n)\rangle \delta(t' - t'') \tag{9}$$

(angular brackets mean the ensemble averaging), which has a vanishing mean value,

$$\langle g(n,t)\rangle = 0. \tag{10}$$

The kinetic coefficient B in the resulting FPE at any given time t is proportional to the dispersion of $g(n)$:

$$B = \frac{\langle g^2(n)\rangle - \langle g(n)\rangle^2}{2} = \frac{\langle g^2(n)\rangle}{2}. \tag{11}$$

Let us consider a process which includes two kinds of random events: absorption and desorption. If the corresponding stochastic functions $p(n,t)$ and $q(n,t)$ are delta-correlated functions of time and

$$\begin{aligned} \langle p(n,t)\rangle &= P, \\ \langle q(n,t)\rangle &= Q, \end{aligned} \tag{12}$$

then we can use them in Eq. (8), assigning

$$A = P - Q, \tag{13}$$

$$g(n,t) = p(n,t) - P - [q(n,t) - Q]. \tag{14}$$

The substitution of relation (14) into (11) gives

$$B = \tfrac{1}{2}(\langle p^2\rangle - P^2 + \langle q^2\rangle - Q^2 - 2\langle (p - P)(q - Q)\rangle). \tag{15}$$

In the case in which stochastic functions p and q are statistically independent, the last term in Eq. (15) disappears and the kinetic coefficient B is determined by the sum of dispersions of p and q. If absorption and desorption are Poisson processes, then their dispersions coincide with the mean values and Eq. (15) further reduces to Eq. (6).

Thus, the validity of the conventional expression (6) implies that monomer absorption and desorption by clusters are independent Poisson processes. The Poisson property is usually a reasonable assumption [27], but the independence of absorption and desorption processes requires special consideration.

As discussed in the Introduction, the point defect absorption and desorption cannot generally be considered as statistically independent, because the absorption includes, in part, recently detached monomers. It is possible, however, to suggest a physical approach that guarantees the independence of absorption and desorption [28]. It is physically clear that when monomers emitted by a cluster move too far from it, they become involved in so complicated interactions with other clusters, that the probability of their return becomes completely uncorrelated with the emission event. Hence, it is possible to specify around each cluster its "zone of influence" [29] and demand that an emitted monomer leaving this zone becomes a part of the "average" monomer concentration and keeps no memory about its former kinetics. The sizes of the influence zones are roughly comparable to the average distance between the clusters (or, where the monomer diffusion is described in terms of effective-medium approach, the concentration screening length [30]). Although an isolated subcritical nucleus is rather an emitter of monomers, their ensemble as a whole necessarily provides the monomer sink as a source of its formation and maintenance. The limited influence zone has a crucial importance in the 2D case, where it leads to the exponentially distributed return time of a monomer random walk [31,32] and can justify the adiabatic principle, allowing the steady-state solution of a 2D diffusion problem [22].

When defining the absorption rate P, we demand that it is equal to the average number of monomers arriving into the influence zone from memory-free average monomer concentration. Correspondingly, Q includes only that part of the emitted monomers that leave the zone of influence. Thus, defined "net" absorption and desorption processes are *independent* from each other by definition.

This treatment is closely related to the problem of the correlation factor for defect-mediated diffusion [33,34], though we deal here with the diffusion in the cluster size space, rather than in the real space.

III. KINETIC COEFFICIENTS AND NUCLEATION BARRIER

In this section we apply our approach to the nucleation in two-dimensional geometry. To be specific, we model the decay of a supersaturated solution of adatoms on the surface of a solid. However, the approach can be equally well applied to other 2D problems (clustering in layered structures, growth of thin films, etc.), as well as the nucleation in three-dimensional systems.

A. Monomer absorption and desorption rates

Let the new phase nuclei be monolayer disk islands with radii R, determined by the numbers n of monomers that they contain,

$$R = \sqrt{\frac{n\omega}{\pi}}, \tag{16}$$

where ω is the island area per monomer. An island grows and dissolves via monomer absorption and desorption, the rates of which are determined by the diffusional supply of adatoms from the surface outside the island and by the adatom interaction with the island edge.

The rates of monomer absorption and desorption at a cluster of fixed size will be determined here in the effective-medium approximation. That is, instead of explicit separation of the surface into zones of influence for each individual cluster, we will assume that each cluster is immersed into an effective medium with the sink strength k^2 exactly equal to the ensemble-averaged sink strengths of all available islands. This approach gives essentially the same monomer currents as the explicit cells [30], but allows us to avoid the inessential complications of solving diffusion equations in finite influence zones of complicated shape.

In order to find the net absorption rate of monomers, we consider only monomers coming to the edge of a selected island outside of its zone of influence, which corresponds to monomer current **1** in Fig. 1. This can be achieved by setting the probability of the monomer detachment from the selected island vanishing. The steady-state spatial distribution of monomer concentration C_1 near a sink satisfies the standard effective-medium equation [30],

$$D(\nabla^2 - k^2)\, C_1 = 0. \tag{17}$$

The sink strength k^2 is assumed to be constant during the nucleation stage, though at the later stages of the system kinetics the account of its time dependence can become relevant [35–37].

Having in mind that C_1 includes only monomers, which participate in the events **1** and **4** (Fig. 1), the boundary conditions should be written down as

$$C_1|_{r\to\infty} = C_0, \tag{18}$$

$$\frac{2\pi R}{\omega} D\nabla C_1\bigg|_{r=R} = P_1, \tag{19}$$

where the absorption rate P_1 is proportional to the monomer concentration $C_1(R)$ at the island edge in the layer of about the diffusional jump length λ, and the efficiency of monomer capture at the edge v:

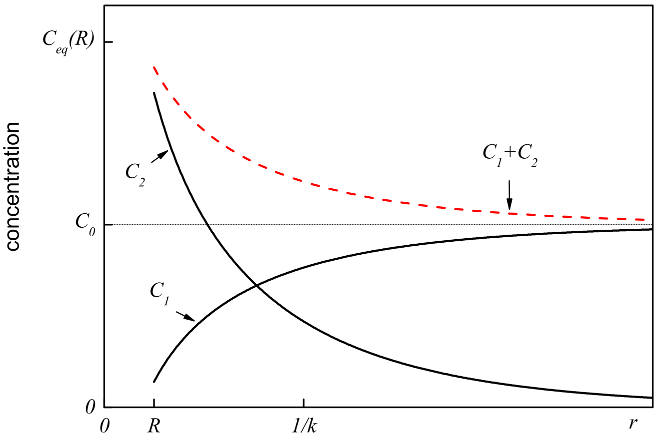

FIG. 2. The concentration profiles of monomers, participating in the separated absorption (C_1) and desorption (C_2) processes. Their sum $C_1 + C_2$ (dashed curve) provides a diffusional profile in the vicinity of a selected island, where both processes are taken into account.

$$P_1 = \frac{2\pi R}{\omega\lambda} v D C_1(R). \tag{20}$$

The diffusion problem (17)–(20) determines the diffusion profile (Fig. 2) and gives the unknown monomer concentration at the island edge in the form [22,23]

$$C_1(R) = \frac{C_0}{1 + u(R)}, \tag{21}$$

where $u(R)$ depends on the sink strength of all clusters:

$$u(R) = \frac{v}{\lambda} \frac{K_0(kR)}{k K_1(kR)}. \tag{22}$$

Here K_0 and K_1 are the modified Bessel functions of zero and the first order, respectively.

The net rate of monomer “escape” from a selected island (current **3** in Fig. 1) can be found from the diffusion equation similar to (17),

$$D(\nabla^2 - k^2)\, C_2 = 0, \tag{23}$$

but with the vanishing average monomer concentration in order to exclude the monomer flux from outside. This corresponds to the following boundary conditions:

$$C_2|_{r\to\infty} = 0, \tag{24}$$

$$\frac{2\pi R}{\omega} D\nabla C_2\bigg|_{r=R} = -Q. \tag{25}$$

The net desorption rate Q in Eq. (25) takes into account only current **3**, while the total rate of the monomer desorption from the island, $Q + P_2$, is determined by the equilibrium concentration at the island edge $C_{\mathrm{eq}}(R)$ and constitutes currents **2** (with the absorption rate P_2 and the necessarily equal desorption rate) and **3**:

$$Q + P_2 = \frac{2\pi R}{\omega\lambda} v D C_{\mathrm{eq}}(R). \tag{26}$$

Similar to Eq. (20), the rate of absorption of previously emitted monomers is given by

$$P_2 = \frac{2\pi R}{\omega\lambda} v D C_2(R). \tag{27}$$

Solving the diffusion problem (23)–(25) for C_2, one easily gets

$$C_2(R) = \frac{u C_{\mathrm{eq}}(R)}{1+u(R)} \tag{28}$$

and

$$Q = \frac{2\pi R}{\omega\lambda} v D \frac{C_{\mathrm{eq}}(R)}{1+u(R)}. \tag{29}$$

The sum of C_1 and C_2 (Fig. 2) coincides with the solution of the full diffusion problem [22,23], which is a consequence of the linearity of the problem.

At this junction, it is worth mentioning that the treatment above is very similar to that used in Refs. [15–17], where even three independent stochastic processes were introduced, corresponding to net absorption, net desorption, and the emission of monomers to be returned (currents **1**, **3**, and **2** in Fig. 1, respectively). However, in our diffusion problem processes **2** and **3** cannot be independent because their sum gives the full emission rate (26), which is determined exclusively by the local structure of the cluster edge and is unaware of the subsequent career of the emitted monomer.

B. Nucleation barrier

In order to demonstrate the advantage of our approach, let us use it for the estimation of the steady-state cluster nucleation rate. In doing it, we assume that the parameters of the island and monomer systems are such that the adiabatic principle can be applied. We also assume that the rate of cluster drift A in Eq. (2) follows the standard assumptions of CNT, namely, it is a monotonically increasing function of island size, which remains negative when n is below a certain critical value $n_c \gg 1$.

The general CNT treatment suggests that, after some time lag, the creation of new clusters (more exactly, the transition of nuclei into the growth region on the size axis, $n > n_c$) occurs for some time at a nearly constant rate, I_{st} [6]. This rate is known to be determined by the steady-state solution of Eqs. (1) and (2) and can be written down as [9]

$$I_{\mathrm{st}} = f_0(n_{\min})\, B(n_{\min}) \sqrt{\frac{1}{2\pi} \left| \frac{d^2\varphi}{dn^2} \right|_{n=n_c}} \exp(-\varphi_c). \tag{30}$$

Here f_0 is the constraint equilibrium size distribution function, which describes the size distribution of heterophase fluctuations under zero nucleation rate conditions [$I_{\mathrm{st}}(f_0) = 0$], $n_{\min}$ is the minimum size starting from which the clusters are identified as clusters, $\varphi_c = \varphi(n_c)$ is the nucleation barrier, and $\varphi(n)$ is the function determined by the FPE kinetic coefficients:

$$\varphi(n) = -\int_{n_{\min}}^{n} \frac{A(n')}{B(n')}\, dn'. \tag{31}$$

Using Eqs. (20) and (29), the kinetic coefficients can be written down in our approach as

$$A = P_1 - Q = \frac{2\pi R}{1+u(R)} \frac{vD}{\omega\lambda} [C_0 - C_{\mathrm{eq}}(R)], \tag{32}$$

$$B = \frac{P_1 + Q}{2} = \frac{\pi R}{1+u(R)} \frac{vD}{\omega\lambda} [C_0 + C_{\mathrm{eq}}(R)]. \tag{33}$$

For the equilibrium monomer concentration at the island edge we use the standard Gibbs-Thomson relation,

$$C_{\mathrm{eq}}(R) = \exp\left(-\frac{\Psi - \gamma\omega/R}{T}\right), \tag{34}$$

where Ψ is the Gibbs energy of monomer evaporation from a flat island edge, and γ is the edge line tension.

Critical islands correspond to the vanishing drift kinetic coefficient in the FPE, $A(n_c) = 0$. This gives the following expression for the critical radius:

$$R_c = \frac{\gamma\omega}{\Psi - T\, \ln(1/C_0)}. \tag{35}$$

In the vicinity of the critical size, where $|\,C_0 - C_{\mathrm{eq}}(R)\,| \ll C_0$, the ratio A/B is reduced to

$$\frac{A}{B} = 2\frac{C_0 - C_{\mathrm{eq}}(R)}{C_0 + C_{\mathrm{eq}}(R)} \approx \frac{C_0 - C_{\mathrm{eq}}(R)}{C_0}. \tag{36}$$

Note that expression (36) does not include $u(R)$, which depends on the island edge barrier ε and the sink strength k^2 and which is related to the deviation of the monomer concentration in the cluster vicinity from the average monomer concentration C_0 in the system. Correspondingly, the nucleation barrier contains no memory about the presence of diffusional profiles and the other clusters,

$$\varphi_c = \frac{\pi\gamma R_c}{T}. \tag{37}$$

In the present formalism, the nucleation barrier (37) coincides with that expected for nucleation in thermodynamic conditions, where it is equal to the minimal work of the cluster formation [7,8]. However, the current approach uses no assumption of thermodynamic equilibrium and is applicable to nonequilibrium systems. A relevant example is met in crystals under irradiation [28], where cluster nucleation involves coprecipitation of radiation-produced vacancies and self-interstitial atoms, making the introduction of the minimal work for cluster formation meaningless.

The preexponential factor in expression (30) for the steady-state nucleation rate can depend on the diffusion profile via $B(n_{\min})$. For the minimum island size one can safely assume $kR_{\min} \ll 1$ and use in Eq. (22) asymptotic relations for the modified Bessel functions, that is, $K_0(x) \sim -\ln x$ and $K_1(x) \sim 1/x$. Thus, for small clusters (with $R \sim \lambda$) $u(R)$ can be approximated by

$$u(\lambda) \sim -v\, \ln(k\lambda). \tag{38}$$

A low efficiency for defect accommodation at the cluster edge ($v \ll 1$) makes $u(\lambda)$ negligible compared to unity and completely eliminates the effect of the diffusion profile on $B(n_{\min})$ and on the nucleation rate. In the opposite case

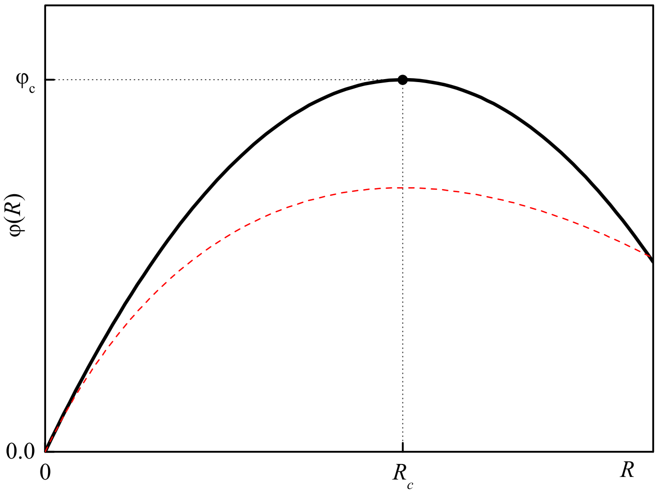

FIG. 3. The island nucleation barrier function $\varphi(R)$ corresponding to Eq. (37). The dashed curve illustrates the estimation using the kinetic coefficient expressions suggested in earlier papers [22,23] with $\upsilon = 0.25$, $k = 0.01\,\lambda^{-1}$.

($\upsilon \gg 1$), the preexponential factor in I_{st} decreases as the logarithm of the sink strength.

The earlier treatments, where the effect of monomer return is not eliminated from the absorption rate [22,23], underestimated the nucleation barrier, since the diffusion term B in the FPE was artificially increased (see Fig. 3). Correspondingly, the nucleation rate, which depends exponentially on the nucleation barrier, could be largely overestimated.

IV. MONTE CARLO SIMULATION OF THE DIFFUSION EFFECT

We have demonstrated that in the domain of the adiabatic principle the adjusted kinetic coefficients (32) and (33) correspond to a decrease of the nucleation rate in the case of diffusional cloud formation. However, the situation beyond the applicability of the FPE requires further analysis. On the one hand, a diffusional cloud in the nucleus vicinity can accumulate the evaporated monomers, making them easier to return [15–17], but on the other hand, it also limits the monomer supply. Even if the effects would compensate each other on average, the cluster mobility in the size space could increase with the process dispersion. In order to estimate the resulting effect let us consider the simplest system with a single intermediate layer between the nucleus edge and some average field of monomers in the bulk [see Fig. 4(a)]. Here $n \geqslant 1$ is the nucleus size (the number of constituent monomers), and C_0 and C_1 are the monomer concentrations in the bulk (assumed to be constant) and within the "diffusional" layer, respectively, so that the transition rates, indicated in the figure, can be written as follows:

$$\begin{aligned} p &= w_1 C_1 \sqrt{n}, \\ q &= \begin{cases} w_1 C_{\mathrm{eq}}(\infty)\sqrt{n}\exp\left[\sqrt{\frac{n_c}{n}}\ln\left(\frac{C_0}{C_{\mathrm{eq}}(\infty)}\right)\right], & n > 1 \\ 0\,, & n = 1. \end{cases} \\ j_1 &= w_0 C_1 \sqrt{n}, \\ j_0 &= w_0 C_0 \sqrt{n}, \end{aligned} \tag{39}$$

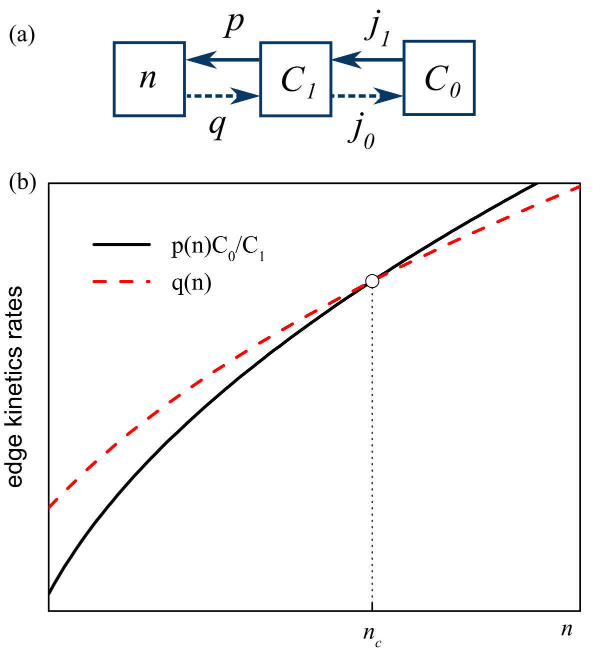

FIG. 4. Monte Carlo simulation scheme (a) and the probabilities of attachment and detachment depending on the island size n (b).

where $C_{\mathrm{eq}}(\infty)$ is the equilibrium monomer concentration at a flat island edge according to (34), w_1 is the coefficient of jumping rate between the island edge and the intermediate layer, which includes also the absorption probability υ and geometric constants from (20), and w_0 is the similar coefficient for monomer transition between the intermediate layer and the bulk. In our model system we assume that the diffusional layer is thin enough to be characterized by the nucleus size $\sqrt{n}$. Cluster size dependences of p and q for given C_1 are sketched in the Fig. 4(b). Their intersection determines the critical size n_c with respect to the bulk monomer concentration C_0. This definition remains consistent with (35) since the critical nucleus does not disturb the monomer solution [22].

Actually the value of w_1 gives the time scale, and the reaction controlled case corresponds to very rapid diffusion $w_0 \gg w_1$, so that the diffusional layer is very fast mixing with the bulk and $C_1 = C_0$. In this case one could obtain the steady-state nucleation rate either via simulation or a FPE solution (30). But in order to take into consideration diffusion-limited processes, when $w_0 \sim w_1$ or even $w_0 \ll w_1$, we will calculate and compare the distribution of the supercritical ($n > n_c$) nucleus formation time $f_c(t)$. For a known time-dependent size distribution function $f(n,t)$ it could be found as [11,31,38]

$$f_c(t) = \frac{\partial}{\partial t} P_c(t), \tag{40}$$

where

$$P_c(t) = 1 - \int_0^{n_c} f(n,t)dn. \tag{41}$$

Alternatively, having the Monte Carlo sampling of the transition rates (39) we can find $f_c(t)$, starting from the

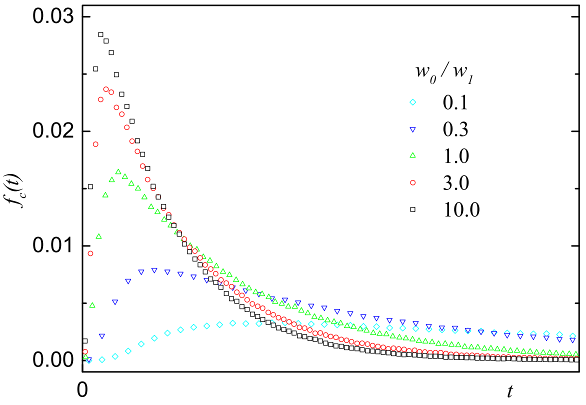

FIG. 5. Distribution function of the supercritical island formation time: Monte Carlo calculations for different kinetic regimes.

initial point

$$n|_{t=0} = n_0 = 1, \quad C_1|_{t=0} = C_0; \tag{42}$$

and summing up the values of $\Delta t = -\tau \ln(\gamma)$ while $n \leqslant n_c$. Here $\tau = 1/(p + q + j_0 + j_1)$ is determined by the total event frequency, and $\gamma \in (0,1]$ is the uniformly distributed random value.

The resulting plots of $f_c(t)$ are shown in the Fig. 5 for several ratios of the diffusion jump frequency w_0 and the reaction rate w_1. For $w_0 \gg w_1$, which in practice means w_0/w_1 more or about 10, the Poisson distribution of the supercritical island formation time is obtained. According to [39] it indicates the steady-state nucleation regime, whereas deviations correspond to a time-correlated process. Thus we can justify the FPE applicability for not extremely large ratios w_0/w_1. However, in the opposite case or even for $w_0 \sim w_1$, it can be seen that the formation time is systematically increasing. This means that the diffusional layer in our model is slowing down the nucleation process, when the diffusion effect turns out beyond the FPE domain.

V. CONCLUSIONS

Our paper demonstrates that the treatment of cluster nucleation in terms of the Fokker-Planck equation formalism meets problems when the cluster growth and dissolution are controlled by the diffusional transport of monomers. First of all, the Fokker-Plank equation is applicable to Markovian processes, which can be justified only provided the diffusion profiles of monomers quickly adjust themselves to the cluster size variations. While this requirement is nearly always satisfied for diluted 3D systems of monomers, in the two-dimensional case it imposes a restriction on the minimum cluster density in the ensemble.

Second, we discuss the problem of uncertainty of FPE kinetic coefficient definition in a system of clusters growing in a diffusion-controlled regime. It is shown that the common expression for the "diffusion" coefficient in an FPE [Eq. (6)] can be employed only if the attachment and detachment of monomers to clusters are statistically independent processes. We demonstrate that this restriction makes the definition of kinetic coefficients unique, and propose a possible approach to the calculation of kinetic coefficients so that the required statistical independence of monomer absorption and desorption was guaranteed.

The above-mentioned general considerations were applied to the problem of adatom island nucleation on solid surfaces, resulting in notably different predictions as compared to the earlier treatments, where these limitations were not considered. For example, the island nucleation barrier turned out to be insensitive to the presence of diffusion profiles and coincided with the conventional thermodynamic expression, regardless of the fact that no thermodynamic equilibrium had been assumed. On the other hand, the preexponential factor of the nucleation rate can explicitly depend on the diffusion profile parameters.

Monte Carlo simulation was used to evaluate the diffusion effect beyond the FPE applicability. The increase of the supercritical nucleus formation time was demonstrated as the intermediate diffusional layer plays a more prominent role in the monomer kinetics.

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