Instability of the axisymmetric shape of two-dimensional nuclei as a function of the relaxation of the order-parameter field

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The instability of the shape of two-dimensional new-phase nuclei is studied using an order-parameter field equation. The criteria of instability of angular perturbations are obtained for systems in which the order-parameter nonconservation processes are negligible. These coincide with criteria obtained within the framework of the phenomenological Zeldovich-Volmer theory and the continual diffusion-limited aggregation model in the diffusive limit. The influence of small angular perturbations on the fractal dimensionality of the nuclei is discussed.

I. INTRODUCTION

Azimuthal-symmetrical nuclei[1–3] as well as structures with complex symmetry[3,4] are observed during experimental studies of the processes of nucleation and subsequent growth of a new phase on surfaces. The value of the index N in the relationship between the number of particles in a cluster and the cluster radius ($N \sim R^{\mathrm{N}}$) is a simple quantitative criterion of deviation of the cluster shape from axial symmetry. The parameter N is called the "fractal dimensionality."[5–11] Asymmetry of the cluster leads to deviation of the N value from the Euclidean dimensionality. In the case of fractal growth, values of N are found to be universal to some extent for a number of systems, (for example, for fractal structures on surfaces $\mathrm{N}=1.5-1.9$).[5–11] In the vast majority of experiments, the clusters grow mainly in the surface plane. For example, such clusters appear during deposition of atoms from the vapor phase onto a surface,[12] electrodeposition from solutions or melts of metals,[13,14] and crystallization of amorphous films on substrates.[15,16] Therefore in this work we shall consider only clusters growing in the surface plane.

There are various theoretical approaches to the problem of determination of the conditions of instability of nuclei with axisymmetric shape and the appearance of nuclei with more complex shapes and different symmetries. These conditions have been studied both theoretically within the framework of the Zeldovich-Volmer theory of first-order phase transitions[17–19] and numerically using various approaches to the cluster growth dynamics.[6–11] In phase-transition theory,[1–4] the main attention was paid to the explicitly anisotropic conditions of nucleus growth connected with surface tension, substrate lattice symmetry, anisotropy of the external fields, etc.[3,4,20–25] However, it was found that the phenomenon of nucleus symmetry breaking took place in symmetrical (isotropic) systems as well.[26–28] It was shown[26] that the nuclei whose growth was controlled by diffusive flow of adatoms possess axial shape instability. The growth rates of the m-fold angular perturbations of the nucleus boundary

$$R(\varphi,t)=R_0(t)+\sum_{m\geq 2} R_m(t)\cos(m\varphi)$$

are

$$\frac{d}{dt}\ln R_m(t)=\rho_0 s C_0 D\frac{(m-1)}{R_0^2}\times\left\{\left[\frac{1}{R_c}-\frac{1}{R}\right]\frac{1}{K_0(R_0/L)}-\frac{m(m+1)}{R_0}\right\}, \tag{1}$$

where D is the diffusion coefficient, s is the area of one adatom in a new phase, $R_c=\rho_0 C_0/(\bar{C}-C_0)$ is the new-phase critical size, $\bar{C}$ is the concentration of the particles far from the nucleus, C_0 is the equilibrium concentration at the linear nucleus boundary, $\rho_0=\gamma s/T$, γ is the surface tension coefficient, T is the temperature, $L^2=D\alpha^{-1}$, α^{-1} is the desorption time, and $K_0(x)$ is the Macdonald function. The criterion of instability $\lambda_m>0$ [where $\lambda_m=(d/d\tau)\ln(R_m/R_0)$ is the instability increment] determines the conditions

$$\frac{R_0}{R_c}\geq\frac{m(m^2-1)}{(m-2)}K_0(R_0/L)\ . \tag{2}$$

If (2) is valid, the m-fold perturbations do not fade. Instability is possible for angular perturbations with $m\geq 3$ when the sizes of the growing nuclei are large enough.

In papers on the application of cluster growth dynamics to different physical systems, several models are used. The diffusion-limited aggregation (DLA) model is historically the earliest and the most frequently used model.[5–11,27–31] There are different modifications of the DLA model: lattice DLA where particles are supposed to jump only between nearest-neighbor positions in the lattice, and nonlattice DLA where particles are free to move in any direction between any two points on the surface plane. In this model, cluster growth is determined by particle adhesion (with some probability) to the cluster boundary on contact. Nonlattice models allow one to eliminate the possible influence of lattice anisotropy on the cluster properties. In the cluster-cluster aggregation

(CCA) model,[5–8] light clusters can move and adhere as well as single particles. Besides the models with diffusive trajectories of particles, models were formulated like the ballistic model of Eden[32] where the particle trajectories were straight.

Computer simulations based on these models show universality in the fractal cluster growth phenomenon. This is supposed to be connected with some common features of the growth process, and these features have been manifested in the primarily symmetrical models like nonlattice DLA. Nevertheless, the influence of anisotropic properties of the system (substrate symmetry, anisotropy of the particle itself, cluster boundary conditions modeling the elastic tension, etc.[20–25]) is apparent, and at some stages of the growth may result in variations of the fractal dimensionality ℕ. Some analytical studies of DLA have been carried out in Refs. 27 and 28. The growth criterion for angular perturbations of the cluster boundary within the framework of the DLA model[27] formally coincides with criterion (2) in the diffusive limit $R \ll L$ (after replacement of the necessary variables).

Thus, the investigations prove that anisotropic properties are not strictly necessary for formation of nonround nuclei and the axial shape instability of the nuclei is connected apparently with the diffusive nature of the growth process. Unfortunately, the models applied to studies of the instability conditions of the nucleus boundary shape[1–4,33] use many external phenomenological parameters and assumptions. The Zeldovich-Volmer theory, for example, needs the surface tension coefficient, the molecular volume of the new phase, the equilibrium concentration of the saturated solution, and conditions at the nucleus boundary. The conditions and assumptions used in this theory are also used in DLA. The latter approach is based on a model of stationary diffusion with fixed boundary conditions which define the rate of movement of the nucleus boundary. It is not clear to what extent the description of the complex structure evolution is determined by phenomenological conditions and parameters. A nondiffusion mechanism of cluster growth on a surface is possible too. It suggests direct sticking of the gas-phase atoms to the cluster perimeter.[34] The dependence of the shape instability on the cluster growth mechanism is not yet clear. Theoretical consideration of the phenomenon within the framework of a more general approach would help to answer these questions.

Besides Zeldovich-Volmer theory and computer simulations, the expansion of the free-energy functional of the system in a power series of the order parameter[35] is used to describe the phase transition and cluster growth. Analysis of the relaxation can be performed using an order-parameter equation (OPE) like the Ginzburg-Landau equation.[35–37] Such an approach to the phase-transition kinetics needs neither additional parameters nor additional assumptions. This method has allowed one to describe domain growth both in bulk and on surfaces, and a number of nontrivial features of second-order phase transition kinetics have been investigated (see, for example, Refs. 38–43). Consideration of three-dimensional (3D) nucleation[36,37] showed that all the parameters, assumptions, and principal results of Zeldovich-Volmer theory can be obtained as a result of the OPE solution. In 2D systems, an approach based on the OPE allows one to obtain various limits of the Zeldovich-Volmer theory for the growth kinetics of axisymmetrical nuclei.[44] Thus we suppose that this method will enable us to investigate the nuclear shape instability caused by the general properties of the growth process without using any additional assumptions and parameters. The purpose of this paper is to analyze the phenomenon of shape instability of 2D nuclei with the help of an OPE-based method.

II. ORDER-PARAMETER EQUATION

The equation which describes the relaxation of the order-parameter field $\xi(\mathbf{r},t)$ to the preferred energy state is[35–37]

$$\dot{\xi}(\mathbf{r},t) = -\hat{\mu}\delta F[\xi(\mathbf{r},t)]/\delta\xi \; . \tag{3}$$

Here $F[\xi(\mathbf{r},t)]$ is the free-energy functional corresponding to the $\xi(\mathbf{r},t)$ field, $\mathbf{r}$ is the coordinate, t is the time, $\hat{\mu}$ is the kinetic operator given by $\hat{\mu} = -\mu_c\nabla^2 + \mu_n$ in the long-wave approximation, μ_c is the kinetic coefficient in the case of conserved field $\xi(\mathbf{r},t)$, μ_n is the kinetic coefficient in case of nonconserved field $\xi(\mathbf{r},t)$, and ∇^2 is the Laplace operator. In application to phase transitions on surfaces, which are under consideration here, the field ξ is the deviation of the adsorbed atom concentration $C(\mathbf{r},t)$ in the new phase from the average concentration $\bar{C}$ on the surface: $\xi(\mathbf{r},t) = C(\mathbf{r},t) - \bar{C}$.

In principle, definition of the kinetic coefficients μ_c and μ_n and the free energy F near the phase-transition point completely determines Eq. (3). So neither additional parameters nor additional assumptions are necessary to explain the kinetics of phase transitions.[35–37] Near the phase-transition point, the expression for the free energy following from the Landau theory[35,36] can be written as

$$F = \int d\mathbf{r}[\lambda\xi^2/2 + \Omega(\nabla\xi)^2/2 - B\xi^3/3 + \Gamma\xi^4/4] \; . \tag{4}$$

Here λ, Ω, B, and Γ generally depend on external parameters and as temperature and adatom concentration.

In case of $B \neq 0$, the free energy (4) describes first-order phase transitions. It is easy to prove that a phase transition take place when $\lambda < 2B^2/3\Gamma = \lambda_c$. This transition proceeds from the state with zero order parameter $\xi = 0$ to another state with $\xi_0 = 2B/3\Gamma$.

The order-parameter equation (3) for the free energy given by (4) has the form

$$\dot{\xi}(\mathbf{r},t) = (\mu_c\nabla^2 - \mu_n)(\lambda\xi - \Omega\nabla^2\xi - B\xi^2 + \Gamma\xi^3) \; . \tag{5}$$

This equation is a Ginzburg-Landau-type equation which is often used in phase-transition theory.[35–37]

Before taking into consideration the order-parameter field relaxation, let us find the connection between the kinetic coefficients μ_c and μ_n in Eq. (3) and observable parameters. This will allow us to choose the physical mechanisms of nuclear growth. In linear approximation Eq. (5), which defines the relaxation of small perturbations on the surface, has the form

$$\dot{\xi}(\mathbf{r},t)=-\alpha\xi+D\nabla^2\xi,\quad \alpha\equiv\mu_n\lambda,\quad D\equiv\mu_c\lambda\ , \tag{6}$$

The phenomenological theory of adsorption uses equations identical to Eq. (6).[45,46,34] D is the adatom diffusion coefficient and α^{-1} is the adatom lifetime determined by either desorption or transition from the surface into the bulk of the solid. Thus, the physical meaning of the kinetic coefficients μ_n and μ_c appears to be clear. The former is connected with adsorption and desorption ($\mu_n=-\alpha/\lambda$), and the latter with adatom diffusion on the surface ($\mu_c=D/\lambda$).

Equation (5) in dimensionless variables $\phi=2\xi/\xi_0-1$, $\boldsymbol{\rho}=\mathbf{r}/\chi$, and $\tau=t/\tau_0$ may be written as

$$\dot{\phi}(\boldsymbol{\rho},\tau)=(l^2-\nabla^2)[\nabla^2\phi+2\phi(1-\phi^2)+h(\phi+1)]\ . \tag{7}$$

Here $\xi_0=2B/3\Gamma$ is the phase order parameter at the phase-transition point, $\chi=\xi_0\sqrt{8\Omega/\Gamma}$, $\tau_0=\chi^4/\mu_c\Omega$, $l^2=\chi^2\mu_n/\mu_c$, and $h=4(1-\lambda/\lambda_c)$ is the degree of metastability. In the old phase $\phi=-1$ while in the new phase $\phi=\phi_n=(1+\sqrt{1+2h}\ )/2$ ($\phi_n\cong 1$ if $h\ll 1$).

There are only two dimensionless parameters h and l in Eq. (7). The degree of metastability h determines how far the system is from the phase-transition point or, in other words, the difference between the new and old energy states. Near the phase transition point we can assume that h is rather small: $h\ll 1$. The parameter l determines the ratio of the contributions of the two distinct mechanisms of nuclear growth: direct sticking and diffusive growth.[44] This parameter varies over a wide range in different physical systems and determines the regimes of system relaxation.

It should be noted that diffusive growth of the new phase occurs more often in experiments. Nuclear shape instability in the diffusive limit has been studied using Zeldovich-Volmer theory[26] and the DLA model.[27,28] This case of the diffusion limit corresponds to $l\ll 1$ and is considered in this paper.

III. SOLUTIONS OF THE OPE

The order-parameter field which corresponds to the critical-sized nuclei minimizes the free-energy functional. Therefore it is a stationary solution of the OPE as may be seen from (3). With a small degree of metastability h, this field can be written with high accuracy as[36,44]

$$\phi_c(\rho)\cong\tanh(a_c-\rho),\quad a_c=\frac{2}{3h},\quad h\ll 1\ . \tag{8}$$

Equation (8) describes a nucleus of the new phase ($\phi=1$) in the old phase ($\phi=-1$). The width of the transition layer between the phases (nuclear boundary) is of the order of unity in dimensionless variables and of the order of χ in dimensional variables.

Let us consider now the nonstationary solutions of the OPE (7). Using the Green function $G(\boldsymbol{\rho})=K_0(\rho l)/2\pi$ of the equation

$$(l^2-\nabla^2)G(\boldsymbol{\rho})=\delta(\boldsymbol{\rho}), \tag{9}$$

we can write (7) in another form as

$$\int G(\boldsymbol{\rho}-\boldsymbol{\rho}')\dot{\phi}(\boldsymbol{\rho}',\tau)d\boldsymbol{\rho}' =\nabla^2\phi(\boldsymbol{\rho},\tau)+2\phi(1-\phi^2)+h(\phi+1)\ . \tag{10}$$

Let us find the solution of (7) and (10) which describes the axisymmetric new-phase nuclei with a size R greater than the transition-layer width $\chi(a\equiv R/\chi\gg 1)$. We shall write this solution in the form of the sum of a nucleuslike term plus some correction function:[36,44]

$$\phi(\boldsymbol{\rho},\tau)=\phi_c(\rho-a(\tau))+w(\boldsymbol{\rho},\tau)\ . \tag{11}$$

The component $\phi_c(\rho-a(\tau))$ is the solution (8) of Eq. (10) for the critical nuclei. Here the substitution $a_c\to a(\tau)$ is made. To consider the axisymmetric shape instability let us introduce the following dependence of the nucleus size a on the azimuthal angle φ:

$$a(\varphi,\tau)=a_0(\tau)+\sum_{m\geq 2}a_m(\tau)\cos(m\varphi)\ . \tag{12}$$

A term with $m=1$ is not included in (12) since it corresponds to the shift of the nucleus as a whole on the surface. To find the conditions of instability it is enough to consider small angular perturbations, i.e., $a_m/a_0\ll 1$.

The correction function $w(\boldsymbol{\rho},\tau)$, as will be seen further, determines the diffusive flows to the nucleus. In the diffusive limit ($l\ll 1$) and in the case of weak metastability $h\ll 1$, w is a small-valued function and slowly changing in space:

$$|w(\boldsymbol{\rho},\tau)|\ll 1,\quad |\nabla^2 w|\ll|w|\ . \tag{13}$$

The process of nucleus size change is the slowest one near the phase-transition point,[34,36,47] i.e., one may assume that the characteristic time τ_w of $w(\boldsymbol{\rho},\tau)$ variation is smaller than the characteristic time of nucleus size variation τ_a:

$$\tau_w\ll\tau_a\ . \tag{14}$$

Note that the quasistationarity condition (for 2D systems) can be disturbed if $l\to 0$ and in this case special consideration is demanded.[48]

At large distances from the nucleus only the old phase exists at any finite time $[\phi(\rho\to\infty,\tau)=-1]$, so the condition for w is

$$w(\rho\to\infty,\tau)=0\ . \tag{15}$$

Substituting the solution (11) into Eq. (10) and using conditions (13) and (14) we obtain

$$-P(\boldsymbol{\rho},\tau)=[1/a-1/a_c-a''/a^2-6w(\boldsymbol{\rho},\tau)]\times\cosh^{-2}(a-\rho)+4w(\boldsymbol{\rho},\tau)\ . \tag{16}$$

Here

$$P(\boldsymbol{\rho},\tau)=\int G(\boldsymbol{\rho}-\boldsymbol{\rho}')\cosh^{-2}(a-\rho')d\boldsymbol{\rho}'\ ,$$

$$a\equiv a(\varphi,\tau),\quad\text{and}\quad a''\equiv\partial^2 a(\varphi,\tau)/\partial\varphi^2\ .$$

It is important for further consideration that, in the case of the diffusive limit $l\ll 1$, the function $P(\boldsymbol{\rho},\tau)$ is smooth and changes on the scale $\sim 1/l$, which is greater than the nucleus transition-layer width (at least in the initial stages of angular perturbation growth). To be convinced of these properties of $P(\rho,\tau)$ let us write this function as

$$P(\rho,\tau)=\sum_{m\geq 0, m\neq 1} \dot{a}_m(\tau)P_m(\rho) \ , \tag{17}$$

where (if $a_m/a_0 \ll 1$)

$$P_m(\rho)=\int G(\rho-\rho')\cos(m\varphi')\cosh^{-2}(a_0-\rho')d\rho' \ .$$

The smoothness of $P_0(\rho)$ can be shown, for instance. The expression under the integral in $P_0(\rho)$ [Eq. (17)] ($l \ll 1$) is a product of two functions. One of them, $\cosh^{-2}(a-\rho')$ is a sharp function differing from zero only near the nucleus boundary $\rho'=a$, and the other, $G(\rho,\rho')\rho'$, is smooth near the boundary [here $G(\rho,\rho')$ is the integral of $G(\rho-\rho')$ (29) over the angular variable of the vector ρ']. These allow one to expand the function $G(\rho,\rho')\rho'$ over the variable ρ' near the maximum $\rho_m(\rho_m \simeq a)$ of the function $\cosh^{-2}(a-\rho')$. The zeroth item of the expansion $G(\rho,\rho')\rho' \simeq G(\rho,\rho_m)\rho_m$ is sufficient for $P_0(\rho)$ (17), so

$$P_0(\rho)=\begin{cases} 2I_0(\rho l)K_0(a_0 l), & \rho<\rho_0, \\ 2K_0(\rho l)I_0(a_0 l)a_0, & \rho>a_0 \ . \end{cases} \tag{18}$$

Here I_0 is the modified Bessel function. Hence the quantity $1/l$ is a characteristic scale of $P_0(\rho)$ variation. Thus, in the diffusive limit when $l \ll 1$, the function $P(\rho)$ is smooth on the scale of the nucleus interface width.

Equation (16) can be simplified outside the boundary transition layer of the nucleus [where $\cosh^{-2}(a-\rho')$ is exponentially small] to

$$-P(\rho,\tau)=4w(\rho,\tau) \ . \tag{19}$$

According to the smoothness of functions $w(\rho,\tau)$ and $P(\rho,\tau)$ [relations (13) and (18)], Eq. (19) should be true everywhere in space, including the nucleus boundary $\rho \simeq a$. As a result, it can be obtained from Eq. (16) that near the boundary

$$w(\rho=a(\varphi,\tau))=\frac{1}{6}\left[\frac{1}{a(\varphi,\tau)}-\frac{1}{a_c}\right]-\frac{1}{6}\frac{a''(\varphi,\tau)}{a^2(\varphi,\tau)} \ . \tag{20}$$

To find the rate of angular perturbation growth let us act on (19) with the operator $(l^2-\nabla^2)$. This leads to

$$\dot{a}(\varphi,\tau)\cosh^{-2}[\rho-a(\varphi,\tau)]=4(\nabla^2-l^2)w(\rho,\tau) \ . \tag{21}$$

Outside the boundary of the nucleus this is just the diffusive equation which defines the atom flow to the growing nucleus. Let us integrate (21) over the transition layer where the function $\cosh^{-2}[a(\varphi,\tau)-\rho']$ differs from zero. It should be taken into account that in the initial stages of angular perturbation growth the ratio $a_m/a_0 \ll 1$ and the angles between the normals to the perturbed boundary and the unperturbed axisymmetric boundary at the same point are small: $\gamma \ll 1$. This allows one to write

$$\begin{aligned}\int d\rho\,\nabla^2 w(\rho,\tau) &\simeq \oint dl'\cos\gamma \left[\left.\frac{\partial w}{\partial\rho}\right|_{a(\varphi,\tau)+0}-\left.\frac{\partial w}{\partial\rho}\right|_{a(\varphi,\tau)-0}\right] \\ &= \int_0^{2\pi} d\varphi\, a(\varphi,\tau)\left[\left.\frac{\partial w}{\partial\rho}\right|_{a(\varphi,\tau)+0}-\left.\frac{\partial w}{\partial\rho}\right|_{a(\varphi,\tau)-0}\right] \ .\end{aligned} \tag{22}$$

So the nucleus-boundary growth rate $\dot{a}(\varphi,\tau)$ is determined by the atom flow $\partial w/\partial\rho$ to the nucleus boundary ($l \ll 1$). Note that, if the value l is not zero, desorption and adsorption processes take place not only outside the nucleus but also inside it. This leads to the appearance of two flows of adatoms to the nucleus boundary: over the virgin substrate surface and over the nucleus surface.

To determine these flows explicitly it is necessary to find the solution of Eq. (21) outside the boundary

$$(\nabla^2-l^2)w(\rho,\tau)=0, \quad |\rho-a(\varphi,\tau)|>1 \tag{23}$$

in the form of an expansion over angular harmonics:

$$w(\rho,\tau)=\begin{cases} w_0\dfrac{K_0(\rho l)}{K_0(a_0 l)}+\displaystyle\sum_{m\geq 2} w_m^{(1)}\dfrac{K_m(\rho l)}{K_m(a_0 l)}\cos m\varphi, & \rho>a(\varphi,\tau) \ , \\ w_0\dfrac{I_0(\rho l)}{I_0(a_0 l)}+\displaystyle\sum_{m\geq 2} w_m^{(2)}\dfrac{I_m(\rho l)}{I_m(a_0 l)}\cos m\varphi, & \rho>a(\varphi,\tau) \ . \end{cases} \tag{24}$$

Here K_m and I_m are mth-order modified Bessel functions. The asymptotic condition (15) $[w(\rho\to\infty,\tau)=0]$ is taken into account in writing the solution (24).

To study the instability of small perturbations $a_m(\tau)$ the boundary condition for the function $w(\rho,\tau)$ (20) should be written in linear approximation over $a_m/a_0 \ll 1$:

$$w(\rho=a(\varphi,\tau))=\frac{1}{6}\left[\frac{1}{a_0}-\frac{1}{a_c}\right] + \sum_{m\geq 2}\frac{(m^2-1)}{6a_0^2}a_m\cos m\varphi \ . \tag{25}$$

Joining solution (24) with (25) gives the coefficients $w_0, w_m^{(1,2)}$ of various harmonics in (24). Therefore the flows $\partial w/\partial\rho$ can be found when $\rho = a(\varphi,\tau)\pm 0$. Finally, in the diffusive limit $l \ll 1$, the equations for azimuthal-perturbation growth and average radius are

$$\dot{a}_0 = -4w_0 \left\{ \frac{l}{2} \left[\frac{K_1(a_0 l)}{K_0(a_0 l)} + \frac{I_1(a_0 l)}{I_0(a_0 l)} \right] + l^2 \right\}, \tag{26}$$

$$\frac{d\ln a_m}{d\tau} = -\frac{1}{3}\frac{(m^2-1)}{a_0^2} \left\{ \frac{l}{2} \left[\frac{K_{m+1}(a_0 l)}{K_m(a_0 l)} + \frac{I_{m+1}(a_0 l)}{I_m(a_0 l)} \right] + l^2 \right\} - 2l^2 w_0 \left\{ \left[\frac{K_1(a_0 l)}{K_0(a_0 l)} \frac{K_{m+1}(a_0 l)}{K_m(a_0 l)} - \frac{I_1(a_0 l)}{I_0(a_0 l)} \frac{I_{m+1}(a_0 l)}{I_m(a_0 l)} \right] - \frac{(m+1)}{a_0 l} \left[\frac{K_1(a_0 l)}{K_0(a_0 l)} + \frac{I_1(a_0 l)}{I_0(a_0 l)} \right] \right\}, \tag{27}$$

where $w_0 = \frac{1}{6}(1/a_0 - 1/a_c)$.

Relationship (26) was studied earlier during analysis of the growth of azimuthal-symmetrical nuclei with the help of the OPE.[44] It describes growth of a round nucleus (if $a_0 > a_c = 2/3h$) due to particle flow to the boundary from inside and outside the nucleus (the first and the second components, respectively) and due to direct particle sticking to the nucleus boundary. This equation is also well known from phenomenological theory,[34] where it has been written in dimensional variables as

$$\dot{R} = s_0 \rho_0 C_\infty \frac{D}{L} \left[\frac{1}{R_c} - \frac{1}{R} \right] \left\{ \left[\frac{K_1(R/L)}{K_0(R/L)} + \frac{I_1(R/L)}{I_0(R/L)} \right] + \frac{\alpha l_0 L}{D} \right\}. \tag{28}$$

Here l_0 is the width of the layer where direct sticking to the nucleus perimeter takes place.

Equation (27) describes relaxation of the m-fold angular perturbations. Let us write the increments of instability to analyze the conditions of perturbation instability:

$$\lambda_m = \frac{d}{d\tau} \ln \frac{a_m}{a_0} = -\frac{1}{3}\frac{(m^2-1)}{a_0^2} \left\{ \frac{l}{2} \left[\frac{K_{m+1}(a_0 l)}{K_m(a_0 l)} + \frac{I_{m+1}(a_0 l)}{I_m(a_0 l)} \right] + l^2 \right\} - 2l^2 w_0 \left\{ \left[\frac{K_1(a_0 l)}{K_0(a_0 l)} \frac{K_{m+1}(a_0 l)}{K_m(a_0 l)} - \frac{I_1(a_0 l)}{I_0(a_0 l)} \frac{I_{m+1}(a_0 l)}{I_m(a_0 l)} \right] - \frac{(m+1)}{a_0 l} \left[\frac{K_1(a_0 l)}{K_0(a_0 l)} + \frac{I_1(a_0 l)}{I_0(a_0 l)} \right] - \frac{1}{a_0} \right\}. \tag{29}$$

Expressions (27) and (29) are obtained for an arbitrary relation between a_0 and l^{-1}. The only conditions are $a_0 \gg 1$ and $l \ll 1$. Let us consider the case when the diffusion length L is larger than the nucleus radius R: $a_0 l \ll 1$. Using the asymptotic relations for $K_m(x)$ and $I_m(x)$ $(x = a_0 l)$,[49] Eqs. (27) and (29) can be written in the form

$$\frac{d\ln a_m}{d\tau} \simeq \frac{2(m-1)}{a_0^2} \left\{ \frac{1}{6} \left[\frac{1}{a_c} - \frac{1}{a_0} \right] \frac{1}{K_0(a_0 l)} - \frac{m(m+1)}{6a_0} \right\},$$

$$\lambda_m \simeq \frac{2}{a_0^2} \left\{ \frac{1}{6} \left[\frac{1}{a_c} - \frac{1}{a_0} \right] \frac{(m-2)}{K_0(a_0 l)} - \frac{m(m^2-1)}{6a_0} \right\}. \tag{30}$$

In dimensional variables these equations correspond to Eqs. (1) and (2) of the phenomenological theory which has been obtained in Ref. 26. Note the fact that in this limit $(a_0 l \ll 1)$ the growth of the shape perturbations (condition $\lambda_m \geq 0$) can be observed only for perturbations with $m \geq 3$ while for $m = 2$ this is impossible for any set of parameters.

Figure 1 shows the conditions of instability for various relations between a_0 and l at $a_c = 100$. The solid lines are obtained for $\lambda_m(a_0, l) = 0$ in the general case (29). They envelope the respective instability areas (i.e., $\lambda_m \geq 0$) of the perturbations with $m = 3, 4, \ldots$. It can be seen that instability is possible only when l is small enough $(l \leq 5.6\times 10^{-5})$, i.e., the diffusive length L is much larger than the transition-layer width χ. It is necessary for the nucleus radius to be large enough, $a_0 \geq a_0^* \simeq 10^4$. Thus at the initial stage of growth when $a_0 < a_0^*$ the nuclei have an axially symmetrical shape. When the values $a_0 = a_0^*$ and $\lambda_m = 0$ are reached, an unstable perturbation starts to grow. In the range $l \leq 3\times 10^{-5}$ the first perturbation to grow [as $a_0(\tau)$ increases] is that with $m = 3$. However, there is an area of parameters $3\times 10^{-5} \leq l \leq 5.6\times 10^{-5}$ where the first unstable perturbation is that with $m = 4$ or 5, while the perturbations with $m = 3$ or 3,4 correspondingly are suppressed. Development of the instabilities starting with perturbations $m \geq 6$ is impossible at any parameter l. Hence, by selection of the physical conditions one may obtain various values of l and therefore satisfy the conditions when the perturbations with symmetries $m = 3$, 4, or 5 grow and at the same time the oth-

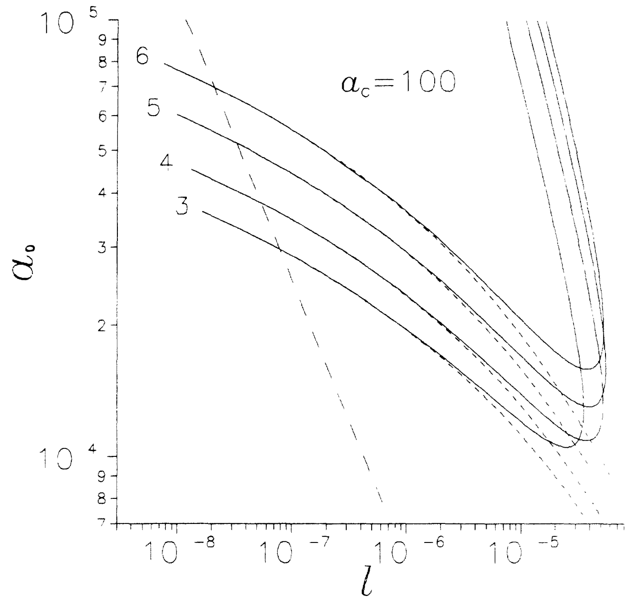

FIG. 1. Solution of Eq. (29) with $\lambda_m(a_0,l)=0$ (solid lines) corresponding to the conditions for the appearance of instability of the angular perturbations for harmonics with $m=3,\ldots,6$ (numbers given near curves) and the critical size $a_c=100$. Short-dashed curves are solutions of (30) for the corresponding harmonics (in the $a_0 l \ll 1$ case). The long-dashed curve is the condition of breaking of diffusive-growth quasistationarity (31).

er perturbations fade.

After the appearance of instability of one of the m-fold perturbations, the criteria for the others can change. Thus, if we consider the growth of an initially stable nucleus, Fig. 1 shows the boundary of the instability area and the indexes of those unstable perturbations which arise first. If it is possible to create such conditions that axially symmetric nuclei fall into the instability area from the very beginning, Fig. 1 shows the perturbation indexes m of the angular harmonics which grow for these nuclei in the initial stage.

Figure 1 also represents the case of $a_0 l \ll 1$ (30) (short-dashed lines). Thus, the phenomenological growth equations (1) and (2) are fulfilled when $a_0 l \ll 1$ and $l \leq 3\times10^{-5}$ (in terms of the variables a_0 and l). The discrepancy between our results and those obtained in Ref. 26 is connected with the growing contribution of the adatom flow over the nucleus surface to its boundary in the region $l \geq 3\times10^{-5}$. This flow sequentially stabilizes the instabilities with $m=3$, 4, and 5, and then all the others.

The fact that the quasistationarity condition (14) for the function $w(\rho,\tau)$ is satisfied (see above) allows one to neglect the term $\dot{w}(\rho,\tau)$ in Eq. (16). Substituting $w(\rho,\tau)$ (24) into (14) and using the nucleus growth rate (26), one can determine the criterion of quasistationarity breaking for the correction function $w(\rho,\tau)$:

$$a_0^3 l^2 I_0(a_0 l) K_0(a_0 l) \simeq 1 \ . \tag{31}$$

This criterion is shown in Fig. 1, too (long-dashed line in the left part of the figure). It is seen that if $l \to 0$ the curves $\lambda_m=0$ meet the area (located to the left of the long-dashed line) where the condition of quasistationarity is broken.

As the value of a_c decreases, the diagram of instability obtained moves as a whole towards smaller sizes a and larger values of l. Thus for $a_c=1$ instability appears already at sizes of the nucleus about 10^2. Further formal decrease of a_c in (29) moves the instability area down to the sizes $a \sim 1$, i.e., enables one to realize shape instability at the initial stages of cluster growth. However, the critical sizes $a_c \sim 1$ are too small to be used in analytical studies of the OPE performed in this paper. This is because the degree of metastability is becoming high, $h \sim 1$.

There are several physical causes for decreasing a_c, for example, variations of boundary conditions, change in the linear surface tension, and adhesion coefficients. These alterations (occurring at the same cluster size) can lead to development of structures of different shapes (different sets of unstable harmonics at the initial stages of growth). This in turn leads to variation of the fractal dimensionality.

IV. COMPARISON OF THE OPE AND THE CONTINUOUS DLA MODEL IN THE DIFFUSIVE LIMIT

Let us make comparison of the OPE-based approach and the DLA model. Analytical equations and boundary conditions of the latter model are usually written in the form[5–11,27,28]

$$\nabla^2 u(\rho)=0 \ , \tag{32a}$$

$$u|_b = 1-\kappa(\rho_b) \ , \tag{32b}$$

$$u(\rho_{\text{cluster}})=1, \quad u(\rho\to\infty)=0 \ , \tag{32c}$$

$$\bar{v}_n = -\left.\frac{(\mathbf{n},\nabla u)}{4\pi}\right|_b \ . \tag{32d}$$

Here the index b means that the value is considered at the cluster boundary, $\kappa(\rho)$ is interpreted as the cluster boundary curvature, and $\bar{v}_n$ is the normal growth rate of the boundary. It is easy to see that the function $u(\rho)$ in the DLA model is an analog of the field w (11). Indeed, the equation for the function u (32a) and the condition at large distances (32c) correspond to Eq. (23) (in the diffusive limit $l \to 0$) and condition (15) for the field w. The growth rate given by (32d) coincides with the growth rate $\dot{a}$ given by (21) and (22) (see also the discussion after these relations) to the accuracy of the numerical coefficient when $l \to 0$ and $a_m/a_0 \ll 1$. To determine the relation between boundary conditions (32b) and (20), let us rewrite (20) in terms of the curvature. If perturbations of the axisymmetric shape of the nucleus are small, the curvature k can be represented in the form

$$k(\varphi,\tau)=\frac{a^2+2(a')^2-aa''}{[a^2+(a')^2]^{3/2}} \simeq \frac{a-a''}{a^2} \ . \tag{33}$$

Using this relation, the condition (25) for the field w at the interface can be written as

$$w(\rho,\tau)=-\frac{1}{6a_c}[1-k(\varphi,\tau)a_c] . \quad (34)$$

It is seen that the conditions (32b) and (34) are identical, and the relations between OPE and DLA values are

$$w=-u/6a_c,\quad k=\kappa/a_c,\quad v_n=\bar{v}_n 4\pi/3a_c ,$$
$$v_n=\dot{a}\cos\gamma\simeq\dot{a} . \quad (35)$$

Hence, in the case of $a_c \sim 1$, the parameters of the OPE are similar to those in the DLA model.

In this work we study the growth of small azimuthal perturbations of the cluster boundary by solving the order-parameter equation. At the same time in the models of fractal growth[5–11,27–31] the value of the fractal dimensionality N is used as the basic criterion. Let us study the influence of angular perturbations of the boundary upon N. Let a 2D cluster have only one unstable harmonic m:

$$a(\varphi)=a_0+a_m\cos(m\varphi) . \quad (36)$$

From the definition of fractal dimensionality (see the Introduction) it follows that the cluster area is proportional to R^{N} [where R is the maximum size, which in case (36) is $R=a_0+a_m$]. Generally speaking the concept of fractal dimensionality is used to describe structures in the late stages of instability development, when cluster shape is not determined by relation (12), or (36) as a particular form of (12). However, it is useful to reserve this term for nuclei like (36). Thus the expression for the value $\mathrm{N}=\mathrm{N}_m$ corresponding to the cluster (36) is

$$\mathrm{N}_m=2\frac{\ln[a_0(1+\delta_m^2/2)^{1/2}]}{\ln[a_0(1+\delta_m)]} . \quad (37)$$

It is seen that (37) does not depend on the harmonic number m, but only on amplitudes a_0 and a_m. The appearance of a harmonic with $m\neq 0$ leads to deviation of the N value from the Euclidean dimensionality $n=2$. As the ratio δ_m increases, the N value decreases monotonically (see Fig. 2). An increase in the amount of unstable harmonics leads to an even stronger decrease in the fractal dimensionality. It is easy to see that a cluster with two unstable harmonics (m and p) has the fractal dimensionality $\mathrm{N}_{m,p}<\{\mathrm{N}_m,\mathrm{N}_p\}$. For example, in the initial stages of growth, the following relation is valid:

$$\mathrm{N}_{m,p}=\mathrm{N}_m+\mathrm{N}_p-2 . \quad (38)$$

Thus variations of the structure of the unstable mode leads to variations in fractal dimensionality. At the same time, these variations of the unstable-mode structure are possible when the boundary conditions at the cluster interface change. This agrees with the results of computer simulations of fractal growth, where a link between boundary conditions and the value of N is explicitly seen.

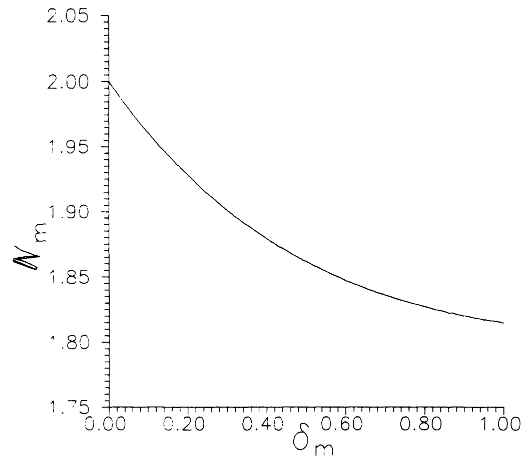

FIG. 2. Fractal dimensionality (37) of the cluster as a function of the amplitude $\delta_m=a_m/a_0$ of the growing mth harmonic.

V. CONCLUSION

In this paper, analysis of the instability of the axial shape of 2D clusters is performed using a Ginzburg-Landau-type equation for the order-parameter field. The criteria for m-fold perturbation instability are obtained. These criteria are determined by two parameters: a_0, the cluster size, and l, the ratio of the contributions of two mechanisms of cluster growth which correspond to conserving and nonconserving order-parameter field processes. It is shown that instability develops when the principal mechanism of cluster growth is of a diffusion type (diffusion of the adatoms upon the substrate surface). As the rates of the processes which do not conserve the order parameter increase (adsorption, desorption), the flow of atoms upon the cluster surface increases and suppresses the instability. In the limit $a_0 l \ll 1$ the criterion obtained for the instability agrees with results of work[26] based on Zeldovich-Volmer phenomenological theory. In the diffusive limit ($l\to 0$) and when $a_c\sim 1$, description of clusters on the basis of the OPE leads to equations based on the DLA model. It is shown that growth of the m-fold angular perturbations and increase in their number leads to decrease of the fractal dimensionality.

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