Formation of islets of a new phase on a surface as relaxation of the order parameter

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The growth kinetics of two-dimensional new-phase islets is investigated with the aid of the equation for the order-parameter field. Equations are obtained for the islet growth in various regimes. A connection between the developed approach and the phenomenological Zel'dovich–Volmer theory is established. The onset of various types of conditions imposed in the phenomenological theory on the islet boundary is considered.

1. INTRODUCTION

Phenomena occurring when atoms and molecules are adsorbed in material surfaces are attracting great attention (see, e.g., the reviews[1-3]). The most interesting is the islet-growth stage, which is characterized by formation of seeds of a new phase on the surface. The kinetic laws governing the phase transitions in the adsorbing layers are usually characterized by the exponent n of the power-law growth of the dimension R of the new-phase islets with time, $R \propto t^n$. The experimental value of the exponent n varies in a wide range: $0.1 \leqslant n \leqslant 1$ (Refs. 3–9).

Several approaches are used to a theoretical description of the kinetics of the macroscopic adsorption-layer changes due to the onset of various islet structures. The most widely used approach is based on the classical Zel'dovich-Vollmer (ZV) theory.[10-13] This theory can describe the growth of individual new-phase seeds in first-order phase transitions, as well as the relaxation of the growth of an ensemble of such seeds during various stages.[3,5,6-9,14] While physically simple, this approach contains an appreciable number of phenomenological parameters and supplementary conditions. Thus, assuming that the energy of a two-dimensional new-phase islets is represented by "volume" and "surface" parts, it is easy to find that the growth of islets is energywise favored when their dimension R exceeds a critical value

$$R_c = \gamma s/\Delta\mu, \tag{1}$$

where γ is the surface-tension coefficient of the islet boundary, s is the area per atom in the new phase, and $\Delta\mu$ is the change of the chemical potential of the atom as it goes from the old phase to a new one. To describe the growth kinetics, conditions are postulated in the ZV theory on the islet boundary for the flux of adatoms or for their density. It is usually assumed that equilibrium is established on the boundary, and that the following relation holds for the adatom density[11-13]

$$C(r=R) = C_R = C_0(1+\rho_0/R), \quad \rho_0 = \gamma s/T. \tag{2}$$

Here C_0 is the density of the saturated adatom solution and T is the temperature. The flow boundary conditions make it possible to take into account the deviation of the adatom density around the seed from the equilibrium value (2) (Ref. 3).

The growth rate $\dot{R}$ of an individual new-phase seed is expressed in the ZV phenomenological theory on the basis of the conservation laws and is determined by the total atom flux J through the seed boundary:

$$\dot{R} = sJ. \tag{3}$$

The flux J is produced by the following mechanisms of atom supply to the islet: diffusion of adatoms over the surface and adsorption of atoms from the gas directly on the islet perimeter, where it is directly trapped into the islet.[3,4] In the diffusion mechanism, the atom fluxes adsorbed by the islets and by the clean surface lead to the growth equation

$$\dot{R}(t) = sC_0 \frac{D}{L} \rho_0 \left\{ \frac{K_1(R/L)}{K_0(R/L)} + \frac{I_1(R/L)}{I_0(R/L)} \right\} \left(\frac{1}{R_c} - \frac{1}{R} \right). \tag{4}$$

Here D is the diffusion coefficient, $L = (D/a)^{1/2}$, a^{-1} is the characteristic adatom lifetime and is governed by desorption processes or by escape of the adatoms into the bum of the material, and K_i and I_i are modified Bessel functions.[15]

Lowering of the rates of the processes connected with nonconservation of the particle number ($a \to 0$) produces a singularity indicative of two-dimensional systems: no stationary distribution of the adatoms is reached. The reason is that the diffusion equation for a two-dimensional system is gauge-invariant.[16] For this case there was obtained only an asymptotic expression[7,8] for the long-time growth rate $\dot{R}$ of the islet[7,8]

$$\dot{R}(t) = sDC_0\rho_0 \left(\frac{1}{R_c} - \frac{1}{R} \right) \left\{ R \ln\left[2 \frac{(Dt)^{1/2}}{R} \right] \right\}^{-1}. \tag{5}$$

The value that follows for the power-law exponent n from Eq. (5) is close to[7,8] (0.5). The same value was obtained by computer simulation[17-20] and was observed in experiment for a number of systems (see, e.g., Refs. 21 and 22). The value $n = 0.5$ is obtained also from Eq. (4) when the islet dimensions are small compared with the diffusion length L ($R \ll L$). If $R \gg L$, however, the value of n obtained by direct integration of (4) is unity. This value of n was observed in experiment for several systems,[6,9,23] for example for exidation of nickel.[9,23] Note that allowance for the diffusion interaction of the islets and for their coalescence lowers the exponent n (Refs. 3 and 7).

When the direct-capture mechanism predominates, the islet-growth equation takes the simple form[3,9]

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$$\dot{R}(t)=sC_0\alpha\rho_0\chi_0\left(\frac{1}{R_c}-\frac{1}{R}\right) \tag{6}$$

Here χ_0 is the width of the region that surrounds the islet and in which direct capture into the islet takes place. It is easy to verify that in this case the exponent n tends to unity with time.

Another approach to the kinetics of phase transitions is based on an equation describing the relaxation of the order parameter $\xi(r,t)$ to an energywise more favorable state[24,27]:

$$\dot{\xi}(\mathbf{r},\ t)=-\hat{\mu}\delta F[\xi(\mathbf{r},\ t)]/\delta\xi. \tag{7}$$

Here $F[\xi(\mathbf{r},t)$ is a free-energy functional corresponding to the field $\xi(\mathbf{r},t)$, $\mathbf{r}$ is the coordinate, t is the time, $\hat{\mu}$ is a kinetic operator given in the long-wave approximation by $\hat{\mu} = -\mu_c\Delta + \mu_H$, where μ_c and μ_H are the kinetic coefficients in the case of a conserved and nonconserved field ξ, respectively. In the considered conversions on the field, ξ is the deviation of $C(r)$ density of the adsorbed atoms in the new phase state from the average adatom density $\overline{C}$ on the surface: $\xi(\mathbf{r},t) = C - \overline{C}$.

In principle, the kinetic coefficients μ_c and μ_H and the free energy F in the vicinity of the phase-transition point determine Eq. (7) completely, and description of the phase-transition kinetics requires neither additional parameters nor assumptions. This approach has made it possible to describe for second-order phase transitions in the bulk and on the surface the growth of the domains and a number of nontrivial features of the structural-transition kinetics (see, e.g., Refs. 26–31). A description[25] of seed formation in three-dimensional systems has shown that all the parameters, assumptions, and main results of the ZV theory can be obtained by solving the equation for the order parameter. By its very nature the approach based on the concept of an order parameter should constitute a microscopic verification of the phenomenological theory.

We use in this paper the order-parameter field to investigate the kinetics of the growth of new-phase islets. This approach makes it possible to obtain by a single procedure different limiting cases of the phenomenological theory and determine the system parameters that lead to various values of the power-law exponent.

2. ORDER-PARAMETER EQUATION. BASIC PARAMETERS OF THEORY

We write for the free energy in the vicinity of the phase-transition point an expression that follows from the Landau theory:[24,32]

$$F=\int d\mathbf{r}\left(\frac{\lambda\xi^2}{2}+\frac{\Omega(\nabla\xi)^2}{2}+\frac{B\xi^3}{3}+\frac{\Gamma\xi^4}{4}\right). \tag{8}$$

Here λ, Ω, B, and Γ are coefficients that depend in general on external parameters, such as the temperature and density of the adatoms.

The free energy (8) describes a first-order transition when $B \neq 0$. It is easy to verify that a phase transition takes place at $\lambda \leqslant 2B^2/9\Gamma$ and constitutes a transition from a state with a zero order parameter $\xi = 0$ into a state with ξ 2B/3Γ.

The order-parameter equation (OPE) (7) for the free energy (8) takes the form

$$\dot{\xi}(\mathbf{r},\ t)=(\mu_c\Delta-\mu_H)(\lambda\xi-\Omega\Delta\xi+B\xi^2+\Gamma\xi^3). \tag{9}$$

Before we proceed to investigate the relaxation of the order-parameter field, let us find the connection between the kinetic coefficients μ_c and μ_H of Eq. (7) and the observable quantities, so that we can separate the physical mechanism of the seed growth. We write Eq. (9) in the linear approximation in $\xi(\mathbf{r},t)$, which describes the relaxation of small perturbations in the old phase:

$$\dot{\xi}(\mathbf{r},\ t)=-\alpha\xi+D\Delta\xi,\quad \alpha\equiv\mu_H\lambda,\quad D\equiv\mu_c\lambda. \tag{10}$$

An identical equation is used in the phenomenological theory of atom adsorption.[7,33] In this case the quantity D corresponds to the adatom-diffusion coefficient and a^{-1} corresponds to the adatom characteristic lifetime governed by their desorption from the surface or by their departure into the bulk of the crystal. This explains the physical meaning of the kinetic coefficients μ_H and μ_c. The first is connected with atom adsorption and desorption ($\mu_H = \alpha/\lambda$), and the second with adatom diffusion over the surface ($\mu_c = D/\lambda$). These are the mechanisms which have been considered in the phenomenological theory [see Eqs. (4)–(6)].

For further convenience, we express (9) in terms of the dimensionless variables $\varphi = 2\xi/\xi_0 - 1$, $\boldsymbol{\rho} = \mathbf{r}/\chi$, $\tau = t/\tau_0$:

$$\dot{\varphi}(\rho,\ \tau)=(l^2-\Delta)[\Delta\varphi+2\varphi(1-\varphi^2)+h(\varphi+1)]. \tag{11}$$

Here $\xi_0 = 2B/3\Gamma$ is the order parameter of the new phase at the phase transition point,

$$\chi=\xi_0(8\Omega/\Gamma)^{1/2},\quad \tau_0=\chi^4/\mu_c\Omega,\quad l^2=\chi^2\mu_H/\mu_c,$$

and the quantity $h = 4(1-\lambda/\lambda_c)$ has the meaning of the degree of metastability. The dimensionless order parameter φ is equal to -1 in the old phase and $\varphi = \varphi_H \equiv [1 + (1+2h)^{1/2}]/2$ in the new one ($\varphi_H \approx 1$ for low degrees of metastability $h \ll 1$).

Equation (11) contains only two dimensionless parameters, h and l. The degree of metastability h measures the proximity to the phase-transition point, the difference between the new and old energy states. The parameter h can be regarded as small near the phase-transition point, $h \ll 1$. The parameter l (11) determines in fact the ratio of the contributions of two different growth mechanisms of the new-phase islets—direct capture and diffuse growth. The parameter l varies in a wide range in different physical systems, and will in fact determine the different relaxation regimes of the system.

We emphasize that the equation obtained for the field of the order parameter (11) is universal, and the relaxation kinetics in actual physical systems differs only because the parameters ξ_0, χ, τ_0 and l are different. We now go on to solve the OPE (11).

3. CRITICAL NUCLEI OF NEW PHASE—STATIONARY SOLUTIONS OF OPE

We consider the non-uniform order-parameter field distributions $\varphi(\boldsymbol{\rho},\tau)$ produced in two-dimensional phase transitions. It is known that the new-phase seeds are solutions of the equation for the order parameter.[25] The free-energy functional (8) makes it possible to determine the explicit form of the order-parameter field $\varphi_c(\boldsymbol{\rho})$ for a new-phase seed with critical dimension. This field corresponds to an extremum of the free-energy functional and is therefore a stationary solution of Eq. (7), in accord with the fact that critical seeds neither grow nor are dissolved.

The result is an equation for the order-parameter field $\varphi_c(\rho)$ of the critical seed:

$$\delta F/\delta\varphi=0\to\Delta\varphi_c+2\varphi_c(1-\varphi_c^2)+h(\varphi_c+1)=0. \tag{12}$$

Let us write down the boundary conditions for Eq. (12) The order parameter corresponds at large distances from the seed to the old phase, $\varphi(\rho\to\infty)=-1$, and inside the seed to the new phase, $\varphi(\rho=0)=\varphi_H$.

For a two-dimensional system with axial symmetry the solution of (12) for critical seeds at low degrees of metastability, $h\ll 1$, can be represented in the form

$$\varphi_c(\rho)\approx\operatorname{th}(a_c-\rho),\quad a_c=2/3h. \tag{13}$$

Here $R_c\equiv\chi\alpha_c$ is the critical dimension of the seeds. It follows from (13) that χ assumes the role of the width of the transition layer between the phases.

The analytic solutions (13) are compared in Fig. 1 with the numerical solutions of (12), which describe the field of the order parameter of critical seeds. Evidently the analytic solutions agree well with the exact ones up to metastability degrees $h\approx 0.1$. At higher metastabilities ($h>0.1$) spreads out, by analogy with three-dimensional systems.[34]

The obtained order-parameter field distribution (13) yields the connection between the phenomenological parameters in Eq. (1) and the free-energy coefficients (8). Integration of the free energy (8) over the transition layer of the new-phase seed (13) yields for large seeds a linear tension coefficient

$$\gamma=(2\Gamma\Omega)^{1/2}\xi_0^3/12. \tag{14}$$

Using the solution (13), we can calculate also the change of the chemical potential on going from the old phase to the new:

$$\Delta\mu=h\Gamma\xi_0^3/16. \tag{15}$$

The energy (8) corresponding to an order-parameter field given by (13) can be represented as

$$E(R)=2\pi R\gamma+\Delta\mu s\pi R^2. \tag{16}$$

Here $s\equiv\xi_0^{-1}$ has the meaning of the molecular area of the new phase. Note that the subdivision of the energy (16) into "bulk" and "surface" parts was used to obtain R_c (1). Thus, for large-radius critical seeds ($\alpha_c\gg 1$) the Zel'dovich–Vollmer and Landau theories are in full agreement.

Relation (16) can be written only for large seeds exceeding the width χ of the transition layer. With increase of the metastability degree h the critical dimension $R_c=\chi\alpha_c$ of the seed decreases. At large h the concept of critical dimension becomes too vague, for at $R_c\sim\chi$ the seed energy does not separate into bulk and surface parts. At the same time a solution for the critical-seed field $\varphi_c(\rho)$ does exist in this range of parameters (Fig. 1).

4. EQUATION FOR ISLET GROWTH

We proceed to find the nonstationary solutions of Eq. (11) for the order parameter and show that the growth and dissolutions of the islets can be described without additional assumptions and phenomenological parameters.

Using the Green's function $G(\rho)=K_0(\rho l)$ of the equation

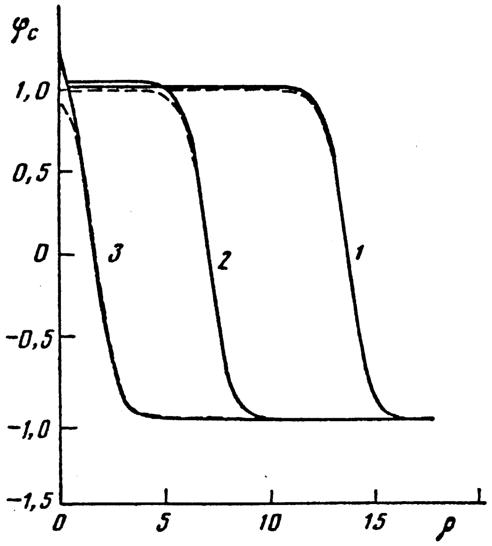

FIG. 1. Order-parameter field $\varphi_c(\rho)$ of critical islets [solid line—solution of Eq. (12), dashed-analytic relation (13)]: 1—$h=0.05$; 2—$h=0.1$; 3—$h=0.5$.

$$(l^2-\Delta)G(\rho)=\delta(\rho) \tag{17}$$

we rewrite Eq. (16) in the form

$$\int G(\rho-\rho')\dot\varphi(\rho',\tau)\,d\rho'=\Delta\varphi(\rho,\tau)+2\varphi(1-\varphi^2)+h(\varphi+1). \tag{18}$$

We seek for Eqs. (11) and (18) solutions that describe the formation of new-phase islets of size R large compared with transition-layer width $\chi(\alpha\equiv R/\chi\gg 1)$, in the form of a seed plus a certain correction:

$$\varphi(\rho,\tau)=\varphi_c(\rho-a(\tau))+w(\rho,\tau). \tag{19}$$

Here $\varphi_c(\rho-\alpha(t))$ is the solution of Eq. (12) for the critical seed but with the substitution $\alpha_c\to\alpha(\tau)$. The correction $w(\rho,\tau)$ will be shown below to determine the diffusion fluxes to the seed, and in the diffusion limit of small l it is a slowly varying function of the coordinates:

$$\Delta w\ll w. \tag{20}$$

For weak metastability $h\ll 1$ the increment $w(\rho,\tau)$ to the solution φ_c can also be regarded as small:

$$w(\rho,\tau)\ll 1. \tag{21}$$

Near the phase-transition point ($h\ll 1$) the change of the seed dimension is usually the slowest process,[25,35] i.e., it can be assumed that the characteristic time τ_w for the establishment of the distribution w is short compared with the time τ_α in which the size of the seed changes:

$$\tau_w\ll\tau_a. \tag{22}$$

At any finite instant of time τ, only the old phase $[\varphi(\rho\to\infty,\tau)\to -1]$ exists at large distances from the seed. Since $\varphi_c(\rho\to\infty,\tau)\to -1$, $w(\rho,\tau)$ satisfies the condition

$$w(\rho\to\infty,\tau)=0. \tag{23}$$

Substituting the solution (19) in Eq. (18) and using the conditions (20), (21), and (22) we obtain

$$-\dot{a}(\tau)P(\rho,\ \tau)=(1/a-1/a_c-6w(\rho,\ \tau))\,\mathrm{ch}^{-2}(a-\rho)+4w(\rho,\ \tau), \tag{24}$$

$$P(\rho,\ \tau)\equiv\int G(\rho-\rho')\,\mathrm{ch}^{-2}(a-\rho')d\rho'.$$

The investigations that follow will involve the solution of Eq. (24) which determines the growth rate of the islets in a field $w(\rho,\tau)$. In the diffusion limit ($l\to 0$), as will be shown below, it is necessary to take into account in (24), for two-dimensional systems, the discarded terms $\sim\dot{w}$. This will be done for $l=0$.

The parameter l that determines Eq. (11) for the order parameters enters in (24) only via the Green's function (17) and correspondingly through the integral $P(\rho)$ of Eq. (24). Therefore the characteristic features of the kinetics are determined by the properties of the integral $P(\rho)$ at various values of l. It is convenient to represent the parameter l, which determines the contributions of the various growth mechanisms, as the ratio χ/L of the seed transition-layer width χ to the characteristic diffusion length L during the adatom lifetime. The quantities χ and L are indicative of the dimensions of the layers in which the mechanisms of direct capture and diffusion growth supply adatoms to the islet [χ corresponds to $\chi_0(6)$]. We investigate the properties of the function $P(\rho)$ to various limiting cases with $l\ll 1$ and $l\gg 1$, and obtain the corresponding growth equations.

5. ISLET GROWTH IN THE DIFFUSION REGIME ($l\ll 1$)

Consider the case when the diffusion length L exceeds the width χ and let the adatom desorption be weak:

$$L\gg\chi,\ l=\chi(\mu_{\text{н}}/\mu_c)^{1/2}\ll 1. \tag{25}$$

The integrand in expression (24) for $P(\rho)$ at $l\ll 1$ contains a product of an abrupt function $\cosh^{-2}(\alpha-\rho')$, which differs from zero in the vicinity of the seed boundary $\rho'=\alpha$, and a function $G(\rho,\rho')\rho'$, which is fluent in this vicinity [here $G(\rho,\rho')$ is the function $G(\rho-\rho')=K_0(|\rho-\rho'|l)$ of Eq. (17), integrated over the directions of the vector ρ']. This circumstance makes it possible to expand the function $G(\rho,\rho')\rho'$ in terms of the variable ρ' near the maximum value $\rho'=\rho_m$, ($\rho_m\approx a$) of the function $\cosh^{-2}(\alpha-\rho')$:

$$G(\rho,\rho')\rho'\approx G(\rho,\rho'=\rho_m)\rho_m + \left.\frac{\partial(G(\rho,\rho')\rho')}{\partial\rho'}\right|_{\rho_m}(\rho'-\rho_m)+\dots \tag{26}$$

Confining ourselves to the zeroth approximation of the function $G(\rho,\rho')\rho'$ in (26), we obtain for $P(\rho)$ (24)

$$P(\rho)\approx P_0(\rho)=\begin{cases}2I_0(\rho l)K_0(al)a, & \rho<a\\ 2K_0(\rho l)I_0(al)a, & \rho>a\end{cases}. \tag{27}$$

It follows hence that the characteristic scale of the variation of the function $P(\rho)\approx P_0(\rho)$ is $1/l$. In the diffusion limit, when $l\ll 1$, the function $P(\rho)$ is thus smooth over scales of the order of the size of the transition layer of the seed.

Consider now Eq. (24) outside the seed boundaries. The function $\cosh^{-2}(\alpha-\rho)$ is here exponentially small, so that the equation simplifies to

$$-\dot{a}(\tau)P_0(\rho)=4w(\rho,\ \tau). \tag{28}$$

Since the functions $w(\rho,\tau)$ and $P_0(\rho,\tau)$ are smooth [relations (20) and (27)], Eq. (28) should be satisfied in all of space, including on the seed boundary at $\rho\approx\alpha$. It follows hence that the first term in the right-hand side of (24) is zero, and the following relation holds on the islet boundary

$$w(\rho=a)=w_c\equiv\frac{1}{6}\left(\frac{1}{a}-\frac{1}{a_c}\right). \tag{29}$$

Using (27) and (29) it is easy to obtain from (28) the islet growth rate in the diffusion regime:

$$\dot{a}(\tau)=\frac{1}{3}\left(\frac{1}{a_c}-\frac{1}{a}\right)\left(\frac{K_1(al)}{K_0(al)}+\frac{I_1(al)}{I_0(al)}\right). \tag{30}$$

When account is taken of the function $P(\rho)$ [Eq. (27)] the behavior of the perturbation $w(\rho,\tau)$ can be determined in all of space:

$$w(\rho,\ \tau)=w(\rho=a)\begin{cases}K_0(\rho l)/K_0(al), & \rho>a\\ I_0(\rho l)/I_0(al), & \rho<a\end{cases}. \tag{31}$$

From the explicit form of the perturbation (31) it follows that at finite l there are two different fluxes $J\propto-\nabla w$, one from the outside and the other from the inside towards the boundary. It is these two fluxes that determine the growth rate (30) of the seed.

It was assumed above that $w(\rho,\tau)$ is a smooth enough and slowly varying function of the coordinates and the time [the conditions (20), (21), and (22)]. Using the explicit form (31) of the function w we easily verify that the conditions (20) and (21) are certainly satisfied in the region of low degrees of metastability ($h\ll 1$) for large seeds ($l\gg 1$). The same result was obtained in Ref. 25 for the three-dimensional case. On the other hand, the quasistationary condition (22) may be violated at short times, when the seeds are small and the following relation holds:

$$a^3l^2I_0(al)K_0(al)\approx 1. \tag{32}$$

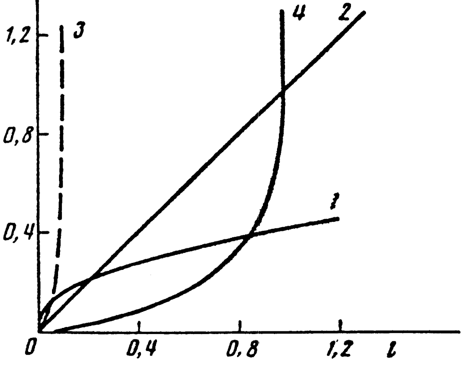

FIG. 2. Diagram of relaxation regimes of a two-dimensional system: *1*—line [(22,32)] of violation of quasistationary-growth condition; *2*—line of admissible dimensions $a>1$; *3*, *4*-line of equilibrium violation (45) on islet boundary (*3*—$\beta=0.1X$, where $X=\frac{1}{2}\,aI_0(al)K_0(al)$, *4*—$\beta=X$).

As l tends to zero, when the role of the processes that do not conserve the number of adatoms becomes negligibly small, this time and space region broadens. Figure 2 shows the regions of seed dimensions for various values of the parameter l, where various relaxation regimes are realized. The size region in which growth takes place in the quasistationary regime lies below curve *1*. This region is bounded from below by line *2* which determines the permissible dimensions $a > 1$. It is seen from Fig. 2 that there is nonstationary growth if $l > 0.2$.

Let us consider the kinetics of the islet growth (30) in the diffusion regime. Figure 3 (lines *1–4*) shows the time dependences (30) of the islet dimensions for different values of the parameter l. A nonstationary relaxation regime exists for the curves to the right of line *3*. The region of the parameters of this regime lies below the dashed curve *7*. Figure 4 (lines *1–4*) shows the effective power-law exponents $n \equiv \dot{a}t/a$ for the same parameters as in Fig. 3. In the case of the diffusion relaxation mechanism (at small l) we have $n \to 0.5$. With enhancement of the processes that do not conserve the number of particles on the surface (desorption, penetration into the bulk of the material), the asymptotic values of the exponent increase.

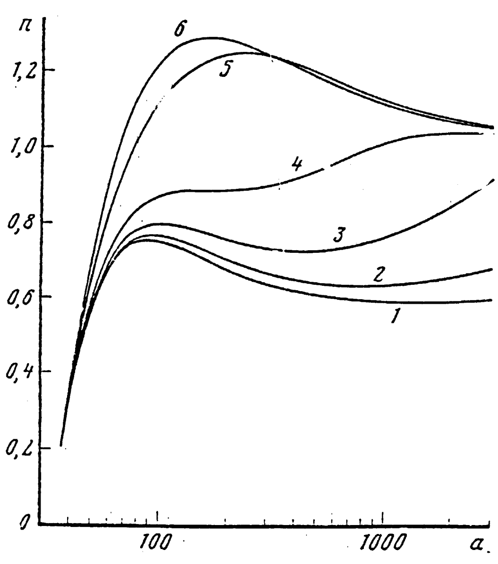

FIG. 4. Dependence of effective power-law exponent $n \equiv \dot{a}t/a$ on the dimension a: *1*—$l = 2\cdot 10^{-5}$, *2*—10^{-4}, *3*—$5\cdot 10^{-4}$, *4*—$2\cdot 10^{-3}$, *5*—10^{-2}, *6*—0.2 (the remaining parameters are the same as in Fig. 3).

6. OPE AND PHENOMENOLOGICAL-THEORY PARAMETERS

We start by showing that at $l \ll 1$ the seed-growth equation is determined by the conservation laws, just as in the case of the phenomenological theory [Eq. (3)]. We rewrite Eq. (28) in differential form, by applying it to the operator $(l^2 - \Delta)$:

$$-\dot{a}(\tau)\,\mathrm{ch}^{-2}(a-\rho) = 4(l^2-\Delta)\,w(\rho,\tau). \tag{33}$$

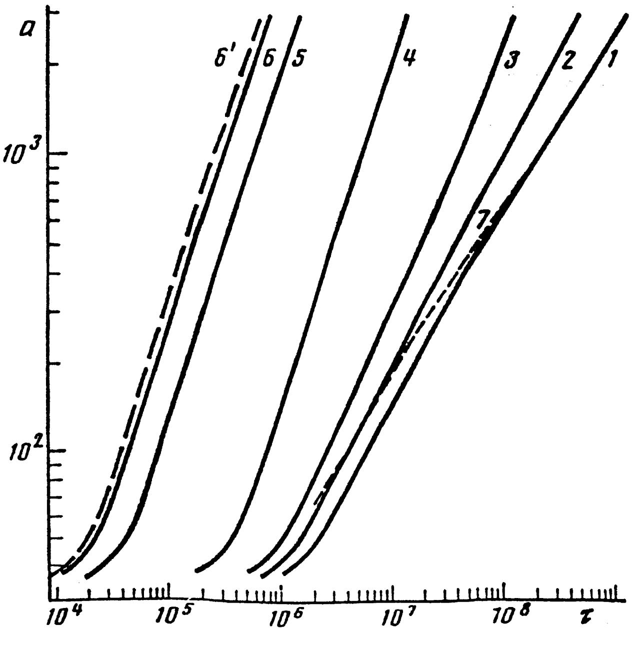

FIG. 3. Dependence of islet dimension a on the time τ for $\alpha(\tau = 0) = 32$, $\alpha_c = 30$, and different values of the parameter *l* [lines *1–4* and *6'*—solutions of Eq. (30); lines *5* and *6*—solutions of Eq. (43)]: *1*—$l = 2\cdot 10^{-5}$, *2*—$2\cdot 10^{-4}$, *3*—10^{-3}, *4*—10^{-2}, *5*—0.1, *6*, *6'*—0.2.

We integrate this equation over the boundary layer, where the function $\cosh^{-2}(a-\rho)$ differs from zero. The result is an equation for the seed growth rate in the case $l \ll 1$:

$$\dot{a}(\tau) = 2\left(\nabla w|_{\rho=a+0} - \nabla w|_{\rho=a-0} - l^2 w|_{\rho=a}\right). \tag{34}$$

The first two terms in (34) describe the diffusion fluxes towards the seed boundary from the inside and the outside, while the last term is the flux due to the creation (adsorption) of particles on the seed boundary itself. This term is proportional to l^2, and therefore diminishes rapidly as $l \to 0$. Note that with decrease of l (slowing down of the processes connected with nonconservation of the number of particles) the contribution to (34) from the flow from the interior of the seed also decreases and vanishes altogether in the limit as $l \to 0$. If l is small but finite, particles are produced inside the seed by adsorption and flow towards the boundary.

The growth rate of the seeds is determined by relations of the form (34) in systems of any dimensionality ($\geqslant 2$), when the nonconservation of the number of particles is insignificant ($l \ll 1$). A change of the dimensionality changes only a numerical coefficient and the form of the function $w(\rho,\tau)$ that determines the particle fluxes towards the seed boundary.

We show now that the value (29) obtained for the function $w(\rho,\tau)$ on the seed boundary from the order-parameter equation agrees with the phenomenological condition (2) corresponding to equilibrium on the boundary. We use the expression for the critical dimension R_c [Eq. (1)] expressed in the low-density approximation, $R_c = \rho_0 C_0/(\bar{C} - C_0)$ (Ref. 35), and rewrite the boundary condition (2):

$$C(r=R) - \bar{C} = C_0\rho_0(1/R - 1/R_c). \tag{35}$$

Changing in (29) from the dimensionless quantities a to the dimensional $R = \chi a$ we readily verify that expressions (29) for $w(r=R)$ and (35) for $C(r=R) - \overline{C}$ coincide, and a connection exists between the parameters of the phenomenological theory and the coefficients of the order parameter:

$$C_0\rho_0 = \xi_0\chi/12. \qquad (36)$$

Since an expression in the form (29) is obtained for w only in the diffusion limit $l \ll 1$, equilibrium is reached on the boundary only when the diffusion length L exceeds the characteristic scale χ of the boundary layer between the phases, in which direct capture of atoms from the gas into the new phase is possible.

7. DEVIATION FROM QUASISTATIONARY GROWTH REGIME ($l=0$)

We have considered above the case (22), when the time to establish the distribution $w(\rho,\tau)$ was neglected compared with the time to change the islet dimension, so that the term $\sim \dot w$ could be left out of Eqs. (24) and (33). There exists, however, also a parameter region in which the quasistationarity condition (22) is violated (Fig. 2). This condition is certainly not met at $l = 0$. Let us consider the growth of islets in just this case. We must write them in place of (33)

$$-\dot a(\tau)\,\mathrm{ch}^{-2}(a-\rho) = -4\Delta w(\rho,\tau) + \dot w(\rho,\tau). \qquad (37)$$

Outside the seed boundary, where the left-hand part of (37) is zero, this is the usual equation of nonstationary two-dimensional diffusion. Solution of the diffusion equation with allowance for the asymptotic condition (23) can be written in the long-time limit $4\tau^{1/2} \gg \alpha$ in the form[8,36]

$$w(\rho,\tau) \approx \begin{cases} A\left(1 - \ln(\rho/a)/\ln(4\tau^{1/2}/a)\right), & a \leqslant \rho \leqslant 4\tau^{1/2} \\ 0, & \rho \geqslant 4\tau^{1/2} \end{cases} \qquad (38)$$

Here A is a slowly varying function of the time, which can be conveniently determined from the behavior of the system near the islet boundary. Inasmuch as for sufficiently long times $4\tau^{1/2} \gg \alpha$ the perturbation wave $w(\rho,\tau)$ (38) propagates over large distances from the islet boundary, the function $w(\rho,\tau)$ near the islet can be regarded at $\rho \approx a$ as quasistationary, so that $\dot w$ can be disregarded in this region when Eq. (37) is solved. Equation (24) therefore remains in force near the boundary. This circumstance makes it possible to obtain the boundary conditions (29), and for long times we have $A = w_c$ in (38). Integrating (37) over the transition layer of the seed [by analogy with (33)] and substituting the explicit form (38) of $w(\rho,\tau)$, we obtain an asymptotic expression for the growth rate in a two-dimensional system with a conserved order parameter (at $4\tau^{1/2} \gg a$):

$$\dot a(\tau) = \frac{1}{3}\left(\frac{1}{a_c} - \frac{1}{a}\right)\frac{1}{a\ln(\tau^{1/2}/a)}. \qquad (39)$$

This equation coincides with Eq. (5) of the phenomenological theory (apart from the nondimensionalizing parameters). The exponents n of the power-law growth of the islet size, which appear when equations such as (39) are solved, have been considered in Ref. 8 and are close to 0.5 owing to the weak dependence of the function $\ln(4\tau^{1/2}/a)$ on the argument. As a result the solutions of Eq. (39) are similar[7,8] to the solutions of the equation

$$\dot a(\tau) = \frac{1}{3}\left(\frac{1}{a_c} - \frac{1}{a}\right)\frac{1}{a}. \qquad (39a)$$

Just such an expression was obtained in Ref. 37 for the islet growth rate in investigations of the relaxation of a conserved order parameter in a two-dimensional system. Our analysis above shows that Eqs. (39) and (39a) are asymptotic and describe the behavior of the system after long times.

8. DEVIATION FROM EQUILIBRIUM ON THE BOUNDARY OF THE SEED ($l \leqslant 1$)

We have considered above the case $l \ll 1$, when the influence of the processes that do not conserve the number of particles was manifested only far from the islets, at large distances compared with the transition-layer width χ. Equilibrium $w(\rho = \alpha) = w_c$ was reached in this case on the boundary of the islet (this condition is satisfied at $l = 0$ only for long times $4\tau^{1/2} \gg \alpha$). Analysis of the processes that do not conserve the number of particles on the boundary should lead to deviation from equilibrium. To take formal account of the influence of these processes on the boundary condition it is necessary to retain in (26) the terms that follow the zeroth term of the expansion and permit allowance for small but finite values of $l(l \leqslant 1)$. Thus, the quantity $P(\rho)$ defined by (24) takes in the linear approximation the form

$$P(\rho) = P_0(\rho) + \delta P(\rho). \qquad (40)$$

The function $P_0(\rho)$ [Eq. (27) varies over scales $1/l$. Direct substitution of the liner term of the expansion (26) into relation (24) for $P(\rho)$ shows that the function $\delta P(\rho)$ differs form zero only in the region of the seed boundary. This means that outside the boundary Eq. (24) takes as before the form (28), and the function $w(\rho,\tau)$ is just as smooth as $P_0(\rho)$. Since the functions $w(\rho,\tau)$ and $P_0(\rho)$ are smooth, the relation $-\dot\alpha(\tau)P(\mathrm{p}) = 4w(\mathrm{p},\tau)$ is valid near the boundary $\rho \approx a$. Equation (24) takes then in the vicinity of the boundary the form

$$-\dot a(\tau)\,\delta P(\rho) = [1/a - 1/a_c - 6w(\rho,\tau)]\,\mathrm{ch}^{-2}(a-\rho). \qquad (41)$$

We integrate this equation over the transition layer of the seed, using the abrupt dependence of the functions $\cosh^{-2}(a-\rho)$ and $\delta P(\rho)$. The result is

$$w(\rho = a) = w_c + \dot a(\tau)\,\beta/3. \qquad (42)$$

$$\beta = \int_{-\infty}^{+\infty} \delta P(\rho)\, d\rho,$$

[$\beta = \pi^2/12$ in the linear approximation (26)], w_c is the equilibrium value of the field $w(\rho,\tau)$ (29) on the seed boundary.

Note that the quadratic and subsequent terms of the expansion (26) introduce into $P(\rho)$ a term that varies both over scales comparable with $1/l$ and over scales of the order of the width of the transition layer. The terms of the former type renormalize $P_0(\rho)$ and change the flows to the seed, while those of the second renormalize $\delta P(\rho)$ and accordingly β in (42).

By considering jointly Eq. (28) and the boundary condition (42), we obtain the growth rate of the seeds at $l \leqslant 1$:

$$\dot a(\tau) = \left(\frac{1}{a_c} - \frac{1}{a}\right)\frac{1}{3aI_0(al)K_0(al) + 2\beta}. \qquad (43)$$

in the limit of small l we can neglect β in the denominator of (43), in which case the growth equation (43) coincides with (30).

Using relation (43) for the growth rate, we rewrite the boundary condition (42):

$$w(\rho=a)=w_c\frac{aI_0(al)K_0(al)}{aI_0(al)K_0(al)+2\beta/3}. \tag{44}$$

It is easily seen that equilibrium is reached on the islet boundary (29) only under the condition

$$aI_0(al)K_0(al)\gg\beta. \tag{45}$$

The islet-dimension regions where the influence of processes violating the condition of equilibrium on the boundary becomes substantial, are indicated in Fig. 2. The contribution of the processes on the islet boundary to the right of curve *3* exceeds 10% [i.e., $\beta > 0.1X$, where $X=\frac{3}{2}\alpha I_0(\alpha l)K_0(\alpha l)$], and becomes decisive on the right of curve *4* ($\beta > X$). If $l < 0.1$, equilibrium is reached on the boundary only for islets of sufficient size, $a > a^*$. It is easy to show that a^* increases when l decreases. The equilibrium in the interval $0.2 < l < 1$, starting with $a \geqslant 1$, is violated on the boundaries of seeds of all sizes, in the $0.2 < l < 1$ interval, and at $l > 1$ this violation becomes predominant: $w(\rho=\alpha) < \frac{1}{2}w_c$.

We rewrite the obtained boundary condition (42), using the general relations for the growth rate $\dot{a}(\tau)$ [Eq. (34)] for the growth rate of an islet, and for the total flux J of particles to the boundary of the islet:

$$J=\frac{3}{2\beta}[w(\rho=a)-w_c], \tag{46}$$

or in dimensional form

$$J=\frac{3}{2\beta}\frac{D}{\chi}[C(r=R)-C_R\}. \tag{46a}$$

A condition such as (46a) is used for the flow of particle through the boundary of a seed in the ZV phenomenological theory. This is a more general boundary condition that (2) and (29). It takes into account the finite rate of the processes that occur on the boundary of the seed.[3,6] From the explicit form of the expression obtained for the flow it is seen that the velocity v of passage of the particles through the boundary is determined in this case by the velocity of a diffusion jump of length χ, which is indicative of the width of the transition layer of the seed:

$$v=\frac{3}{2\beta}\frac{D}{\chi}.$$

The quantity β [Eq. (42)] is thus connected with the finite flow rate of the particles through the boundary.

Let us examine the influence of the finite rate of the processes at the boundary of an islet on the growth kinetics of the new phase. Curves *1–4* of Fig. 3, which constitute solutions of Eq. (30) for $l \leqslant 10^{-2}$, agree within 10% with the solutions of Eq. (43) which takes the processes on the boundary into account. On the left of line *5* ($l > 0.1$) are located curves for which the contribution of the processes on the boundary exceed 10% [lines *5* and *6*—solutions of Eq. (43)]. By way of example, Fig. 3 shows the solution of both Eq. (43) (line 6) and Eq. (30) (line *6'*) for $l=0.2$. The power-law exponents calculated with the aid of Eq. (43) exceed 0.5 and tend to unity for large values of *1* (curves *5* and *6* of Fig. 4).

9. NONDIFFUSION LIMIT $l \gg 1$

A situation far from equilibrium sets in when processes in which the number of particles is not conserved, $l \gg 1$, dominate. The phase transitions are described in this case by a nonconserved order parameter. Relaxation of a non-conserved order parameter was investigated in sufficient detail[25,37] for systems with various dimensionalities. The following growth equation [in the dimensionless form (11)] was obtained for the seeds in Ref. 25:

$$\dot{a}(\tau)=l^2\left(\frac{1}{a_c}-\frac{1}{a}\right). \tag{47}$$

This equation is easily obtained in the framework of the proposed method. For $l \gg 1$, in fact, the Green's function G [Eq. (17)] can be assumed, up to scales of the order of the boundary width, to be $G=l^2\delta(\rho)$. As a result, the integral $P(\rho)$ differs from zero only on the boundary, the growth equation takes the form (47). Note that the perturbation $w(\rho,t)$ is zero for $l \gg 1$, so that the same nonequilibrium adatom density obtains near the islet as at large distances, and there are no diffusion fluxes. The islet growth rate (47) is fully determined by the particle adsorption on its boundary [by analogy with (6)].

The growth equation (47) leads for large islets to a power-law exponent $n=1$. The islet size increases thus linearly both if $l \gg 1$ and if $l \ll 1$ (see Sec. 8). Since the growth exponent is a monotonic function of the parameter l, one can expect n to be close to unity also in the intermediate region $l \gg 1$.

10. CONCLUSION

The theory of relaxation of metastable states[25] is applicable to two-dimensional systems of adsorbed atoms. The main advantage of the developed approach is its universality: the entire variety of relaxation regimes reduces to variation of two dimensionless parameters h and l, one of which (h) determines the degree of metastability of the system and the other (l) the ratio of two growth mechanisms, viz., diffusion of adatoms to an islet and direct landing of atoms from the gas phase above the surface on the perimeter of the islet. We have investigated here the growth kinetics of new-phase islets in various regimes. The obtained power-law exponents of the growth of an islet (occurring after long growth times) varies in the interval from 0.5 (in the diffusion limit $l \to 0$) to 1 (in the cases $l \sim 1$ and $l \gg I$).

A connection was established between the developed approach and various generalizations of the ZV theory for two-dimensional systems. Relations were obtained between the coefficients of the order parameter and the parameters of the ZV theory. Solution of the order-parameter equation led to the conditions produced on the islet boundary in various cases. It was shown that an equilibrium adatom density is produced near an islet boundary only in the diffusion limit ($l \ll 1$), and deviation from this limit violates the equilibrium and leads automatically to a flow-like boundary condition.

Application of the developed approach to actual systems requires derivation of an expansion of the free energy in powers of the order parameter in the vicinity of the phase transition point, or indirect derivation of an order-parameter equation. A similar microscopic approach was implemented for certain physical systems.[38–40] The free energy of an adatom system can be expanded on the basis of the potential of paired long-range interactions between the adatoms.[41,42]

Note that the theory of relaxation of order-parameter fields can be used to consider individual seeds as well as their ensembles. It is possible to derive in a regular manner an equation for the seed flux in dimension space and to study formation of seeds, their coalescence, and other effects.[25] The distinguishing features of two-dimensional systems with different growth-mechanism ratios requires a separate analysis of the relaxation of an ensemble of islets.

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