

Influence of adsorption or desorption and surface diffusion on the formation kinetics of open half-monolayer coverage

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The formation kinetics of open half-monolayer films on solid substrates is studied by the deposition of particles from a gaseous (vapor) phase to a cold substrate (room temperature) provided the lateral interaction between the particles of adsorbed layer (adlayer) is attractive. A detailed analysis of two limiting cases is presented: when the half-monolayer film formation rate is limited by the adsorption of particles from the gas phase and when the formation of the half-monolayer film surface is determined by the rate of surface diffusion of the adsorbed particles. The asymptotic analysis of the coverage dispersion evolution and the characteristic spatial scale of coverage inhomogeneities at the early and late stages of relaxation of a submonolayer film after quenching under the spinodal is carried out. It is found that separation of the adlayer occurs, so inhomogeneities of submonolayer films at the later stages of the process tend to equilibrium values of coverage in any case. However, asymptotic and numerical analysis shows that in the second case for some relationship between the kinetic and thermodynamic parameters of the adlayer an intermediate asymptotic relaxation process can be observed. It testifies to a kinetic slowdown of the separation process at the spinodal values of coverages. This fact manifests as the appearance of the intermediate plateau in the evolution curves for the coverage dispersion and nonmonotonic change of the characteristic spatial scale of coverage inhomogeneities. Moreover, at the early stages of the coverage evolution, the incubation period is revealed in the development of its inhomogeneities. It is shown that at the later stages of the separation of the half-monolayer film, the characteristic spatial scale of coverage inhomogeneities increases with time according to the law $\tau^{1/2}$ and the width of the transition region between enriched and depleted regions of adlayer decreases as $1/\tau^{1/2}$.

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I. INTRODUCTION

The problem of obtaining homogeneous ultrathin (sub-monolayer) films with the desired properties is of special interest, in particular for application in micro- and optoelectronics. The control of the layer-by-layer formation process is of great importance. A significant role in forming such films belongs to the adsorption of alien atoms or molecules on the surface of solids. From a physical viewpoint, the adsorption layer (adlayer) is a two-dimensional system located on the boundary between vapor and solid. The study of these properties is interesting not only for practical aims, but also for fundamental physics [1,2].

The main difficulty in the generalization and an adequate description of physical phenomena in such films is related to the process of evolution determined by many factors. Even though the adsorbed film grows upon an atomically smooth surface, it is not evident that homogeneous submonolayer coverage will form. Another important aspect of film formation is the structure of the coverage, which can be ordered or amorphous. The quality of that structure is determined not only by the sorption capability of the substrate, but by the character of the intralayer (lateral) interaction of the sorbate atoms or molecules also [3]. If this interaction has a repulsive character, then a phase transition of the order-disorder type by temperature should be observed in the film at low temperature. The processes of two-dimensional ordering are especially important for submonolayer films, which is why a number of experimental [4–7] and theoretical works [8–10] have been devoted to investigations in films like these. Otherwise, under attractive lateral interaction, the coverage will have a tendency

[11] to separate upon the regions enriched and depleted by adatoms, specifically at low temperatures. In particular, phase separation of the spinodal type [12] can be observed under certain conditions in such films.

It should be noted that spinodal decomposition has been studied by computer simulation methods in adsorbed films of different nature (liquid, polymeric, semiconductor, and ferromagnetic ones). Experimental detection of phase separation of spinodal type in thin semiconductor films in a number of cases can be carried out by means of photoluminescence and TEM [13] and also by differential ac chip calorimetry [14] and atomic force microscopy [15].

For theoretical research of spinodal decomposition in polymeric films, the methods of computer simulation are often used, namely, the molecular dynamics method [16] and Monte Carlo simulation scheme [17,18]. A phenomenological approach to the description of the kinetics of spinodal decomposition in an unstable region in both liquid [19,20] and polymeric [21–23] films is based on the numerical solution of the Cahn-Hilliard equation, where the coverage or thickness of films is used as the order parameter. Under this approach in the case of polymeric films, originally, the existence of two stages of phase separation of spinodal type [21] was ascertained theoretically and then three stages of this process were found [22]. Experimental confirmation of the many-stage character of the above-mentioned phenomena, i.e., the existence of the early, late, and intermediate stages of spinodal phase separation, was presented in [23] by studying the spinodal decomposition in polymeric films. It should be noted that all of these works [21–23] studied many-stage phase separation in thin but still multilayer films. As will be seen below, the

many-stage nature of the spinodal decomposition is inherent in this type of film with low coverage, i.e., it can be observed even in half-monolayer films on solid substrates.

It should be mentioned that in all of the above theoretical studies [16–22], the separation processes of thin films (spinodal decomposition) was discussed without accounting for material contact with the gaseous phase, i.e., when the total number of atoms or molecules adsorbed on the substrate has been fixed. In fact, due to adsorption and desorption processes of particles from the gas phase, a number of the particles in the film itself do not stay unchanged. Therefore, constructing the theory of formation of the films in each case requires a valid account of the exchange process adlayer particles and the gas phase with the condition of particle deposition on the substrate [24]. It should be noted that attempts to take into account the arrival of the particles from the gas phase were made before [25–27]. However, in Ref. [25], spinodal decomposition was considered for the directed flux of adsorbate particles from a gaseous phase. This condition corresponds to receiving the films by molecular-beam epitaxy, not to the case of gas-phase deposition that we consider below. In [26,27], the adlayer was treated as an open system and described by a Landau-Khalatnikov equation with a nonconserved order parameter. However, such a statement cannot explicitly take into account the source of inflowing particles in the adlayer.

The aim of this work is to study theoretically the dynamic interplay between processes of adsorption or desorption and surface diffusion in ultrathin film with coverage ϑ close to 0.5 (half monolayer) when the lateral interaction is attractive. Moreover, we consider that the adlayer is obviously an open system that is not only in thermal contact with the substrate, but in material contact with the gas phase. In the framework of the phenomenological approach, we establish how the temperature of the substrate and the relationship between the adsorption or desorption and surface diffusion affect the phase separation of the half-monolayer film at all its stages.

The paper is structured as follows. In Sec. II, in the framework of nonequilibrium thermodynamics, a phenomenological approach is developed for the description of adlayer formation deposited onto a cold substrate and subjected to rapid quenching. In Sec. III a derivation of the dynamic equation describing the subsequent temporal evolution of a half-monolayer film coverage is given. Taking into consideration that the coverage fluctuations at the initial moment of time have a random character, in order to describe the subsequent process of half-monolayer film formation, we use a statistical approach developed in Sec. IV. Section V contains a detailed analysis of the evolution of coverage dispersion and the characteristic scale of inhomogeneities in the case of slow surface diffusion. In Sec. VI an analogous treatment is given for the case of rapid diffusion processes. Section VII analyzes the temporal evolution of the width of the transient region between enriched and depleted regions of adlayer. The article concludes with a briefly summary of the results.

II. NONEQUILIBRIUM THERMODYNAMICS OF THE ADSORPTION LAYER

We consider a massive monocrystalline substrate with an atomically smooth surface placed in a vacuum camera, which

is filled with vapor sorbate under low pressure. Since the deposition of atoms (molecules) will occur on a cold substrate, its surface is assumed to be sufficiently rigid. We consider the situation when the energy of adatoms (molecules) interact with the substrate, i.e., the adsorption energy u_0 is negative. Under vacuum deposition, the adsorption prevails over the desorption processes. Therefore, the atomic adsorption will proceed on the substrate surface even in the case when the value of the pressure P in the vapor phase is comparatively small. Since the pressure of vapors of the deposition material above the substrate usually does not exceed 10^{-4} – 10^{-3} Torr, that gaseous phase can be considered as an ideal gas.

We assume that the substrate, on which atoms from the vapor phase are deposited, is massive and the adsorption layer is small. Therefore, the adlayer acquires instantly the substrate temperature and is in thermal equilibrium with the substrate. For simplicity, we assume that there is only a nearest-neighbor pair interaction between adatoms in the adsorbed layer and the lateral interaction energy u_L is negative. To be specific, but without loss of generality, we assume that the substrate has a bcc crystal structure, so the coordination number of interstitials on the substrate surface is 4. Then we assume that the adsorption layer grows by the Frank–van der Merwe mechanism (layer-by-layer growth), corresponding to complete wetting. Here we study the formation of the first monolayer. Since it is assumed that the process of deposition of the adlayer occurs at low temperatures and the lateral interaction is considered to be weak, in this case, a good approximation is the mean field approximation. In this approximation, the specific free energy of the atomic submonolayer per one available place for adsorption (interstitial) on the surface of the substrate has the form

$$f(T, \vartheta) = -u_0\vartheta - 2u_L\vartheta^2 + T[\vartheta \ln \vartheta + (1 - \vartheta) \ln(1 - \vartheta)], \quad (1)$$

where $\vartheta = N_a/N$ is the coverage defined as a ratio of the number of adatoms N_a to the total number N of seats on the substrate available for adatoms, $0 < \vartheta < 1$. Since the substrate is maintained at a low temperature, atom evaporation from the substrate will not occur. Consequently, the number of substrate atoms, as well as the number of seats on the substrate N , will remain fixed over all time. In Eq. (1) and below, the temperature T is measured in energetic units. In addition, for convenience, the absolute values of the adsorption energy and lateral interaction are denoted by u_0 and u_L , respectively.

The expression (1) for the specific free energy $f(T, \vartheta)$ was written on the assumption that the coverage ϑ is homogeneous. We are interested in the evolution of heterogeneities of the coverage, so we consider ϑ as a function of coordinates on the surface and time hereinafter. As we are dealing with an open system, the thermodynamic potential Ω of the grand canonical ensemble should be used for the description of evolution of inhomogeneities. Thus, the expression for the adlayer potential Ω has the form of the functional

$$\Omega = \int_S [f(T, \vartheta) + \frac{1}{2}\gamma(\vec{\nabla}\vartheta)^2 - \mu_g(P, T_g)\vartheta] \sigma dS, \quad (2)$$

where σ is the surface density of the number of seats available for adatoms, γ is a constant evaluated as $\gamma \approx r_0^2 u_L$, and r_0 is the characteristic radius of the lateral interaction. The function

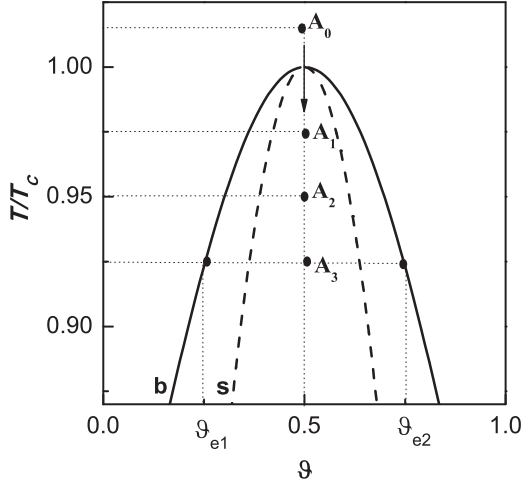


FIG. 1. Phase diagram of the adsorption layer. Here s is a spinodal, b is a binodal, ϑ_{e1} and ϑ_{e2} are the binodal values of coverage, A_0 is a point corresponding to the state of the adlayer until quench with initial temperature T_0 , and T_c is a critical temperature. The points A_1 , A_2 , and A_3 correspond to quenching temperatures T_1 , T_2 , and T_3 , respectively.

$f(T, \vartheta)$ is described by expression (1). The last term in (2) takes into account the material contact of the adlayer with the gas phase, i.e., an exchange of particles. Under equilibrium, the chemical potential of the adlayer $\mu = \partial f / \partial \vartheta$ is equal to the chemical potential of the gas μ_g , which is determined by its pressure P and temperature T_g ,

$$\mu_g = (P, T_g) = T_g \ln (P / P_{T_g}). \quad (3)$$

In the case of a single-atom gas, the value of P_{T_g} has dimensionality of pressure and it is defined by the relation

$$P_{T_g} = T_g \left(\frac{m T_g}{2\pi \hbar^2} \right)^{3/2}, \quad (4)$$

where m is the mass of a sorbate atom or molecule. The temperature of the gas T_g can be considered independent from the temperature of the substrate T since establishing thermal equilibrium between the substrate and the gas required a certain amount of time, particularly if it is a rarefied gas, and the substrate is small in volume compared to the volume of the vessel.

With knowledge of the specific free energy $f = f(T, \vartheta)$, we can build a T - ϑ diagram of the adsorption layer. Differentiating the function f with respect to the coverage ϑ , we obtain a curve that responds to the equilibrium values of the coverage ϑ_e and is called binodal (Fig. 1).

In the homogeneous case, the equilibrium values of the coverage ϑ_e are defined by the equality of chemical potentials of the adsorbed film and gas ($\mu = \mu_g$), i.e., by the equation

$$\mu = \left. \frac{\partial f}{\partial \vartheta} \right|_{\vartheta=\vartheta_e} = -u_0 - 4u_L \vartheta_e + T \ln \frac{\vartheta_e}{1 - \vartheta_e} = \mu_g. \quad (5)$$

As can be seen from (5), the equilibrium coverage ϑ_e depends on temperature and the chemical potential of the thermostat, whose role is played by the substrate. The simplest and theoretically most interesting and practically significant case is realized when the equilibrium coverage is close to 50%

and the chemical potential of the gas is close to the chemical potential of the adlayer ($\mu_g \approx -u_0 - 2u_L$). In this case, Eq. (5) is transformed into

$$T \ln \frac{\vartheta_e}{1 - \vartheta_e} = 4u_L \left(\vartheta_e - \frac{1}{2} \right), \quad (6)$$

whence it follows that the value of coverage $\vartheta_e = 1/2$ (half monolayer) is equilibrium. At high temperatures ($T > u_L \equiv T_c$) this state of the film is homogenous and stable. However, if we make the temperature of the substrate lower abruptly and with it the adlayer temperature $T < T_c$, the homogeneous state with coverage $\vartheta_e = 1/2$ becomes unstable. Instead, two other equilibrium states appear, $\vartheta_{e1} = 1/2 - \nu_e$ and $\vartheta_{e2} = 1/2 + \nu_e$, which are symmetric relative to $\vartheta_e = 1/2$. Both of these equilibrium states are stable. Here the value ν_e denotes equilibrium deviation of the coverage from the value $1/2$ in a half-monolayer film. Therefore, if a homogeneous equilibrium film with a coverage of 0.5 forms at high temperature $T_0 > T_c$ by rapid quenching to cool down to the substrate temperature $T < T_c$, it will tend to decompose on the parts with equilibrium (binodal) coverages ϑ_{e1} and ϑ_{e2} .

Doubly differentiating the function $f = f(T, \vartheta)$ with respect to the coverage ϑ and equating the obtained result to zero

$$\frac{\partial^2 f}{\partial \vartheta^2} = -4T_c + \frac{T}{\vartheta(1 - \vartheta)} = 0, \quad (7)$$

we obtain the dashed curve on the T - ϑ diagram, which is called a spinodal (Fig. 1). The region below the spinodal curve (miscibility gap) corresponds to the absolute thermodynamic instability of the half monolayer. If the adlayer is transferred rapidly into this unstable region, for example, by means of rapid quenching of the substrate, then the adlayer will tend to separate on the regions enriched and depleted of adatoms instantly, as a result of its thermodynamic instability. The equilibrium diagram (Fig. 1) demonstrates that in the present high-symmetry case, the adlayer (half monolayer) will be divided eventually on the regions with coverages ϑ_{e1} and ϑ_{e2} , i.e., the decomposition will occur on the regions with equilibrium coverages located on the binodal curve (but not on the spinodal one). This fact is determined by the openness of the system. Subdivision of the separation process into individual stages and significant details of separation kinetics is controlled, as we will see later, not only by the observation temperature T , but also by the temperature T_0 , from which the quenching starts. The relation between the characteristic time of adsorption and the characteristic time of surface diffusion is also important. Our aim is to describe the separation kinetics of the adlayer over all its stages.

III. DERIVATION OF THE DYNAMICAL EQUATION

We assume that under certain high temperatures $T_0 (T_0 > T_c)$ the homogeneous half-monolayer coverage forms. If we rapidly cool down the substrate, the subsystem of adsorbed atoms instantly acquires the temperature of the substrate due to the good thermal contact. As a result, when the adlayer turns out to be below the spinodal curve due to the process of quenching, the accidental frozen high-temperature fluctuations of the coverage ϑ remain within it. In this case the

thermodynamic equilibrium in the system of the adsorption layer and gaseous phase is disturbed. However, since the adsorbed layer is an open system, then either the adsorption of atoms on substrate or desorption occurs, depending on the relationship between the chemical potentials of the gas and the adsorbed layer. The diffusion process takes place in the adsorbed layer at the same time. So rearrangement of adatoms will proceed on the substrate. Thus, for the description of the kinetics of these two simultaneous processes in the adlayer, we suggest the use of the equation of material balance in the form of the continuity equation with the sources or sinks

$$\frac{\partial \vartheta}{\partial t} + \operatorname{div} \vec{J} = \left(\frac{\partial \vartheta}{\partial t} \right)_{\text{ext}}. \quad (8)$$

The driving force of the gas adsorption process onto the substrate is the difference between the chemical potentials of the gaseous phase and the adsorbed layer. Then the right-hand of Eq. (8) is responsible for the adsorption (or desorption) of gas atoms (or molecules) onto the substrate (or from the substrate) and it can be represented in the form

$$\left(\frac{\partial \vartheta}{\partial t} \right)_{\text{ext}} = \beta(\mu_g - \mu) = -\beta \frac{\delta \Omega}{\delta \vartheta}. \quad (9)$$

The constant β may be approximated by the value $\beta \sim (t_a u_0)^{-1}$, where t_a is the characteristic time of adsorption (the average time an adatom stays on the substrate). It can be easily seen that with regard to relation (9), Eq. (8) obtains the universal character, combining features of both the Cahn-Hilliard equation and the Landau-Khalatnikov one. Moreover, the coverage in (8) acts simultaneously as a nonconserved order parameter and as a concentration of the atoms (molecules) deposited on the substrate. According to [28], an expression for the adatoms density flow \vec{J} on the surface substrate may be written as

$$\vec{J} = -M \vec{\nabla} \frac{\delta \Omega}{\delta \vartheta}. \quad (10)$$

Here M is generalized mobility of adatoms

$$M = b \vartheta (1 - \vartheta), \quad (11)$$

where b is a temperature-dependent constant. We will consider the situation when the depth of quenching of the adsorbed layer under the spinodal is small. Then we can assume that the coverage ϑ in the adlayer is not very different from 1/2, i.e., the coverage in the adsorbed layer can be written as

$$\vartheta = \frac{1}{2} + v(x, t), \quad (12)$$

where $v(x, t)$ is a small variation of the coverage from 1/2, i.e., $v(x, t) \ll 1$.

Substituting Eqs. (9)–(12) into Eq. (8), with regard to the v function, which is small, we get the evolution equation in the form

$$\frac{\partial v}{\partial \tau} = 4\varepsilon v \left(\alpha - \frac{4}{3} v^2 \right) + (\varepsilon - \alpha + 4v^2) \Delta v - \frac{1}{4} \Delta(\Delta v), \quad (13)$$

where Δ is a two-dimensional Laplace operator with respect to coordinates in the plane of the adlayer. Equation (13) has been

made dimensionless with respect to the spatial coordinates and time by using the relation

$$\xi = \frac{r}{r_0}, \quad \tau = \frac{t}{t_d}, \quad t_d = \frac{r_0^2}{D_s}, \quad D_s = b u_L, \quad (14)$$

where D_s is the surface diffusion coefficient. Under the surface diffusion coefficient we are referring to the single-particle (or tracer) diffusion coefficient.

In Eq. (13), one of the basic operating parameters determining the character of adlayer evolution is the thermodynamic parameter $\alpha(T)$ characterizing the supercooling degree of the adlayer

$$\alpha(T) = 1 - T/T_c \quad (15)$$

related to the depth of the adlayer quenching by temperature under the spinodal. The second is the kinetic parameter ε , which is equal to the ratio between the characteristic time of surface diffusion t_d and the characteristic time of adsorption or desorption t_a ,

$$\varepsilon = \frac{t_d}{t_a}. \quad (16)$$

Thus, the value ε characterizes the ratio of the rates of two basic processes in a half-monolayer film, namely, surface diffusion and adsorption or desorption, respectively. If $\varepsilon \ll 1$ ($t_d \ll t_a$), surface diffusion takes place in a submonolayer film, whereas the processes of adsorption (or desorption) go on slowly. Conversely, if $\varepsilon \gg 1$ ($t_d \gg t_a$), adsorption (or desorption) are the main processes influencing the film formation and surface diffusion may not be taken into account in this case [29].

The parameter ε introduced here may be expressed through the physical constants, evaluated directly from experiment [27,30], in the form

$$\varepsilon = \frac{r_0^2 v}{D_s^0} \exp\left(\frac{E_d - E_a}{T}\right), \quad (17)$$

where $D_s^0 = a^2 v_d$ is the preexponential factor of the surface diffusion coefficient, v is the preexponential factor of adsorption, v_d is vibration frequency of an adatom on the substrate, a is the nearest-neighbor distance, and E_d and E_a are the activation energies of surface diffusion and adsorption, respectively. As an example of a similar situation, we can point to experimental investigations of the deposition of CO molecules onto the Ni (111) substrate [30,31], where all the parameters in formula (17) were defined, namely, $v = 10^{17} \text{ s}^{-1}$, $D_s = 1, 2 \times 10^{-9} \text{ m}^2/\text{s}$, $r_0 = 3 \times 10^{-10} \text{ m}$, $T = 220 \text{ K}$, $E_d = 0.3 \text{ eV}$, and $E_a = 1.1 \text{ eV}$. Using these values and expression (17), we obtain that the value of ε is very small.

In this work we will develop a theory for arbitrary values of ε since in different specific cases the value of ε may be varied within a wide range. For example, using values of the characteristic time of surface diffusion t_d and the adsorption (or desorption) time t_a for different temperatures at the deposition of NO molecules onto the Pt (110) substrate [32] and substituting them in (16), we obtain that the parameter $\varepsilon < 1$ at $T = 313 \text{ K}$ but $\varepsilon > 1$ at $T = 385 \text{ K}$.

The following shows the role of evaluating the different terms on the right-hand side of Eq. (13). We notice that the

first term is connected with the sources (sinks) in Eq. (8), i.e., it describes the processes of atom adsorption (or desorption) on the substrate. At the late stages, it causes decomposition of the adlayer on regions with two thermodynamic equilibrium (binodal) values of coverage ϑ_{e1} and ϑ_{e2} . The second term is a diffusive one that prevails at the early stages. It describes the uphill diffusion subject to the condition that $\varepsilon \ll \alpha$, i.e., it causes decomposition of the adlayer on the regions with intermediate (spinodal) values of coverage; however, it gives rise to blurring of the heterogeneities at $\varepsilon > \alpha$. Finally, the last term provides the smoothing of transition regions between the enriched and depleted (with an adsorbate) sections of the film.

IV. CORRELATION ANALYSIS OF THE EVOLUTION EQUATION

The initial condition for the coverage as a function of coordinates should be added to Eq. (13) for consistent consideration of adlayer relaxation kinetics:

$$v(\vec{\rho}, \tau)|_{\tau=0} = v_0(\vec{\rho}), \quad (18)$$

where $\vec{\rho}$ is a two-dimensional radius vector located in the plane where the adsorbed film is formed. Since the high-temperature fluctuations of the coverage are fixed by rapid quenching of the substrate, the function $v_0(\vec{\rho})$ appearing at the initial condition should be considered as a random function of coordinates. It follows that the solutions of Eq. (13) will be random functions of coordinates also. Therefore, there it is necessary to use a statistical analysis to determine Eq. (13) with the random initial condition (18). Specifically, it is a question of finding the correlation function of the random field $v(\vec{\rho}', \tau)$. The characteristics of the correlation function (dispersion and correlation radius) provide a basic understanding of the coverage evolution.

After multiplying both parts of Eq. (13) by $v(\vec{\rho}', \tau)$ and averaging over the ensemble of random field realization, we obtain an equation of the form

$$\frac{\partial K(\vec{s}, \tau)}{\partial \tau} = a(\tau)K(\vec{s}, \tau) + b(\tau)\Delta K(\vec{s}, \tau) - \frac{1}{2}\Delta^2 K(\vec{s}, \tau). \quad (19)$$

Here

$$K(\vec{s}, \tau) = \langle v(\vec{\rho}', \tau)v(\vec{\rho}, \tau) \rangle \quad (20)$$

is the required second-order correlation function, with $\vec{s} = \vec{\rho}' - \vec{\rho}$. For convenience of the following analysis, we introduce the notation

$$a(\tau) = 8\varepsilon\left[\alpha - \frac{4}{3}K(0, \tau)\right], \quad b(\tau) = 2[\varepsilon - \alpha + 4K(0, \tau)] \quad (21)$$

in Eq. (19). As for the initial correlation function of the random field of v , it would be reasonable to select the correlation function in a Gaussian form

$$K(\vec{s}, 0) = D_0 \exp(-s^2/R_0^2), \quad (22)$$

where $D_0 \equiv K(0, 0)$ is the initial dispersion and R_0 is the initial correlation radius.

We have made some assumptions to obtain the equation (19) for the second-order correlation function (20). Apparently,

under the aforesaid procedure, besides the second-order correlation function, the fourth-order correlation function will appear. Therefore, for a constructive solution of the problem it is necessary to use a procedure for uncoupling the fourth-order correlation function for a random function $v(\vec{\rho}, \tau)$ on the product of second-order correlation functions. We note that for a random field of arbitrary type, uncoupling the fourth-order correlation function on the product of the second-order correlation function is not quite correct. However, it is known that two limiting cases exist when this procedure is accurate, namely, the random field is Gaussian or it has two values. Taking into account that at the late stages, i.e., in the thermodynamic limit, the coverage ϑ takes only two thermodynamic equilibrium values ϑ_{e1} and ϑ_{e2} , i.e., permitting the random field of coverage $v(\vec{\rho}, \tau)$ to have two values, then we may approximately write an uncoupling in the form

$$\langle v^3(\vec{\rho}', \tau)v(\vec{\rho}, \tau) \rangle \approx K(0, \tau)K(\vec{s}, \tau). \quad (23)$$

Notice that the uncoupling in the form (23) at the early stages reduces to a qualitatively correct result also.

If we apply the Fourier transformation on the \vec{s} coordinate to Eq. (19), it takes the form

$$\frac{dK(\vec{q}, \tau)}{d\tau} = a(\tau)K(\vec{q}, \tau) - b(\tau)q^2 K(\vec{q}, \tau) - \frac{1}{2}q^4 K(\vec{q}, \tau). \quad (24)$$

Since Eq. (24) is an ordinary differential equation of first order with separating variables, then its solution can be written formally in the form

$$K(\vec{q}, \tau) = K(\vec{q}, 0) \exp\left(-\frac{q^4 \tau}{2}\right) \exp\left(\int_0^\tau [a(\tau') - b(\tau')q^2] d\tau'\right). \quad (25)$$

In order to find the $K(0, \tau)$ function, i.e., coverage dispersion, equality (25) should be integrated in the variable \vec{q} . Then we obtain

$$K(0, \tau) = (2\pi)^{-2} \int \int_{-\infty}^{\infty} dq_x dq_y K(\vec{q}, 0) \exp\left(-\frac{q^4 \tau}{2}\right) \times \exp\left(\int_0^\tau [a(\tau') - b(\tau')q^2] d\tau'\right). \quad (26)$$

Applying the Fourier transformation on the \vec{s} to the initial correlation function (22), we can find the Fourier transform of $K(\vec{q}, 0)$ [from (26)]:

$$K(\vec{q}, 0) = \pi R_0^2 D_0 \exp(-q^2 R_0^2/4). \quad (27)$$

Substitution of the expression (27) into (26) gives

$$K(0, \tau) = \frac{\pi R_0^2 D_0}{4\pi} I(\tau) \exp\left(\int_0^\tau a(\tau') d\tau'\right), \quad (28)$$

where the following notation is introduced:

$$I(\tau) = \int_{-\infty}^{\infty} \exp\left(-\frac{q^4 \tau}{2} - \rho(\tau)q^2\right) dq_x dq_y, \quad (29)$$

$$\rho(\tau) = \frac{R_0^2}{4} + \int_0^\tau b(\tau') d\tau'.$$

After calculating the integral $I(\tau)$ in (29), we obtain the integral equation relative to the function $K(0, \tau)$ in the form

$$K(0, \tau) = k \frac{D_0 R_0^2}{\sqrt{\tau}} [1 - \Phi(x(\tau))] \exp \left(x^2(\tau) + \int_0^\tau a(\tau') d\tau' \right), \quad (30)$$

where $\Phi(x)$ is the error integral [33], $k = \sqrt{\pi}/(4\sqrt{2})$ is some constant, and the functions $x(\tau) = \rho(\tau)/\sqrt{2\tau}$ and $a(\tau)$ are expressed in terms of $K(0, \tau)$ according to (29) and (21). The integral equation (30) is the self-consistent condition for the function $K(0, \tau) \equiv D(\tau)$, where $D(\tau)$ is the time-dependent coverage dispersion. Then the solution of Eq. (30) and finding the temporal dependence of the coverage dispersion enable us to retrace the character of the evolution of inhomogeneities under the phase transition of the adlayer over all the stages.

In order to elucidate how the characteristic spatial scale of inhomogeneities of the adlayer coverage changes over time, we identify it (the scale) with the correlation radius R_c , i.e., with a characteristic distance where the correlation function (20) decreases. The parameter R_0 used in the definition of the initial correlation function (22) is in fact the initial value of the correlation radius $R_c(0)$. In general, the correlation radius can be determined in various ways. In our case it is suitable to introduce it in the following way. We suggest that the volume, limited by the surface corresponding to the two-dimensional correlation function, is equal to the volume of some cylinder. The height of this cylinder is equal to the dispersion $K(0, \tau) \equiv D(\tau)$ and the radius is equal to the correlation radius of this function, i.e.,

$$\pi R_c^2 D(\tau) = \iint K(\vec{s}, \tau) ds_x ds_y, \quad (31)$$

where integration occurs over the whole two-dimensional space (s_x, s_y) . From the definition of the Fourier transform of the correlation function on the spatial coordinates

$$K(\vec{q}, \tau) = \iint K(\vec{s}, \tau) \exp(-i\vec{q} \cdot \vec{s}) ds_x ds_y, \quad (32)$$

it follows that the right-hand side of (31) is nothing but the Fourier transform of the correlation function at $\vec{q} = \vec{0}$, i.e.,

$$K(\vec{q}, \tau)|_{\vec{q}=\vec{0}} = \iint K(\vec{s}, \tau) ds_x ds_y. \quad (33)$$

On the other hand, using the obtained expression (25) for the Fourier transform of the correlation function on the spatial coordinates, we get

$$K(\vec{q}, \tau)|_{\vec{q}=\vec{0}} = \pi D_0 R_0^2 \exp \left(\int_0^\tau a(\tau') d\tau' \right). \quad (34)$$

Taking into consideration (30), (31), and (34), we obtain the expression for the correlation radius

$$R_c(\tau) = \tau^{1/4} \{k \exp[\rho^2(\tau)/2\tau] [1 - \Phi(\rho(\tau)/\sqrt{2\tau})]\}^{-1/2}. \quad (35)$$

The integral equation (30) for the coverage dispersion cannot be solved analytically. However, before a numerical solution, we should carry out the asymptotic analysis of the dispersion behavior $D(\tau)$ and the correlation radius (35) at the

early and late stages after rapid quenching of the adsorption film down to the temperature below the critical one. Separately, we will analyze two limiting situations, namely, when $\varepsilon \gg \alpha$ and the opposite limiting case when $\varepsilon \ll \alpha \ll 1$.

V. ANALYSIS OF SLOW SURFACE DIFFUSION

At first, we suppose that we deal with such adsorbates and substrates when the adsorption processes occur faster than the processes of surface diffusion, i.e., when $\varepsilon \gg \alpha$. Then, after using the integral equation (30) and applying the asymptotic expansion for the error integral [33]

$$\Phi(x) \approx 1 - \frac{\exp(-x^2)}{x\sqrt{\pi}} \left(1 - \frac{1}{2x^2} \right), \quad (36)$$

a coverage dispersion during the early stages of the process can be approximated by the analytical expression

$$D(\tau) \approx D_0 \left(1 - \frac{16\tau}{R_0^4} \right). \quad (37)$$

Here we take into account that for early stages of the process ($\tau \ll 1$), the value $D(\tau)$ may be replaced by the initial coverage dispersion D_0 . As can be seen, the coverage dispersion decreases at the early stage of the process (i.e., at $\tau \ll 1$) by linear law and independent from the parameters ε and α .

Now we consider the behavior of the correlation radius $R_c(\tau)$ in this situation. When $\tau \ll 1$, (35) is approximated by the relation

$$R_c(\tau) \approx R_0 [1 + (4\varepsilon\alpha + 8/R_0^4)\tau]. \quad (38)$$

Therefore, the characteristic spatial scale of the adlayer coverage inhomogeneities increases by linear law at the early stages of separation process.

As for the evolution of coverage at the late stages ($\tau \gg 1$), the analysis of Eq. (30) shows that in this case the coverage dispersion $D(\tau)$ tends to a constant value by the law

$$D(\tau) \approx \frac{3}{4} \left(\alpha - \frac{1}{8\varepsilon\tau} \right). \quad (39)$$

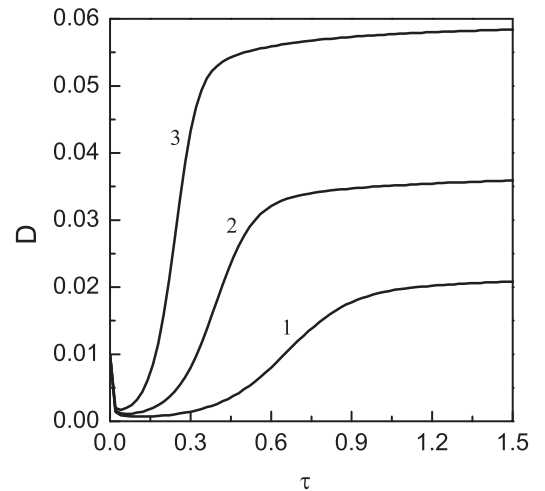


FIG. 2. Evolution of the coverage dispersion for $\varepsilon = 10$ in the case of $\varepsilon \gg \alpha$. Curves 1–3 correspond to $\alpha_1 = 0.03$, $\alpha_2 = 0.05$, and $\alpha_3 = 0.08$, respectively.

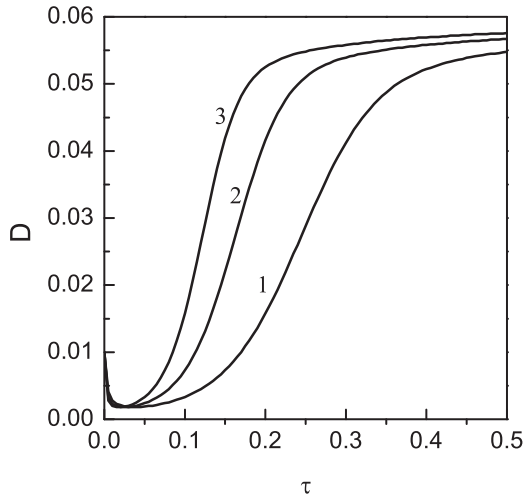


FIG. 3. Evolution of the coverage dispersion for $\alpha = 0.08$ in the case of $\varepsilon \gg \alpha$. Curves 1–3 correspond to $\varepsilon_1 = 40$, $\varepsilon_2 = 60$, and $\varepsilon_3 = 80$, respectively.

The asymptotic analysis of the expression (35) at the late stages ($\tau \gg 1$) shows that the characteristic spatial scale of the adlayer coverage inhomogeneities increases by the square root law, namely,

$$R_c(\tau) \approx 4\sqrt{\varepsilon\tau}. \quad (40)$$

In order to analyze the evolution of the coverage dispersion over all stages of the separation process, the numerical solution of Eq. (30) is carried out. The dispersion behavior is studied with respect to the quenching depth of the adlayer under the spinodal $\alpha(T)$ (Fig. 2) and to the parameter ε (Fig. 3).

The curves presented in Fig. 2 show that the deeper the quenching film under the spinodal, the greater the coverage dispersion in the adsorbed layer will be. As for the parameter ε , as Fig. 3 shows, its value only affects the separation kinetics of the half-monolayer film. The greater the value of ε , the higher the rate of the separation processes in the adlayer will be. Similarly, in order to analyze the behavior of the correlation

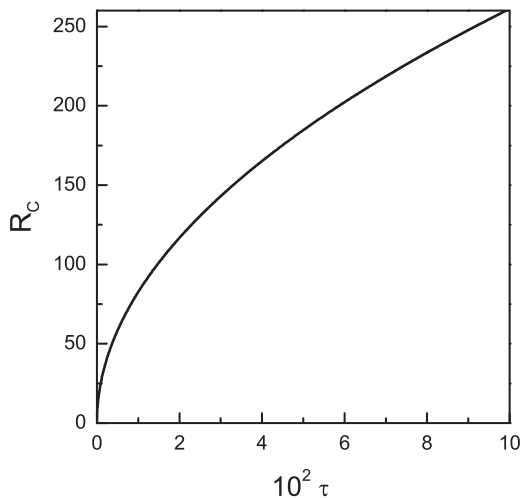


FIG. 4. Evolution of the correlation radius in the case of $\varepsilon \gg \alpha$ for $\varepsilon = 8$ and different values of α ($\alpha_1 = 0.03$, $\alpha_2 = 0.05$, and $\alpha_3 = 0.08$).

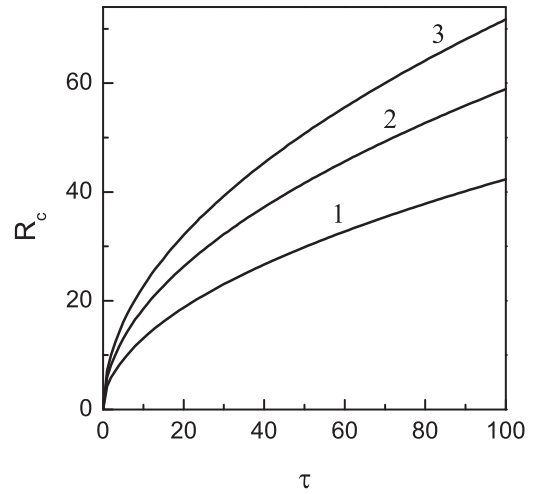


FIG. 5. Evolution of the correlation radius for $\alpha = 0.08$ in the case of $\varepsilon \gg \alpha$. Curves 1–3 correspond to $\varepsilon_1 = 2$, $\varepsilon_2 = 4$, and $\varepsilon_3 = 6$, respectively.

radius at all stages of evolution, the numerical investigation of relationship (35) is carried out.

As can be seen in Fig. 4, the monotonic growth of the correlation radius is observed independently on the parameter $\alpha(T)$ since curves for different values α_1 , α_2 , and α_3 are merged into a single curve. At the early stages of evolution, the rapid increase of the characteristic spatial scale of coverage inhomogeneities occurs by the linear law (38). At the final stage it is transformed to a slow asymptote by the root law (40).

In addition, the effect of the parameter ε on the correlation radius evolution is analyzed. It turns out that the correlation radius always increases at large values of ε ($\varepsilon \gg \alpha$) and the rate of growth is proportional to the value of the above-mentioned parameter (Fig. 5).

VI. ANALYSIS OF RAPID SURFACE DIFFUSION

Let us consider the opposite case, when the processes of surface diffusion go faster than adsorption processes, i.e., when the relation $\varepsilon \ll \alpha \ll 1$ is satisfied. The asymptotic behavior of dispersion $D(\tau)$ at the early and the late stages at $\varepsilon \ll \alpha$ has the same form as in the case $\varepsilon \gg \alpha$. Namely, at the early stages, the dispersion decreases by the linear law (37). At the late stages, it tends to a certain constant value by the law, which is described by the relation (39). However, in contrast to the case of slow surface diffusion ($\varepsilon \gg \alpha$) considered above, an intermediate asymptote of the separation process of the submonolayer film is observed in the case of rapid surface diffusion ($\varepsilon \ll \alpha$) in the defined range of ε and α . It corresponds to the stages when the function $\rho(\tau)$ has a negative value. After analyzing the dispersion at these stages, we establish that the coverage dispersion approaches slowly (from the bottom) the spinodal values of coverage by the law

$$D(\tau) \approx \frac{1}{4}(\alpha - \varepsilon) - \frac{\ln(\tau/\tau_{cr})}{16\sqrt{\tau}}, \quad (41)$$

where $\tau_{cr} = (4kD_0R_0^2/\alpha)^2$ is the certain characteristic time depending on the frozen initial fluctuations of coverage.

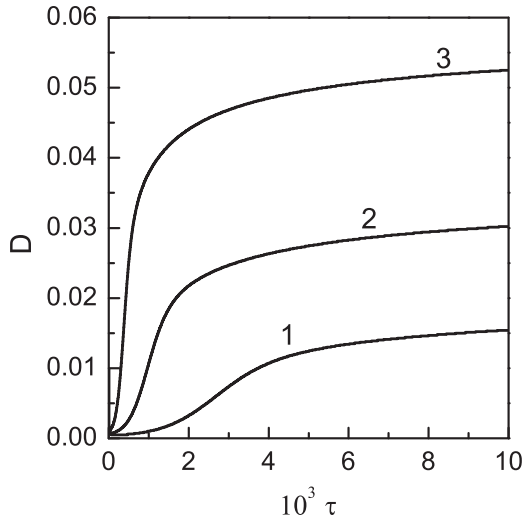


FIG. 6. Evolution of the coverage dispersion for $\epsilon = 8 \times 10^{-3}$ in the case of $\epsilon \ll \alpha$. Curves 1–3 correspond to $\alpha_1 = 0.03$, $\alpha_2 = 0.05$, and $\alpha_3 = 0.08$, respectively.

The presence of an intermediate asymptote indicates that the dispersion approach to equilibrium coverage does not occur immediately, i.e., a kinetic slowdown of the process for spinodal values of coverage takes place. The intermediate dispersion value depends on both the quenching depth by temperature under the spinodal $\alpha(T)$ and the parameter ϵ .

The asymptotic behavior of the correlation radius $R_c(\tau)$ at the early and late stages at $\epsilon \ll \alpha$ has the same form as in the case $\epsilon \gg \alpha$. Namely, at the early stage, the correlation radius grows by the linear law (38), but at the late stages it obeys the root law (40). However, for the case $\epsilon \ll \alpha$ at those stages of the process, when dispersion has an intermediate asymptote, the correlation radius also behaves in a nonmonotonic way. At the intermediate stages, when $\rho(\tau) < 0$, the correlation radius increases by the law of $\tau^{1/4}$, but at the late stages of evolution, when $\rho(\tau) > 0$, it increases by the law of $\tau^{1/2}$.

In order to verify and illustrate our asymptotic expressions, the numerical analysis of the coverage dispersion over all stages of evolution was carried out. The results of this analysis

are presented in Figs. 6 and 7, which show the dependence of the coverage dispersion on both a parameter $\alpha(T)$ (Fig. 6) and a parameter ϵ (Fig. 7). Figure 7(a) represents the earlier and Fig. 7(b) describes the later stages of the spinodal decomposition process of film, respectively.

It could be seen from Figs. 6 and 7(a) that if the system will be quenching under the spinodal (Fig. 1), the coverage dispersion decreases at the early stages. Then it increases and over time tends to approach a constant value independently of the parameter ϵ . This means that the half-monolayer film with heterogeneous coverage on the substrate always forms under these conditions. The time of the dispersion approach to the limiting value depends on the parameter ϵ . This limiting value is determined by the quenching depth $\alpha(T)$ of the film under the spinodal.

As is evident from Fig. 7(a), the incubation period in waiting for the adlayer separation is observed at the early stages of the process. This is related to the fact that for heterogeneous film formation some time is needed to decrease the energy of frozen high-temperature coverage fluctuations at the expense of standard diffusion. At this stage the smoothing of the small-scale coverage heterogeneities proceeds. The duration of the incubation period depends on the adsorption rate. Namely, the smaller adsorption rate, the longer the incubation time will be and the later the formation of a large-scale heterogeneity of the coverage will be.

As the numerical calculations indicate, in the case $\epsilon \ll \alpha$ the intermediate asymptote for coverage dispersion is observed. This is related to the fact that the spinodal precipitates are formed at the intermediate stages of the separation process, at the expense of uphill diffusion. However, binodal decomposition with the formation of thermodynamic equilibrium values of coverage proceeds only at the later stages [Fig. 7(b)]. Therefore, a conclusion about the existence of the kinetic retarding stage of the film separation at the spinodal values of coverage can be made.

Thus, depending on the quenching depth by temperature $\alpha(T)$, formation of heterogeneous film with one or another value of the coverage dispersion [the quenching under the spinodal (Fig. 1)] takes place. The parameter ϵ influences both on the duration of the incubation period and on the rate of the separation process of the coverage.

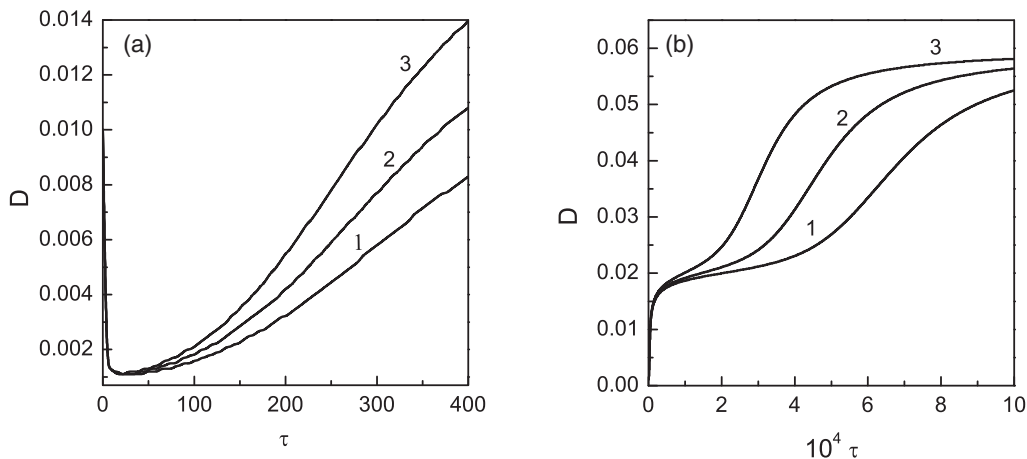


FIG. 7. Evolution of the coverage dispersion at the (a) early and (b) late stages of separation for $\alpha = 0.08$ in the case of $\epsilon \ll \alpha$. Curves 1–3 correspond to $\epsilon_1 = 10^{-3}$, $\epsilon_2 = 5 \times 10^{-3}$, and $\epsilon_3 = 8 \times 10^{-2}$, respectively.

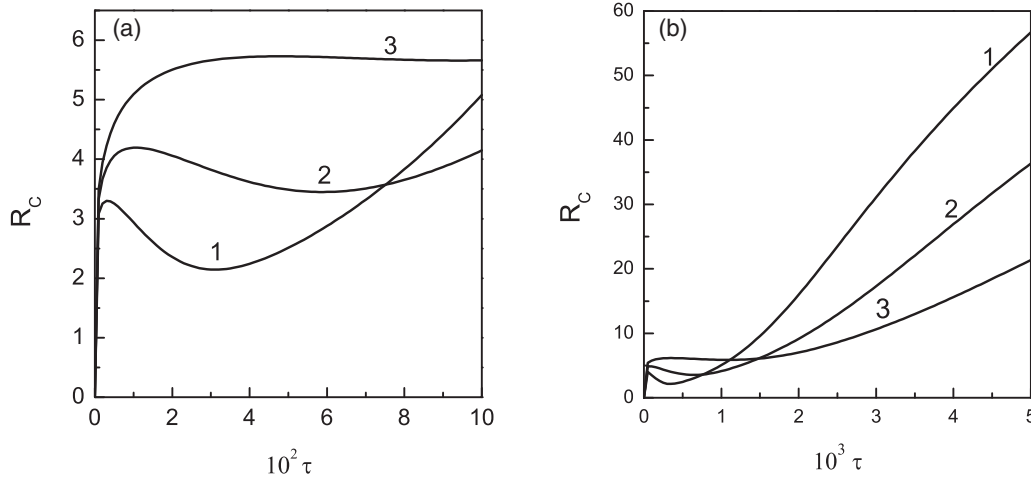


FIG. 8. Evolution of the correlation radius at the (a) early and (b) late stages of separation for $\epsilon = 8 \times 10^{-3}$ in the case of $\epsilon \ll \alpha$. Curves 1–3 correspond to $\alpha_1 = 0.03$, $\alpha_2 = 0.05$, and $\alpha_3 = 0.08$, respectively.

Let us consider now the curves describing the dependence of correlation radius on the quenching depth $\alpha(T)$ at the early and late stages of process (Fig. 8).

As is seen in Figs. 8(a) and 8(b), the deeper the quenching is, the greater correlation radius will be, i.e. the larger a spatial scale of coverage inhomogeneities of half-monolayer film will be.

We now consider the evolution curves describing the time dependence of correlation radius for different values of ϵ at the early and late stages of separation of the half-monolayer film (Fig. 9).

As is seen in Fig. 9(a), at the early stages, the correlation radius increases rapidly by the linear law, and then it decreases slightly during a little time interval, i.e., it behaves in non-monotonic way. If we compare this curves for the correlation radius [Fig. 9(a)] with behavior of the dispersion at the early stages [Fig. 7(a)], it may be seen that the maximum of the correlation radius at the early stages of the process is directly related to the incubation time of expectation of nucleus by the

coverage dispersion. In other words, the characteristic spatial scale of inhomogeneities increases just at the same stage when the coverage dispersion decreases.

Analyzing behavior of the dispersion [Fig. 7(b)] and the correlation radius [Fig. 9(b)] on the intermediate stages of separation, we have noted, that kinetic slowdown of film separation is observed simultaneously both by the dispersion and by the characteristic spatial scale of inhomogeneities.

Thus, we have found that the nonmonotonic behavior of the correlation radius is observed only in the case $\epsilon \ll \alpha$. At the late stages of separation, regardless of the situation considered, the correlation radius certainly increases with time nonproportionally to $\tau^{1/2}$, i.e., by the root law. As one can see, the results of our work are sufficiently well correlated with the numerical experiments using the Monte Carlo method [18], for which it was shown that the characteristic spatial size of inhomogeneities increases by the root law at the late stages, namely, $\langle d \rangle \approx \beta t^{1/2}$, where $\beta = \text{const}$.

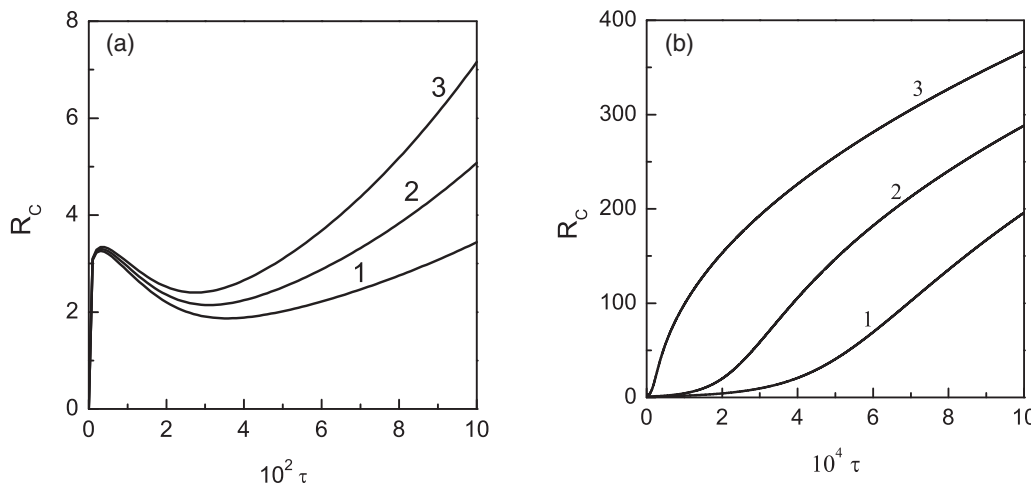


FIG. 9. Evolution of the correlation radius at the (a) early and (b) late stages of the separation process for $\alpha = 0.08$ in the case of $\epsilon \ll \alpha$. Curves 1–3 correspond to $\epsilon_1 = 4 \times 10^{-4}$, $\epsilon_2 = 8 \times 10^{-4}$, and $\epsilon_3 = 8 \times 10^{-3}$, respectively.

VII. ANALYSIS OF THE WIDTH OF THE COVERAGE TRANSITION REGION

Let us evaluate the width of a transient layer between the enriched and depleted regions of the adsorption layer in order to establish the way of its time evolution. We assume that the region enriched (or depleted) of adsorbate has a circular form with radius $R_c(\tau)$ and the transient region is in the form of a ring. The area of the enriched region may be estimated as $S \sim R_c^2(\tau)$, therewith the area of the transient region (border layer) will be equal to $\Delta S \sim R_c(\tau)\delta(\tau)$. Taking into account that at the late stages the correlation radius at $\varepsilon \gg \alpha$ and $\varepsilon \ll \alpha$ varies by the law (40), we estimate the variation of the value v^2 with a transition from the enriched regions to a depleted one

$$\Delta(v^2) \sim \frac{\alpha\delta}{R_c(\tau)} \sim \frac{\alpha\delta}{\sqrt{\tau}}. \quad (42)$$

On the other hand, for the case $\tau \rightarrow \infty$, in accordance with (39), the variation of v^2 obeys the law

$$\Delta(v^2) \sim 1/\tau. \quad (43)$$

When we compare the relations (42) and (43), the qualitative temperature and time dependence of the transient layer width is obtained as

$$\delta(T, \tau) \sim \frac{1}{\alpha(T)\tau^{1/2}}. \quad (44)$$

Thus, at the later stages, the width of the transient layer between the enriched and depleted regions of the film is inversely proportional to the quenching depth $\alpha(T)$ and decreases with time by the inverse root law, i.e., $\sim 1/\tau^{1/2}$.

VIII. CONCLUSION

The present study has been devoted to the theoretical analysis of the formation of a half-monolayer film on a cold substrate by the deposition of atoms (or molecules) from the gaseous phase. The power sources of the particles arriving in the adlayer were not specified, but depend on the state of the adlayer–gaseous phase system. For adequate consideration of such a situation, when the adlayer is an open system, we suggested to describe its temporal evolution using the continuity equation with sources (8). This dynamic equation has a universal character since it takes into account the processes of adsorption (or desorption) and surface diffusion simultaneously. As a result, we investigate in detail both possible limiting situations, namely, when the relaxation processes in the film are limited by the adsorption (or desorption) processes and the opposite limiting case, when the processes of surface diffusion of atoms (or molecules) are determinative.

We note that as the result of rapid quenching of the substrate the random spatially inhomogeneous fluctuations of coverage occur in the adsorption layer. To describe their subsequent temporal evolution, we used a statistical approach that is based on the introduction of the correlation functions of the order parameter, i.e., the coverage $v(\bar{\rho}, \tau)$. As a result, we obtained a self-consistent condition for the dispersion function of coverage in the form of the integral equation (30). In addition, we obtained an analytical expression for the correlation radius as a function of time, which allowed us to study the temporal evolution of the characteristic scale of spatial inhomogeneities of coverage.

An asymptotic and numerical analysis of the integral equation (30) for the dispersion coverage allowed us to establish the objective laws of developing the coverage inhomogeneities over all stages of the process, when the half-monolayer film approaches thermodynamic equilibrium. In particular, it was shown that at the early stages of the evolution the coverage dispersion decreases over time by the linear law, independently of the relationship between the governing parameters (ε and α) of the process. Therewith, an incubation period of waiting for a separation of the adlayer is always observed. The lower the adsorption rate, the longer the duration of the incubation period will be and hence the later the coverage formed by large-scale inhomogeneities will be. The law of the dispersion approach to a constant value corresponding to the binodal (i.e., thermodynamic equilibrium) coverages was found at the late stages of the adlayer evolution. In thermodynamic equilibrium, the value of coverage dispersion is proportional to the quenching depth of the adlayer under a spinodal. For the case of rapid diffusion processes (i.e., when $\varepsilon \ll \alpha$), the existence of an intermediate asymptote of the relaxation process was established, which occurs as a result of the kinetic slowdown of phase separation film on the spinodal values of coverage.

In addition, the asymptotic analysis of the expression (35) allowed us to find the temporal dependence of the correlation radius at the early and late stages of its evolution. It was found that at the early stages of the evolution the characteristic spatial scale of inhomogeneities increases linearly over time and at the later stages by the root law. The width of the transient region between the enriched and depleted regions of film decreases with time, according to the law of inverse root at the late stages of the separation process. Numerical analysis of the temporal dependence of the correlation radius (35) allowed us to reveal its nonmonotonic character at the intermediate stages of the process for the case when the evolution of the film is controlled by surface diffusion processes.

The results obtained above will help in attaining a deeper understanding of the formation of ultrathin films on the solid substrates and will also contribute to the development of technology to obtain qualitative thin-film coverages.

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- [1] Yu. G. Ptushinskii, *J. Low Temp. Phys.* **30**, 1 (2004).
 [2] T. V. Krachino, M. V. Kuz'min, M. V. Loginov, and M. A. Mittsev, *Phys. Solid State* **42**, 566 (2000).
 [3] B. Lehner, M. Hohage, and P. Zeppenfeld, *Chem. Phys. Lett.* **379**, 568 (2003).

- [4] A. Fedorus, D. Kolthoff, V. Koval, I. Lyuksyutov, A. Naumovets, and H. Pfnür, *Phys. Rev. B* **62**, 2852 (2000).
 [5] N. V. Petrova and I. N. Yakovkin, *Surf. Sci.* **519**, 90 (2002).
 [6] A. Fedorus, G. Godzik, A. Naumovets, and H. Pfnür, *Surf. Sci.* **565**, 180 (2004).

- [7] A. G. Fedorus, A. A. Mitryaev, M. A. Mukhtarov, H. Pfnür, Yu. S. Vedula, and A. G. Naumovets, *Surf. Sci.* **600**, 1566 (2006).
- [8] E. P. Feldman, K. V. Gumennyk, and L. I. Stefanovich, *Surf. Sci.* **604**, 1854 (2010).
- [9] M. Presber, B. Dünweg, and D. P. Landau, *Phys. Rev. E* **58**, 2616 (1998).
- [10] H. Shi and J. Ni, *Phys. Rev. B* **65**, 115422 (2002).
- [11] J. Kołaczkiwicz and E. Bauer, *Surf. Sci.* **151**, 333 (1985).
- [12] K. S. Schneider, W. Lu, T. M. Owens, D. R. Fossnacht, M. M. Banaszak Holl, and B. G. Orr, *Phys. Rev. Lett.* **93**, 166104 (2004).
- [13] J. Novák, S. Hasenöhrl, I. Vávra, and M. Kučera, *Appl. Surf. Sci.* **252**, 4178 (2006).
- [14] N.-A. Gotzen, H. Huth, C. Schick, G. Assche, C. Neus, and B. Mele, *Polymer* **51**, 647 (2010).
- [15] A. Karim, J. F. Douglas, B. P. Lee, S. C. Glotzer, J. A. Rogers, R. J. Jackman, E. J. Amis, and G. M. Whitesides, *Phys. Rev. E* **57**, R6273 (1998).
- [16] P. K. Jaiswal, S. Puri, and S. K. Das, *Phys. Rev. E* **85**, 051137 (2012).
- [17] C. D. Adams, D. J. Srolovitz, and M. Atzmon, *J. Appl. Phys.* **74**, 1707 (1993).
- [18] A. Mazor, D. J. Srolovitz, P. S. Hagan, and B. G. Bukiet, *Phys. Rev. Lett.* **60**, 424 (1988).
- [19] L. Ó Náraigh and J.-L. Thiffeault, *Phys. Rev. E* **76**, 035303(R) (2007).
- [20] R. Khanna, N. K. Agnihotri, M. Vashishtha, A. Sharma, P. K. Jaiswal, and S. Puri, *Phys. Rev. E* **82**, 011601 (2010).
- [21] H. Wang and R. J. Composto, *J. Chem. Phys.* **113**, 10386 (2000).
- [22] M. A. Parsa, M. Ghiass, and M. R. Moghbeli, Iran. Polym. J. **20**, 689 (2011), <http://journal.ippi.ac.ir>.
- [23] H. Wang, J. F. Douglas, S. K. Satija, R. J. Composto, and C. C. Han, *Phys. Rev. E* **67**, 061801 (2003).
- [24] Yu. B. Gaididei, V. M. Loktev, A. G. Naumovets, and A. G. Zagorodny, *Condens. Matter Phys.* **16**, 13604 (2013).
- [25] M. Atzmon, D. A. Kessler, and D. J. Srolovitz, *J. Appl. Phys.* **72**, 442 (1992).
- [26] A. V. Osipov, *J. Phys. D* **28**, 1670 (1995).
- [27] S. A. Kukushkin and A. V. Osipov, *Prog. Surf. Sci.* **51**, 1 (1996).
- [28] J. S. Langer, M. Bar-on, and H. D. Miller, *Phys. Rev. A* **11**, 1417 (1975).
- [29] E. P. Feldman, K. V. Gumennyk, L. I. Stefanovich, and Yu. V. Terekhova, *Funct. Mater.* **19**, 88 (2012), <http://www.isc.kharkov.com/journal/contents/19-1/fm191-15.pdf>.
- [30] J. V. Barth, *Surf. Sci. Rep.* **40**, 75 (2000).
- [31] M. Shayegan, E. D. Williams, R. E. Glover, III, and R. L. Park, *Surf. Sci. Lett.* **154**, L239 (1985).
- [32] M. Croci, C. Félix, G. Vandoni, W. Harbich, and R. Monot, *Surf. Sci.* **307–309**, 460 (1994).
- [33] I. S. Gradshteyn and I. M. Ryzhik, in *Table of Integrals, Series, and Products*, edited by A. Jeffrey and D. Zwillinger (Academic, New York, 2007).