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Thin-film condensation processes

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Abstract. The status of knowledge of phase nucleation and growth processes on a solid surface in one- and multicomponent systems is surveyed. The formation kinetics and subsequent evolution of new phase islands are investigated. Models for film growth from the vapor and solution-melt are analyzed which include island distribution by size, the degree of coalescence, island orientation, morphological stability, etc. The Ostwald ripening of the ensembles of multicomponent islands of a new phase is considered for both the isothermal and non-isothermal cases and nonlinear effects involved in the growth of continuous structures are examined. The problem of controllable growth of new phase layers is discussed.

1. Introduction

The surprising progress in micro- and optoelectronics, optics and other fields of engineering that have transfigured the world of information within a short period of time is directly related to the development of thin-film technologies. During film growth, experimenters and technologists are forced to control a whole number of parameters, such as material and structure of the substrate, its temperature, the composition of vapor, and the intensity of its inflow. To obtain the film structure and composition needed, these parameters are selected as a rule empirically. Films of increasingly involved composition and structure have been required of late, for example, high-temperature superconducting films, films of materials with exceptionally low values of saturated-vapor density (TiN, GaN), films containing quantum wires and quantum dots, etc. It is already clear today that further development will be impossible without analysis of the complicated physical phenomena that take place during thin-film growth [1 – 27]. The study of these phenomena began in the mid-1950s. Principal attention was paid to the new-phase nucleation on the solid surfaces. Initially, the main theoretical analysis of new-phase nucleation [12 – 16] was carried out in the framework of the classical nucleation theory by Zel'dovich [28], disregarding the variation of supersaturation during condensation and the more so disregarding the possible change of the growth mechanisms in individual islands. Hence, the comparison of experimental results on surface new-phase nucleation with the Zel'dovich theory revealed a substantial difference between them. This led the researchers to an erroneous deduction for the impossibility of using the concepts of the classical theory of phase transitions in surface processes and the necessity of rejecting them. In particular, it was assumed that such quantity as the specific interphase energy could not be used at all in the description of the early stages of thin-film nucleation. That is why, in the early 1960s, the so-called discrete models appeared that described the new-phase nucleation with the help of the methods of equilibrium statistical mechanics. The most remarkable in this sense

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were the Walton – Rodin [29], Lewis – Cambell [30] and Zinsmeister [31] models. It should be noted that these theories were inapplicable to the description of nucleation of strongly metastable and unstable systems in the same measure as the rejected Zel'dovich model because they ignored the most important effect, namely, the increasing of long-wave density fluctuations in the spinodal region [32, 33]. To establish a correspondence between the theory and experiment, it was actually quite enough to allow for the variation of supersaturation in time and the related possibility of changing growth mechanisms of individual islands [5, 11, 17]. Furthermore, most of the models were constructed for single-component films only, while a wide variety of experiments were carried out with multicomponent systems. The needs of engineering led in the course of time to the necessity of obtaining composite multicomponent films with prescribed properties and composition, and the above-mentioned models could in no way give answers to these questions. They rather 'diverted' the researchers from the straight pathway.

Meanwhile, fundamental studies of the kinetics of first-order phase transitions were being conducted in the same period. It was shown that the kinetics of first-order phase transitions was a complicated multistage process accompanied by various nonlinear phenomena [34 – 55]. Such stages typically include nucleation, the separate growth of new-phase nuclei, coalescence, and the late stage, i.e. Ostwald ripening, where the growth of the larger islands proceeds at the expense of dissolution of the smaller ones. This process is due to the difference of the Laplacian pressures on the large and small nuclei. The indicated processes have widely different time scales. The most rapid stage is the nucleation, then goes the separate growth, and so on. This time hierarchy means that the fast processes have time to 'keep up' with the slow ones [52]. Solution of the equations for fast processes provides, in fact, the initial conditions for the equations of slower processes. It turned out that the solution obtained by Zel'dovich was valid at the nucleation stage only. At later stages it is necessary to take into account the equations of conservation of matter in a system and to solve the corresponding nonlinear problems. The extension of these ideas and methods to film growth processes, as well as the development of a consistent field approach [54] providing a unified standpoint for the description of condensation under any arbitrarily high supersaturations offered quite a new view of the problems of the formation and growth of thin films. The supersaturation levels were found for which it was necessary to employ the classical nucleation theory for the description of the film growth, and also the levels for which it was necessary to use the field approach [54]. All this made it possible to apply a unified approach to the description of condensation of composite multicomponent films irrespective of the type of the initial phase (vapor, gas, liquid, etc.) and condensation conditions. It was shown that the surface brings appreciable diversity to the phase transformation, although the basic stages of this process remain unchanged. It is in this context that the modern ideas of film condensation processes are presented in the review.

Our aim here is to give a general outlook of the whole variety of processes proceeding on a solid surface in the course of new-phase nucleation on it. We consider the growth of single- and multicomponent films from vapor, solution, and melt. Great attention is paid to the nonlinear phenomena accompanying the new-phase nucleus growth and to the methods of their description.

Section 2 is devoted to the formation of a layer of adsorbed particles on a substrate surface and to the main properties, kinetic and thermodynamic, of this layer. Surface nucleation under permanent supersaturation is discussed (a change in supersaturation is a slower process). All possible growth mechanisms of new-phase nuclei are enumerated, and the stability of the form of growing islands is analyzed.

The evolution of the size distribution of phase nuclei with allowance for a decrease of supersaturation, i.e. the kinetics of the proper phase transition is described in Section 3, where the multicomponent case as well as the growth from solution-melt are also examined. Closest attention is given to the possibility of presenting the solution of the main system of equations (in the general case) in the form of a convergent series in powers of the inverse number of particles in critical nuclei under maximum supersaturation. Convergence of the series in this perturbation theory is provided by time renormalization.

Section 4 deals with the interaction of growing islands at the late stage of condensation. The Ostwald ripening with all its features, as well as the methods of film growth control at this stage (the characteristic time of Ostwald ripening is much longer than the nucleation time) are discussed in detail.

Section 5 is concerned with the final stage of thin-film condensation — the formation and evolution of a continuous structure. Much attention is also paid here to the nonlinear processes, in particular, the appearance of nonlinear density waves.

In conclusion we briefly discuss the prospects of the development of the thin-film condensation theory.

2. Elementary processes on solid surfaces

2.1 Types of solid surfaces

An important specific feature of the new-phase nucleation on the substrate surface compared to homogeneous nucleation in the bulk is the presence of various defects on the substrate. Defects are typically divided into point and linear ones, the latter including steps, surface dislocations and scratches. Even an ideal substrate contains such defects as Tamm levels due to the incompleteness of crystal planes. No rigorous theory of heterogeneous new-phase nucleation on a surface has yet been developed. The existing theories of new-phase nucleation on solid surfaces proceed either from the classical nucleation theory [5, 12] modified for the two-dimensional case and allowing for the possible role of defects in nucleation, or from the atomistic Walton – Rodin model [29] (see Section 2.5).

The surfaces of solid bodies can in the general case be both crystalline and amorphous. The modern concepts [3] distinguish between atomically smooth and atomically rough surfaces. The former usually include singular and vicinal facets, while the latter include nonsingular ones. Singular surfaces are characterized by a local minimum in the surface tension σ and a discontinuity in the angular derivative $\partial\sigma/\partial\theta$ (here θ is the angle in the polar diagram [3]). Such traits of σ and $\partial\sigma/\partial\theta$ behaviour are typical of all the directions described by rational Miller indices, the minima being sharpest and deepest in the directions normal to the close-packed planes (with minimum Miller indices). Vicinal planes have a small deviation from the alignment of close-packed facets [3].

In the vicinity of absolute zero temperature, a singular surface is an ideal flat vapor-crystal interface. As the

temperature increases, the role of the entropy term in the free energy increases, and on such a surface equilibrium defects occur, namely, adsorbed proper atoms (adatoms) and surface vacancies [56]. According to the Landau theory [57] even at $T = 0$ those surfaces that have a deviation from a close-packed orientation must be steplike to provide a minimum surface energy. In real crystals containing structure defects, it is practically impossible to obtain sufficiently large singular surfaces because surfaces possessing a macroscopically singular orientation consist as a rule of microscopic domains with orientations close to that of the singular surface. Such step-containing vicinal forms are due to the intersection by the surface of dislocations whose Burgers vector has a screw component normal to the surface. Therefore, when considering atomically smooth surfaces one customarily means vicinal surfaces possessing a certain density of steps aligned with the crystallographic orientation of the surface. At $T \approx 0$, these steps are practically straight, while at $T > 0$ they exhibit ledges.

To describe the atomic structure of vicinal facets, the TLK (terrace, ledge, kink) model [56] is most often used, which allows obtaining the binding energy of atoms that are in different positions. In terms of the TLK model one can calculate both the number of ledges and the spacing between them and can also determine the concentration of atoms in each position, i.e. in atomically smooth regions of the surface, on a step, in a ledge, etc. [56].

Cahn's [58], Jackson's [59], Temkin's [60] and some other models [61] are commonly employed to calculate the parameters of a surface in a liquid–crystal system. In particular, the Jackson model implies that for $q/k_B T < 2$, where q is the latent heat of phase transition per particle, the phase interface is atomically rough, while for $q/k_B T > 5$ it is atomically smooth. For $2 < q/k_B T < 5$, the crystal surface changes from atomically smooth to atomically rough [3, 60]. The growth mechanisms for each type of surfaces will be considered in Section 2.6. The liquid–crystal transition is a first-order phase transition from the thermodynamic point of view. Nevertheless, almost all the corresponding theories treat the solid and liquid phases as a quasi-continuous state. At the same time, the liquid–crystal transition resembles in many respects a second-order phase transition. The models used in theories of this type are similar to those considered in the theory of alloy ordering [62].

Thus, even ideal crystal surfaces having a slight deviation from a close-packed orientation are steplike; at $T > 0$, the steps are covered with ledges; the surfaces of real crystals are rough, contain surface vacancies, surface dislocations, intergrain boundaries, and other defects [3, 63]. They all essentially affect the parameters of the condensation and may serve as orienting centres in epitaxial growth.

2.2 Adsorption, desorption and diffusion of adatoms

The adsorption, desorption and diffusion of atoms over the surface of a substrate have been rather well investigated [3, 25, 64]. In particular, adsorption isotherms for different types of surfaces have been drawn, microscopic theories of all basic processes have been formulated, and the influence of substrate occupancy by adatoms has been taken into account. However, to describe the sufficiently slow processes of thin-film condensation it is not at all necessary to use detailed microscopic theories of fast processes such as adsorption, desorption and diffusive jumps of adatoms to neighbouring sites. It is quite enough to know the averaged macroscopic behaviour of adsorbed particles. Below, we shall therefore present only the simplest models of elementary processes on the solid surfaces in terms of the transition state theory [65]. A detailed description of fast processes can be found in Refs [25, 64, 65].

Adsorption is typically thought of as the first stage of film condensation [1–9]. In condensation from a single-component vapor, monomolecular and dissociative adsorptions are most frequently distinguished [66] which, for small substrate occupation numbers, lead to a uniform appearance of adatoms about the entire unoccupied substrate surface with a constant rate J:

$$J = C_g P (2\pi M k_B T_v)^{-1/2} , \tag{2.1}$$

where P is the vapor pressure, T_v is the vapor temperature, M is the mass of one deposited molecule, k_B is the Boltzmann constant, and C_g is a geometric factor.

The adsorbed atoms can either desorb back into vapor or jump over (diffuse) to one of the neighbouring sites [2, 3, 8]. In the single-component case we distinguish between monomolecular and associative desorption, which are respectively described by the following equations

$$\frac{dn_1}{dt} = -\frac{n_1}{\tau_r} , \qquad \tau_r = \nu^{-1} \exp \frac{E_a}{k_B T} , \tag{2.2}$$

$$\frac{dn_1}{dt} = -D_d n_1^2 , \quad D_d = D_{d0} \exp\left(-\frac{E_a}{k_B T} \right) , \tag{2.3}$$

where n_1 is the surface adatom concentration, t is the time (dn_1/dt is the desorption rate), τ_r is the characteristic time of monomolecular desorption (reevaporation time), D_d is the associative desorption coefficient with dimension of the diffusion coefficient, E_a is the desorption activation energy, and ν and D_{d0} are preexponential factors [66]. The mean distance covered by a diffusing atom in a time t is

$$\langle x^2 \rangle = 2 D_a t , \quad D_a = D_{a0} \exp\left(-\frac{E_d}{k_B T} \right) , \tag{2.4}$$

where D_a is the diffusion coefficient of adatoms, E_d is the diffusion activation energy (it is commonly equal to $E_a/3$), D_{a0} is a preexponential factor. The values of the activation energy and preexponential factors for various systems can be found, for example, in Ref. [66].

We shall now consider the kinetics of substrate surface occupation by adatoms in the absence of thin-film growth, i.e. for $n_1 < n_{1e}$, where n_{1e} is the equilibrium concentration of adatoms. For a constant rate J of arrival of adatoms at the substrate and small substrate occupation numbers in the cases of monomolecular and associative desorptions, we have respectively

$$\frac{dn_1}{dt} = J - \frac{n_1}{\tau_r} , \qquad n_1(0) = 0 , \tag{2.5}$$

$$\frac{dn_1}{dt} = J - D_d n_1^2 , \qquad n_1(0) = 0 . \tag{2.6}$$

The solutions of these equations are as follows:

$$n_1(t) = J\tau_r \left[1 - \exp\left(-\frac{t}{\tau_r} \right) \right] , \tag{2.7}$$

$$n_1(t) = \sqrt{\frac{J}{D_d}} \tanh(\sqrt{J D_d}\, t) . \tag{2.8}$$

Unless otherwise specified, we shall further on consider for simplicity only the case of monomolecular desorption, which is more frequently encountered in practice.

2.3 Thermodynamics of an adsorbed layer

After establishing equilibrium between the surface and the surrounding initial phase, a two-dimensional 'gas' of adatoms with surface density n_1 is formed on the surface of the solid body [5, 12]. In the case of monomolecular desorption, this proceeds approximately within a time τ_r, and in the case of associative desorption — within a time $1/\sqrt{JD_d}$ [see Eqns (2.7), (2.8)]. A large number of papers [27, 54, 64–67] are devoted to the study of the thermodynamic and kinetic characteristics of such an adsorbed 'gas'. The most interesting and important for us are the thermodynamic stability, instability and metastability of these systems because it is just these characteristics that are directly connected with the possibility of phase transformations in adsorbed layers. With this purpose in mind, we shall consider the simplest model. All adatoms are embedded at the sites in a two-dimensional periodic lattice. Their density will be denoted by n_0 (the influence of steps and other inhomogeneities is neglected). Next, we shall introduce the variable n_j as follows: $n_j = 1$ if the site number j is occupied by an adatom, and $n_j = 0$ otherwise. Applying the substitution $n_j \to n(\mathbf{r})$, where $\mathbf{r}$ is the radius vector in the substrate plane, we shall pass over from a discrete description to a continuous one. In this case, nn_0 is none other than the adatom concentration on the substrate. Suppose also that the system is homogeneous and isotropic. In the case of a monolayer adsorbate, this allows the grand thermodynamic potential to be written as

$$\Omega = \frac{n_0^2}{2}\int\int U(|\mathbf{r}_1-\mathbf{r}_2|)n(\mathbf{r}_1)n(\mathbf{r}_2)\,\mathrm{d}\mathbf{r}_1\,\mathrm{d}\,\mathbf{r}_2 + n_0\sigma_s\int n(\mathbf{r})\,\mathrm{d}\mathbf{r} - k_B T\int \ln W_e\,\mathrm{d}\mathbf{r} - \mu n_0\int n(\mathbf{r})\,\mathrm{d}\mathbf{r} + \Omega_0\,, \tag{2.9}$$

where U is the potential energy of interaction between adatoms in the substrate field, σ_s is the energy of interaction between an adatom and the substrate, W_e is the number of ways nn_0 particles can be positioned at n_0 sites, μ is the chemical potential of the two-dimensional gas, and Ω_0 unites all the contributions due to the remaining degrees of freedom.

Expression (2.9) can be simplified by passing over to the variables $(\mathbf{r}_1+\mathbf{r}_2)/2$ and $\mathbf{r}_1-\mathbf{r}_2$, and assuming the potential U to be short-range and then evaluating the entropy summand by the Stirling formula [54]:

$$\Omega = n_0 k_B T\int\left[\frac{T_c}{T}\left(\frac{R_s}{2}\right)^2(\nabla s)^2 + E(s)\right]\mathrm{d}\mathbf{r} + \Omega_0\,, \tag{2.10}$$

$$E(s) = \frac{1}{2}\left[-\frac{T_c}{T}s^2 + (1+s)\ln(1+s) + (1-s)\ln(1-s) - \lambda s\right], \tag{2.11}$$

where $s = 2n-1$ is the order parameter, and $\lambda = (2k_B T_c - \sigma_s + \mu)/k_B T$ is the parameter of metastability with

$$k_B T_c = -\frac{n_0}{4}\int U(|\mathbf{r}|)\,\mathrm{d}\mathbf{r} = -\frac{\pi n_0}{2}\int_{l_0}^{\infty} rU(r)\,\mathrm{d}r\,, \tag{2.12}$$

$$R_s = \frac{1}{2}\sqrt{\frac{\int_{l_0}^{\infty} r^3 U(r)\,\mathrm{d}r}{\int_{l_0}^{\infty} rU(r)\,\mathrm{d}r}}\,. \tag{2.13}$$

Here T_c plays the role of the critical temperature [54], and R_s is the scale factor. The minimization of Ω with respect to $s(\mathbf{r})$ allows determination of the critical configuration $s_c(\mathbf{r})$ which is in equilibrium with the initial phase [54]. The quantity λ has the meaning of the chemical potential difference, expressed in $k_B T$, between the new and the old phases.

We shall now briefly discuss the properties of the potential (2.10), (2.11) and the consequent equation of state of a two-dimensional adatom population. Let us introduce the concept of the volume V occupied by a substance of unit mass, $V = 1/n$. Then the pressure in the adatom system is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = n^2\left(\frac{\partial F}{\partial n}\right)_T, \tag{2.14}$$

where $F(n) = k_B T[n\ln n + (1-n)\ln(1-n)]/n - 2k_B T_c n$ is the free energy of the substance of unit mass. From this follows the equation of state

$$\frac{P}{k_B T_c} = \frac{T}{T_c}\ln\frac{1}{1-n} - 2n^2\,. \tag{2.15}$$

For $T < T_c$, $P < P_c = (\ln 2 - 1/2)k_B T_c$, the $P(V)$ isotherms contain a characteristic van der Waals loop testifying to a first-order phase transition of gas–liquid type. In real systems such a transition occurs only in the interval $T_t < T < T_c$ between the triple and the critical points. Since the potential (2.10), (2.11), being homogeneous and isotropic, bears no information about the crystal structure of the new phase, the given model (the same as other models of this type) describes only the phase transition of gas–liquid type (amorphous state), i.e. the amorphous film condensation and the first stage of the crystalline film condensation, which proceeds by the vapor → liquid → crystal mechanism. In spite of the simplifications made, this continual model satisfactorily describes many principal features of the behaviour of the adatom system.

We shall introduce new universal variables $P' = P/P_c$, $V' = V/V_c = 1/2n$, and $T' = T/T_c$ after which the equation of states will not depend on the characteristics of the substance:

$$P' + \frac{b_0}{2V'^2} = b_0 T'\ln\frac{1}{1-1/2V'}\,, \tag{2.16}$$

where $b_0 = (\ln 2 - 1/2)^{-1} \approx 5.177$. The $P'(V')$ isotherms are drawn in Fig. 1 for various T'. Similar isotherms are obtained for systems of solid discs, solid squares, and particles on a lattice in simulations by the Monte-Carlo and molecular dynamics methods using various interaction potentials [68]. The Maxwell rule allows determination of the equilibrium concentrations $n_{1e}(T)$ and $n_{2e}(T)$ between which occurs the phase transition shown by the horizontal straight line in Fig. 1. The application of the Maxwell rule to the equation of state (2.15) or (2.16) gives the phase equilibrium curve

$$\frac{T}{T_c} = \frac{2(1-2n)}{\ln(1/n-1)}\,. \tag{2.17}$$

From Eqn (2.17) one finds the equilibrium concentration n_{1e} of adatom gas and the equilibrium density n_{2e} of the amorphous state. In particular, over the region $T/T_c < 0.4$

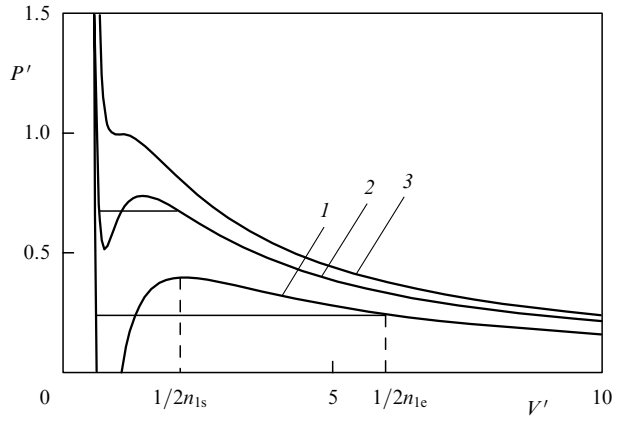

Figure 1. Dependences of P' on V' for various T': *1* — $T' = 0.7$; *2* — $T' = 0.9$; *3* — $T' = 1$. The horizontal lines are drawn by the Maxwell rule. Curve *1* shows the interval from the equilibrium concentration n_{1e} to the concentration n_{1s} of a spinodal corresponding to a supersaturated gas of adatoms.

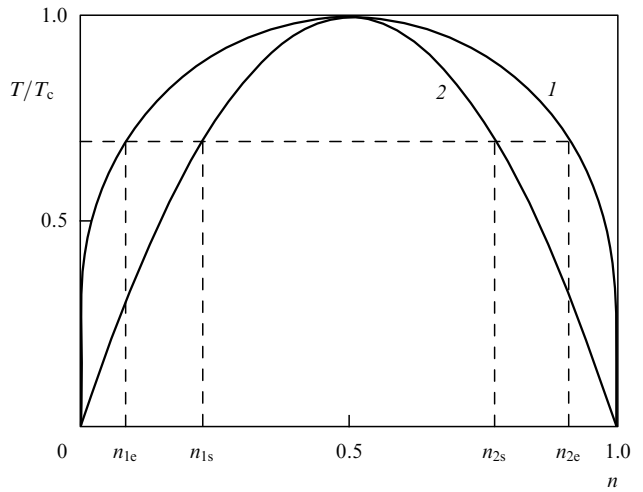

Figure 2. Phase-equilibrium curve (*1*) and spinodal curve (*2*) obtained from Eqns (2.17) and (2.20), respectively. The values of n_{1e}, n_{1s}, n_{2s}, and n_{2e} are given for $T/T_c = 0.7$.

the approximation holds [54]:

$$n_{1e}(T) = \exp\left(-\frac{2T_c}{T}\right), \tag{2.18}$$

$$n_{2e}(T) = 1 - \exp\left(-\frac{2T_c}{T}\right). \tag{2.19}$$

Comparison of Eqn (2.18) with experimental data gives the estimate for T_c. For example, comparing the data of Refs [69, 70] with (2.18), we find $T_c = 3600$ K for Au/NaCl and $T_c = 4000$ K for Au/KBr. The range of n values between the points of maximum and minimum P is the region of unstable states because in this case we have $(\partial P/\partial V)_T > 0$. The region $n_{1s} < n < n_{2s}$ is called the spinodal region. The initial state located in this region decays to n_{1e} and n_{2e} owing to the increase of periodic fluctuation of substance concentration [32, 54]. The spinodal curve can be found from the condition $(\partial P/\partial V)_T = 0$:

$$\frac{T}{T_c} = 4n(1-n), \tag{2.20}$$

which implies

$$n_{1s}(T) = \frac{1}{2}\left(1 - \sqrt{\frac{1-T}{T_c}}\right), \tag{2.21}$$

$$n_{2s}(T) = \frac{1}{2}\left(1 + \sqrt{\frac{1-T}{T_c}}\right). \tag{2.22}$$

The phase-equilibrium and spinodal curves are plotted in Fig. 2. The region of metastable states, $n_{1e} < n < n_{1s}$, corresponds to a supersaturated vapor, and the region $n_{2s} < n < n_{2e}$ to a superheated liquid. It is precisely in the region $n_{1e} < n < n_{1s}$ that the film condensation proceeds through nucleation, and for $n = n_{1s}$ the critical nucleus consists of only one particle. The quantity $\xi_{max} = n_{1s}/n_{1e} - 1$ has the meaning of maximum attainable supersaturation. For supersaturations exceeding ξ_{max}, the adatom population becomes unstable and a spinodal decomposition begins in it [32, 54]. Let us make very simple estimations. For $T/T_c = 1/4$ we have $n_{1e} = 3.7 \times 10^{-4}$, $n_{1s} = 3.2 \times 10^{-2}$ and $\xi_{max} = 96$, and for $T/T_c = 1/10$ — $n_{1e} = 2.1 \times 10^{-9}$, $n_{1s} = 2.6 \times 10^{-2}$ and $\xi_{max} = 1.2 \times 10^{7}$. Consequently, both the equilibrium adatom concentration and the maximum supersaturation in a real temperature range may change radically.

Concluding the section we note that in weakly metastable systems with $\xi \ll \xi_{max}$, the metastability parameter and supersaturation are related as $\lambda = \ln(\xi + 1)$, where $\xi = n_1/n_{1e} - 1$ is supersaturation. In strongly metastable systems, where ξ approaches ξ_{max}, this dependence is violated [54].

2.4 Thin-film growth regimes

The thin-film growth regimes are typically divided into layer-by-layer, island, and intermediate [1, 2, 8].

The layer-by-layer, or the Frank – van der Merwe regime is realized in the case when the atoms of a deposited substance are bound with the substrate more strongly than with each other. Monatomic layers in this regime are occupied in turn, i.e. two-dimensional nuclei (one atom thick) of a subsequent layer are formed on the upper part of the nuclei of the preceding layer after the latter is occupied. The equilibrium form of the nuclei is found by the Wulf theorem [3]. The theoretical description of the layer-by-layer growth is customarily given in the framework of the Kashchiev model [71] or its modifications [72, 73].

The island, or Volmer – Weber regime is realized in the opposite case, i.e. for the atoms of a deposited substance bound with each other more strongly than with the substrate. Island growth can only be realized under the condition [8, 9]

$$\sigma_s < \sigma_d + \sigma_{s-d} - \text{const} \times k_B T \ln(\xi + 1), \tag{2.23}$$

where σ_s is the free energy of a unit substrate surface, σ_d is the free energy of a unit adsorbate surface, and σ_{s-d} is the free energy of a unit substrate – adsorbate interface. Otherwise the layer-by-layer regime holds. In the island regime, small nuclei are formed straight on the substrate surface and then grow transforming into large islands of the condensed phase [8]. Thereupon these islands merge to form a continuous film after the channels between them are filled [8, 74].

In the intermediate, or Stranskiĭ – Krastanov regime, the first to be realized is layer-by-layer growth and then, after one

or two layers are occupied, island growth begins. There may be several reasons for the change of the growth mechanisms [8]. The principal cause is that the lattice parameter cannot remain unchanged upon occupation of an immediate layer. Its variation entails a strong increase of the adsorbate–intermediate layer interface energy, which provides fulfilment of the island regime criterion (2.23). A large number of examples illustrating all three thin-film growth conditions and experimental methods of their investigation are presented in reviews [2, 8].

In paper [75], it has been shown that under certain conditions the faceting of cap-shaped clusters at the Ostwald ripening stage may lead to a replacement of the island mechanism by the layer-by-layer one. In this regime, condition (2.23) holds at first and then the change in the condensate symmetry causes its violation.

Thus, the material of the substrate and the type of its surface determine the film growth regime.

2.5. The nucleation processes

We shall briefly discuss the methods used to describe the nucleation processes on the surface in the cases of single- and multicomponent films. The most widely employed is the so-called capillary model first formulated by Volmer and Weber, Becker and Döring [18, 19], and Zel'dovich [28]. This model postulates the following. Positive free-energy fluctuations that lead to overcoming the activation barrier are necessary for the condensation of a new phase from a supersaturated vapor in the metastable state (i.e. over the region $n_{1e} < n_1 < n_{1s}$) [20, 28]. The presence of such a barrier is connected with the fact that the free energy of nucleation from a supersaturated vapor has a maximum at a certain critical point.

Nuclei on a substrate may have various shapes [1, 2, 7–9] but theoretically they are most frequently assumed to look like a disc or a hemisphere according to the film growth mechanism [12], because many films grow by the vapor → liquid → crystal mechanism. The free energy F of the formation of disc-shaped clusters on an ideal substrate, found in Ref. [12], can be written in the form

$$F(i) = 2\sqrt{ai} - i\ln(\xi+1) - \ln\frac{n_0}{n_1}\,. \tag{2.24}$$

Here i is the number of particles in a nucleus, $a = (\sigma/k_BT)^2\pi w/h$, σ is the effective interphase energy per unit length of the disc boundary, h is the disc height, w is the volume occupied by one particle in the nucleus, and F is expressed in k_BT units. The first term in Eqn (2.24) is the energy of the surface tension, the second is the chemical potential difference between the new and the old phases, and the third is a statistical correction due to the distribution of n_1 atoms over n_0 lattice sites [12]. The maximum of the free energy (2.24) is positioned at the point

$$i_c = \frac{a}{\ln^2(\xi+1)}\,, \tag{2.25}$$

and is equal to

$$F(i_c) = \frac{a}{\ln(\xi+1)} - \ln\frac{n_0}{n_1}\,. \tag{2.26}$$

The nucleus has to overcome just such a potential barrier of height $H(\xi) = F(i_c)$ owing to heterophase fluctuations in order that it might grow further regularly.

According to the capillary model, an elementary act changing the nucleus size is either an attachment to it or, on the contrary, a loss of one molecule (the merging of nuclei is ignored). As regards sufficiently large nuclei containing $i \gg 1$ particles, this change is small, and therefore the evolution of large nuclei is described by the Fokker–Planck equation [20]

$$\frac{\partial g}{\partial t} = -\frac{\partial I}{\partial i}\,, \qquad I = -W(i)\left[\frac{\partial g}{\partial i} + g\frac{\mathrm{d}F(i)}{\mathrm{d}i}\right], \tag{2.27}$$

where $g(i,t)$ is the distribution function of nuclei over the number of particles i in them, I is the nucleation rate (it vanishes for an equilibrium distribution $g_e = \text{const} \times \exp[-F(i)]$), and $W(i)$ is the diffusion coefficient in the dimension space, which is equal to the number of molecules coming into the nucleus from the ensemble of adatoms per unit time. The stationary solution of this equation has the form [28]

$$g_s(i) = I\exp\left[-F(i)\right]\int_i^\infty W^{-1}(i')\,\exp F(i')\,\mathrm{d}i' \tag{2.28}$$

(the standard boundary condition: $g_s \exp F(i) \to 0$ as $i \to \infty$ was taken into account here). The probability of fluctuations described by the second derivative of g with respect to i in (2.28) increases rapidly with decreasing size. Hence, the store of subcritical nuclei may be regarded as supplemented so rapidly owing to the fluctuations that their number remains in equilibrium in spite of the permanent outflow of the flux I. Consequently, the boundary condition to Eqn (2.27) takes the form: $g_s(i) \to n_1\exp[-F(i)]$ as $i \to 0$, and therefore from (2.28) we find

$$I = n_1\left[\int_0^\infty W^{-1}(i')\exp F(i')\,\mathrm{d}i'\right]^{-1}. \tag{2.29}$$

The integrand in (2.29) has a sharp maximum at the point $i = i_c$, which allows us to calculate the integral using the Laplace method:

$$I = n_1\sqrt{-\frac{F''(i_c)}{2\pi}}\,W(i_c)\exp\left[-F(i_c)\right]. \tag{2.30}$$

The square root in (2.30) is sometimes called a nonequilibrium Zel'dovich factor. Let us estimate the quantity $W(i_c)$, which is the frequency with which adatoms are attached to a critical nucleus. To this end we shall use the lattice model. Let R_c be the radius of the critical nucleus linear boundary, l_0 the length of diffusive jumps of adatoms, v the desorption frequency, and E_d the activation energy of surface diffusion. Then we have

$$W(i_c) = 2\pi R_c n_1 l_0\frac{v_d}{4}\exp\left(-\frac{E_d}{k_BT}\right) = 2\pi R_c n_1\frac{D_a}{l_0}\,, \tag{2.31}$$

where $D_a = (l_0^2 v_d/4)\exp(-E_d/k_BT)$ is the diffusion coefficient of adatoms. From this, for disk-shaped nuclei we arrive at [5]

$$I(\xi) = C_1 n_{1e} n_0 D_a(\xi+1)\ln^{1/2}(\xi+1)\exp\left[-\frac{a}{\ln(\xi+1)}\right]. \tag{2.32}$$

Similarly, for nuclei in the shape of a hemisphere we have

$$I(\xi) = C_2 n_{1e} n_0 D_a (\xi + 1) \ln(\xi + 1) \exp\left[-\frac{b}{\ln^2(\xi + 1)} \right]. \tag{2.33}$$

Here $C_1 = (2w/hl_0^2)^{1/2}$, $C_2 = 2\sin\theta[\sqrt{(3/2)\pi} l_0^3 (1 - \cos\theta)^2 \times (2 + \cos\theta)/w]^{-1/3} b^{-1/2}$, $b = 4\pi(\varepsilon/k_B T)^3 w^3 (2 + \cos\theta) \times (1 - \cos\theta)^2/3$, ε is the interphase energy per unit area, and θ is the contact angle. The time t_s of setup of a stationary nucleation rate has been repeatedly evaluated by various authors, all the values being coincident in the order of magnitude [76–79]. The mean value is as follows:

$$t_s = \frac{1}{-F''(i_c) W(i_c)}. \tag{2.34}$$

In thin-film condensation, this time is usually very short (10^{-4}–10^{-8} s) both for disc- and cap-shaped nuclei, and therefore in practice it suffices only to calculate the stationary flow of nuclei I. The method of making allowance for nonstationary effects (necessary for the description of very fast processes) was proposed, for example, in Refs [78, 79].

In the case of multicomponent films, the free energy of a nucleus depends on the number of particles of each component. Its calculation is a separate, fairly complicated problem [80]. The Fokker–Planck equation becomes multidimensional, and accordingly the boundary condition at the zero point becomes more complicated. The method of its solution is based on the simultaneous diagonalization of both the equation and the boundary condition by way of a linear change of variables [81]. Then it turns out that the nucleation rate I can be estimated in the order of magnitude as

$$I = n_0 \left(\sum_{k=1}^{m} d_k \right) \exp(-H_0), \tag{2.35}$$

where d_k are the diffusion coefficients for each of the m components in the dimension space for $i = i_c$ [80], and $H_0 = H + \ln(n_0/\sum_{k=1}^{m} n_{1k})$ is the nucleation barrier height without the entropy correction.

It has been assumed above that the nucleation proceeds on an ideal substrate, namely, in a homogeneous way. However, various substrate defects very frequently initiate nucleation by reducing the activation barrier height H. In particular, the work of heterogeneous nucleation at the step of a substrate has recently been found in Ref. [12], where it has also been shown that steps may substantially increase the nucleation rate. This is confirmed by numerous experimental data [1, 2, 7, 8, 10]. The activation barrier of nucleation on a step can be so small ($\sim k_B T$) that a nucleus consisting of two particles will already be supercritical, i.e. $F(2) < F(1)$ (or $n_1 > n_{1s}$). In this case, as has already been mentioned, a new phase will be formed not through conventional nucleation, but through a spinodal decomposition, namely, an increase of the periodic fluctuations of substance concentration [32, 54]. At the same time, the size distribution of new-phase islands on the step and their spatial distribution will already be different.

There exist many modifications of the classical capillary model of nucleation on a substrate, in which various corrections to the height of the activation barrier are calculated, in particular, the correction due to internal degrees of freedom of a cluster [20], the correction due to free energy variation upon separation of a group of i molecules from a large ensemble [12], the correction due to cluster boundary smearing (see Ref. [82]), corrections due to cluster faceting [3] and diffusion field fluctuations [83], due to merging of migrating nuclei, electrostatic and nonisothermal effects [84], and so on. These corrections are, as a rule, relatively small and, moreover, have different signs. The most significant is obviously the correction due to the influence of nucleus surface curvature upon the interphase energy [85, 86]. It leads to a 10^2–10^6-fold increase of the nucleation rate.

We recall that the capillary model described above is only applicable for $i_c \gg 1$, because it is only in this case that the attachment and detachment of particles to and from critical nuclei can be described by the differential Fokker–Planck equation (2.27). An alternative to this model for $i_c < 10$ is the atomistic Walton model [29] exploiting the methods of equilibrium statistical mechanics. It allows I to be expressed in terms of i_c, but does not give the dependence of i_c on ξ. Moreover, it is invalid for $i_c = 1$ and $i_c = 2$, when the increase of long-wave density fluctuations is appreciable.

The equation for the rate of first-order phase transition in melts was obtained in the model [87] intended for the description of film growth from melt. The derivation of this equation (but not the equation itself) differs from the conventional Zel'dovich approach in that the model at hand uses the relations between the atomic emission and absorption probabilities defined in advance and not the equilibrium distribution function for subcritical nuclei. The flows of the viable nuclei of a new phase were evaluated for several cases not previously investigated.

From what has been said it is clear that the models for calculating the quasi-stationary nucleation rate are fairly numerous, and it is only on the basis of the corresponding analysis of experimental conditions that a particular model can be chosen.

2.6. Growth mechanisms of new-phase nuclei

After the appearance of nuclei of a new phase on the substrate surface they start growing and interacting with atoms of the old phase of which they were formed. This latter phase may be a single- or multicomponent vapor, a single- or multicomponent solution-melt, an amorphous phase, a solid solution, etc. [17]. Accordingly, the island growth mechanisms also differ substantially. Thus, the diffusion flux of atoms of the old phase towards the surface of the nuclei is responsible for their growth from vapor medium. Both the removal of the latent heat of phase transformations and the diffusion of atoms of the old phase are responsible for the island growth from solutions-melts and from an amorphous medium. If the film growth is due to decomposition of a supersaturated solid solution, the islands will grow through the presence of a diffusion flux of atoms of the old phase. In case the film growth proceeds in the course of another type of phase transformation, for instance, a film decay caused by elastic strains [88, 89] occurring at film–substrate interfaces, the islands grow owing to the diffusion atomic flux induced by elastic strains. The surface introduces an appreciable diversity into the nucleus growth mechanisms compared to the growth in the bulk of solids [90, 91]. According to contemporary concepts [17], the following basic ways of atomic migration and energy, in particular, heat transfer over the surface are distinguished: three-dimensional or volume diffusion of atoms and three-dimensional heat removal; two-dimensional atomic diffusion over the substrate surface and two-dimen-

sional heat removal; one-dimensional atomic diffusion along substrate steps, surface dislocations and other linear defects. Islands may also grow owing to an immediate arrival of atoms from a vapor onto their surface. The ultimate goal of the study of island growth mechanisms is the determination of their growth rate as a function of their radius and the degree of supersaturation. With this purpose, the corresponding heat and mass transfer equations are solved [17, 92–94]. Such problems are typically referred to as Stefan problems [3, 17, 61, 62]. They have been widely examined for three-dimensional systems [66], in particular, for crystal growth from single-component and binary melts. Similar calculations for the diffusion mechanism of island growth on surfaces have been made by Sigsbee [95], Chakraverty [96] and others [2, 15]. But the authors of these papers have analyzed only one of the possible mechanisms of island growth, namely, island growth due to surface diffusion of adatoms. It has also turned out that the island growth rate is notably governed by nonstationary effects induced by the nucleus boundary motion [97]. These effects become predominant for small values of $R/\sqrt{D_a\tau_r}$, where R is the island radius, and $\sqrt{D_a\tau_r}$ is the diffusion path length of adatoms. Below we shall only consider the quasi-stationary approximation for the island growth rate, which holds for high values of $R/\sqrt{D_a\tau_r}$.

The structure of diffusion fields in the bulk of a vapor phase, on a substrate surface, and at linear defects was investigated in detail and the expressions for the island growth rate v_R were found in Refs [17, 88, 98]. Islands usually grow simultaneously through several atomic diffusion mechanisms. It is however more convenient to consider each mechanism of island growth separately. According to Refs [93, 94], the expression for the new-phase island growth rate v_R can be written in the following general form for each of the mass transfer mechanisms:

$$v_R = -M^{2-d'} w \frac{J_{DR}\Psi(\theta)}{R^{3-d'}} . \tag{2.36}$$

Here w is the volume per atom in the islands of a new phase; d' is the dimension of the space in which the diffusion fluxes propagate: $d' = 3$ for mass transfer in the bulk of a phase, $d' = 2$ for mass transfer over the surface, and $d' = 1$ for one-dimensional atomic diffusion along substrate steps or other linear defects (in this formula $2 - d'$ is assumed to take only nonnegative values); J_{DR} is a diffusion flux of atoms onto the island surface, which is found from the corresponding diffusion equations (for more details see Refs [17, 93]), and $\Psi(\theta)$ is the function taking into account the island geometry. For caplike islands we have $\Psi(\theta) = 2(2 - 3\cos\theta + \cos^3\theta)^{-1} \times (1 - \cos\theta)$ when the diffusion of atoms proceeds in the bulk of a gas phase, $\Psi(\theta) = 2\sin\theta/(2 - 3\cos\theta + \cos^3\theta)$ for the diffusion of atoms over the substrate surface, and $\Psi(\theta) = [2\pi(2 - 3\cos\theta + \cos^3\theta)]^{-1}$ for the one-dimensional atomic diffusion, and, finally, M is the number showing how many linear defects are crossed by an island during its growth. To find the atomic diffusion flux of atoms J_{DR} to a nucleus, one has to solve the corresponding diffusion equations. The form of these equations, the boundary conditions on them and the methods of their solution can be found in Refs [5, 17, 92, 93]. The general expression for the new-phase island growth rate has the form

$$v_R = \frac{K_p}{R^{p-1}} \left(\frac{R}{R_c} - 1 \right) . \tag{2.37}$$

Here K_p is a constant involving the parameters which characterize the material of the island and the kinetic parameters of its growth (particular values of K_p in different cases can be found in Refs [5, 11, 17, 92]), and the number p assumes the values 2, 3, 4 depending on the mass transfer mechanism. For our further purposes it is convenient to express the number p in terms of the island dimension $d = 2, 3$ and the growth index m, which takes the values 1, 3/2, 2, 3 depending on the island shape and the type of the limiting stage: $p = d/m + 1$. At the initial stages of phase transformation, the island radius is $R \gg R_c$, and therefore the unity in the right-hand side of Eqn (2.37) is customarily ignored as being negligibly small compared to R/R_c. Furthermore, it is convenient to write this equation not in terms of the radius growth rate but via the change of the number of atoms in the nucleus. Then Eqn (2.37) will be rewritten in the form [5, 11]

$$\frac{di}{dt} = m \frac{\xi}{t_0} i^{(m-1)/m} , \tag{2.38}$$

where ξ is supersaturation, and t_0 is a constant having the dimension of time and called the characteristic time of island growth. It is expressed through the constant K_p and the constants relating supersaturation to the critical radius [55].

It has been shown theoretically and experimentally [17, 88] that the new-phase island growth is determined by two principal processes — substance transfer to the island, i.e. diffusion proper, and the passage of atoms through the old phase – new phase interface, i.e. the boundary kinetics. We note that the necessity of allowing for the boundary kinetics during nucleus growth was discussed in a number of theoretical papers [88, 99], where island growth controlled not only by the diffusion rate but also by the velocity of passage of atoms through the boundary between the diffusion source and the island was considered. Island growth control using boundary kinetics was convincingly demonstrated in a number of experiments, the results of which were summarized in the monograph [88]. It was shown, in particular, that between an island and an adatom vapor there may exist a potential barrier preventing the passage of the atoms in only one direction, namely, toward the island [100].

Having passed through the phase interface, an atom joins the island surface. The island surface, the same as the surface of any crystal (see Section 2.1), can be atomically rough, atomically smooth or vicinal. The ways in which the atom joins the island surface are different and depend on the type of surface [17]. So, phase interfaces rough at the atomic level grow by the normal mechanism of growth. Atomically smooth surfaces grow by way of two-dimensional nucleation on their facets. Vicinal surfaces grow either through the motion of already existing steps or through the use of screw dislocations appearing on their surfaces. Island growth by the two-dimensional nucleation, as well as the evolution of an ensemble of such islands was described in the paper [101]. In Refs [17, 75], a rigorous analysis of island growth due to the motion of dislocations over their surfaces was carried out and the conditions under which this growth mechanism is realized, were found.

The next stage represents incorporation of adatoms into a new-phase island. The growth rate (2.37), namely the constant K_p and the index p, are significantly influenced by which of the processes is limiting. For the particular form of the constant K_p for each type of mass transfer mechanism, see, for example, Refs [5, 11, 17].

We shall now consider peculiarities of growth of the multicomponent islands. Multicomponent systems may be divided into two groups. One of them includes systems with solid solutions as islands [17, 102, 103], and the other involves systems with islands consisting of stoichiometric compounds [5, 90–94, 98]. We shall first dwell on the growth of multicomponent stoichiometric islands and then pass over to an examination of growth processes in islands of solid solutions.

In the course of formation of multicomponent thin films, atoms arrive at the substrate surface and they may initiate islands of various chemical compounds. For example, during growth of high-temperature superconducting films, islands of Y_2O_3, BaO, and CuO compounds appear [104]. Many of the islands of these compounds represent an intermediate phase in the course of growth of other phases. Islands of a chemical compound will further on be referred to as the phase s. As in single-component systems, the growth of multicomponent islands is due to the same mass transfer mechanisms [17, 92, 93]. However, there is one important difference in that the chemical components of which an island of phase s is formed, may diffuse towards it in different ways. One of the components may arrive at the island surface through surface diffusion, and another through gas diffusion. Furthermore, these components may have different limiting stages. In this situation one usually has to find the component responsible for the limitation and by this component determine the main flow of substance towards the island. The growth rate of a multicomponent island of an arbitrary phase s will as before be described by Eqn (2.36) in which, however, instead of the product of the atomic flux J_{DR} by the volume w there stands the sum of the products of an atomic flux from each component by their volume w_i, i.e. $\sum_{i=1}^{n^s} w_i^s J_{iR}^s$, where the subscript i stands for the corresponding sort of atoms. Since the islands have a stoichiometric composition, it follows that on their surfaces, according to Refs [5, 11, 17, 90–93], the stoichiometry condition $J_{iRr}^s/v_i^s = J_{i'Rr}^s/v_{i'}^s$ holds. This condition allows us to express the quantity $\sum_{i=1}^{n^s} w_i^s J_{iR}^s$ in terms of the product of the flux of one of the components i by the volume w_m^s of a molecule of the chemical compound of phase s, i.e. $J_{iR}^s w_m^s/p_i^s$, where $w_m^s = \sum_{i=1}^{n^s} p_i^s w_i^s$ is the volume per molecule of phase s, and $p_i^s = v_i^s/\sum_{i=1}^{n^s} v_i^s$. Thus, to calculate the growth rate of a multicomponent island, it suffices to find the flux J_{iR}^s of only one arbitrary component. In Refs [92, 98], all possible mechanisms of substance transport in multicomponent systems were investigated and analytical expressions for any type fluxes J_{iR}^s were found. Their substitution into an equation of growth rate of the type (2.36) leads to an equation of motion for an island of phase s, which has the form (2.37), where the constant K_p is replaced by a generalized constant containing kinetic and some other coefficients of each component entering the phase s [17]. The critical radius R_c in Eqn (2.37) is replaced by the critical radius R_c^s for a given phase.

The exact calculation of the growth rate of solid solution islands is much more sophisticated than that for stoichiometric compounds. If the diffusion processes inside the islands are slowed down compared to the same processes outside the islands, the island composition along their radii will be inhomogeneous. Only provided the diffusion rate inside the islands appreciably exceeds the rate of variation of their radius, the island composition may be thought of as homogeneous. To determine the island growth rate, it is necessary to know in what proportion the components are built-in in an island. This question can only be answered after the mixing entropy of the components is calculated [80]. The solution of this problem can be approached differently, namely, one may use the state diagram relating the composition of the old and the new phases [17, 102, 103, 105]. Solid solution islands are formed as a rule from the vapor phase and melts. Any state diagrams of substances in which there are no chemical interactions can be represented in the form of one or other modification of the two simplest state diagrams, namely, the diagram describing melting–crystallization of substances insoluble in each other when in solid state (Fig. 3a — the diagram with an eutectic point) and the diagram describing melting–crystallization (evaporation-condensation) of substances that form a continuous solid-solution series (Fig. 3b) [106]. Islands produced from systems of the first type are single-component substances of composition A or B, respectively. At a eutectic point (see Fig. 3b), there simultaneously appear islands of both A and B compositions. In Refs [17, 102, 103], it was shown that whenever the volume diffusion in the island matrix was fast enough, the expression for the growth rate remained the same (2.36), but the flux J_{DR} already consisted of the difference of atomic fluxes of components A and B. The average composition of islands changed during their growth by a definite law (see Section 4.6).

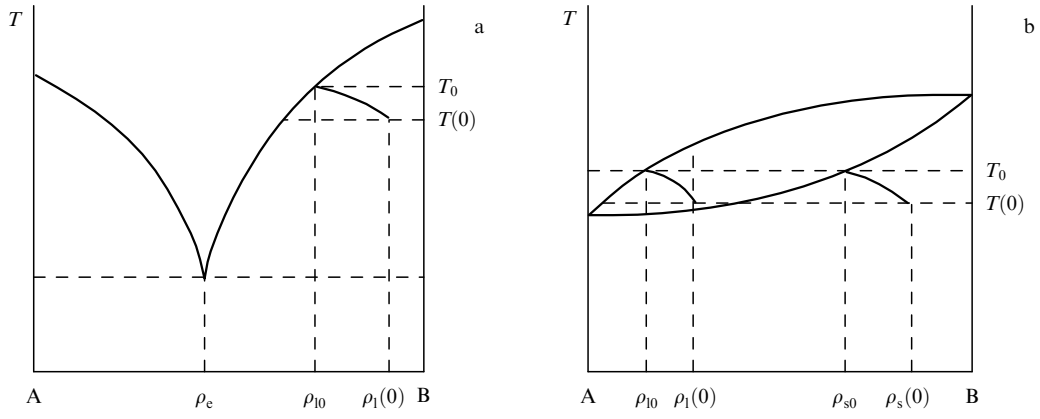

Figure 3. State diagrams of binary systems: (a) system with a eutectic point; (b) system with infinite component solubility in the solid phase; ρ_s and ρ_l are equilibrium concentrations in the solid and liquid phases, respectively; T_0 is an equilibrium temperature, $T(0)$ and $\rho(0)$ are respectively the temperature and the composition at the onset of island growth.

The examination of island growth from single-component melts has shown that the principal mechanisms of island growth are as follows: three-dimensional heat removal into the melt, three-dimensional heat removal into the substrate, and two-dimensional heat removal from the nucleus along the substrate. The limiting stages in this process are the thermal conductivity proper and the mechanism of atomic incorporation into an island, which depends on the crystalline structure of its surface. The general expression for the island growth rate for each heat transfer mechanism takes the form

$$v_R = w\frac{J_{TR}\Psi(\theta)}{qR^{3-d'}}\,, \tag{2.39}$$

where q is the latent heat of phase transition per atom. Concrete expressions for the heat flows and the island growth rates can be found in Refs [17, 107 – 109].

If the islands grow from multicomponent melts, their growth rate is determined by the intensity of substance supply and the intensity of heat removal from their surface. In this case the substance and the heat can be supplied and removed through absolutely different channels. All these possibilities are analyzed in Ref. [17], where the expressions for the growth rates and the flows are also presented. Several fundamental mechanisms of island growth are sketched in Fig. 4.

At the eutectic point, islands of compositions A and B simultaneously precipitate. In the series of works [17, 103, 110, 111] it was established that the growth of nuclei of eutectic composition depends on the sum of supersaturations over all the components. As a result, in a eutectic melt an identical critical radius of the nuclei forms, determined by the supersaturation in both components. In paper [111], we described the properties of a diffusion 'dipole', i.e. a diphase object located in a melt or in a solid solution of eutectic composition, in which two nuclei of distinct compositions are united by a common diffusion field.

Thus, the mechanism of island growth defines its rate v_R which enters the main equations of film condensation kinetics and hence ultimately determines the structure and composition of the growing film, as will be shown below.

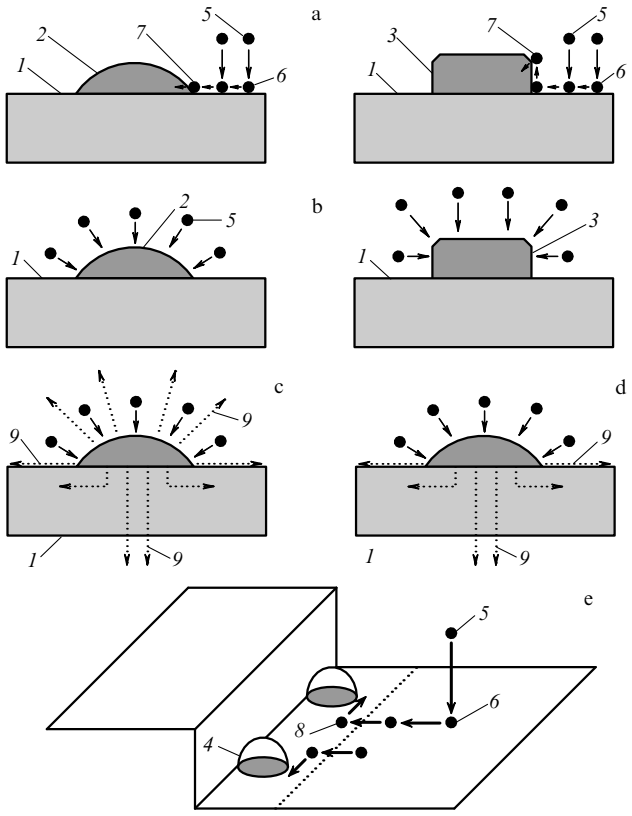

Figure 4. Schematic diagram of the fundamental mechanisms of island drowth: (a) growth of edged and unedged islands, when the limiting stage is the surface diffusion of adatoms; (b) limiting process — the diffusion of atoms in the vapor phase or evaporation-condensation; (c) the growth of unedged islands, when the process is controlled by the entry of atoms from the vapor phase, but the heat removal occurs over all their surfaces; (d) the same, but with the heat removal through the substrate only; (e) the growth of islands through linear diffusion along the steps of the substrate: *1* — substrate, *2* — unedged island, *3* — edged island, to the surface of which atoms join only in specific places, *4* — the island at a substrate step, *5*, *6*, *7*, *8* — the atom in the vapor phase, on the substrate surface, on an island surface, and at a substrate step, respectively, *9* — heat flows.

2.7. Morphological stability

The main problem of the theory of morphological stability is to find out whether a given particular form of a vapor-, solution-, or melt-grown island is stable under small distortions. The analysis of stability is carried out by the following scheme: one assumes the shape of an island or a crystal to be slightly distorted, and then finds out whether this distortion increases or disappears. The necessity of examining stability stems from the fact that crystals often grow in the form of dendrites. Dendrites, or treelike crystals consist of a central trunk and primary, secondary, etc. branches off. They are often observed in nature and in laboratory conditions in melt crystallization. A quantitative analysis of the stability of the form of the growing crystal was first carried out in the classic paper by Mullins and Sekerka [112]. Before the appearance of this paper, the crystal had been assumed to preserve its shape as a whole during growth. Later, Lyubov, Cahn, Cornell, Parker and many other researchers [3, 5, 61 – 63] were engaged in these studies.

Numerous experiments on film growth show that the form of nuclei on the surface changes as they grow. It either becomes edged or, on the contrary, unstable or dendritelike [61, 62, 113]. This fact significantly influences both the nucleation and the Ostwald ripening and, accordingly, the structure of continuous films. The growth of islands on the surface from vapor medium differs noticeably from the melt growth of three-dimensional crystals. This is first of all associated with the fact that deposited atoms are permanently supplied to the substrate surface and, having a finite lifetime (see Section 2.2), leave the surface by evaporating. This introduces essential changes and thus has a crucial effect upon the physics of the process.

In line with Ref. [114] we shall discuss the following particularly simple model. Let us assume the shape of a flat island of height h, growing on a substrate as the result of adatom diffusion, to differ only slightly from the shape of a disc of height h and radius R_0. Then the equation for the island surface in polar coordinates (with the origin at the island centre) will have the form

$$R(\varphi) = R_0\left(1 + \sum_{v=0}^{\infty}\varepsilon_v \cos v\varphi\right), \tag{2.40}$$

where $\varepsilon_v \ll 1$ are the coefficients of the expansion in cosines of the island shape deviation from a disc, and φ is the polar

angle. A change of the quantities ε_v with time means a change in the island shape during its growth. The change of the shape is induced by a competition of two forces. On the one hand, a ledge on the island surface appears to be in the region of higher concentration gradients of adatoms and must, therefore, increase in size. On the other hand, a ledge increases the curvature and thus raises the saturated vapor density at this point, which in turn slows down the growth rate of the ledge compared to the neighbouring points of the nucleus boundary. The analysis of the corresponding diffusion equation [114] has shown that for sufficiently large islands and a small critical radius R_c the equation

$$\frac{d\varepsilon_v}{dt} = \frac{w\sqrt{D_a\tau_r}}{hR_0}\left(J - \frac{n_{1e}}{\tau_r}\right)\left(1 - \frac{R_1}{R_0}\right)\left(\frac{R_2}{R_0} - 1\right)\varepsilon_v \quad (2.41)$$

holds, where R_1 and R_2 are parameters depending on the number of the mode v. If $R_c/\sqrt{D_a\tau_r} \ll 1$, then $R_1(v) = R_c$, $R_2(v) = [(v^2-1)/2]\sqrt{D_a\tau_r}$. For each $v \geqslant 2$, the modes with corresponding numbers increase only in the interval $R_1(v) < R_0 < R_2(v)$ and reach a maximum value ε_v^{max} for $R_0 = R_2$ [114]. The description of the island form evolution and the allowance for additional effects are presented in Ref. [114].

The analysis of the morphological stability of nuclei growing from eutectic melts [111] has shown that the perturbations occurring in the system may cause a change in the nucleus shape if its radius $R > 25R_c$ (R_c is a double critical radius of the eutectic system). The perturbed modes here can be represented in the form of Legendre polynomials $P_n(\cos\theta)$ with odd n. The first to excite is the mode with $n = 3$, then the one with $n = 5$, and so on. It turns out that during nucleus growth from eutectic melts the mode with $n = 3$ dominates, which induces a change in the nucleus shape in the direction perpendicular to its axis. The nuclei then elongate to form strips, flakes or needles. Their lateral branches are typical of nucleus growth from melts of pre-eutectic and post-eutectic compositions.

An interesting parallel between the growth of dendrites and the formation of brittle cracks in an elastic medium (in particular, in a thin film) was revealed in Ref. [115]. At the initial stage of cracking, a brittle material exhibits microcavities (pores) due to expansion and compression stresses, which is analogous to the new-phase nucleation. The cracks themselves result from morphological instability of the form of these microcavities. Viewed like this, a crack is analogous to a crystalline dendrite occurring in a supercooled melt. The critical stresses for which cracking is possible and the geometry of cracking were obtained in the course of a rigorous analysis of morphological instability [115].

2.8 The surface migration of islands

Numerous experimental studies demonstrate that at the initial stages of crystal film condensation on foreign crystalline substrates the nuclei of a new phase can rather rapidly transfer over the substrate surface [4, 116, 117]. This process serves as an important link in the film structure formation [1–3]. Such migrations proceed under the action of various external forces: collisions with fast particles of the flow, the temperature gradient, the electric and magnetic fields, the entrainment by moving steps, etc. As concerns the mechanism of island migration, only two basic models describing the island transfer have been used up to now [4]. In the first, particle diffusion proceeds only across the island surface, and particles attached to the boundary surface remain immobile about it. In the second, an island is assumed to slide over the substrate surface. Many concrete mechanisms of the morphological change of the island and of the sliding process have been proposed, but all of them yield relatively low values for the migration velocity and the diffusion coefficient compared to those actually observed in some cases [116, 117]. In the models of first type this is associated with the low values of the coefficients of self-diffusion of adatoms which cannot provide sufficiently fast island migration. In models of the second type this is caused by the high values of the sliding friction forces between the island and the substrate (i.e. the high activation energy of slide) particularly during epitaxial growth. We have recently proposed [118] an essentially different model of transfer of orientedly growing islands over a foreign substrate. As is well known, under certain conditions mismatch dislocations are generated on the island–substrate interface [119]. If the Burgers vector lies in the slip plane, the motion of the island can be provided by the motion of these dislocations (solitons) [118]. Such a mechanism looks preferable to the usual sliding because during the motion of the dislocation at every instant of time almost all the atoms of the island remain immobile with respect to the substrate, and it is only a very small group of atoms that move. The passage of a dislocation (compression or rarefaction waves) from one end of an island to the other is equivalent to island displacement by one lattice constant of the substrate [118, 120]. If the dislocation (soliton) velocity is much smaller than the velocity of sound in the material of the film, then the energy losses during its motion are very small, i.e. in such displacement of an island there is almost no friction against the substrate. The estimate of the 'effective' mass of an island migrating over a substrate owing to soliton motion takes the form [118]

$$M_{eff} = 4cM \ln\frac{1}{\epsilon - \epsilon_c}, \quad (2.42)$$

where M is the island mass, c is the ratio of forces acting on an atom from the side of other atoms of the island to those from the side of the substrate, ϵ is the parameter of lattice mismatch between the film and substrate, and ϵ_c is the critical lattice mismatch parameter corresponding to the onset of generating mismatch dislocations [118].

3. Kinetics of thin-film condensation at the initial stage

Among the whole variety of processes accompanying thin film growth, the principal one is undoubtedly the new-phase nucleation in islands, i.e. the first-order phase transition proper. It is at this initial stage of condensation that the number of islands of a new phase is determined and the bases of thin-film structure formation are laid.

3.1. Condensation theories for low supersaturations

The description of the real kinetics of new-phase nucleation and the occupation of a condensation surface by the nuclei is one of the most important problems of the theory of first-order surface phase transitions. A large number of papers of both classical and nonclassical direction have been devoted to this issue [7, 8, 30, 31, 55, 121–128]. The corner stone of any theory is a correct account of the nonlinear feedback between supersaturation and the size distribution function of new-phase islands. Indeed, growing islands absorb adatoms and

thus diminish the supersaturation which is responsible for the nucleation rate and the growth rate of the islands, i.e. ultimately for the distribution function [55].

One of the first models describing film condensation kinetics was posed by Zinsmeister [31]. He was the first to investigate the influence of a supersaturation decrease due to cluster growth upon the nucleation kinetics. This model has at least three shortcomings. First, the cluster growth rate is thought of as independent of cluster size. Second, the number of particles in a critical nucleus is always assumed to be equal to unity and not to increase with falling supersaturation (the decay of all the clusters is ignored). Third, the nucleation rate I is assumed to be equal to const $\times n_1^2$ over the entire nucleation stage (the possibility of a spinodal decomposition is neglected altogether). As a result, the island concentration given by the model is greatly overestimated and increases with time without restriction. This model was further developed in many papers where the decay of all the clusters was also disregarded and it was assumed that $I \propto n_1^2$ over the entire film formation stage [1].

A whole number of papers have been devoted to the calculation of the maximum surface cluster concentration $N_{\max}$ by the equation

$$I(N_{\max}) = V_{\text{coal}} N_{\max}^2 , \tag{3.1}$$

where V_{coal} is the rate of pair cluster coalescence (see Section 4.1) calculated from various geometric considerations [122], and I depends in a certain way on $N_{\max}$ through the supersaturation ξ. Such models typically ignore the fact that the limitation on the number of clusters is not only due to coalescence, but largely due to the deterioration of supersaturation and the associated abrupt decrease of the nucleation rate I.

An important step in the development of film condensation kinetics was the model of the rate equations [124]. It is based on the division of all nuclei into subcritical and supercritical and the use of averaged condensation characteristics, such as the average number of particles in supercritical nuclei, the average rate of particle trapping by supercritical nuclei, the average radius of particles, etc. This model is frequently employed in numerical computations [129], which determine various characteristics of condensation. The shortcomings of the model [124] also include the absence of analytical results, the absence of data on the size distribution function of nuclei, as well as a forced assumption of an identical rate of adatom consumption by growing clusters of various sizes.

We should specially mention the nonstandard Kikuchi model which represents the nucleation and thin film growth as an irreducible cooperative process and exploits the so-called path probability method [130]. Kikuchi deduces nine probabilities of various processes, of which three are independent. The variations in a system within the period of time from t to $t + \Delta t$ are determined using the so-called path parameters, which are the probabilities of transitions of one configuration of the system into another. The probability of realizing a change of state determined by a set of path parameters is called the path probability P. The change of the macrostate corresponds to the most probable path defined by the maximum P found from the path parameters for fixed initial conditions. The search for the maximum P leads to kinetic differential equations for three independent probabilities, which bear information on the onset of film formation and on film growth in the pair approximation. The numerical solution of these equations was analyzed in Ref. [130]. The method of path probabilities also determines the equation of state for a system of adatoms on a lattice.

The microscopic theory [131] applies the methods of the modified adsorption theory to the description of the earliest stage of thin film growth. Within its framework one can calculate the time variation of film roughness.

The cluster model [21] describes the nucleation, growth, and coalescence of islands of a new phase using the microscopic stochastic equations reformulated in terms of 'clusters'. 'Clusters' are defined as independent fluctuations of the local order parameter [21]. The division of all the variables into 'relevant' and 'irrelevant' ('irrelevant' properties induce random transitions in 'relevant' coordinates, which are described by the Markov master equation) allows simplification of the kinetic equation. This equation is thoroughly examined in Ref. [21].

The stochastic models [132 – 134] describe the film growth by various approximate stochastic equations. The characteristic feature of such models is the scaling behaviour of various parameters of a growing film, for instance, its roughness.

The ballistic model [135] represents nucleation as a Poisson process and is intended to describe the structure – zone characteristics of a growing film.

The kinetic theory [55, 126] yields analytical expressions for all the basic characteristics of film condensation at the initial stage using specially developed methods for an approximate account of the nonlinear feedback mentioned above.

And finally, the continual model [54] represents thin film condensation as the order-parameter field relaxation, the surface adatom density being the order parameter in this case. This approach is apparently the most general [136 – 139] because it allows a description of film deposition both in terms of nucleation and spinodal decomposition, and for low supersaturations it becomes a standard kinetic model. Furthermore, there is an opinion that it is precisely this approach that will allow us to describe the appearance of the crystalline order during film growth from a vapor or melt.

3.2 Perturbation theory

The variety of approaches to the description of thin film growth is largely due to the impossibility of an exact analytical solution of the main system of equations of film formation in the opening stage, i.e. the system consisting of the equation of conservation of matter on the substrate and the kinetic equation for the size distribution function of nuclei (this system is derived using the division of the whole size axis into three portions: subcritical, critical, and supercritical [55]). Practically all the above-mentioned models apply approximate methods for the solution of this system, which are based on some small parameter of the theory. From the physical point of view, the 'principal' small parameter is the inverse number of particles in a critical nucleus (at the moment of maximal supersaturation). It is just this parameter that stands in the denominator of the nucleation rate exponent. Expanding all the quantities in power series of the small parameter directly, one obtains series that diverge for sufficiently long times, i.e. not uniformly valid series. In order to provide convergence of the series, it is necessary to use a rigorous perturbation theory [140]. It should be noted that the presence of a small parameter does not always allow the solution to be represented in the form of a convergent series,

i.e. it is not always possible to provide a uniform validity of the series by way of a particular renormalization [140]. Therefore, it should be specially emphasized that the system of equations governing kinetics of the first-order phase transition in general and of thin film condensation in particular admits an analytical solution in the form of a power series of the small parameter [128]. The uniform convergence of this series is provided by the time renormalization procedure. We shall consider this technique in more detail.

Let us represent the main system of equations of film condensation kinetics in the following form [55, 141]:

$$\frac{\xi_0}{\xi(t)} - 1 = \frac{(k+1)\tau_r}{n_{1e}t_0}\int_0^\infty \rho^k g(\rho,t)\,d\rho\,, \tag{3.2}$$

$$\frac{\partial g}{\partial t} + \frac{\xi(t)}{t_0}\frac{\partial g}{\partial \rho} = 0\,, \qquad g(0,t) = \frac{I\big(\xi(t)\big)t_0}{\xi(t)}\,, \qquad g(\rho,0) = 0\,. \tag{3.3}$$

Here the term $\tau_r\xi'/\xi$ is ignored because of the smallness of τ_r [55], $\xi(0)$ is assumed to be equal to ξ_0, t_0 is the characteristic cluster growth time involved in the law of growth of stable islands (2.38), and $g(\rho,t)$ is the size distribution function of stable clusters ρ ($\rho = i^{1/(k+1)}$). The merging of the islands and the Ostwald ripening are disregarded in (3.2) and (3.3). In the capillary nucleation model the nucleation rate $I(\xi)$ entering (3.3) has the form [see (2.32), (2.33)]

$$I(\xi) = P(\xi)\exp\big[-H(\xi)\big]\,, \tag{3.4}$$

where H is the nucleation barrier height, and P is the pre-exponential factor depending on supersaturation. The most important parameter Γ of the phenomenological theory is connected with the function H as follows [141]:

$$\Gamma = -\xi_0\left.\frac{dH}{d\xi}\right|_{\xi=\xi_0}. \tag{3.5}$$

For films growing from vapor medium and high values of ξ_0 we have $\Gamma \sim i_c \gg 1$, where i_c is the number of particles in critical nuclei for $\xi = \xi_0$. Consequently, the quantity

$$\varepsilon = \frac{1}{\Gamma} \tag{3.6}$$

is the small parameter of the given problem.

To find the solution of the system (3.2)–(3.4) in the form of a power series in ε, we shall introduce new dimensionless variables

$$x = \frac{\xi_0 t/t_0 - \rho}{\varepsilon}\,, \qquad \tau = \frac{t}{t_0} - \varepsilon\omega_1(\tau) - \varepsilon^2\omega_2(\tau) - \dots \tag{3.7}$$

and represent the functions ξ, g, H in the following way

$$\xi(\tau) = \xi_0\big[1 + \varepsilon\psi_1(\tau) + \varepsilon^2\psi_2(\tau) + \dots\big]^{-1}, \tag{3.8}$$

$$g(x,\tau) = -\varepsilon g\big(\rho(x,\tau), t(\tau)\big) = -\varepsilon g_1(x,\tau) - \varepsilon^2 g_2(x,\tau) - \dots\,, \tag{3.9}$$

$$H\big(\xi(\tau)\big) = H(\xi_0) + \psi_1(\tau) - \varepsilon\big[K\psi_1^2(\tau) - \psi_2(\tau)\big] + \dots\,, \tag{3.10}$$

where

$$K = 1 - \frac{\xi_0^2}{\Gamma}\left.\frac{d^2H}{d\xi^2}\right|_{\xi=\xi_0}.$$

To avoid the appearance of secular terms, the expansion of ξ in ε is chosen in the form of series (3.8). According to the rigorous perturbation theory [140], the functions $\omega_1, \omega_2, \dots$ participating in the time renormalization (3.7) should be chosen so as to cancel the secular summands in the expansion (3.9). Substituting (3.7)–(3.10) into (3.2)–(3.4) and equating the coefficients of terms with equal powers of ε, one can readily obtain the equation describing the evolution of the quantities ψ_1, g_1, ψ_2, g_2, etc. In particular, in the first order in ε we have

$$\psi_1(\tau) = \frac{(k+1)\tau_r\xi_0^k}{n_{1e}t_0}\tau^k\int_{-\infty}^{b_0(\tau)} g_1(x,\tau)\,dx\,, \tag{3.11}$$

$$\frac{\partial g_1}{\partial \tau} + \xi_0\psi_1\frac{\partial g_1}{\partial x} = 0\,, \quad g_1\big(b_0(\tau),\tau\big) = \frac{I(\xi_0)t_0}{\xi_0}\exp\big[-\psi_1(\tau)\big]\,, \quad g_1(x,0) = 0\,. \tag{3.12}$$

In the second-order approximation, the equation for g_2 takes the form

$$\frac{\partial g_2}{\partial \tau} + \xi_0\psi_1\frac{\partial g_2}{\partial x} + \xi_0\psi_2\frac{\partial g_1}{\partial x} - (\omega_1' - \psi_1)\frac{\partial g_1}{\partial \tau} = 0\,. \tag{3.13}$$

The secular term $(\omega_1' - \psi_1)\partial g_1/\partial\tau$ responsible for the divergence can be eliminated by putting

$$\omega_1(\tau) = \int_0^\tau \psi_1(\tau')\,d\tau'\,. \tag{3.14}$$

Repeating this procedure for the other powers of ε, it is easy to find ω_2, ω_3, etc., for example, one obtains

$$\omega_2(\tau) = \int_0^\tau \frac{\psi_2^2(\tau')}{\psi_1(\tau')}\,d\tau'\,.$$

This provides convergence of the series for all t. Our further calculations will be restricted to the first order in ε. This approximation suffices for many purposes because it is valid over the entire time variation region. Obviously, the system of equations (3.11), (3.12) is appreciably simpler than (3.2), (3.3) and can be readily solved analytically. All the unknown functions will be expressed here in terms of the auxiliary function $\varphi_k(x)$ specified by the equation

$$\frac{d\varphi_k}{dx} = \exp(-x^k\varphi_k)\,, \qquad \varphi_k(0) = 0\,. \tag{3.15}$$

The dependence of φ_k on x is plotted in Fig. 5. We shall only present the net result to the first approximation in powers of ε [128]:

$$\xi(t) = \frac{\xi_0}{1 + (1/\Gamma)T^k(t)\,\varphi_k\big(T(t)\big)}\,, \tag{3.16}$$

$$I(t) = I(\xi_0)\frac{\exp\big[-T^k(t)\varphi_k(T(t))\big]}{1 + (1/\Gamma)T^k(t)\varphi_k(T(t))}\,, \tag{3.17}$$

$$N(t) = I(\xi_0)t_k\varphi_k\big(T(t)\big)\,, \tag{3.18}$$

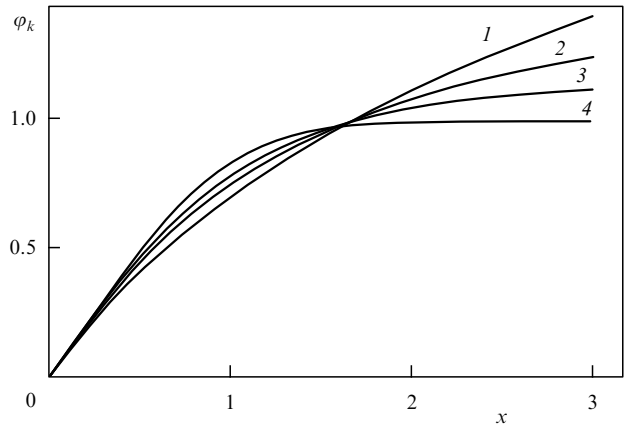

Figure 5. Dependence of the function φ_k on x: *1* — $k = 0$; *2* — $k = 1/2$; *3* — $k = 1$; *4* — $k = 2$.

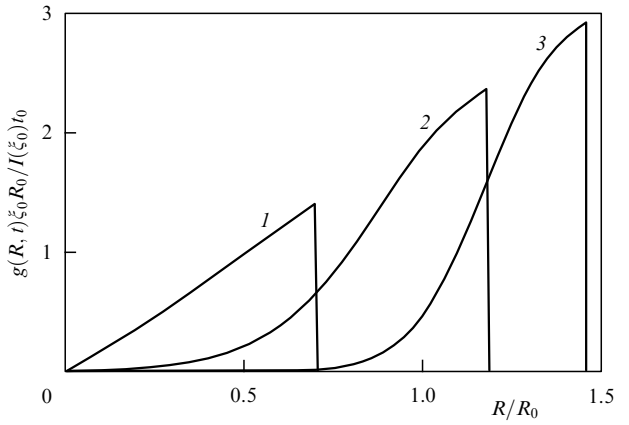

Figure 7. Size distribution function of new-phase islands for $\Gamma = 10$, $k = 2$: *1* — $t = 0.54t_k$; *2* — $t = 1.7t_k$; *3* — $t = 4.4t_k$.

$$g(\rho, t) = \begin{cases} \dfrac{I(\xi_0)t_0}{\xi_0}\exp\left[-\left(T(t) - \dfrac{t_0\rho}{t_k\xi_0}\right)^k \varphi_k\left(T(t) - \dfrac{t_0\rho}{t_k\xi_0}\right)\right], & \rho \leqslant \xi_0 \dfrac{t_k}{t_0} T(t)\,, \\ 0, & \rho > \xi_0 \dfrac{t_k}{t_0} T(t)\,, \end{cases} \tag{3.19}$$

$$T = \frac{t}{t_k} - \frac{1}{\Gamma}\int_0^T x^k \varphi_k(x)\,\mathrm{d}x\,,$$
$$t_k = \frac{t_0}{\xi_0}\left[\frac{n_{1e}\xi_0}{(k+1)\Gamma I(\xi_0)\tau}\right]^{1/(k+1)}. \tag{3.20}$$

The time dependences of the nucleation rate and the size distribution function of new-phase islands are illustrated in Figs 6, 7. The results obtained agree well with those of the phenomenological kinetic model [55] (with a distinction of the order of 20%), but the present ones are asymptotically exact. For example, in the framework of the phenomenological theory, the denominator in expression (3.17) should be put equal to unity because it yields much more weaker dependence on t than the exponent of $H(\xi(t))$. Nevertheless, within the perturbation theory it is rigorously calculated because for long times it changes the asymptotics of the function $I(t)$. The quantities ψ_1, g_1, and ω_1 having been found, one can, in principle, calculate ψ_2, g_2, ω_2, etc. The same method can be used to describe the growth of multicomponent films as well as inhomogeneity effects [128]. The shortcoming of the small parameter technique is the impossibility of describing a phase transition for arbitrary τ_r, Γ, and t_0, which can only be done numerically by solving the equations of condensation kinetics (3.2), (3.3).

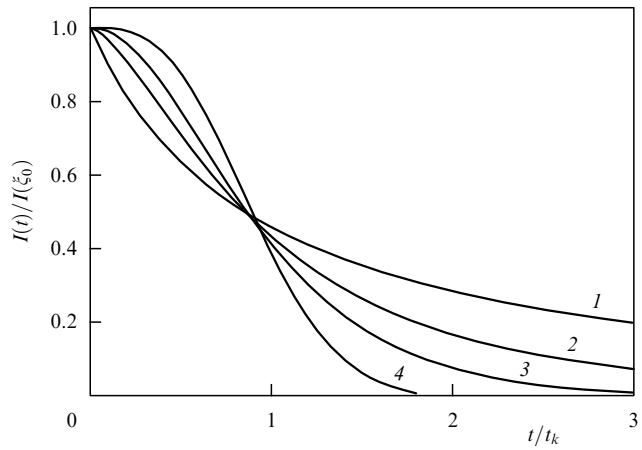

Figure 6. Time dependence of the nucleation rate for $\Gamma = 10$: *1* — $k = 0$; *2* — $k = 1/2$; *3* — $k = 1$; *4* — $k = 2$.

3.3 Film condensation upon high supersaturation

If the external source of deposited particles has a large power such that a one-particle nucleus is energetically more advantageous than a two-particle nucleus, i.e. $F(2) > F(1)$, then in the ensemble of adatoms a spinodal decomposition starts [21, 32, 54]. Any thermodynamic fluctuations increase in this case, the long-wave fluctuations increasing faster. A theory of spinodal decomposition in a system of adatoms was formulated in Ref. [54].

If the external source of deposited particles has such a power that in a metastable system it creates a supersaturation ξ close to $\xi_{\max}$, which corresponds to approximately $i_c = 2 - 4$, then the character of the nucleation process radically changes. Firstly, the correlation radius in the system may exceed the average cluster size (for $i_c = 1$ the correlation radius is equal to infinity). Secondly, the distribution of subcritical nuclei may be other than equilibrium, and, thirdly, for small i_c the structure of critical nuclei and, therefore, the character of the interphase energy significantly change. Hence, strongly metastable systems should be considered separately [142, 143]. It is appropriate to describe them in the framework of the continual theory [54], which represents a phase transition as a relaxation of the order-parameter field φ:

$$\gamma\frac{\partial\varphi}{\partial t} = -\frac{\delta\Omega}{\delta\varphi} + f_*\,, \tag{3.21}$$

where γ is the kinetic coefficient, Ω is the grand thermodynamic potential, and f_* is a random force describing thermal fluctuations [32, 54]. Let us represent the function $E(s)$ entering (2.10) in the form of a series in the neighbourhood of the point $s_0 = -\sqrt{1 - T/T_c}$ corresponding to the boundary of a metastable region ($s_0 = 2n_{1s} - 1$, $E''(s_0) = 0$):

$$E(s) = E(s_0) + \frac{\lambda_c - \lambda}{2}(s - s_0) - \frac{h_0}{6}(s - s_0)^3 + \ldots\,, \tag{3.22}$$

where $h_0 = -E'''(s_0) = 2(T_c/T)^2\sqrt{1 - T/T_c}$, and λ_c is the critical value of the parameter of metastability which corresponds to ξ_{max}. Assuming the supersaturation to be sufficiently close to ξ_{max} for s to be close to s_0, we shall restrict our consideration to the first three summands in (3.22). Following Ref. [54], we shall introduce the variable $\varphi = (s - s_0)/s_*$, where $s_* = [(\lambda_c - \lambda)/h_0]^{1/2}$, and measure the length in the units $R_* = R_s\{2(T_c/T)[h_0(\lambda_c - \lambda)]^{-1/2}\}^{1/2}$ and the energy in the units $E_* = k_B T_c n_0 R_s^2(\lambda_c - \lambda)/2h_0$. Then the grand thermodynamic potential of the system will take the form

$$\Omega[\varphi] = \int \left[\frac{\nabla\varphi^2}{2} + 2\varphi\left(1 - \frac{\varphi^2}{3}\right)\right] d\mathbf{r} + \text{const}. \qquad (3.23)$$

The value $\varphi = -1$ describes a homogeneous equilibrium state of adatoms in these variables. Measuring the time in the units $t_* = 2/(\gamma k_B T_c n_0 R_s^2)$ and f_* in the units E_*/s_*, we shall write the equation of the order-parameter field relaxation in the form [54]

$$\frac{\partial\varphi}{\partial t} = \Delta\varphi + 2(\varphi^2 - 1) + f_*. \qquad (3.24)$$

Equation (3.24) does not depend on any parameters of the thermodynamic potential, and therefore the phase transition kinetics in the vicinity of the spinodal is described similarly for any real $E(s)$ (only the units of measurements are changed). This equation was thoroughly examined for the two-dimensional case in Ref. [54]. In particular, the equilibrium configuration φ_c describing the critical nucleus was determined, the spectrum of a linearized kinetic operator and the corresponding eigenfunctions were found and the nucleation rate was calculated.

Thus, there exist three ways of relaxation of a supersaturated adatom population. The first is realized in weakly metastable systems where the supersaturation ξ is much lower than $\xi_{max} = n_{1s}/n_{1e} - 1$. In this case the critical nucleus is so large ($i_c \gg 1$) that its fluctuations lead to a change of only the coordinate of its boundary, although it has a considerable thickness. The structure of the nucleus itself will remain unchanged. In this event it is convenient to apply the capillary model, in particular, formula (2.32). The second way of relaxation takes place for $\xi \leqslant \xi_{max}$. Here the critical nucleus contains only a few particles and is so small that its fluctuations affect not only the boundary, but the whole nucleus. In other words, the internal structure of the critical nucleus itself changes during fluctuations. The nucleation rate in this case depends on the supersaturation as

$$I(\xi) = I(\xi_{max}) \exp\left[-\text{const}(\xi_{max} - \xi)^2\right]. \qquad (3.25)$$

And, finally, the third way of relaxation lies through spinodal decomposition. It is realized for $\xi \geqslant \xi_{max}$. In this event the system is unstable, $i_c = 1$, and thermal fluctuations generally destroy the structure of critical nuclei and lead to an increase of periodic fluctuations of substance concentration. This periodicity is a consequence of the fact that near a growing new-phase island no other islands are produced, and the whole ensemble of islands is strongly interacting [54].

3.4 The kinetics of film condensation from a solution-melt

Let us consider a pure single-component melt with a crystallization temperature T_c. If the melt is supercooled, i.e. its temperature is below T_c, the formation of a solid phase begins in it [59, 144–146]. The rate of this process increases sharply with elevation of supercooling [146]. If a foreign substrate is placed in a supercooled melt, it may initiate new-phase nucleation even for fairly low degrees of supercooling. Moreover, if heat is removed from the substrate, nucleation will begin even in a superheated melt with a temperature above T_c, because the substrate forms a layer of supercooled melt around itself.

In some liquid-phase epitaxy methods, a substrate is rotated in a melt. As is shown in Ref. [17], in order to make the control over the ensemble of new-phase nuclei occurring on the substrate easier, it is necessary to rotate the substrate parallel to the melt plane with a constant frequency ω. Then a boundary layer with a thickness of the order of $(\nu/\omega)^{1/2}$, where ν is the kinematic viscosity, appears around the substrate. This boundary layer noticeably affects the temperature distribution around the substrate and sometimes results in the onset of the Ostwald ripening stage [17]. It is conventional to think that a cooled substrate initiates new-phase nucleation only in a narrow melt layer of thickness λ_{eff}, adjoining the condensation surface and intimately related to it. The ensemble of new-phase islands generated in this layer further forms a thin crystalline film on the substrate surface. If the melt temperature in this layer is assumed to be unchanged and equal to T (this nucleation layer is analogous to a layer of adsorbed particles in a vapor-grown film), the process of film nucleation from a melt will be identical to the growth from a vapor. Indeed, the main system of equations of film crystallization, which consists of the law of heat conservation in the near-surface layer and the kinetic equation for the distribution function of nuclei by size, is completely analogous to the corresponding system of equations for a vapor (they differ only in coefficients) [5, 146]. It can be solved, in particular, with the help of the perturbation theory considered above. In this case one finds the time dependences of the supersaturation $\xi = (T_c - T)/T_c$, of the nucleation rate, of the nucleus surface concentration, size distribution, etc.

A single-component film can be obtained not only from a pure melt of a given substance, but also from a melt with a considerable fraction of impurity or solvent that forms eutectics with the film material. In a certain range of temperatures (from the pure material crystallization temperature to the temperature of the eutectics) and concentrations (exceeding saturation level), a given substance can also be crystallized from a binary solution-melt. However, as follows from the general theory of cluster growth from a binary melt [17], the growth mechanism will differ from the preceding case. Indeed, the driving force of the crystallization process is now supersaturation rather than supercooling, and the islands now grow owing to diffusion rather than thermal conductivity. The process of film nucleation from a solution is therefore much slower than that from a melt, and under identical nucleation conditions a solution-grown film has finer grains than a melt-grown one. Using perturbation theory one can also calculate here all the basic characteristics of condensation [146].

Thus, in the film nucleation from a solution-melt, the driving force of new-phase island formation is supercooling or supersaturation in a thin nucleation layer surrounding the substrate and the clusters that grow on it. The effective thickness of this layer is determined by the character of interparticle interaction of substrate molecules, of molecules from the solid and the liquid phases. The flow of substance

from the solution into this layer (or a heat flow from the melt) depends on the properties of the boundary layer of the liquid phase surrounding the substrate and induced by substrate rotation in a viscous medium [146]. Changing the velocity of rotation one can change the relaxation time τ of the driving force of nucleation and, thus, change the number of generated islands. In solutions, for a constant ξ_0 an increase of ω lowers τ and raises N. In melts, an increase of ω at a constant melt temperature T_∞ far from the substrate lowers ξ_0 and, therefore, $I(\xi_0)$ and N. Consequently, in this case an increase of ω makes the film more large-grained. Mathematically, the nucleation of films from melts, solutions, and vapor proceeds identically. However, the rate of variation of the driving force of phase transition and its duration differ strongly in all the three cases, because the thermal diffusivity χ in a melt greatly exceeds the diffusion coefficient D in a solution and the latter, in turn, is much larger than the coefficient D_a of adatom diffusion across the substrate (customarily, $\chi \sim 10^{-6}\,\mathrm{m^2\,s^{-1}}$, $D \sim 10^{-9}\,\mathrm{m^2\,s^{-1}}$, and $D_a \sim 10^{-12}\,\mathrm{m^2\,s^{-1}}$). This leads to the fact that a melt-grown film is the most large-grained, while a vapor-grown one is the most fine-grained [146]. Such a conclusion is confirmed by many experimental results on the study of initial film growth stages [1–4].

3.5 Multicomponent nucleation

If an adsorbed vapor is multicomponent, the nuclei grown from it will also be multicomponent, their most probable composition being determined by the minimum free energy of nucleation [80]. Let us estimate the mean time t_p of particle involvement into a phase transition. For the rate of particle attachment to a nucleus $I_a \sim 10^{20}\,\mathrm{m^{-2}\,s^{-1}}$ and the surface concentration of adsorbed particles $n_1 \sim 10^{17}\,\mathrm{m^{-2}}$, we have $t_p \sim n_1/I_a \sim 10^{-3}\,\mathrm{s}$. As the supersaturation elevates, the quantity t_p rapidly decreases. Simultaneously with this process, adatoms can undergo a chemical reaction [147]. In the lattice model of adsorbed gas, the mean time t_c of particle involvement into a chemical reaction is estimated as $(D_a n_1)^{-1} \exp(E_c/RT)$, where E_c is the chemical reaction activation energy, R is a molar gas constant, T is the vapor temperature, and D_a is the coefficient of particle diffusion across the substrate. For high-rate chemical reactions with $E_c = 10$ kkal mol^{-1} at $T = 500$ K and $n = 10^{17}\,\mathrm{m^{-2}}$, $D_a = 10^{-12}\,\mathrm{m^2\,s^{-1}}$ we obtain $t_c \sim 0.2\,\mathrm{s}$, that is, $t_p \ll t_c$. For sluggish and moderate-rate reactions with $E_c \sim 15$–40 kkal mol^{-1}, the t_c is still higher.

Thus, if a system is supersaturated, the first to occur is generally a phase transition and only after does a chemical reaction begin. Very high-rate (ionic type) reactions with $E_c < 5$ kkal mol^{-1} are an exception, but such reactions do not frequently occur in the vapor growth of solid films. If however $t_c \ll t_p$, the first to occur is a chemical reaction and only afterwards a film is condensed from the single-component vapor produced in the reaction. Such single-component film nucleation is a particular case of the multicomponent nucleation, in which supersaturation sets-in only in a chemical reaction. Accordingly, for certainty one can assume that $t_p \ll t_c$. In this case, the boundary of the concentration region in which condensation proceeds from a multicomponent vapor has the form $H^{-1} = 0$, where H is the activation barrier height.

We shall show how H can be calculated for the nucleation from a multicomponent vapor. Since a chemical reaction in a vapor has not yet begun, the new-phase nuclei make up a mixture of particles of different components. We shall assume such a mixture to be a regular solid solution. Let m be the number of vapor components, and $i_1, i_2, \ldots, i_m$ the number of particles of each component in a nucleus. Then the free nucleation energy F expressed in the thermal units $k_B T$ is equal to [85]

$$F(i_1,\ldots,i_m) = \sigma(i_1,\ldots,i_m)S - \sum_{j=1}^{m} i_j \ln\frac{n_j}{n_{j\text{e}}(i_1,\ldots,i_m)} - \ln\frac{n_0}{\sum_{j=1}^{m} n_j}\,, \tag{3.26}$$

where σ is the specific interphase energy, S is the area of the nucleus phase boundary, n_j is the surface concentration of the component j, $n_{j\text{e}}$ is the vapor concentration of the component j which is in equilibrium with the nucleus of this particular composition, and n_0 is the concentration of the lattice sites on which atoms are adsorbed. The nucleus composition is determined by the set of molar concentrations $\{v_k\}$ of each component, where

$$v_k = \frac{i_k}{\sum_{j=1}^{m} i_j}\,, \qquad \sum_{j=1}^{m} v_j = 1\,. \tag{3.27}$$

The dependence of σ and $n_{j\text{e}}$ on v_k for a regular solid solution with a given heat of mixing of components is calculated within the thermodynamic theory of solutions [148]. In particular, if a nucleus is an ideal solution then

$$\sigma = \sum_{j=1}^{m} \sigma_j v_j\,, \qquad n_{j\text{e}} = n^0_{j\text{e}} v_j\,, \tag{3.28}$$

where σ_j and $n^0_{j\text{e}}$ are the interphase energies and densities of a saturated vapor of pure components. Solution of the system of equations $\partial F/\partial i_j = 0$ gives the number of particles of each component $i_{j\text{c}}$ in the critical nucleus, after which one can readily calculate the height of the activation barrier $H = F(i_{1\text{c}},\ldots,i_{m\text{c}})$. The equation $H^{-1}(n_1,\ldots,n_m) = 0$ specifies the surface that separates the regions of concentrations with and without nucleation. In the simplest case of an ideal solution with equal σ_j, this equation takes the form [147]

$$\sum_{j=1}^{m} \frac{n_j}{n^0_{j\text{e}}} = 1\,. \tag{3.29}$$

Along with nuclei containing all m components, those involving a smaller number of components can be formed on the substrate, and therefore the whole range of concentration variation is divided into different phase regions with the help of $2^m - 1$ interfaces of the type $H^{-1}(n_j) = 0$, $H^{-1}(n_j, n_k) = 0$, etc. In particular, for $m = 2$, three dividing lines $H^{-1}(n_1) = 0$ $(n_1 = n^0_{1\text{e}})$, $H^{-1}(n_2) = 0$ $(n_2 = n^0_{2\text{e}})$, and $H^{-1}(n_1, n_2) = 0$ specify five phase regions (Fig. 8).

In region a no new-phase formation is observed, in region b only two-component islands nucleate, in region c two-component islands and those of the atoms of the second component, in region d two-component islands and those of the atoms of first component, and in region e two-component islands and islands of the atoms of each component (the nucleation rate for islands of a mixture is as a rule much higher than the single-component nucleation rate). In the newly appeared islands of a new phase a reaction begins among the components or (if the components cannot make up a chemical compound) a eutectic decay, or the formation of a

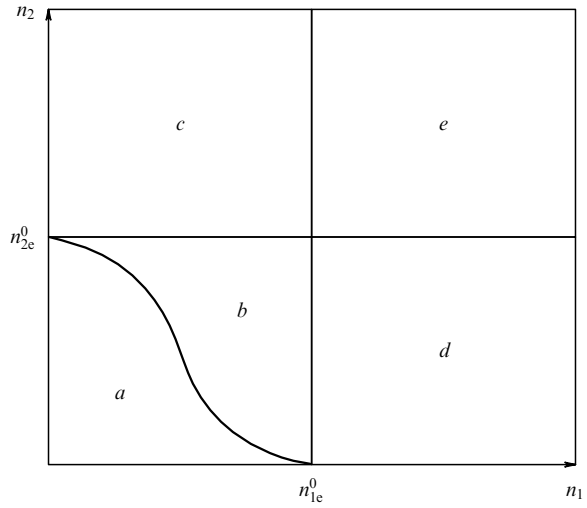

Figure 8. Phase diagram of a binary system.

solid solution. The behaviour of the system is determined by the type of the corresponding state diagram for a solid mixture. In particular, for a binary system there exist five main types of state diagrams for a solid mixture [5, 147]. All possible cases of condensation are accordingly divided into 25 variants. All of them are considered in detail in Ref. [147]. Systems with three or more components are analyzed similarly but with a significantly greater number of versions.

The analysis of the behaviour of an ensemble of adsorbed particles shows that all the versions of multicomponent film condensation make up a set of processes, each proceeding at a certain stage [147]. We shall enumerate the processes that play the key role:

(1) chemical reaction in an adsorbed multicomponent gas with a simultaneous nucleation of the final product of the reaction;

(2) formation of nuclei representing a mixture of components;

(3) chemical reaction in such nuclei;

(4) growth of islands of a new phase from a supersaturated adsorbed vapor;

(5) separation of a eutectic mixture;

(6) evaporation of nuclei.

The methods of description of processes 1–6 are presented in Ref. [5].

3.6 Computer simulation of film growth

All the methods of computer simulation can conditionally be divided into three main types:

(1) analytical simulation, which is a numerical solution to the equations of the theories of nucleation and growth of films;

(2) statistical simulation employing the Monte-Carlo or molecular dynamics methods as well as various random processes for the description of the behaviour of atoms or clusters;

(3) stochastic simulation based on the solution of nonlinear stochastic differential equations that generalize the Langevin equation.

Models of the first type were utilized in the classical papers [8, 124], their modern modifications appeared in Refs [129, 149] and in the works [150–154] devoted to the evolution of an ensemble of decorated substrate steps. A great many of papers on numerical simulation of film growth pertain to the second type (see, for example, Refs [155–165]). The advantages and disadvantages of the majority of the models, as well as the results obtained in their terms are discussed in the review [165]. It should be emphasized that a common shortfall of statistical models is a disregard of the possible decay of subcritical nuclei. The increase in the number of particles in critical nuclei and the decrease of the nucleation rate, which both are induced by a lowering of the supersaturation during condensation, are thus ignored. The papers assuming $i_c = 1$ (i.e. a two-particle nucleus never decays and is thought of only as growing) generally describe the spinodal decomposition of an unstable adatom population rather than nucleation in a metastable system, as was claimed in the statement of the problem.

The works on stochastic simulation largely investigate the time evolution of a rough film surface [132–135]. The classification and the description of various stochastic approaches are presented in the review [166]. The most frequently applied model is that due to Kardar, Parisi, and Zhang [167] according to which the profile of a growing surface is specified by the equation

$$\frac{\partial h(\mathbf{x},t)}{\partial t} = D_{\text{eff}}\Delta h + \frac{\varkappa_0}{2}(\nabla h)^2 + \eta_0(\mathbf{x},t)\,. \tag{3.30}$$

Here $h(\mathbf{x},t)$ is the film thickness at a point $\mathbf{x}$ at an instant of time t, D_{eff} is the effective diffusion coefficient, $\varkappa_0$ is the constant determining the lateral growth rate, and η_0 is a random variable related to a random particle flux onto the substrate. The system was shown to obey the law of dynamic scaling

$$\omega_s \equiv \sqrt{\langle \overline{h^2} - \bar{h}^2 \rangle} \approx L^{\alpha} f\left(\frac{t}{L^z}\right). \tag{3.31}$$

Here ω_s is the mean thickness of a growing surface, L is the substrate size, and α and z are the scaling factors typical of a particular model.

In conclusion we note that the scaling behaviour is inherent in many quantities describing nucleation and growth processes [5, 37], namely, the size distribution of nuclei in the course of liquid coalescence [158, 168] and at the Ostwald ripening stage [17], the new-phase island growth rate [169–175], the distribution over the spacing between them [176], the interface thickness [167], etc.

3.7 Comparison with experiment

We shall first compare the theory with experiment at the initial stage of film nucleation from vapor. It should be immediately stressed that a sufficiently complete quantitative comparison is impossible in this case because of the high level of errors in both theoretical and experimental data. Therefore only a qualitative comparison can be made. The linear dependence of n_{1e} on $1/T$ is experimentally confirmed, for example, for the systems Au/NaCl and Au/KCl [69, 70] as well as for some semiconducting films [177], which makes it possible to estimate the quantity T_c (see Section 1.3). The dependence of n_{1s} on T has not obviously been measured, and it is hence impossible to compare this dependence and $\xi_{\max}(T)$ with experiment. The dependence of the nucleation rate I on the temperature T and the rate J of particle supply to the substrate is fairly involved. In many cases, however, we can restrict ourselves using the exponential approximation according to which the whole dependence of I on ξ and T is

expressed in terms of $\exp[-H(\xi)/k_B T]$. The pre-exponential factors are then assumed to be constants, i.e. one obtains

$$I = I_p \exp\left[-\frac{H(\xi)}{k_B T}\right]. \tag{3.32}$$

In particular, for cap-shaped nuclei with a curvature-independent interphase energy we have $H/k_B T = b'/(k_B T)^3 \times \ln^2(J\tau_r/n_{1e})$, where $b' = 4\pi\varepsilon^3 w(2+\cos\theta)(1-\cos\theta)^2/3$. Taking into account the dependences of τ_r and n_{1e} on T: $\tau_r = \tau_{r0}\exp(E_a/k_B T)$, $n_{1e} = n_0\exp(-2T_c/T)$, where E_a is the desorption activation energy, we find from (3.32)

$$\ln\frac{I}{I_p} = -\frac{T_I}{T}, \qquad T_I = \frac{b'/k_B}{\left[E_a + 2k_B T_c + k_B \bar{T}\ln(J\tau_{r0}/n_0)\right]^2}, \tag{3.33}$$

where $\bar{T}$ is the mean temperature in the investigated interval (the use of a mean temperature is justified only if $k_B(T-\bar{T})\ln(J\tau_{r0}/n_0) \ll E_a + 2k_B T_c$). The linear dependence of $\ln I$ on $1/T$ has been observed in very many experiments (see, for example, the references in the reviews [1–4, 8]). The measurement of the inclination of this straight line allows one to find from experimental data the quantity b', which is the basic constant in the capillary nucleation theory (dependence (3.33) with a different T_I is valid for disk-shaped clusters as well). The dependence of I on J at constant T is also given by formula (3.33) with $\bar{T} = T$. It contains two parameters and agrees well with the experimental curves presented, for instance, in Ref. [8]. Accounting for the preexponential factors changes formula (3.33) only slightly.

It should be stressed that the atomistic Walton model [29] also leads to a linear dependence of $\ln I$ on $1/T$ with a disregard of the dependence of i_c on T. Some authors who believe that in their experiments the quantity i_c is very small (it is most often assumed that $i_c = 1$), compare their data with the Walton model for small i_c and claim a good agreement between the theoretical and experimental data. The results of such a verification should apparently be treated with scepticism, first, because actually i_c strongly depends on T and, second, because the time within which $i_c = \text{const}$ is typically extremely short, and within such a short time it is thus impossible to measure the rate of appearance of very small nuclei (for large i_c it is much simpler to carry out such experiments). Third, if $i_c = 1$ then the new-phase clusters in the usual sense of the word are altogether absent. There are only periodic changes of concentration with increasing amplitude, and the period of these changes is determined by the maximum of the gain factor [32] (and so it is unclear what exactly the experimenters registered in this case). We emphasize that in systems where i_c is indeed equal to unity, the structure of the new phase is absolutely different from that in ordinary nucleation. Some cases of solid solution decomposition or binary melt crystallization [32, 62] may serve as examples. The temperature dependence of the maximum cluster concentration for $m > 1$ and at sufficiently high T is determined from (3.18) in the exponential approximation

$$N_{max} = N_p\left(\frac{I}{I_p}\right)^{(m-1)/m}, \tag{3.34}$$

where $N_p = \text{const}$, and m is the cluster growth index, from which we find

$$\ln\frac{N_{max}}{N_p} = -\frac{m-1}{m}\frac{T_I}{T}. \tag{3.35}$$

For $m = 1$, the increase of the number of clusters is restricted not only by a decrease of supersaturation, but also by coalescence (see Section 4.1). From Eqns (3.33) and (3.35) it follows that comparing the inclination of the dependences of $\ln(I/I_p)$ on $1/T$ and $\ln(N_{max}/N_p)$ on $1/T$ for one and the same J, one can find the quantity m from experimental data and, therefore, establish the cluster growth mechanism. It should be stressed that with temperature variation the growth mechanisms may at times change, which is explained by a strong temperature dependence of the kinetic coefficients (in this case the dependence of $\ln(N_{max}/N_p)$ on $1/T$ has the form of a broken line). Dependence (3.35) is also confirmed by a large number of experimental data obtained for different materials [1–4, 8]. The dependence of N_{max} on J at constant T is also given by formula (3.35) with allowance for the dependence of T_I on J. In particular, for cap-shaped nuclei we find from (3.35)

$$\ln\frac{N_{max}}{N_p} = -\frac{\text{const}}{(\text{const} + \ln J)^2}. \tag{3.36}$$

Selecting two constants entering (3.36), one can readily make this dependence coincident with the experimental results.

It has already been pointed out that because of the short duration of the nucleation stage and the small nucleus size it is extremely difficult to obtain reliable experimental data on the nucleation rate, the size distribution of nuclei, etc. for the vapor-grown films (for the solution-melt growth of films the nucleation stage is still shorter). Nevertheless, there exist systems in which the first-order phase transition is rather long ($10^2 - 10^4$ s) and the nuclei are rather large (10^{-5} m). Such systems are perfectly suited to comparison of the theory with experiment. One such system is a lead zirconate–titanate film in which the first-order phase transition from the pyrochlore phase through nucleation into a new perovskite phase is observed at a temperature above 710 K [178]. The high value of the effective heat of phase transition caused by substantial mechanical stresses in the film and by the piezoeffect leads to fairly slow nucleus growth (owing to thermal conductivity) and a large nucleus size [178].

With the purpose of verifying the above-mentioned theoretical results, a special series of experiments was carried out that determined the dependences of all the basic characteristics of phase transition on time and on the maximum relative superheating ξ_0 (an analog of initial supersaturation) [178]. Figures 9–13 present the experimental data obtained together with the theoretical findings. The difference between them does not as a rule exceed 7%, which testifies to the high degree of their accord. The decrease of the number of new-phase nuclei after 7000 s of heating in Fig. 10 is explained by liquidlike coalescence (see Section 4.1). The inclination of the dependence of $\ln I$ on $1/\xi_0^2$ in Fig. 11 is twice that for the dependence of $\ln N_{max}$ on $1/\xi_0^2$ shown in Fig. 12, and therefore the cluster growth index m is equal to two [see Eqns (3.33), (3.35)], which completely coincides with the data of direct observation: $m = 2.02 \pm 0.05$. The size distribution function of new-phase islands demonstrated in Fig. 13 also agrees well with the corresponding theoretical result (3.19) [178].

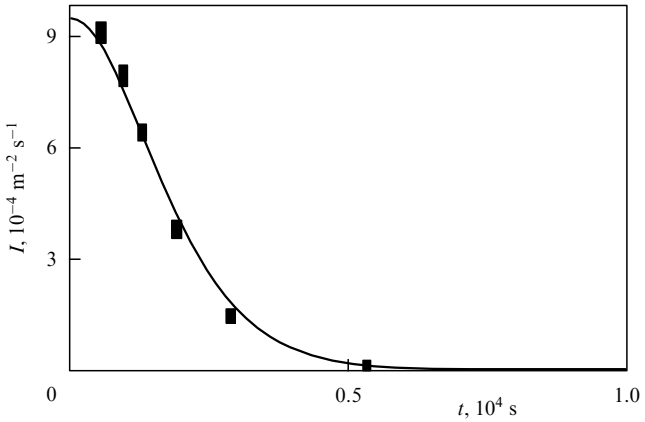

Figure 9. Time dependence of the nucleation rate for $\xi_0 = 0.1$ (solid line — theory, rectangles — experiment).

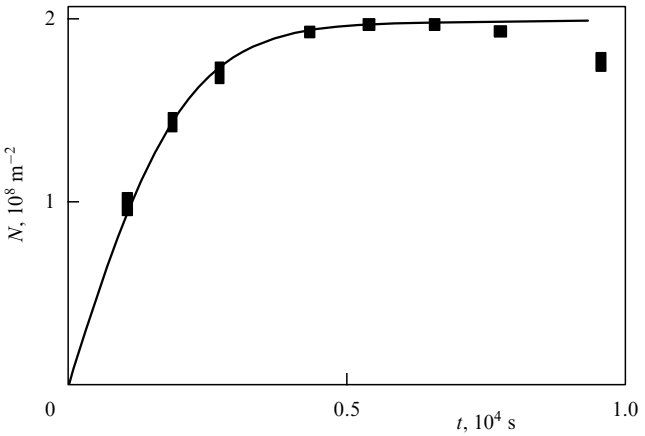

Figure 10. Time dependence of nucleus concentration for $\xi_0 = 0.1$ (solid line — theory, rectangles — experiment).

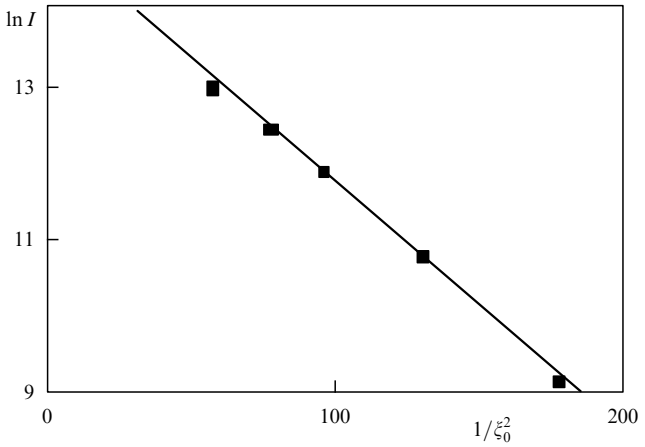

Figure 11. Dependence of the nucleation rate (in m^2 s^{-1}) on relative superheating (solid line — theory, rectangles — experiment).

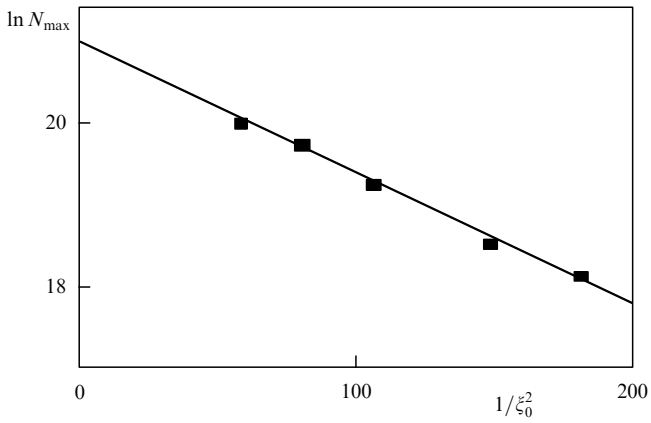

Figure 12. Dependence of the maximum nucleus concentration (in m^{-2}) on relative superheating (solid line — theory, rectangles — experiment).

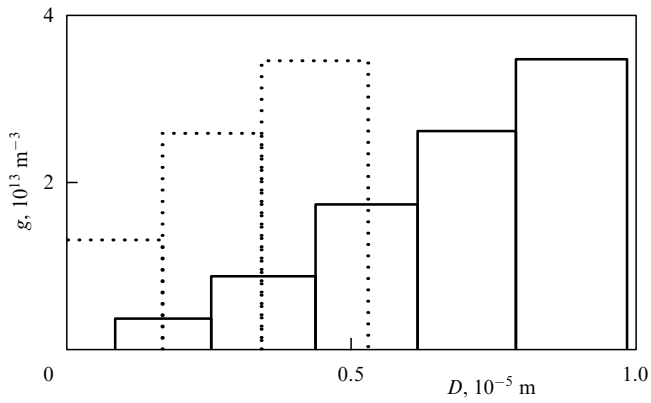

Figure 13. Distribution function of new-phase islands over the diameter for $\xi_0 = 0.1$ as observed in the experiment: dotted columns — $t = 2 \times 10^3$ s; solid columns — $t = 4 \times 10^3$ s.

4. The kinetics of thin-film condensation at the late stage

The late stage of thin film growth is characterized by the fact that the new-phase islands generated earlier begin to interact. There exist three main types of cluster interaction. The first is cluster merging due to their migration over the surface (the migration mechanisms were briefly discussed in Section 2.8). The second is cluster merging due to their lateral growth [168, 179]. The third is the growth of larger clusters at the expense of the evaporation of smaller ones [the so-called Ostwald ripening (OR) stage]. The latter type of interaction is realized through the generalized diffusion or temperature field [17]. The first two types are discussed in Section 4.1, and the third in the subsequent sections.

4.1 Cluster coalescence

All the ways of new-phase island merging on a substrate are customarily reduced to two types for the sake of simplicity: liquidlike (like two liquid drops) or solid-phase (like the adhesion of two solids) [1, 7, 11]. The central problem in the theoretical description of coalescence (merging) of islands is the nonlinearity and even the nonlocality of this process in the dimension space [180, 181]. This nonlocality leads to a whole number of interesting physical effects established experimentally, namely, the appearance of several maxima in the size distribution function of nuclei [182], a nonmonotone time dependence of substrate occupancy, the appearance of a clearly pronounced maximum in the surface concentration of islands, and so on. Furthermore, in the film growth of some materials coalescence is responsible for the percolation transition [183, 184]. It is at the coalescence stage that the structure of a growing film is formed, and therefore control-

ling the coalescence one can control the structure and some properties of the films. In spite of the very rich experimental material, there are almost no theories of coalescence or merging of new-phase islands because it is difficult to describe a nonlocal, nonlinear interaction. There exist only two main approaches to the description of this phenomenon, namely, the geometric theory of solid-phase adhesion based on the Avrami – Kolmogorov model [185], and the kinetic theory of liquidlike coalescence employing the Smoluchowski model [186].

In the geometric model, the nonlocality problem in the dimension space is successfully solved by the introduction of fictitious nuclei growing inside a new phase by a certain law. According to this model, the substrate occupancy by islands is equal to [185]

$$Z(t) = 1 - \exp\left\{ -\pi \int_0^t I(t') \left[\int_{t'}^t v_0(t'' - t')\, \mathrm{d}t'' \right]^2 \mathrm{d}t' \right\}, \tag{4.1}$$

where $v = \mathrm{d}R/\mathrm{d}t$ is the rate of growth of new-phase islands which is assumed to be independent of R. The distribution of islands by size in the Avrami – Kolmogorov model was calculated in Ref. [187]. The kinetics of substrate occupation with allowance made for a decrease of supersaturation is discussed in Ref. [188].

Liquidlike coalescence cannot already be described in the framework of the geometric model, and therefore the integral transformation technique is used here to solve the nonlocal integral equation for the distribution function. The liquidlike island merging due to their migration was described by Kashchiev [189] in the framework of the Lushnikov – Piskunov approximation [180] (where lateral island growth is absent). In particular, it was shown that for a certain form of coalescence nucleus the cluster distribution over radii has the form

$$g(R,t) = g_{\max}(t) \left(\frac{R}{R_{\max}(t)} \right)^{2(\mu+1)} \times \exp\left\{ -\frac{2}{3}(\mu+1) \left[\left(\frac{R}{R_{\max}(t)} \right)^3 - 1 \right] \right\}, \tag{4.2}$$

where $g_{\max}$ is the maximum value of g, $R_{\max}$ is the value of R corresponding to $g_{\max}$, and $\mu > -1$ is the nucleus growth index [189].

Liquidlike coalescence of clusters due to their lateral growth was described in Refs [168, 179] in the framework of the kinetic model. The size distribution function of clusters, the nucleation rate, the cluster concentration, the substrate occupancy by clusters and other coalescence parameters were calculated.

In view of the importance of this process, we shall consider it more extensively. We suppose that all the islands of the condensed phase are of the same shape and their merging proceeds instantaneously. Then we can introduce the distribution function g of stable clusters over the number of particles in them i normalized so that $N(t) = \int_{i_0}^{i} g(i,t)\, \mathrm{d}i$ is the cluster concentration on the substrate (i_0 is the minimal number of particles in a stable aggregate). Assuming the system to be sufficiently rarefied and allowing therefore only for pair island collisions, we shall write the kinetic equation for the function g in the following form

$$\frac{\partial g}{\partial t} + \frac{\partial (vg)}{\partial i} = \frac{1}{2} \int_0^i \beta(i - i', i') g(i - i') g(i')\, \mathrm{d}i' - g \int_0^\infty \beta(i, i') g(i')\, \mathrm{d}i', \tag{4.3}$$

$$g(i_0, t) = I(t) \left[1 - Z(t) \right] v^{-1} \big|_{i=i_0}, \quad g(i,0) = 0, \tag{4.4}$$

where $v = \mathrm{d}i/\mathrm{d}t$ is the cluster growth rate, I is the nucleation rate, Z is the substrate occupancy by islands, and β is the coagulation nucleus [185] [we assume that $g(i,t) = 0$ for $i < i_0$]. The boundary condition (4.4) is imposed in accordance with the principle of the division of the condensation process into stages [55]. Since the functions v and I depend on the supersaturation $\xi(t)$, equation (4.3) should necessarily be closed by the law of conservation of matter. In what follows, for the sake of definiteness we shall mainly consider a layer-by-layer film growth, for which

$$Z(t) = n_0^{-1} \int_0^\infty i g(i,t)\, \mathrm{d}i, \tag{4.5}$$

$$\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{J}{n_{1e}} - \frac{(\xi+1)}{\tau} - \left(\frac{n_0}{n_{1e}} - 1 - \xi \right) (1 - Z)^{-1} \frac{\mathrm{d}Z}{\mathrm{d}t}. \tag{4.6}$$

In an island regime of the thin-film growth we have $Z = \mathrm{const} \times n_0^{-1} \int i^{2/3} g(i,t)\, \mathrm{d}i$, and accordingly the equation of balance of matter will change.

We shall make an important remark concerning the coagulation nucleus β. By definition, $\beta(i,i')$ is the probability of merging of two islands containing i and i' particles on a unit substrate area per unit time. Assuming that the merging is caused only by the growth of motionless clusters, we obtain

$$\beta(i,i') = \left[\frac{\mathrm{d}R(i)}{\mathrm{d}t} + \frac{\mathrm{d}R(i')}{\mathrm{d}t} \right] \frac{P\big(R(i) + R(i')\big)}{N(t)}, \tag{4.7}$$

where $R(i)$ is the radius of the contiguity region between the island and the substrate, $P(r)\, \mathrm{d}r$ is the probability for an island at a time t to be at a distance of r to $r + \mathrm{d}r$ from a distinguished cluster. If the aggregates are randomly distributed over a flat substrate, then we arrive at

$$P(r) = 2\pi r N(t). \tag{4.8}$$

For almost all the growth models, the quantity $\mathrm{d}R/\mathrm{d}t$, the same as R, depends on i in a power-law manner, and therefore the nucleus β is a homogeneous function, i.e. one obtains

$$\beta(ki, ki') = k^\mu \beta(i,i'), \tag{4.9}$$

where μ is the nucleus growth index. This property is also inherent in the nucleus of coagulation due to cluster diffusion across the substrate surface [189]. This circumstance substantially simplifies the search for solutions of the system of thin-film condensation equations (4.3) – (4.6) because it allows us to apply the Laplace transformation [186]. If coalescence between only nearest neighbours is involved, then for high cluster concentrations β becomes an inhomogeneous function. The same effect is observed provided that the correlation between islands is taken into account [190].

Concrete solutions of the system (4.3) – (4.7) for some very simple nuclei, which were obtained using the Laplace transformation and the moment equation method, and the dependence of the asymptotics of the distribution function on the index of nucleus homogeneity were presented in Ref. [179] where, in particular, the nonmonotone character of the functions $N(t)$ and $Z(t)$ was shown to be one of the consequences of the coalescence. For example, for constant coalescence nuclei N reaches its maximum at approximately $Z = 0.38$.

4.2 Ostwald ripening

The Ostwald ripening stage is the late stage of the phase transition. It begins only when the sources of evaporated adatoms are sufficiently weak and the supersaturation ξ on the substrate is small and tends to zero. No new islands are formed in this situation. The estimate of the starting point of this stage can be found in Refs [17, 90, 91, 128, 142]. The physical meaning of OR is as follows. At a late stage of evolution of an ensemble of islands they begin to interact in a peculiar manner. This interaction is realized through a generalized self-consistent diffusion field. On a substrate, this field can be established by adatoms with a concentration $\bar{\rho}_a$, vapor atoms with a density $\bar{\rho}_r$ or, if the substrate surface contains linear defects, by adatoms ($\bar{\rho}_l$) adsorbed at the steps.† This field depends on the size distribution function $f(R, t)$ of islands and is in equilibrium with islands of critical size R_c. Islands of size $R < R_c$ are dissolved in the diffusion field because near them the equilibrium concentration ρ_R of atoms exceeds the mean field concentration: $\rho_R > \bar{\rho}_a$, $\rho_R > \bar{\rho}_l$, or $\rho_R > \bar{\rho}_e$. Islands of size $R > R_c$ grow because for them $\rho_R < \bar{\rho}_a$, $\rho_R < \bar{\rho}_l$. The critical size R_c itself goes on increasing because the islands absorb the substance from the substrate thus lowering the supersaturation.

For this interaction and, therefore, the OR stage to take place, it is necessary that the two-dimensional island density would satisfy the inequalities [17, 191]

$$\left[\pi(\bar{R} + \lambda_i)^2\right]^{-1} < N_s < (\pi \bar{R}^2)^{-1}, \tag{4.10}$$

where N_s is the two-dimensional island density, $\bar{R}$ is the mean island radius, $\lambda_i = \lambda_s$ for mass transfer over the substrate surface, and $\lambda_i = \lambda_l$ for mass transfer along the steps, λ_s and λ_l being respectively the mean free path along the substrate surface and along the steps. Otherwise, if $N_s \geqslant (\pi R^2)^{-1}$, the islands will 'collide' and for $N_s \leqslant [\pi(R + \lambda_i)]^{-1}$ the adatoms on the substrate will evaporate and will not participate in the OR process provided that $\lambda_i = \lambda_s$. When $\lambda_i = \lambda_l$, the adatoms can leave the step and will not participate in ripening of the ensemble of islands located at the step.

The Ostwald ripening of an ensemble of islands in thin films was first investigated by Chakraverty [96, 192]. He examined the evolution of an ensemble of single-component islands with the shape of a spherical segment and located on solid substrates in the regime of complete condensation and also in the presence of atoms sputtered onto the substrate. The main idea of the OR analysis of such systems took root in the pioneering paper by Lifshits and Slezov [193]. These authors showed that any disperse systems containing new-phase nuclei and old-phase atoms‡ possess a whole number of common properties inherent only in disperse systems and appeared in the course of their evolutionary growth. From the thermodynamic point of view, this common property of disperse systems is their deviation from equilibrium state simultaneously in many parameters. One of the main signs showing that a disperse system resides in a nonequilibrium state is the presence of a fairly extended phase interface associated with an excess free energy. At heightened temperatures, when an appropriate diffusion mechanism becomes valid, some processes proceed in disperse systems that lead to a relaxation of the excess energy. These processes must be accompanied by a diffusive mass transfer which is responsible for the emergence of OR. This process was named after the German scientist W Ostwald who, at the beginning of the century, examined this phenomenon experimentally during precipitation ripening§. The principal system of equations describing this process has been presented in numerous works generalized in reviews [5, 11, 90, 91, 191] and monographs [17, 88]. When describing the nonisothermal ripening below, we propose a more general system of equations, a particular case of which is the one given. The OR stage was also thoroughly investigated by Wagner [195], Ardell [196], Kahlweit [197], Oriani [198], Cahn [199], Voorhees and Cliksman [200 – 201], Enomoto, Kawasaki, Tokuyama [203, 204] and many other authors [205 – 219].

An investigation of the OR stage raised the following two questions:

(1) Is the size distribution function of nuclei, obtained by Lifshits and Slezov, asymptotic (as the other time dependences) or not?

(2) Why does the Lifshits – Slezov distribution function terminate at a 'blocking' point [193], whereas the experimental distribution functions have asymptotically decreasing tails?

As concerns the second question, Lifshits and Slezov answered it in their second paper [212] where they showed that the tails resulted from nucleus coalescence (merging). Obviously, that paper was noticed by few researchers. To answer the first question, various mathematical methods were used, including perturbation theory, scaling theory, etc. The most widely known is the paper by Kahlweit [197]. He believed that the Lifshits – Slezov distribution was not uniformly valid and was therefore not asymptotic. However, he pointed out an erroneous reason for the appearance of nonuniformity, for which he was justly criticized [90, 91]. Margusee and Ross [205] suggested that the solution of the kinetic OR equations should be sought directly in the form of a series in t:

$$f(R, t) = t^{-y_0}\left[f_0(z) + t^{-y_1} f_1(z) + t^{-y_2} f_2(z) + \ldots\right], \quad z = \frac{r}{t^{\beta}}, \tag{4.11}$$

where f is the distribution function of new-phase nuclei over the radius R, t is time, and $\beta, y_0, y_1, \ldots$ are positive constants.

† The generalized field is formed, as a rule, by all concentrations, but as the analysis [17] shows, it is difficult to obtain an analytical solution of the OR problem. It is hence more convenient to investigate the evolution of an ensemble of islands for each field separately and to choose the main mass transfer mechanism (see Section 2.6).

‡ The authors of Ref. [193] analyzed a diffusive decompostion of supersaturated solid solutions.

§ In the scientific literature there are two terms denoting this process. In the Russian literature it is called 'coalescence' [17, 90, 91, 193, 194] and in the rest of the world 'Ostwald ripening'. However, the term coalescence means merging (coagulation), i.e. the process considered in Section 4.1 above. Therefore, to avoid misunderstanding, we shall henceforth use the term OR for the phenomenon investigated in the present section.

Using an original technique, they managed to uncouple the equations for f_0 and f_1 and to find their solutions. In so doing the function f_0 turned out to coincide with the corresponding result of the Lifshits – Slezov theory, from which Margusee and Ross concluded that this was just an asymptotic solution. Actually this is not at all an asymptotic solution, but a solution corresponding to the Lifshits – Slezov zeroth approximation, because the series (4.11) is divergent at least at the blocking point. The convergence of the series (4.11) was not examined in the paper [205] at all while, as shown in Ref. [213], the blocking point gives rise to nonuniform validity of the series (4.11) already in the next order, i.e. $f_1(z)/f_0(z) \to \infty$ as z tends to the blocking point. As is well-known, this is the most crucial point of any asymptotic or perturbation theory [140]. Similar error was also made in some other papers on the OR theory. In paper [213] we constructed a rigorous asymptotic theory of the OR stage, using a uniformly valid solution, to find out that at the OR stage there exists a stable asymptotic state characterized by the universal distribution function. This leads to the peculiar evolution of an ensemble of new-phase nuclei which is considered below.

So, Chakraverty [96, 192] believed that mass transfer between islands is realized only through a surface diffusion of adatoms and that the island growth rate can be controlled by both the surface diffusion (heterodiffusion) of adatoms and by the rate of consumption and emission of atoms by the islands, i.e. by boundary kinetics. He assumed that the emission and absorption (building-in) of atoms are realized not by the island contour, but by its whole surface. Such an assumption corresponds to the fact that self-diffusion flows along a free island surface must exceed the heterodiffusion flows on the substrate surface. This statement should have been additionally grounded.

This problem was solved more exactly by Geguzin and Kaganovkiĭ [88, 192]. They studied the evolution of an ensemble of islands growing by the following mechanisms: surface diffusion of atoms, gas diffusion of atoms, evaporation-condensation of atoms, one-dimensional atomic diffusion along steps and surface dislocations on a substrate (see Section 2.6) with allowance for a possible island growth control by boundary kinetics.

Later, the OR stage of an ensemble of single-component islands with allowance made for all possible growth mechanisms and in the presence of atoms sputtered on the substrate was investigated by Vengrenovich [214], Olemskoĭ and Paripskiĭ [215], and others [17]. The authors of these papers found the laws of variation of the critical radius, height (if the islands had the shape of a flat disc), the island density in time, as well as island size distribution to a zeroth approximation. The analysis has shown that these characteristics depend substantially on the island growth mechanism and the intensity of atomic supply onto the substrate. According to Refs [5, 11, 17], if a flux of atoms coming onto a substrate has a power-law asymptotics: $g(t) \to ng_0 t^{n-1}$, where $n \geqslant 0$ and g_0 is the constant, then there exist only two types of sources, namely, weak with $n < d/p$ and strong with $d/p \leqslant n$. According to the rigorous results obtained in Ref. [213], the asymptotic laws of variation of the critical radius, the height and the density of islands coincide with those of Ref. [193], whereas the asymptotic size distribution function differs from the functions obtained in the zeroth approximation. Therefore, we present below the expressions of the general laws of island evolution for sources with $n < d/p$ in accordance with the results obtained in Ref. [213]. The general form of these laws is as follows:

$$\bar{R}(t) = \text{const} \times R_c(t)\,, \tag{4.12}$$

$$R_c(t) = (\text{const} \times A'_{pd} t)^{1/p}\,, \tag{4.13}$$

$$h(t) = (\text{const} \times A''_{pd} t)^{1/p}\,, \tag{4.14}$$

$$N(t) = \text{const} \times t^{n-d/p}\,, \tag{4.15}$$

$$f(R,t) = \frac{N(t)}{R_c(t)}\, P_p\left(\frac{R}{R_c(t)}\right), \tag{4.16}$$

$$P_p(u) = \frac{u^p}{u^{p+1} - (p+1)u + p} \times \exp\left[\frac{d - n(p+1)}{2} \int_u^{u_p} \frac{x^p\,\mathrm{d}x}{x^{p+1} - (p+1)x + p}\right]. \tag{4.17}$$

Here $P_p(u)$ is the distribution function normalized to unity, so that $\int_0^\infty P_p(u)\,\mathrm{d}u = 1$, and

$$v_p(u) = \frac{p^p (p-1)^{-(p-1)}(u-1) - u^p}{p u^{p-1}}\,, \tag{4.18}$$

$u = (p-1)R/pR_c$ (Fig. 14 shows the functions $P_p(u)$ obtained by Lifshits and Slezov for $p = 2$ and $n = 0$ and in the paper [213]), u_p are constants determined from the normalization condition $\int P_p\,\mathrm{d}u = 1$, A'_{pd} and A''_{pd} are kinetic coefficients depending on mass transfer coefficients and on other constants of the deposited material.

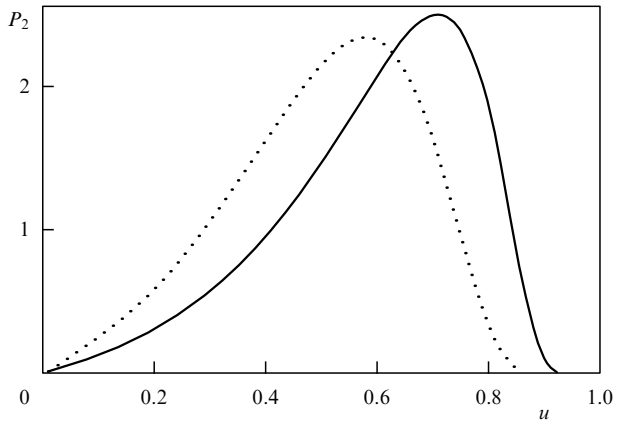

Figure 14. Functions $P_p(u)$ for $p = 2$ and $n = 0$, obtained in Ref. [213] (solid line) and by Lifshits and Slezov (dotted line).

In the case of atomic sources with $d/p \leqslant n < d/(p-1)$, both for cap-shaped and disc-shaped islands the critical radius is also specified by equation (4.13) and the distribution function can be calculated within the kinetic nucleation model [see Eqn (3.19)].

The basis for the analysis of the OR process is the Fokker – Planck equation (2.27) in which the term with the second derivative of the distribution function is omitted. As a result, the remaining equation of continuity governs a determinate Ostwald ripening process. Stochastic ripening with the second derivative in the Fokker – Planck equation was investigated in Refs [219, 220].

The influence of the volume fraction of a new phase on the OR stage has been of great interest for many researchers for a

long time [90, 91, 196, 208]. This influence consists in fact in the interaction of islands caused by the direct overlap of their diffusion fields. The effect of such interactions on the OR process will be particularly strong in the presence of sputtered atoms because the volume fraction of nuclei will increase under such conditions. For an analysis of such interactions various methods are used [204, 206, 208]. We should specially mention paper [218] in which the author used the method based on the classical diagram technique, and the paper by Slezov [91] in which this interaction is reduced to a one-particle problem in an effective medium with a renormalized diffusion coefficient dependent on the mean particle radius in an ensemble.

4.3 Thermal ripening

After new-phase islands have been formed on the substrate surface in the growth from solution-melt (see Section 3.4), they start enlarging and decrease the melt supercooling. After a time, the thermal ripening stage, similar to the diffusive ripening stage, is reached in the system since the thermal-diffusivity equation is totally analogous to the diffusion equation.

In line with Refs [17, 107–109] we shall consider thermal ripening of ensembles of islands. At the initial stage, when the supercooling ξ is still sufficiently high, the islands grow independently of one another and have practically equal sizes [17, 145, 220, 221]. With time, the supercooling decreases owing to the heat liberated in crystallization, and the islands will interact with each other by means of their generalized temperature field. Indeed, according to the Gibbs–Thomson equation, the portion of a crystal bounded by a surface with a large curvature melts at a lower temperature than the corresponding portion of a flat surface [17, 107–109]:

$$T_R = T_c - \frac{(d-1)\sigma_{SL} T_c w}{qR} . \tag{4.19}$$

Here T_R is the equilibrium temperature at the surface of an island of radius R, σ_{SL} is the interphase energy of the boundary surface, q is the latent crystallization heat per atom, and w is the volume per atom.

Thus as $\xi \to 0$, larger islands that liberate heat will grow at the expense of smaller ones that absorb the heat and melt. Such a process can obviously be called 'thermal' Ostwald ripening. It should be taken into account that during diffusion ripening the flows are opposite to those occurring in thermal ripening.

We shall now consider a substrate of thickness l which adjoins a single-component melt with one of its planes. On this plane there is an ensemble of islands with the initial distribution function $f(R,0) = f_0(R)$. The islands can have the shape of either a spherical segment or a cylinder. Above the substrate there is a melt layer with a thickness of the order of the average island size $\bar{R}$. Otherwise the initial melt supercooling will not decrease. As shown in Refs [17, 109], thermal ripening is in principle possible when the melt thickness is infinite, but the substrate must then be rotated in the melt with a certain frequency ω. Such a rotation creates a hydrodynamic layer immediately adjacent to the substrate surface. The properties of this layer differ from those of the remaining part of the liquid because complete mixing occurs in the layer and its temperature is constant (see Section 3.4). In this case, either the removal or inflow of heat will occur in the system, i.e. ripening will proceed with heat sources (sinks).

A complete system of equations governing the thermal OR of an ensemble of new-phase nuclei in the presence of heat sinks and heat sources was derived and the heat fluxes (which depend on the Prandtl numbers) removed from the melt were determined in Refs [17, 107–109]. This system of equations differs from that for the diffusion ripening in that instead of the equation of mass balance it contains the equation of heat balance. It is precisely this equation that ultimately specifies the behaviour of the ensemble of nuclei at the OR stage. The solution to this system of equations coupled with one of the equations for the nucleus growth rate (2.38) was discovered in Refs [107–109] and in the general case it has the form (4.12)–(4.18) because irrespective of the physical nature of the system the phase transition proceeds by unified laws†. At the same time, the kinetic constants A'_{pd} and A''_{pd} will naturally be different.

4.4 Nonisothermal ripening in multicomponent films

The general OR theory in nonisothermal conditions was constructed in Refs [17, 92–94, 102, 103]. The OR processes in multicomponent systems are richer and more diverse than similar processes in single-component systems. In multicomponent systems, substance redistribution is a consequence of not only the Gibbs–Thomson effect, but also of the chemically nonequilibrium state. Islands of a chemical substance (phase s) may be stable from the point of view of the Gibbs–Thomson effect but unstable from the point of view of the thermodynamics of chemical reactions. At the OR stage in multicomponent systems, when the component concentration is $\rho_j(0) \ll 1$ (here $\rho_j(0)$ is the concentration of the component j by the onset of OR), new islands are not formed and all the islands of the ensemble interact with each other through their generalized diffusion field. Islands of phase s with radius R smaller than the critical radius R_c^s are dissolved in the diffusion field, while islands with a radius exceeding the critical one grow. In a multiphase system, not only islands of the same phase, but also those of different phases will interact, and of all the stable phases only those for which the solution is supersaturated will be stable. For low component concentrations, when the law of mass action can be applied to the proceeding chemical reactions, this law can be written in the form

$$\sum_j \nu_j^s \mu_j^s = \ln \frac{\Pi_s j(\rho_j(0))^{\nu_j^s}}{K_\infty^s} \geqslant 0 . \tag{4.20}$$

Here K_∞^s is the equilibrium constant of the sth chemical reaction, s^j is the number of the phase containing the j-component, μ_j^s is the chemical potential of the j-component. If the islands generated in the system do not contain common components, condition (4.20) is necessary and sufficient since they will grow independently. Providing the islands contain common components, during their growth substance redistribution among the islands is possible and, although the solution was at first supersaturated in separate components, it may further appear to be unsaturated. In this case condition (4.20) is only necessary for a selection of islands capable of further competitive growth.

† We note that the distribution functions found in these papers are not asymptotic and should be replaced by the functions (4.17) obtained in Ref. [213].

In multicomponent systems, in the course of OR heat is liberated in chemical reactions, which affects the reaction constants. The thermal fields induced due to the heat liberation in chemical reactions affect the size distribution of islands in a nonlinear manner. The equilibrium concentration of the dissolved substance is not constant, but increases with temperature. The supersaturation will then tend to zero faster than in the isothermal case; however, the substance concentration gradient decreases in the process, which leads in turn to a decrease of the island growth rate. The amount of heat liberated in the course of phase transformation therewith decreases (if the system is conservative), which brings about stabilization of the equilibrium concentration, i.e. the diffusion and thermal fields become self-consistent. Thus, the system temperature heightening may lead to a decay of some phases.

A complete system of equations governing the evolution of an ensemble of multicomponent and multiphase islands at the OR stage looks like this [17, 92, 93]:

$$\frac{\partial f^s(R,t)}{\partial t}+\frac{\partial f^s(R,t)v_R^s}{\partial R}=0\,, \tag{4.21}$$

$$\chi^s\sum_{s^j}\int_0^\infty f^s(R,t)R^{3-d}h^{3-d}J_{DR}^s\,\mathrm{d}R=n_1|g_{D_j}|t^{n_1-1}\,, \tag{4.22}$$

$$\prod_{j=1}^{n^s}(\rho_{jR}^s)^{v_j^s}=K_R^s(T_R)\,, \tag{4.23}$$

$$\frac{J_{jr}^s}{v_j^s}=\frac{J_{j'R}^s}{v_{j'}^s}\,, \tag{4.24}$$

$$\sum_{s=1}^{K}\chi^s q^s\int_0^\infty f^s(R,t)R^{d-1}h^{3-d}J_{TR}^s\,\mathrm{d}R=n_2|g_T|t^{n_2-1}\,, \tag{4.25}$$

$$q^s\sum_{j=1}^{n^s}v_j^sJ_{jR}^s=J_{TR}^s\,, \tag{4.26}$$

$$K_R^s=\varphi(T_R^s)\,. \tag{4.27}$$

Here $f^s(R,t)$ is the size distribution function of islands of phase s, J_{jR}^s is the flux of atoms of the j-component onto an island of phase s, J_{TR}^s is the heat flux liberated during the growth of phase s, ρ_j is the mean concentration of the j-component on the substrate (or in a vapor), χ^s is the coefficient dependent on the island shape, q^s is the chemical reaction heat liberated during growth of islands of phase s per molecule of phase s, $|g_{D_j}|$, and $|g_T|$ are the intensities of the fluxes of j-component and heat, respectively, and, finally, n_1 and n_2 are damping exponents.

A method for the solution of this type of system was developed in papers [92, 93]. This method allows reduction of the system of equations (4.21)–(4.27) to a single-component system [213]. The general solution has the form (4.12)–(4.18) in which all the quantities, i.e. the critical and the mean radii, the density and the distribution functions of islands belong to a certain phase s, while the kinetic constants A_p' entering the laws of time-dependent variation of the critical and mean radii of islands are replaced by the generalized quantities $A_{TP}'^{os}$. The values of these constants are given in papers [92, 93] for all the cases of heat and mass transfer which can be realized in the course of evolution of an ensemble of islands. As an example, we only present the value of $A_{TP}'^{os}$ for the case where the principal mechanism is the surface diffusion of adatoms and the heat is transferred over the substrate surface. In this case, one obtains

$$A_{TR}'^{os}=\frac{27D_s^{os}\sigma^s n_0K_{sb}lT_0^s(w_0^s)^2\psi_1(\theta)}{32\left[D_s^{os}n_0(q^s)^2\ln(H/R_1^s)+K_{sb}\lambda_{\mathrm{eff}}k_{\mathrm{B}}(T_0^s)^2\right]}\,, \tag{4.28}$$

where

$$D_s^{os}=\left(\sum_{j=1}^{n^s}\frac{(p_j)^2\ln(\lambda_j/R_1^s)}{D_{\mathrm{a}j}\rho_{j\infty}^s}\right)^{-1}$$

is a generalized surface diffusion coefficient for $\lambda_{sj}\gg R_1^s$, $D_{\mathrm{a}j}$ is the coefficient of Brownian motion of adatoms of the j-component, $\psi_1(\theta)=2(2-3\cos\theta+\cos^3\theta)^{-1}$ with θ as the contact angle, and the other designations were presented above. The solution also showed [17] that at the OR stage $N_{\mathrm{an}}\sum_{s=1}^{K}q^s|g_D^s|=|g_T|$ and $n_1=n_2$, i.e. the powers of sources (sinks) of all the phases and heat are related to one another and vary in time by one and the same law. Otherwise, the ripening process is impaired. The equations allowing the determination of regions in the concentration and temperature space which demonstrate the coexistence of phases were obtained in Refs [17, 92, 93]. A schematic phase diagram of the evolution of islands of two phases which are chemical compounds of three components (one of which simultaneously enters both phases) are given as an example in Fig. 15.

Thus, in multicomponent systems the conditions of quasi-thermodynamic equilibrium are favourable to the distribution of the substance of components in a most advantageous way over phases and to the establishment of the regions of phase coexistence, while the action of the surface tension leads to a universal size distribution of islands of the existing phases. Notice that such a distribution is only possible for low component concentrations, when the law of mass action can be applied to the chemical reactions proceeding in the system.

We shall now turn to OR of solid-solution islands. Islands of such composition are mainly produced in the growth of

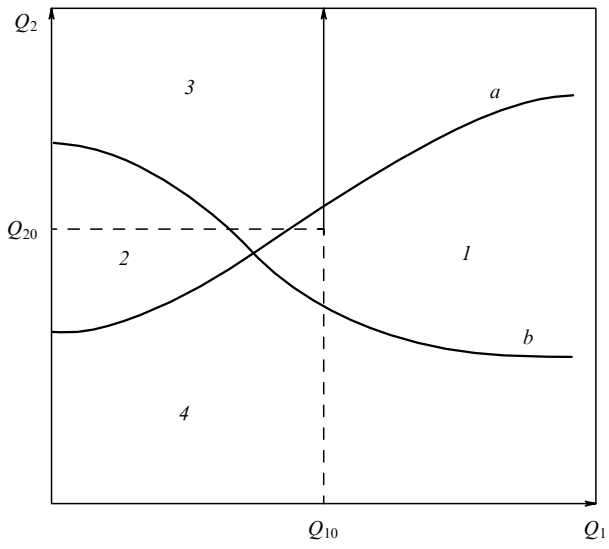

Figure 15. Phase diagram of the evolution of a two-phase ternary disperse system in the projection onto the plane Q_1, Q_2: region *1* corresponds to phase I, *2* to phase II, *3* to phases I and II, and *4* to the absence of phases; lines *a* and *b* indicate phase boundaries; Q_{10} and Q_{20} are the initial amounts of components. The arrow indicates the trajectory of the system's evolution in the presence of sources of the second component.

films from melts which have a 'cigar' type diagram of state (see Fig. 3b). The theory of OR of islands growing from binary melts of this type was developed by a number of authors (see references in [5, 11, 17]). In particular, Voorhees [202], independently of the authors of works [102, 103], described the ripening of new-phase nuclei in binary melts allowing for the fact that their growth is due to both the diffusion and the removal of the latent crystallization heat into the melt. Notice that the hypothesis of a nonisothermal OR was first suggested in Refs [102, 103], where the system of equations governing the evolution of an ensemble of islands and determining the kinetic growth diagram was derived. In these papers it was also shown that generalized diffusion-thermal fields are induced in the course of OR in binary melts. Such fields result from crystallization heat removal during the growth of islands, which causes a temperature increase in the system. This leads in turn to a change of equilibrium concentrations and the diffusion coefficients of atoms as well as to the appearance of an involved nonlinear relation between supersaturation and supercooling on the one hand, and the size distribution and the growth rate of islands on the other. A more extensive consideration of these questions is presented in monograph [17].

The OR theory for islands growing from a eutectic melt (Fig. 3a) was formulated in Refs [103, 110]. It turned out that in the course of evolution of ensembles of nuclei growing from a eutectic solution-melt, the nucleus growth at the OR stage proceeds by the thermal OR mechanism (see Section 4.3), i.e. only due to a decrease of supercooling. The solution-melt supercooling becomes equal for islands of both components, and their critical sizes and the distribution functions appear to be interrelated and similar to each other. It has been established that among some substance constants (crystallization heat, surface tension) there hold simple relations allowing us to calculate the constants of one substance through those of the other.

4.5 Ripening in inhomogeneous conditions

By inhomogeneous conditions we usually understand conditions under which macroscopic material and heat flows may occur on the substrate, being resulted either from substrate inhomogeneity or nonuniformity of the flows of the substance and heat coming to the substrate. In the paper by Lifshits and Slezov [193], the influence of the crystal edge on the OR of an ensemble of pores was already considered. Later, in papers [88, 191] it was demonstrated that if new-phase nuclei are located on the surface of a polycrystal, the grain boundaries are ideal sinks and the island – substrate interphase energy is distinct on disoriented and contacting grains. Since the grain boundary is an ideal sink, a flow of adatoms whose sources are islands will be directed toward this boundary, i.e. near the boundary the islands will dissolve and a region free of them will appear. The law of time variation of the width of this region is as follows

$$\xi(t) \propto t^{3/8} .$$

The analysis of OR of islands on grains of different orientations has shown that from some grains the substance recondensed onto other grains whose orientation is advantageous from both thermodynamic and kinetic points of view [17, 88, 191]. The theory of melt crystallization in inhomogeneous conditions was constructed in paper [222]. The finiteness of the dimensions of systems in which melts solidify leads to the emergence of material and heat flows. While near the boundary the melt gets supercooled at a certain instant of time and undergoes a phase transition accompanied by a new-phase nucleation, it can be still superheated far from the boundary. In the layer, in which nucleation took place, the OR stage may set-in. However, the OR zone will be under conditions quite different from those investigated above. These conditions are a consequence of a nonuniform distribution of heat and material flows over the system. The analysis carried out in [222] allowed the equation of motion of a continuous new-phase crust and the size, coordinate and composition distribution functions of the nuclei for each phase to be obtained. For example, the equation of motion of the crust for each phase $x^s(t)$ has the form

$$xs = \sqrt{\frac{2\lambda^s a^s \chi}{L\rho^s(1-1/p)}}\, t^{(p-1)/2p} . \tag{4.29}$$

Here $\lambda = 2\sigma_{SL}T_k/(L\rho^s A_p^{1/p})$, L is the latent crystallization heat, ρ^s is the density of the material of s-phase islands, and χ is the thermal diffusivity of the melt.

The late stage of the growth of islands produced on the substrate through chemical decomposition of multicomponent gases was examined in paper [223]. Such a film growth process is typical of gas-transport deposition and MOCVD methods. The structure and composition of films obtained by these methods are as a rule inhomogeneous across the substrate area. A system of equations governing the evolution of a film of the island type at the OR stage under conditions typical of the gas-phase deposition was obtained in Ref. [223]. The solution of this system made it possible to obtain the dependences of all the basic characteristics of films of the island type.

4.6 Evolution of the properties of growing films at the OR stage

It is a well-known fact that the properties of films are mainly determined by their composition. It is precisely the composition that determines the majority of electrophysical, optical, strength and other properties. To gain an insight into the evolution of film composition so as to be able to control this composition during film growth is one of the most important problems of thin-film physics. It was shown in Refs [102, 103] that at the OR stage the radius of solid solution islands and their composition are in a one-to-one correspondence. Later, a rigorous theory describing the evolution of phase composition of ensembles of such islands at the OR stage was formulated in Ref. [224]. In particular, the composition distribution function of islands $\varphi(1/\rho_R, t)$ in the presence of substance sources with $0 \leqslant n < d/p$ has the form

$$\varphi\left(\frac{1}{\rho_R, t}\right) = N(t)\Delta(t)P_p(U) . \tag{4.30}$$

The average film composition changes according to the law

$$\bar{\rho}(t) = \frac{2\sigma w \rho_{L0}(1+\gamma)}{k_B T(A_p^0 t)^{-1/p}} . \tag{4.31}$$

Here σ is the specific interphase energy of the island – vapor boundary; ρ_{L0} is the equilibrium concentration of one of the components, for example, A (Fig. 3b) in the liquidus line, i.e. in the liquid or vapor phase; γ is the slope of the straight line joining the liquidus and solidus lines (Fig. 3b). Figure 16 presents the dependences of the island composition on size

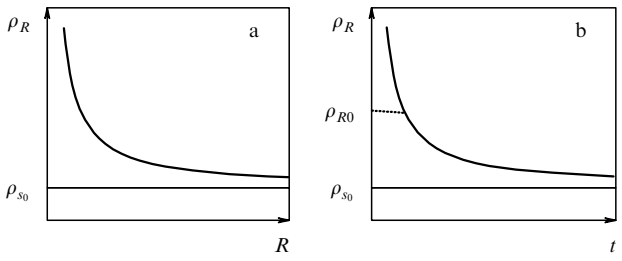

Figure 16. Dependences of the island composition on size (a) and on time (b).

and time. Paper [224] also analyzes the evolution of islands of stoichiometric compounds and determines the function relating the composition to the properties of films.

4.7 Film growth control at the OR stage

It has already been mentioned that independently of the methods of obtaining films they undergo a number of stages during growth that are typical of any first-order phase transition [225]: nucleation of clusters or islands of a new phase, their growth, coalescence and the related processes (autocoalescence, mutual correlation in the position of islands, migration, etc.), Ostwald ripening, and continuous film formation. If a nucleation proceeds with a high supersaturation, the density of new-phase islands and the substrate occupancy will be high and the stages following nucleation may fail to set-in. The composition and structure will then be determined by the nucleation processes which, as shown above, have an involved nonlinear character. Therefore, the film growth parameters are most conveniently controlled at the OR stage when the nucleation of new islands does not happen and a continuous film has not yet formed. The control is feasible because at this stage an ensemble of new-phase islands interacts in a peculiar manner with generalized diffusion-thermal fields induced on the substrate surface and with atomic fluxes incident on it. Neither the asymptotic size distribution of islands nor their composition depend on the initial distribution, but they do depend on the mass and heat transfer mechanism realized during island growth and on the intensity of substance and heat supply onto the substrate.

The theory developed in Refs [17, 98] considers all the presently available methods of film growth control and suggests a unified approach to them. This approach is based on the choice of time dependence of the temperature or the degree of power variation in the sources of atoms coming onto the substrate. Experimental and technical researchers customarily keep these parameters unchanged, and if they do change these parameters, they do it randomly. On an example of single-component systems we shall consider the feasibility of continuous-film structure control through the control of the evolution processes proceeding in ensembles of islands.

Let the islands have, for example, a cylindrical form and let the kinetics of their growth be determined by the processes of the building-in of atoms irrespective of whether the mass transfer is realized in the bulk phase or on the surface of a substrate. Suppose that the islands grow under isothermal conditions in the course of vacuum deposition. It was shown in Ref. [17] that for the island size

$$\bar{h} \approx \frac{l_0 (k_B T)^{1/2} \tau_r}{n_0 w (2\pi m)^{1/2}} , \qquad (4.32)$$

where $\bar{h}$ is the average island height, l_0 is the substrate lattice parameter, $n_0 = 1/l_0^2$, and m is the mass of a single atom, the mass transfer mechanisms will change. If the island height in an ensemble is $h < \bar{h}$, the mass transfer is mainly realized through surface diffusion, while for $h > \bar{h}$ it occurs through gas diffusion.

Depending on the structure and composition of the substrate, the lifetime τ_r may vary within broad limits. As follows from Eqn (4.32), this may lead to a change of the mass transfer mechanism. So, the value of τ_a and, accordingly, the height $\bar{h}$ will be different for one and the same ensemble of islands located on different substrates at the same temperature. For a strong adatom – substrate interaction, the quantity τ_a and, accordingly, $\bar{h}$ are large, while for a weak adatom-substrate interaction the quantity $\bar{h}$ is small. If on both substrates the island height in an ensemble is, for example, h_a, on the substrate strongly coupled with adatoms it may be $h_a < \bar{h}$, in which case the surface diffusion mechanism is operative, whereas on the substrate with weak coupling the same height is $h_a > \bar{h}$, i.e. the vapor diffusion mechanism is operative. This leads to a nonuniform size distribution of islands in an ensemble under the conditions that the substance flow onto the substrate is constant in time, i.e. its damping exponent $n = 1$. Indeed, if the surface diffusion mechanism is realized, then sources with the exponent $n = 1$ are strong and the size distribution function of islands will be determined by the nucleation stage and the growing films will be small-block ones. The size and composition of these blocks will be almost identical. For the case where in an ensemble of islands the vapor diffusion mechanism is operative, sources with the same exponent $n = 1$ will be weak. This will lead, in particular, to a distribution function of the form (4.17) and the source density will decrease with time.

If the sources of substance are weak, then in addition to the distribution of islands over sizes there will appear a distribution over composition. However, if it is necessary to obtain large-sized crystallites or to prescribe a certain island orientation which is energetically more advantageous, one should use weak sources of substance. There are, in principle, no theoretical restrictions on the crystallite size since as $t \to \infty$ all nonequilibrium islands must dissolve. It is only necessary to choose specially the sources of substance, but this process may take much time.

The growth is similarly affected by heat sinks, because at the Ostwald ripening stage they are related to the flows of substance. If one and the same ensemble of islands is located on the surface of one and the same substrate but at different temperatures, then it follows from the results of Ref. [17] that the mass transfer mechanism may be changed for another one. This is associated with the strong dependence of $\bar{h}$ on the substrate temperature: $\bar{h} \propto \sqrt{T}\tau_a$, where $\tau_a = \tau_0 \exp(W'a/k_B T)$. At low temperatures, the mechanism of surface diffusion in the ensemble will prevail as a rule, while at high temperatures it will be the vapor diffusion mechanism.

The possibilities of controlling the evolution of an ensemble of solution-growing islands are limited because it is difficult to regulate the flows of components which are in the same solution as the substrate (the solution and the substrate make up a single whole). As the solution temperature changes, the substrate temperature simultaneously changes, while at a constant temperature a constant flow of substance comes to the substrate since as a rule the solution volume considerably exceeds the volume of island film. It has

been shown above that for the OR process to take place in this case, the substrate should be rotated parallel to the solution plane with a frequency ω. For an extensive presentation of this method see Refs [17, 226]. For the growth of films from melts one should bear in mind that the change in the island growth mechanism is also affected by the substrate thickness [17, 109].

More detailed conclusions can be found in Refs [5, 11, 17, 109, 226]. The results on the control of film growth from binary and multicomponent melts are also presented in these works. Some peculiarities of the growth of capillary and layer-by-layer films were considered in Ref. [229] and the possibilities of film growth control by varying the inert gas pressure in the growth chamber were analyzed in Ref. [227]. The regions of phase coexistence in multicomponent disperse systems on the surfaces of solid substrates, formed in the course of island film evolution, were determined in Refs [17, 224, 226]. Such an approach can be used to obtain films of semiconducting and superconducting materials of a prescribed chemical composition.

The time of continuous structure formation and thicknesses of continuous films as functions of substance flux intensities are given in Refs [17, 93, 98, 228].

4.8 Comparison with experiment

The first correct comparison of theoretical and experimental results was made in Ref. [228] on an example of the evolution of island gold films on the (100)-surface of an NaCl single crystal. As a result, the mass transfer mechanism was determined and the coefficient of gold adatom surface heterodiffusion was found. Later, the OR of single-component island films was investigated by many researchers [17, 88, 191]. Owing to the results obtained the coefficients of surface heterodiffusion were determined for different substances on various substrates.

Experimental studies of the evolution of ensembles of islands at the ripening stage do not only provide unique information on the mechanisms of mass transfer over the surface and such kinetic constants as diffusion coefficients and coefficients of boundary kinetics, but also allow the prediction of specific technological conditions for obtaining continuous films of a given structure and composition.

In the series of works referred to in papers [5, 11, 17], experiments were carried out investigating the OR of islands of a number of multicomponent A^2B^6 compounds and, in particular, films of cadmium selenide (CdSe), cadmium oxide, cermets (Cr_2Si_3 and SiO_2), and titanium nitride (TiN). Moreover, the experimental results obtained for the condensation of films of A^4B^6 compounds, in particular, lead telluride (PbTe) were processed in Ref. [229], and the OR of multicomponent islands of compounds formed in the condensation of high-temperature superconducting films were examined in Ref. [230]. Figure 17 demonstrates the experimental and theoretical curves of the time variation of the mean height and the mean radius of islands. A detailed comparison of theoretical and experimental size distribution functions of islands was carried out in Ref. [17], where comprehensive information on the methods of obtaining island films of these compounds and the processing of the experimental results of research at the OR stage was also presented.

As concerns the experimental investigation of the OR of nuclei growing from solution-melt, the ripening of new-phase nuclei in bulk single-component melts was first experimentally established by Voorhees and Cliksman [201] for the example of white phosphorus (α-P) crystallization. They confirmed the law of time-dependent variation of the mean radius of new-phase nuclei, namely, $R^3 \propto t$, found in Ref. [107]. The ripening of ensembles of islands in solutions-melts were examined in Ref. [231] for the example of solid-solution $Bi_{12}Ti_xSi_{1-x}O_{20}$ film growth. In particular, all stages of film growth from this solution, from nucleation to continuous-structure formation, were analyzed. The analysis was carried out on singular, vicinal, and atomically rough facets of $Bi_{12}SiO_{20}$ single crystals possessing cubic symmetry. The analysis of the results obtained for singular facets of $Bi_{12}SiO_{20}$ single crystals showed that at a certain stage the newly appeared solid-solution islands begin ripening. The theoretical conclusion that the ripening of ensembles of islands growing from large solution-melt volumes can only proceed in diffusion layers with a thickness δ_D satisfying the relation $\delta_D \geqslant \bar{R}$, was confirmed in Ref. [231]. For example, the average sizes of solid-solution $Bi_{12}Ti_xSi_{1-x}O_{20}$ islands were of the order of $\bar{R} \sim 10^{-4}$ m and their ripening was only observed for the same value of the diffusion boundary layer thickness, which corresponded to a substrate rotation frequency of $\omega = 0.3\,s^{-1}$. If the latter changed so that $\delta_D < \bar{R}$ or $\delta_D \gg \bar{R}$, then no Ostwald ripening was observed.

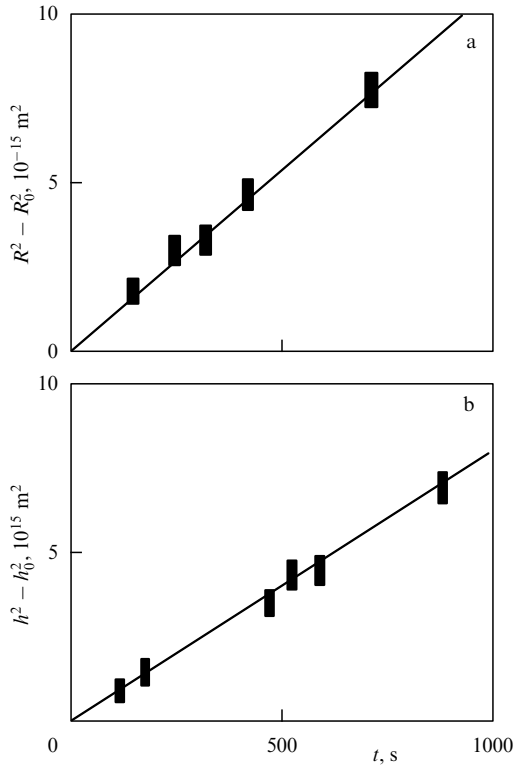

Figure 17. Time dependences of the variation of mean radius (a) and mean height (b) of CdSe islands at the OR stage.

5. The formation and growth of continuous structures

The presently available film growth methods can conditionally be divided into three large groups. The first includes film growth from the gaseous phase, namely, ion-plasma deposition, the MBE method, laser sputtering, vacuum deposition from vapor, gas-transport reactions, and the MOCVD method [17]. The second group involves methods of film

growth through an intermediate solid-phase layer, i.e. solid-phase epitaxy [232]. The methods of film growth from solutions-melts, i.e. liquid-phase epitaxy, belong to the third group [17, 233]. The theoretical arguments described above refer to all three groups and provide insight into the growth of films of any systems, obtained by any of the above-mentioned methods.

The prime concern of thin-film technology is obtaining continuous film structures† of a prescribed composition, thickness and structure. Depending on the sphere of applications, the films may be amorphous, polycrystalline, or epitaxial (single-crystal). Polycrystalline films are as a rule grown on nonorienting substrates, or on orienting ones but under conditions far from equilibrium. To obtain amorphous, i.e. frozen metastable structures, special methods of creating high supersaturations or supercoolings should be employed. The question of what the principal orienting growth factor is remains open. It is believed that a necessary condition for the growth of oriented structures is closeness of film and substrate lattice parameters (it typically suffices that the difference between them should not exceed 15%). This condition is however not at all sufficient because new-phase islands participate in various evolutionary processes. It is rather difficult to decide which of them exerts a decisive influence on orientation. Below we shall consider only a few of the models of the oriented growth.

5.1 Layer-by-layer growth of continuous structures

Beginning with the classical work [56] which laid the foundation of the TLK-model (terrace, ledge, kink), the studies devoted to crystal growth and those concerned with film nucleation go in parallel and develop independently of each other. If the former mainly investigate the motion of steps, the stability of crystal surfaces, etc. (assuming that the nuclei initiating crystal growth are initially present on the surface), the latter largely deal with the new-phase nucleation and the further evolution of the nuclei.

Such a difference is first of all due to the fact that crystals grow from their own vapor, solution or melt, while film growth proceeds on foreign substrates. Depending on the growth conditions, the time within which a continuous film is formed, the substrate occupancy, and film thickness are estimated either by the Kolmogorov formula [75] or, if the film coalescence proceeds at the OR stage, by the formulae of Refs [17, 93]. After a substrate has been covered with a layer of film material, its growth will be governed by the same laws as for crystal growth [3, 61]. If the surface of new-phase blocks is a smooth close-packed single-crystal surface, a subsequent film layer will again be formed owing to nucleation. Later these nuclei will grow and occupy the surface layer by layer. Each block here plays the role of a peculiar crystal seed. There are many such seeds on the surface, and therefore an oriented growth may be violated at high supersaturations. Block boundaries, screw surface dislocations or other linear defects may serve as sources of two-dimensional nucleation. For oriented growth it is necessary that no new nuclei appear and that the film growth be realized by atoms successively adjoining these defects. If the film surface is an atomically rough layer similar to a rough crystal surface, then each point of such a surface may be a place of atomic attachment, and the film will grow in unfavourable conditions as well.

† If one needs island structures for some purpose, the film growth should be terminated at this particular stage.

Original methods of obtaining highly oriented films were proposed in Ref. [234]. Such films usually grow at heightened temperatures (to provide appropriate adatom mobility) in conditions close to equilibrium. So, CdTe films typically grow at a substrate temperature of the order of 800 K. But the authors of Ref. [234] described methods of obtaining epitaxial films at a temperature of 228 K. A variation of substrate temperature in both directions led to a worsening of the film structure. In paper [235], such an orientation was assumed to be caused by the motion of islands as a whole due to the soliton mechanism of atomic transport investigated in Ref. [118]. There exists however an alternative explanation associated with the two-dimensional liquid layer on the substrate surface, which is formed either immediately or thanks to the appearance of liquid CdTe drops directly at the substrate surface. Heightening the substrate temperature results in the destruction of this two-dimensional layer, and its lowering to the creation of a notable supercooling and a violation of the OR stage. With a further lowering of temperature amorphous films begin to grow.

5.2 The growth on vicinal surfaces

It was established in Refs [6, 231, 236–238] that linear defects have an appreciable effect on the mechanism of heteroepitaxial film growth. For instance, in paper [231], for the example of $Bi_{12}Ti_xSi_{i-1}O_{20}$ it was demonstrated that the film growth mechanism substantially changes depending on the substrate face orientation. It was associated there with the presence of steps on the substrate that have an orientation different from that of the singular facet. Under certain conditions, these steps led to the formation of cigar-shaped structures which exert a great influence upon further oriented growth of the film. Similar effects are also observed for other materials, in particular, in the growth of YBa_2Cu_3 on vicinal MgO [236].

The assertion that it is the substrate relief elements and, in particular, steps that present orienting centres of growing film structures has been qualitatively discussed in many papers, and in Ref. [239] this question was investigated quantitatively. The main ideas suggested there are as follows. Since the vicinal surface is a train of parallel steps separated by terraces of equal widths, the atoms deposited on this surface are adsorbed near steps with a greater probability than on the terraces. Then new-phase islands form with their density on the steps largely exceeding that on the smooth substrate areas, because a step is an effective adatom sink and because steps and other defects typically suppress the work on the formation of a critical nucleus [6].

We note that the nucleation on a step is strongly dependent on the step height. An enlargement of the step height causes not only more intense nucleation on it, but an increase of its capacity to orient the new phase. In particular, the minimum step height capable of orienting a growing condensate was estimated in a number of papers [4, 6, 12]. The estimate coincides in the order of magnitude with the height of the critical nucleus. Therefore, one may assume to a first approximation that if the size of the critical nucleus on a step does not exceed $(1-2)h$, where h is the step height, the growing condensate will be oriented (the nucleation rate on smooth substrate regions should be sufficiently low). After that, the islands located at the steps coalesce to form decorated steps, which in Ref. [239] are called 'cigars' because such formations are extended along the initial substrate steps. These 'cigars' are aligned with the substrate orientation. If now the external sources of atoms are so

chosen that all the nonoriented islands on the terraces dissolve and cigar-shaped islands grow, then a layer-by-layer film growth can be realized in full accord with the layer-by-layer growth of single crystals. Such calculations were carried out in Ref. [239], where the necessary conditions for realization of this growth mechanism were found.

In most papers, the behaviour of a train of steps is described in terms of the Mullins model [3, 61], in which each point of the crystalline surface is assumed to be a source or a sink of atoms. These theoretical arguments may only be applied to nonsingular surfaces which at the elementary level are atomically rough (see Section 2.1). The variation of the macrorelief of these surfaces is realized by the normal growth mechanism in exactly the same manner as the Ostwald ripening of unfaceted islands. If the crystal surfaces are vicinal, the Mullins theory is inapplicable. This fact was first mentioned in Ref. [240], but with some mathematical errors. In Ref. [239], solutions of the step-train evolution equations were found in the most general form, which described both the film and crystal growth. Under certain conditions, the cigar density turns out to be governed by a Burgers type equation

$$\frac{\partial\rho^{(1)}}{\partial\xi} - 2a\rho^{(1)}\frac{\partial\rho^{(1)}}{\partial\chi} - D_0\frac{\partial^2\rho^{(1)}}{\partial\chi^2} = 0\,, \tag{5.1}$$

where $\rho^{(1)}$ is the first term of the expansion of the dimensionless cigar density $\rho = \rho_c/\rho_0$ in a power series of a small parameter, ρ_0 is the initial position of the density [239], ξ and χ are dimensionless variables related to the time t and the coordinate x, a is a quantity depending on the supersaturation, $D_0 = \chi\tanh r$, $r = 1/2\rho_0\lambda_0$, $\lambda_0 = \sqrt{D_a\tau_r}$, and D_a is the diffusion coefficient of adatoms. For small D_0 values, a substantial contribution to the amplitude of ρ can be made by the next term of the expansion of ρ in a power series of a small parameter [239], the dispersion effects playing a more significant role than the dissipative ones. In this case, the cigar density is governed by the Korteweg–de-Vries equation

$$\frac{\partial\rho^{(1)}}{\partial\xi} - 2a\rho^{(1)}\frac{\partial\rho^{(1)}}{\partial\chi} - b^2\frac{\partial^3\rho^{(1)}}{\partial\chi^3} = 0\,, \tag{5.2}$$

where $b = (r/2)^{3/2}\cosh^{-1}r$.

The analysis carried out in Ref. [239] showed that the variation in the relief of a growing film (crystal) is completely determined by the initial conditions. Depending on the initial conditions and some constants, triangular shock waves, kinks, solitons, knoidal waves, etc. can be originated. After some time, all of them begin smearing under the action of diffusion. The very fact of the appearance of a background solution and solitons, as well as their number also depend on the initial conditions. Nevertheless, in the overwhelming majority of cases the film roughness first increases during growth and then begins decreasing, which makes this quantity controllable. This approach substantially generalizes the kinematic theory [3, 61], in which the flux of steps was assumed to be dependent on the step density only. But it follows from Ref. [239] that actually the step flux also depends on the first and second derivatives of the step density.

On the basis of this approach, the method of growing well-oriented films of various compounds, in particular, diamond-like ones, was proposed in Ref. [239]. For this purpose, the atomic flux intensity should first be kept sufficiently high to provide new-phase nucleation on steps, and then at $t_1 < t < t_2$ the intensity should decrease in a power-law manner: $g(t) = g_0 t^{-k} = g_0\, t^{-(p+1)/2p}$, after which the quantity $g(t)$ may be fixed at a constant level (the level should be low enough to avoid fresh nucleation). Figure 18 presents the general form of the law of variation of a flux of deposited atoms under which the layer-by-layer mechanism of continuous film growth can be operative.

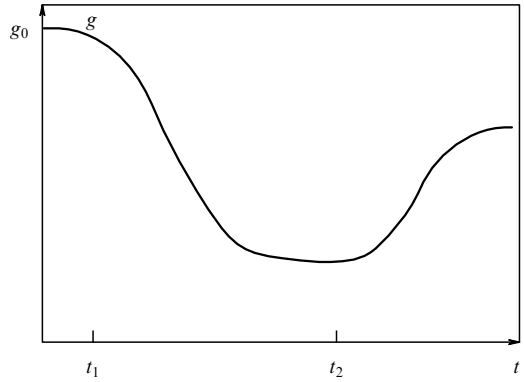

Figure 18. General form of the law of atomic flux variation making the layer-by-layer continuous-film growth mechanism possible.

5.3 The evolutionary processes in continuous films

Various processes may proceed inside continuous films under the action of external factors because the substrate–film system is essentially nonequilibrium. This nonequilibrium state is a consequence of stresses in the film and substrate. In the presence of an appropriate mass transfer mechanism these stresses will relax, which causes the loss of film continuity [88, 241]. Moreover, in polycrystalline films with grains stressed in different ways, recrystallization may take place. A rigorous theory of such processes has not yet been formulated, but nevertheless all these processes may be referred to first-order phase transitions in one way or another.

If a film is a solid solution, inside it there may occur processes of decay into components accompanied by new-phase nucleation and further evolution of the nuclei, which will proceed exactly by the laws described above, and one should only choose appropriately the corresponding coefficients. Notice that solid-phase reactions with the formation of new compounds may develop in multicomponent film systems. If the reactions proceed with the release of gas, the film will contain pores [242].

6. Conclusions

We have presented all the basic modern theoretical concepts and experimental results describing both the new-phase nucleation and further evolution of nuclei, as well as growth processes of films as a whole. The material presentation was based on the classical and field approaches allowing a unified standpoint in the investigation of processes on the substrate surface and in the surrounding volume upon film deposition from the gaseous, liquid, amorphous, and solid phases. The processes of film degradation due to elastic stresses were not considered. The influence of charges and electromagnetic effects upon thin-film growth was also beyond the scope of this paper because the corresponding theoretical models are presently in their early stages. Future progress in both the

theoretical description and practical application obviously lies in this particular field. The theory of nucleation of multicomponent systems requires further development of it. The formulation of a rigorous theory allowing the composition of growing films to be calculated in advance is still far from completion. The theory of vapor – liquid – crystal phase transition including intrinsic symmetry variations should be thoroughly investigated. Of particular interest is an account for the cause of the appearance of such diversified structures during film growth from eutectic melts. The approaches presented in this paper constitute the initial stage of creation of a self-consistent conception of this phenomenon.

It can be said that the front of studies of the physics of surfaces and surface new-phase nucleation is exceedingly wide. The authors hope that the present publication will help the reader to gain insight into these processes and to better and more quickly comprehend the range of questions described.

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