Diffusive mass transfer in island films

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A systematic review is made of the experimental and theoretical investigations of the mechanism and kinetics of mass transfer in a system of islands of substance A deposited on a solid substrate of substance B in which A is insoluble. The analysis is carried out on the assumption that the total amount of matter present jointly in the islands and in a two-dimensional gas of adsorbed atoms is constant. Behavior of systems of islands at rest and in motion is discussed. Coalescence of islands is considered in the case of diffusive mass transfer between islands at rest and also in the case of direct collisions between moving islands. "Dispersion hardening" of the surface by a system of islands, which hinders evaporation and growth of a crystal, is described. Considerable attention is devoted to reporting experimental investigations carried out mainly by electron microscopy. Some new effects are predicted, including a possible phase transition during coalescence of islands, size effect in recrystallization, one-dimensional coalescence, etc.

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CONTENTS

I. INTRODUCTION

The last fifteen or twenty years have seen the beginning and growth of research into physical processes in island films, i.e., in systems of islands of one substance located on the surface of another. Such systems are attracting interest mainly because experiments on island films are a source of important and sometimes unique information on the physics of surface phenomena, particularly on the kinetic constants (surface diffusion coefficients D_S and specific boundary fluxes β_S) and on the nature of the interaction between atoms migrating on the surfaces of a crystal and elements of the real crystal structure, such as steps, defects (including charged centers), points of emergence of dislocation lines on the surface, etc. Moreover, island films often provide convenient and easily visualized models of processes occuring in heterogeneous bulk systems.

The knowledge of the properties of island films is also needed for the understanding of the physics of formation of continuous films from the vapor phase, when an island film is just a stage in reaching the final goal.

From the thermodynamic point of view an island film is a system which is far from equilibrium in respect of many parameters at the same time. One of the principal signs of lack of equilibrium of island films is the presence of very highly developed free and interphase surfaces, with which an excess energy is associated. Naturally, at high temperatures when the necessary diffusion mechanism is active, certain processes occur in island films which tend to release the excess energy. These processes must be accompanied by diffusive mass transfer which results in the formation of intermediate island film structures representing a stage toward equilibrium, when all the matter in an island film collects into one macroscopic drop, whose shape is governed by the capillary constants of the island and substrate materials. Our reviews will be devoted precisely to this aspect of the subject of island films.

The range of processes and phenomena which we shall

discuss is restricted to those which occur when the total amount of matter Q in an island film inside a closed system remains constant:

$$Q = \varkappa \int_0^\infty f(R, t) R^3 \, dR + Q_0, \tag{I.1}$$

where $f(R, t)$ is the island-size distribution function, which varies with time; R is the radius of an island; $\varkappa$ is a dimensionless factor which represents the island geometry; Q_0 is the total amount of the island material present as two- and three-dimensional gases of atoms of this material. We shall at best only touch upon the phenomena which occur when $Q \neq$ const, i.e., when nucleation and growth of new islands or evaporation and diffusion of the newly formed islands into the substrate take place. This range of phenomena belongs not so much to the subject of island films as to the kinetic effects discussed in many reviews of monographs,[1-10] including the formation of nuclei of a new phase, growth of crystals from the vapor phase, role of the real surface structure and of the surface layer in the nucleation and growth processes, etc.

From the point of view of the effects of interest to us, there are two fundamentally different situations in an island film: all the islands can be at rest or islands may be in motion on the substrate for one reason or another. In the first situation the diffusion fluxes may determine the transformation of the shape of the islands at rest and diffusive atomic transfer of matter from one island to another. In the second situation the processes just mentioned form a background to mutual collisions of islands which result in their diffusive coalescence. Both situations occur under real conditions and are discussed in the present review.

The entire presentation will be restricted mainly to the "isotropic crystal" approximation. Since the purpose of the review is to consider the transfer of mass, it follows that the diffusion coefficients D and kinetic coefficients β occurring in the equations are phenomenological constants irrespective of their relationship to the actual mechanism of the elementary events.

II. SYSTEM OF ISLANDS AT REST

Islands at rest may participate simultaneously in two diffusion processes: their shape may be transformed so as to minimize the free energy associated with an island and the islands may emit or absorb atoms and thus participate in the minimization of the free energy of the system as a whole. Both these processes occur in the presence of the interaction between islands and a two-dimensional gas of adsorbed atoms (adatoms) of the island material on the surface of the substrate crystal.

1. Interaction of an island with a gas of adatoms

In many real situations encountered in island films the linear size of an island varies with time because of the surface migration of adatoms to or from an island, which is induced by the lack of equilibrium between the islands and a two-dimensional gas of adatoms. A measure of this lack of equilibrium is the difference between the chemical potential of the island atoms μ_R and the chemical potential of the adatoms far from an island $\bar\mu$, governed by the average concentration of these adatoms $\bar\xi$.

A quasisteady distribution of the chemical potential of adatoms near an isolated island is described by a radially symmetric function $\mu(r)$, which satisfies the equation[11]

$$\lambda^2 \Delta\mu - (\mu - \bar\mu) = 0, \tag{1.1}$$

where $\lambda = \sqrt{D_a \tau}$ is the average diffusion length of an adatom; D_a is the diffusion coefficient of adatoms of the island material on the substrate surface; τ is the average lifetime in the adsorbed state at the end of which an adatom is either desorbed or is captured by a trap on the surface. In the latter case, λ represents the average distance between traps. Equation (1.1) represents the law of conservation of matter in which allowance is made for the condensation from the vapor, which is in equilibrium with the island system, and for the desorption (or for the equilibrium of adatoms with traps on the surface).

Equation (1.1) satisfies the boundary conditions

$$\left.\begin{array}{l} \mu\,|_{r\to\infty} = \bar\mu, \\[4pt] D_\mu \dfrac{\partial\mu}{\partial r}\Big|_{r=R_1} = \beta_\mu\,[\mu\,(R_1) - \mu_R]. \end{array}\right\} \tag{1.2}$$

The first condition gives the quasisteady value of the chemical potential $\bar\mu$ far from an island. The second allows for the connection between the diffusion and boundary fluxes along the perimeter of the island base (R_1 is the radius of this base).

The kinetic coefficients D_μ and β_μ are related to the diffusion coefficient D_a and the specific boundary flux β_a[11-14] by the expressions[11]

$$D_\mu = D_a N_0 \left(\frac{\partial\xi}{\partial\mu}\right)_{T,P}, \quad \beta_\mu = \beta_a \left(\frac{\partial\xi}{\partial\mu}\right)_{T,P}. \tag{1.3}$$

The specific boundary flux β_a represents the number of adatoms which become attached to a unit length of the island perimeter per unit time in the presence of a unit concentration gradient at the island boundary;[1] $N_0 \approx 1/a^2$ is the surface density of the adsorption sites, a is the lattice parameter.

The solution of Eq. (1.1) subject to the boundary conditions (1.2) is

$$\mu(r) = \frac{\beta_\mu \lambda\,(\bar\mu - \mu_R)}{D_\mu K_0'\,(R_1/\lambda) - \beta_\mu \lambda K_0\,(R_1/\lambda)} K_0\left(\frac{r}{\lambda}\right), \tag{1.4}$$

where K_0 and K_0' are a modified Bessel function and its derivative with respect to the argument. The fluxes J_S of adatoms migrating toward an island, calculated subject to Eq. (1.4), are found to depend on the ratio of the radius R_1 to the distance λ. This is due to the fact that a change in the relationship between R_1 and λ alters a characteristic linear size which governs the adatom concentration gradient near a given contour and, therefore, the flux toward this contour.

We shall now consider two important limiting cases.

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[1] The coefficient β_a introduced in this way ($[\beta_a] = cm^{-1}\cdot sec^{-1}$) differs by a factor a^2 from the corresponding coefficient β with the dimensions of velocity.[11]

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(1) $R_1 \ll \lambda$. In this case the flux of adatoms toward or away from an island is given by the expression

$$J_S = -\frac{\tilde{D}_S N_0}{kT} \frac{\bar{\mu} - \mu_R}{R_1}, \quad \tilde{D}_S = \frac{D_S \beta_S a^2 R_1}{D_S + \beta_S a^2 R_1 \ln(\lambda/R_1)}, \quad (1.5a)$$

where $D_S = D_a \xi_0$ is the surface heterodiffusion coefficient; ξ_0 is the equilibrium concentration of adatoms of the island material on the substrate; $\beta_S = \beta_a \xi_0$.

(2) $R_1 \gg \lambda$. We now have

$$J_S = -\frac{\tilde{D}_S N_0}{kT} \frac{\bar{\mu} - \mu_R}{\lambda}, \quad \tilde{D}_S = \frac{D_S \beta_S a^2 \lambda}{D_S - \beta_S a^2 \lambda}. \quad (1.5b)$$

It follows from Eqs. (1.5a) and (1.5b) that the flux of adatoms is governed by surface heterodiffusion only if $D_S \ll \beta_S a^2 R_1 \ln(\lambda/R_1)$ or $D_S \ll \beta_S a^2 \lambda$. In this case we have $\tilde{D}_S = D_S$. For the opposite inequalities, the flux is governed by the rate of acquisition or emission of adatoms by an island and is of the form $J_S = -(\beta_S/kT)(\bar{\mu} - \mu_R)$ in both cases considered above.

The reality of the boundary kinetics in the interaction of islands with an adatom gas has been demonstrated convincingly in the experiments of Shrednik et al.,[15-18] who used an electron projector to investigate the kinetics of growth and dissolution of two-dimensional hafnium and zirconium islands on the surface of tungsten or niobium carrying, respectively, a supersaturated or an undersaturated two-dimensional vapor of adatoms of the island material. Their experiments demonstrated that the temperature dependences of the rate of growth and dissolution of the islands were governed by different activation energies: the activation energy of the dissolution process was approximately 2–3 times greater than that of the growth process. This asymmetry between the growth and dissolution processes in the case of known values of $\bar{\mu}$ and μ_R, governed by the adatom concentrations is—according to Eq. (1.5)—possible only in the case when the change in the direction of a given process alters its limiting stage. It is likely that the rate of growth of islands is limited by the surface heterodiffusion and the rate of dissolution by the boundary kinetics, i.e., by the rate of emission of atoms by islands.

We can use the expressions for the fluxes in considering the problem of the interaction of an island with an adatom gas making specific assumptions about the physical factors responsible for the difference $\bar{\mu} - \mu_R$. By way of example we shall consider the kinetics of the growth of an island in the form of a spherical segment of radius R, which varies in accordance with

$$\frac{dR}{dt} = -\frac{J_S \omega}{R} \psi(\theta). \quad (1.6)$$

where $\psi(\theta) = 2\sin\theta/(2 - 3\cos\theta + \cos^3\theta)$, θ is the angle of contact; ω is the atomic volume. The quantity $\bar{\mu} - \mu_R$ in Eq. (1.4) can be expressed in the following form if the supersaturation is weak:

$$\bar{\mu} - \mu_R = kT\left(\frac{\delta\xi}{\xi_0} - \frac{\alpha}{R}\right) = \frac{2\gamma_1\omega}{R^*}\left(1 - \frac{R^*}{R}\right). \quad (1.7)$$

where $\delta\xi = \bar{\xi} - \xi_0$; $\alpha = 2\gamma_1\omega/kT$; $R^* = \alpha\xi_0/\delta\xi$ is the critical radius; γ_1 is the surface tension of the island material. The relationships (1.4), (1.5a), (1.6), and (1.7) are sufficient to obtain the following equation which de-

termines the time dependence of the rate of growth of an island:

$$\frac{dR}{dt} = \frac{2\psi_1(\theta)}{R^* R^2} \frac{\tilde{D}_S \gamma_1 \omega^2 N_0}{kT}\left(1 - \frac{R^*}{R}\right),$$

where $\psi_1(\theta) = \psi(\theta)/\sin\theta$.

The problem of the growth of an island which has formed at an active center of charge q can be considered in a similar manner[19,20] (see Sec. 4).

It is worth noting the following feature of the kinetics of island growth, which is associated with the electrostatic interaction of a charged center with adatoms.[20] This interaction can be regarded as a reduction in the potential barrier hindering the diffusion of an adatom to a charged center; the reduction is by an amount

$$\Delta Q = \frac{\partial u(r)}{\partial r} \frac{a}{2}, \quad (1.8)$$

where $u(r) = -pq^2/r^4$ is the energy of the interaction between the center and the adatom, which can be represented as the energy of the interaction of a dipole with a point charge; p is the polarization coefficient of the adatom. In view of the strong dependence $u(r)$ we may find that at some value $r = R_0$ the reduction in the barrier height ΔQ is equal to Q_m, which is the migration energy of the adatom. This means that inside a circle $r = R_0$ an adatom migrates toward a charged center in an activation-free manner. The radius R_0 of the "adatom capture zone" of a center follows from Eq. (1.8):

$$\frac{R_0}{a} = \left(\frac{2pq^2}{a^4 Q_m}\right)^{1/5}. \quad (1.9)$$

which can be considerably greater than the lattice parameter for a resonable relationship between the constants. For example, for $p \approx 10^{-23}$ cm^3,[21] $q \approx 5e = 2.5 \times 10^{-9}$ cgs esu, $a = 3 \times 10^{-8}$ cm, and $Q_m = 0.3$ eV, we find that $R_0/a \approx 3$–4.

A similar estimate is obtained by postulating that an adsorbed atom has an effective charge $\bar{q}$ and by regarding $u(r) = -q\bar{q}/r$ as the energy of the Coulomb interaction between the adatom and the center under consideration. For $q \approx 0.1e \approx 5 \times 10^{-11}$ cgs esu, we again obtain $R_0/a \approx 3$–4.

It should be noted that this effect and the existence of a capture zone are similar to a "pulsating" vacancy and its instability zone in the bulk of a crystal, discussed earlier by Koshkin et al.[22,23]

2. Transformation of the shape of an island to equilibrium shape. Coalescence during shape transformation

The general problem of the equilibrium shape of an island in the case of anisotropic surface tension can be considered conveniently using the Wulff construction[24,25] and bearing in mind that, in constrast to free surfaces characterized by a surface tension γ_1, the interface between an island and its substrate should be regarded as having a tension $\gamma_{12}-\gamma_2$, where γ_{12} is the tension of the interface between the two phases and γ_2 is the surface tension of the substrate material. This definition follows from variation of the free surface energy of the island–substrate system:[26]

$$\delta F_S = \delta \int_{S_{12}} (\gamma_{12} - \gamma_2)\, dS + \delta \int_{S_1} \gamma_1\, dS = 0. \qquad (2.1)$$

Equation (2.1) is derived on the assumption that $dS_{12} = -dS_2$; the index 1 refers to the island material and the index 2 to the substrate material. An example of the Wulff construction is shown in Fig. 1. A similar construction for an amorphous island leads to the well-known rule governing the angle of contact
$$\theta = \cos^{-1}[(\gamma_2 - \gamma_{12})/\gamma_1].$$

It is difficult to solve exactly the problem of the transformation of an arbitrary shape of an island to an equilibrium shape. However, we can easily estimate the characteristic times for conversion of the shape of an island whose dimensions vary little with direction so that spontaneous breakup into smaller islands is unlikely from the thermodynamic point of view.[27]

We shall now consider the kinetics of formation of an equilibrium shape of an island in the isotropic approximation. Mass transfer necessary for the formation of a drop of isomeric shape may generally be due to bulk or surface self-diffusion or due to diffusion via a gas. However, the surface fluxes predominate if $R < \tilde{R} = D'_S a / D'_V$ (D'_S and D'_V are the surface and volume or bulk self-diffusion coefficients). Even at high temperatures when the ratio D'_S/D'_V has its minimum value ($\approx 10^4$), we find that $\tilde{R} \approx 10^{-4}$ cm. This means that the fluxes of interest to us in real islands are of the surface type.

Estimates of the characteristic time τ of establishing an isomeric shape can be obtained by assuming that the surface fluxes may be limited not by the actual kinetics of self-diffusion of adatoms on the island surface but also by the rate of detachment of atoms from parts of the surface with a curvature K greater than the average value $\bar{K}$ or by the rate of attachment to those parts of the surface where the curvature is less than average. The average curvature of an island may be defined by $\bar{K} = \int K(S)dS / \int dS$, where $K(S)$ is the local curvature of a surface region of area dS. The rate of emission or acquisition can be represented by the specific boundary flux β', normalized to a unit surface area of the island ($[\beta'] = cm^{-2}\,sec^{-1}$).[13,14]
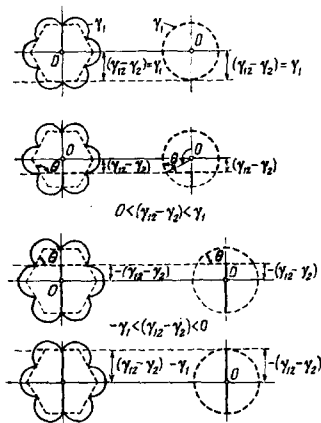

FIG. 1. Examples of the Wulff construction for determination of the equilibrium shape of an island on a substrate for various relationships between γ_1, γ_2, and γ_{12}. On the right the value of γ_1 is isotropic and on the left it is anisotropic.[26]

The flux of adatoms along the surface of an island can be written in the form $J_a = -D'_\mu \nabla \mu_a$, where μ_a is the chemical potential of adatoms measured from the value μ_0 representing atoms in an island of infinite dimensions; $D'_\mu = D'_S N'_0 /kT$; N'_0 is the surface density of island atoms. The value of μ_a at any point on the island surface generally differs from the local chemical potential of the island atoms $\mu_S = K\gamma_1 \omega^{28}$ (also measured from the value of μ_0); this is why emission or acquisition of adatoms may limit the process of shape conversion. We find that $\mu_a > \mu_S$ in regions with $K < \bar{K}$ and that $\mu_a < \mu_S$ in regions where $K > \bar{K}$.

Simple calculations give the following estimate of the value of τ:
$$\tau \approx kT \frac{\bar{R}^4}{\tilde{D}'_S \gamma_1 \omega^2 N_0}, \quad \tilde{D}'_S = \frac{D'_S \beta'_S a^2 R^2}{D'_S + \beta'_S a^2 R^2}, \qquad (2.2)$$

where $\beta'_S = \beta' \xi'_0$; ξ'_0 is the equilibrium concentration of adatoms of the island material on the island surface.

We shall now consider the two limiting cases of restriction on the rate of transformation of the shape of an island.

(a) $D'_S \ll \beta'_S a^2 R^2$. In this case the rate is limited by the surface self-diffusion. We then have $\tilde{D}'_S \approx D'_S$ and $\tau \propto R^4$.

(b) $D'_S \gg \beta'_S a^2 R^2$. The rate of transformation of the shape of an island is now limited by the rate of adatom acquisition or emission. In this case we have $\tilde{D}'_S = \beta'_S a^2 R^2$ and the characteristic relaxation time of the island shape is $\tau \approx kTR^2/\beta'_S \gamma_1 \omega^2$, i.e., $\tau \propto R^2$.

We shall estimate τ for metal island films on the assumption that the process is limited by diffusion. Substituting in Eq. (2.2) the values $R \approx 10^{-6}$ cm, $kT \approx 10^{-13}$ erg, $D'_S \approx 10^{-8}$ cm^2/sec, $\gamma_1 \approx 10^3$ erg/cm^2, and $\omega^2 N_0 \approx 10^{-30}$ cm^4, we obtain $\tau \approx 10^{-3}$ sec. If $R \approx 10^{-4}$ cm, then $\tau \approx 10^5$ sec. These estimates, made on the assumption of isotropy of γ_1, can be used also when an island has crystal faceting because the characteristic difference between the chemical potentials governing the relevant fluxes is not very sensitive to the details of the island geometry. However, in such a case it is more likely that the shape relaxation time will be governed by the specific boundary flux because of the difficulty of detachment (attachment) of atoms from (to) mirror-smooth surfaces forming the island facets.

Islands are frequently disk-shaped with an angle of contact less than the equilibrium value.[29-31] In this case the relaxation of the shape towards its equilibrium configuration results in a contraction of the island and in a reduction of the area of contact with the substrate. This process is sometimes called autocoalescence.[30]

In the course of shape modification to the isomeric form it may happen that two adjacent nonisomeric islands come into contact and coalescence by diffusion. This occurs if the distance between neighboring nonisomeric islands is less than the sum of the radii of islands of equilibrium shape. We can easily estimate the characteristic time for diffusion coalescence τ_c of islands which have come into contact (for simplicity, we shall assume that their volumes are the same). We can use in

this case Eq. (2.2) to estimate the coalescence time of interest to us. The smallness of τ_c creates an illusion of liquid-like coalescence, which has been observed frequently in experimental studies[32-34] of the kinetics of the growth of island films *in situ*.

If the angle of contact is sufficiently large ($\theta \approx \pi$), the coalescence time of islands can be determined more accurately employing a relationship describing the kinetics of merging of spheres as a result of surface diffusion:[35]

$$x^6 \approx 25 \frac{D_S' \gamma_1 \omega^2 N_0'}{kT} R^2 t, \tag{2.3}$$

where x is the radius of the contact "neck" and R is the initial radius of the spheres. Assuming in Eq. (2.3) that $x \approx R$, we find that τ is given by an expression which differs from Eq. (2.2) by a factor of 25 in the denominator.

Merging of islands is frequently accompanied by recrystallization in which one of the islands assumes the orientation of the other, which has a lower free surface energy (allowing for the island–substrate interface). Since the difference between the chemical potentials of atoms in islands coming into contact is inversely proportional to the dimensions of the islands, the recrystallization of island (and more generally, thin) films should be subject to the size effect. Estimates indicate that the predicted size effect should be of magnitude sufficient for experimental detection.

3. Two-dimensional diffusive coalescence on a smooth surface of a single crystal

The basic idea underlying the calculation of the kinetics of this process can be found in the paper by Lifshits and Slezov,[36] where the theory of the coalescence of a system of inclusions in the bulk of a crystal is developed. According to Lifshits and Slezov,[36] variation of the radius of a given island with time is a consequence of its diffusive interaction not with the nearest neighbors but with a generalized diffusion field. In the case of a two-dimensional system of islands we mean here either a generalized reservoir of atoms in the three-dimensional vapor phase above the island film surface or the generalized field of adatoms.

The generalized diffusion field can be described by an adatom concentration $\bar{\xi}$ which depends on the island-size distribution function $f(R, t)$ and which is in equilibrium with islands of critical size R^*. Islands of radii $R < R^*$ dissolve in the diffusion field because near them the equilibrium adatom concentration is $\xi_R > \bar{\xi}$, whereas islands with $R > R^*$ grow because they are characterized by $\xi_R < \bar{\xi}$. This model is valid provided the diffusion field concept does not lose its meaning, i.e., provided the two-dimensional density of islands satisfies the inequalities $[4(\bar{R}+\lambda)^2]^{-1} < N_S < (4\bar{R}^2)^{-1}$.

The problem of kinetics of diffusive coalescence of a system of islands can be reduced to the solution of the equation of continuity in the space of island sizes for the function $f(R, t)$:

$$\frac{\partial f(R, t)}{\partial t} + \frac{\partial}{\partial R}\left[f(R, t) \frac{dR}{dt} \right] = 0, \tag{3.1}$$

where Eq. (I.1) from the Introduction (Sec. I) is used.

The method developed by Lifshits and Slezov[36] gives a solution of the system (3.1)–(I.1) if we know the R-dependence of dR/dt, the rate of change (with time) of the radius of a single island which is in a diffusion field corresponding to the average concentration of atoms of the island material.

We shall now consider various mechanisms of two-dimensional coalescence.

a) *Diffusion of atoms in the gaseous phase.* Time dependence of the island radius is in this case given by[37]

$$\left(\frac{dR}{dt}\right)_g \approx \frac{\tilde{D}_g}{R}\left(\bar{n} - n_R\right) = \frac{\tilde{D}_g}{R} \omega \frac{\alpha n_0}{R^*}\left(1 - \frac{R^*}{R}\right), \tag{3.2}$$

where $\bar{n} = n_0[1 + (\alpha/R^*)]$; $n_R = n_0[1 + (\alpha/R)]$; $\tilde{D}_g = D_g \beta' \omega R / (D_g + \beta' \omega R)$; D_g is the coefficient of diffusion in a gas; $n_0 = p_0/kT$; p_0 is the saturated vapor pressure of the island material. It follows from Eq. (3.2) that the dependence of dR/dt on R is different in the two limiting cases of restriction on the rate of growth of an island.

1) $D_g \ll \beta' \omega R$. In this case we have $\tilde{D} \approx D_g$. The asymptotic law $\bar{R}(t)$ is given by[2]

$$\bar{R}^3 = \bar{R}_0^3 + \frac{D_g \gamma_1 \omega^2 p_0}{(kT)^2} t, \tag{3.3}$$

where R_0 is the initial average radius of islands in the system.

2) $D_g \gg \beta' \omega R$. In this case, we have $\tilde{D}_g \approx \beta' \omega R$, and the asymptotic law becomes

$$\bar{R}^2 = \bar{R}_0^2 + \frac{\beta' \gamma_1 \omega^3 p_0}{(kT)^2} t. \tag{3.4}$$

b) *Diffusion of adatoms on the surface.* It is clear from Eqs. (1.4)–(1.6) that the expressions for dR/dt and, consequently, the asymptotic laws $\bar{R}(t)$ for this mechanism depend on the ratio of the average radius of the islands at their bases $\bar{R}_1$ to the average diffusion length λ traveled by an adatom on the substrate surface. We shall write $\bar{R}(t)$ for limiting cases of practical importance:[37]

1) $\bar{R}_1 \ll \lambda$; $D_S \ll \beta_S a^2 R_1 \ln(\lambda/R_1)$: (diffusion-controlled regime):

$$\bar{R}^4 = \bar{R}_0^4 + \frac{\psi_1(\theta)}{\ln(\lambda/R_1)} \frac{D_S \gamma_1 \omega^2 N_0}{kT} t, \tag{3.5}$$

where $\psi_1(\theta) = \psi(\theta)/\sin\theta$;

2) $\bar{R}_1 \ll \lambda$; $D_S \gg \beta_S a^2 R_1 \ln(\lambda/R_1)$:

$$\bar{R}^3 = \bar{R}_0^3 + \frac{\psi(\theta) \beta_S \gamma_1 \omega^2}{kT} t; \tag{3.6}$$

3) $\bar{R}_1 \gg \lambda$; $D_S \ll \beta_S a^2 \lambda$:

$$\bar{R}^3 = \bar{R}_0^3 + \frac{\psi(\theta) D_S \gamma_1 \omega^2 N_0}{\lambda kT} t; \tag{3.7}$$

4) $\bar{R}_1 \gg \lambda$; $D_S \gg \beta_S a^2 \lambda$: in this case the law $\bar{R}(t)$ is identical with Eq. (3.6).

The expressions (3.3)–(3.7) describing the dependence $\bar{R}(t)$ can be used to find the time dependences of the two-dimensional density of islands $N_S(t)$ for each of the above cases. Since the amount of matter contained in

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[2] It has been shown[36] that the average radius $\bar{R}$ of islands in a system is practically identical with the critical radius R^*.

the islands is much greater than that present on the surface in the form of isolated adatoms, we can simplify Eq. (I.1) by dropping Q_0 and write $Q = \varkappa N_S(0)\bar{R}_0^3 = \varkappa N_S(t)\bar{R}^3(t)$, which gives

$$N_S(t) = N_S(0)\frac{\bar{R}_0^3}{\bar{R}^3(t)}.$$

It follows from the calculations that the asymptotic island-size distribution functions are in each case independent of the initial distribution and have the form

$$f_n(R, t) = \frac{N_S(t)}{\bar{R}(t)} P_n(u), \quad u = \frac{R}{\bar{R}}.$$

The functions $P_n(u)$ are found to be the same for a given power exponent n ($n = 2, 3,$ or 4), governing the law $\bar{R}(t)$, and they depend only on the dimensionless ratio $u = R/\bar{R}$.[36-40] Tabulated asymptotic functions $P_n(u)$ are plotted in Fig. 2.

The expressions (3.3)-(3.7) can be used, in principle, to determine the kinetic coefficients, controlling the coalescence process, from the known law $\bar{R}(t)$ and to find the form of the asymptotic function representing the size distribution of islands.

Two-dimensional coalesence in metal island films with an effective thickness from 10^{-8} to 10^{-5} cm has been observed experimentally on various substrates by electron[40-44] and optical[45-47] microscopic methods. Typical photomicrographs showing successive stages of coalescence and the corresponding island-size distribution functions are shown in Figs. 3 and 4.

The main difficulties in the interpretation of the experimental results arise in the determination of the mechanism and rate-limiting stage of the process. A comparison of the experssions giving dR/dT for various mechanisms shows[37] that for most metal island films the principal coalescence mechanism at temperatures $T \approx T_{mp}/2$ (T_{mp} is the melting point of the island material) is the surface heterodiffusion.

Identification of the rate-limiting stage is a more difficult task. If the inequality $\bar{R} \ll \lambda$, is obeyed, the diffusion and boundary kinetics give different laws $\bar{R}(t)$ [compare Eqs. (3.5) and (3.6)] and different island-size distributions (Fig. 3), so that we can determine the rate-limiting stage. However, if $\bar{R} \gg \lambda$, the diffusion and boundary kinetics are governed by the same law $\bar{R}^3 \propto t$ [compare Eqs. (3.7) and (3.6)], which makes it more difficult to find the rate-limiting stage. However, we can say that in systems of islands with small (compared with $D_S/\beta_S a^2$) distances $\bar{l}$ between them, the rate-limiting stage is the boundary kinetics. On increase of $\bar{l}$, the "resistance" due to the diffusion mechanism in-
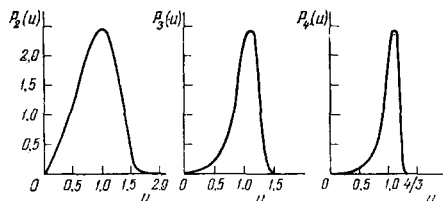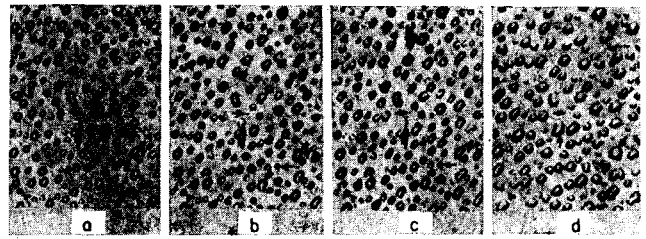

FIG. 3. Successive stages of the coalescence in a silver island film on the surface of nickel at $T = 850°$C applied for different times t (h): a) 0; b) 1.5; c) 4.2; d) 8.2. Arrows are used to identify some of the dissolving and coalescing islands. Magnification ×300 (reproduced here at 213).[46]

creases and then diffusion becomes the rate-limiting stage.

The surface heterodiffusion coefficients have been determined from the kinetics of two-dimensional coalescence[46,47] in which the rate of coalescence (governed by the experimental conditions) has been governed by the boundary and not by the diffusion kinetics. The results of these experiments, together with Eq. (3.5), can be used to determine the coefficient $D_S = D_a \xi_0$. Data on the heterodiffusion coefficients D_S obtained from the coalescence experiments are given in Table I at the end of Sec. 6. The coefficients determined from the coalescence kinetics[47] are close to those found by the labeled atom method.[48] The relatively high activation energies of surface heterodiffusion ($Q_S \approx 30$–50 kcal/mole) deduced from the coalescence experiments (Ni, Ag, Au) determine the temperature dependence of the coefficient $D_S = D_a \xi_0$ and consist of the migration energy of adatoms Q_m and the energy of formation of these atoms Q_0, which may be greater than Q_m.

4. Coalescence of electrically charged islands

Islands may be charged either because of partial ionization of a molecular beam[29] from which an island film is formed or because of the presence-on the surface of an insulating substrate-of electrically charged centers which are nucleation centers in the process of formation of island films.[49,50] The existence of an effective charge q alters, irrespective of its sign, the equilibrium concentration of adatoms near islands because in addition to the compressive Laplace pressure $\approx 2\gamma_1/R$ there is also a stretching "electrostatic" pressure $\approx q^2/2\pi R^4$. Therefore, the expression which gives ξ_R is of the form[51]

$$\xi_R = \xi_0\left(1 + \frac{\alpha}{R} - \frac{s}{R^4}\right), \tag{4.1}$$

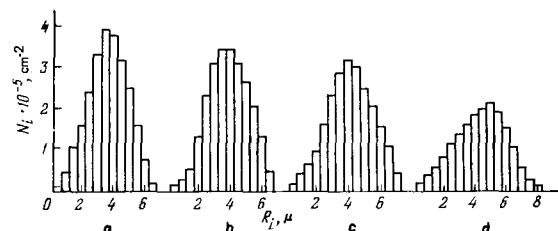FIG. 2. Asymptotic distribution functions $P_2(u)$, $P_3(u)$, and $P_4(u)$.

FIG. 4. Histograms of the island-size distribution corresponding to Fig. 3.

where $s = q^2\omega/2\pi kT$ (Fig. 5a). It is clear from Eq. (4.1) that the influence of charges is important for R of the order of $\tilde{R}$. The value of $\tilde{R}$ can be found by comparing the second and third terms in Eq. (4.1):

$$\tilde{R} = \left(\frac{s}{\alpha}\right)^{1/3} = \left(\frac{q^2}{4\pi\gamma_1}\right)^{1/3}. \tag{4.2}$$

Near an island with $R \approx \tilde{R}$ the equilibrium concentration of adatoms is ξ_0. For $q \approx (5-10)e$, where e is the elementary charge, and $\gamma_1 \approx 10^3$ erg/cm^2, we find that $\tilde{R} \approx 10^{-7}$ cm.

Application of Eq. (4.1) to the diffusion-controlled case allows us to obtain from Eq. (1.7) the following dependence of dR/dt on R:

$$\frac{dR}{dt} \approx \frac{D_S N_0 \omega \psi_1(\theta)}{R^2} \left(\frac{\delta\xi}{\xi_0} - \frac{\alpha}{R} + \frac{s}{R^4}\right), \tag{4.3}$$

which shows that there are two critical radii: $R_1 \approx \tilde{R}$ and $R_2 \approx R^* = \alpha/(\delta\xi/\xi_0)$ (Fig. 5b). The islands with $R = R_1$ should be stable against diffusive dissolution and growth, because according to Eq. (4.1) a reduction in their size lowers the value of ξ_R and an increase in their size enlarges ξ_R. The critical radius R_2 corresponds, like R^*, to the thermodynamically unstable state.

Stabilization of charged metal islands with $R \approx \tilde{R}$ may be regarded also as a quantum effect a small metal island is a potential well for localized electrons, which govern the excess charge. A quantum-mechanical calculation[51] allowing for the presence of one electron per island gives the following estimate of $\tilde{R}$:

$$\tilde{R} \approx \left(\frac{2\pi\hbar^2}{m\gamma_1}\right)^{1/4},$$

where m is the electron mass and h is the Planck constant. For $\gamma_1 \approx 10^3$ dyn/cm, we have $\tilde{R} = 10^{-7}$ cm.

A charge-stabilized island resembles a Krivoglaz phason.[52,53]

In view of the stability of the critical size R_1, the diffusive coalescence of a system of charged islands should have the following features. The island-size distribution function should be described by a cu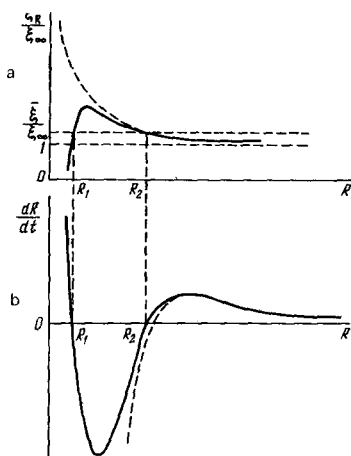rve with two maxima. The width of the first maximum, located near $\tilde{R}$, depends on the distribution of the island charges. The second maximum describes the size distribution of those islands whose radius is sufficiently large to ignore the influence of charges.

The coalescence of charged islands should be slower than in the absence of charge. The process of dissolution of charged islands of subcritical dimensions slows down on approach of their size to $\tilde{R}$, whereas neutral islands dissolve more rapidly on reduction of their radius. An increase in the average size of an island reduces the influence of charges on the coalescence process.

It is reported[51] that the coalescence of a gold film on the surface of NaCl is slower when the average island size is $\bar{R} \approx 10^{-7}$ cm than when it is $\bar{R} \approx 10^{-5}$ cm (Fig. 6). The amount of matter redistributed between islands in a film with $\bar{R} \approx 10^{-7}$ cm and this may be explained by a possible influence of charged defects of the substrate surface on mass transfer.

Charged centers distributed randomly on the surface of a crystal may act as localized sinks of diffusing adatoms.[51,54,55]

5. Coalescence on a rough surface. One-dimensional coalescence

The surface of an arbitrary section through a crystal is covered by natural roughness steps[11,56] whose presence should affect the process of diffusive coalescence in island films. The mechanism of the influence of such steps can be established by considering the role played by an isolated atomic step in the coalescence of a system of islands located along this step. In a real situation if the distance between steps is much less than the linear dimensions of an island, such an island overlaps a large number of identical steps. Under thermodynamic equilibrium conditions we can expect adsorption of the island material atoms at each step and this process can be represented by the adsorption coefficient χ. As a result of adsorption the concentration of adatoms at a
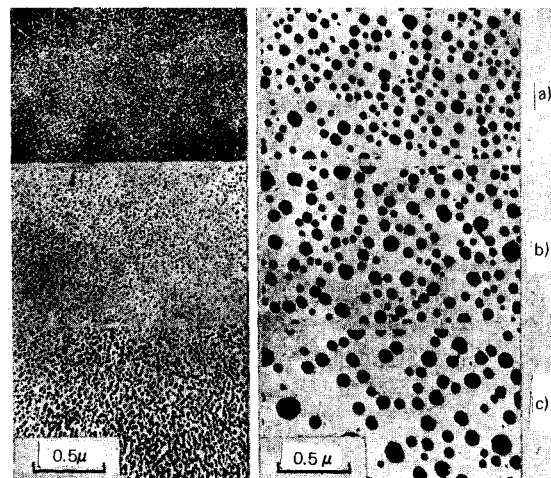

FIG. 5. Schematic dependences of ξ_R (a) and dR/dt (b) on the radius of charged (continuous curves) and neutral (dashed curves) islands.[51]

FIG. 6. Successive stages of the coalescence in Au island films of different degrees of dispersion on NaCl[51] at $T \approx 410°$C applied for different times t (min): a) 0; b) 20; c) 60.

step is now given by $\xi_1 = \chi\xi_0$, and the "linear hetero-diffusion" coefficient is now $D_{S,1} = D_l\xi_1$, where D_l is the coefficient of the Brownian migration of atoms adsorbed by the steps. For a certain value of χ we may find that $D_{S,1} \gg D_S$ even when $D_l < D_a$. This intensifies the diffusive mass transfer between the islands located in the immediate vicinity of a step, so that the islands on the step become larger compared with those located on the "smooth" parts of the surface (other conditions being equal).

The presence of a zone near a step where the concentration of adatoms is higher creates conditions under which islands located along the step become an interacting system.

The criterion of preponderance of the "linear" fluxes of adatoms to islands over the two-dimensional motion is given by the self-evident relationship[37]

$$ m\chi \gg \pi \frac{D_a}{D_l} \frac{R}{a} \frac{d_l}{d_S}, $$

where d_l and d_S are, respectively, the characteristic distances along the step and on the surface governing the variation of the adatom concentration with $\overline{\xi}$ to a value which is in equilibrium with a given island; m is the number of steps intersecting the island.

The problem of linear coalescence has been considered[37,57] under various assumptions concerning the ratio between D_a and D_l. Slezov and Levin[57] calculate the coalescence kinetics on the assumption that $D_l \gg D_a$ ignoring the effects of adsorption. Geguzin and Kaganovskii[37] postulate that $D_l < D_a$, and that the adsorption coefficient is fairly high. The results of these calculations[37,57] can be summarized as follows.

If the number of steps intersecting an island is fixed and the distance between the islands τ is much greater than λ_1, which is the diffusion path of an atom adsorbed at a step, the asymptotic law representing the time dependence of the average size of the islands located along a line is $\overline{R}^4 \propto t$, irrespectively of whether the diffusion or boundary kinetics limits the rate of the process. If islands are located on a rough surface and the number of steps intersecting an island is proportional to its radius, this law becomes $\overline{R}^3 \propto t$. In the $\overline{l} \ll \lambda_1$ case the condition of constancy of the amount of matter in the islands along a step leads to $\overline{l} \propto 1/\overline{R}^3$, so that we then obtain the law $\overline{R}^7 \propto t$.

The predominance of "linear" diffusion in the coalescence of island films of gold on a (100) surface of an LiF single crystal with steps was observed experimentally by Geguzin et al.[58] In these experiments a simultaneous study was made of the coalescence of islands on rough and smooth parts of the surface. Figure 7 shows a photograph illustrating the distribution of the gold islands on different parts of the surface of a growth hump formed by circular concentric layers of approximately the same height ($\approx 5 \times 10^{-7}$ cm). The islands along the steps bounding these layers were (after annealing) considerably larger than those on the smooth terraces between the steps. A typical sequence of electron-micrographs illustrating the process of coal-
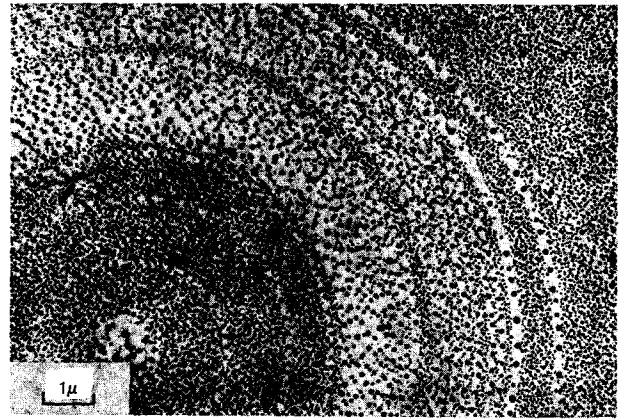

FIG. 7. Gold islands on smooth and stepped parts of the surface of LiF after annealing at $T = 380°C$ for 20 h.[58]

escence of islands on smooth and rough parts of the surface is given in Fig. 8.

6. Coalescence on the surface of a polycrystalline sample

In describing the process of coalescence of islands on the surface of a polycrystalline sample with grain boundaries at rest one has to allow for the possibility of two basic situations associated with the polycrystalline structure of the substrate. One of them is the presence of grain boundaries, which can act as adatom sinks even when the island material is insoluble in the substrate. The other possibility is that the energy of the island–substrate interface and particularly the surface energy of a gain may differ with the orientation of the adjoining grains.
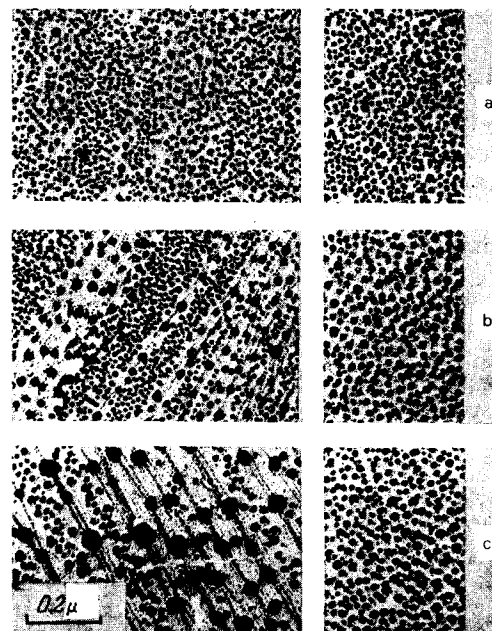
These two circumstances may have a considerable

FIG. 8. Successive stages of the coalescence of Au islands on smooth (on the right) and stepped parts of the surface of LiF.[58] $T = 380°C$ applied for different times t (h): a) 0; b) 6; c) 20.

influence on the coalescence kinetics. We shall now consider this influence.

a) *Substrate grain boundary as a sink.* Since a grain-boundary is a perfect sink and attracts a flux of adatoms originating from islands, it follows that islands near a grain boundary will dissolve and island-free zones will appear on both sides of the boundary. The width of these zones $\zeta_i(t)$ ($i = 1$ or 2) varies with time in accordance with the law

$$\frac{d\zeta_i}{dt} = -J_i \frac{\omega}{h},$$

where h is the effective thickness of an island film and J_i is the flux of adatoms which can be found if the distribution of the chemical potential near the boundary is determined first; under steady-state conditions this distribution obeys

$$\Delta\mu_i = 0. \tag{6.1}$$

This equation may be solved subject to the self-evident boundary conditions

$$\mu_i(0) = \mu_0, \qquad \mu_i(\zeta_i) = \bar{\mu}_i,$$

where $\bar{\mu}_i$ is the average chemical potential of adatoms in the diffusion field far from a grain boundary. The above equations lead to[59]

$$\zeta_i(t) = \frac{4}{\sqrt{3}} \left[\frac{\ln(\lambda/\bar{R})}{\psi_1(0)} \right]^{1/8} \frac{(B_i t)^{3/8}}{h^{1/2}} \propto t^{3/8}, \tag{6.2}$$

where $B_i = D_{si}\gamma_1\omega^2 N_0/kT$ and D_{si} is the heterodiffusion coefficient on the surface of the ith grain.

b) *Allowance for different orientations of neighboring grains.* We shall simplify the problem by assuming that a grain boundary is not an adatom sink. In this case the difference between the orientations of neighboring grains, which is the cause of the difference between the chemical potentials of adatoms, determines the flux directed from one grain to another across the boundary. Clearly, this flux produces a zone where the amount of matter in the islands increases in time (this zone appears on grain 1) and a second zone free of islands (on grain 2). The relevant flux can be found by solving Eq. (6.1) subject to the following boundary conditions

$$\mu_i(-\zeta_i) = \bar{\mu}_i, \qquad \mu_2(\zeta_2) = \bar{\mu}_2,$$
$$\mu_1(0) = \mu_2(0), \qquad D_{s1}\nabla\mu_1(0) = D_{s2}\nabla\mu_2(0).$$

Following the calculation procedure described above, we can find the dependences $\zeta_1(t)$ and $\zeta_2(t)$ which describe the process under discussion.

The quantities $\zeta_1(t)$ and $\zeta_2(t)$ vary with time and obey the following relationship:[59]

$$(\zeta_2 + l)^2 = \frac{16}{3} \frac{B_2}{h} A t^{3/4} + l^2, \tag{6.3}$$

where

$$l = \frac{D_{s2}}{D_{s1}} \zeta_1, \quad A = \left[\frac{\ln(\lambda_1/\bar{R}_1)}{\psi_1(\theta_1) B_1} \right]^{1/4} - \left[\frac{\ln(\lambda_2/\bar{R}_2)}{\psi_1(\theta_2) B_2} \right]^{1/4}.$$

It follows from Eq. (6.3) that the law $\zeta_2(t) \propto t^{3/8}$ is satisfied for $\zeta_2 \gg l$.

The formation of an island-free zone on one side of a grain boundary may have the final result that an island film exists only on certain grains to which the matter

from all other grains is transferred by diffusion.

These features of the coalescence on a polycrystalline substrate with grain boundaries at rest were observed clearly in experiments on chromium island films deposited on copper, silver films deposited on nickel, and copper films deposited on tungsten.[59] These particular systems were selected because their components were not mutually soluble. Typical photomicrographs demonstrating the successive stages of the formation of island-free zones on both sides of a grain boundary (case A) and on one side (case B) are shown in Figs. 9 and 10.

The surface heterodiffusion coefficients were deduced in these experiments from the dependences $\zeta^{8/3} = f(t)$ and from the data on the coalescence kinetics in a region far from the boundaries, where the asymptotic law $\bar{R}^4 \propto t$ was obeyed [see Eq. (3.5)]. The values of D_S found by these two methods were in satisfactory agreement (Table I).

7. Coalescence accompanied by a phase transition

The possibility of influence of a phase transition on the coalescence process follows, in principle, from the circumstance that at temperatures close to the phase transition point the equilibrium phase in the islands of size less than a certain critical value R_{cr} is the high-temperature modification.[60-62] This means that in a system of islands showing different phase states because of the difference between their dimensions, the islands whose size becomes greater or smaller than the critical value in the course of coalescence may be expected to undergo a phase transition. We can easily establish the relationship between the critical size, constants of the system, and temperature.

The critical size R_{cr} is found by equating the chemical potentials of the material in the islands which are in different phase states (I and II):

$$\mu_0^I + \frac{2\gamma_1^I\omega^I}{R_{cr}} = \mu_0^{II} + \frac{2\gamma_1^{II}\omega^{II}}{R_{cr}} \tag{7.1}$$

At a temperature T such that $\Delta T/\tilde{T} = (\tilde{T} - T)/\tilde{T} \ll 1$ ($\tilde{T}$ is the temperature of the phase transition in bulk samples), we find that the difference between the chemical potentials is $\mu_0^I - \mu_0^{II} \approx q\Delta T/\tilde{T}$, where q is the heat of phase transition.[63] Using this relationship and assuming that $\omega^I \approx \omega^{II} \approx \omega$, we find from Eq. (7.1) that

$$R_{cr} = \frac{2\omega\Delta\gamma\tilde{T}}{q\Delta T}. \tag{7.2}$$
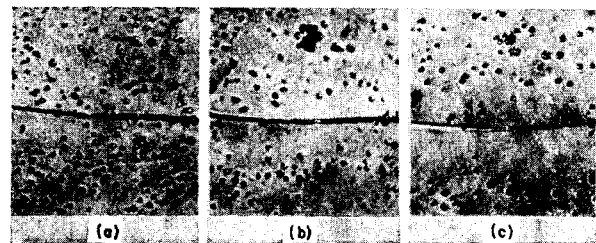
FIG. 9. Successive stages of the formation of island-free zones on both sides of grain boundaries in the case of a Cr film on Cu.[59] $T = 1000°$C applied for different times t (h): a) 3; b) 5; c) 10. Magnification $\times 500$ (reproduced here at $\times 355$).

Ya. E. Geguzin and Yu. S. Kaganovskiĭ
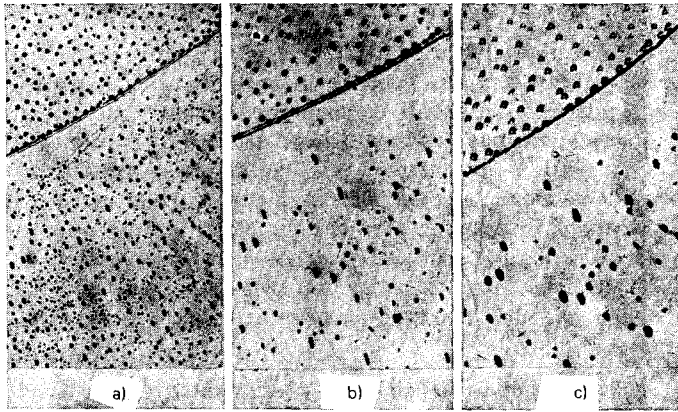
FIG. 10. Successive stages of the formation of a one-sided island-free zone near grain boundaries for a film of Ag on Ni.[59] $T = 800°$ C applied for various times t (h): a) 1; b) 9; c) 18. Magnification ×200 (reproduced here at ×142).

Since $R_{cr} \propto 1/\Delta T$, it follows that at temperature sufficiently close to the phase transition point the effect under discussion can be observed in a system of sufficiently large islands. The reported measurements[64,65] indicate that the melting points of Al and Cu islands of radius $\approx 10^{-6}$ cm are approximately 200 °C lower than the melting points of the bulk materials (further information can be found in other papers[66-68]).

Naturally, the above coalescence process eventually results in an increase of the volume of the low-temperature phase; the rate of increase of this volume V is governed by the diffusion constants of the coalescence process:

$$V(t) = \varkappa \int_{R_{cr}}^{\infty} f(R, t) R^3 dR = \varkappa \int_{R_{cr}/\bar{R}(t)}^{\infty} P_n(u) u^3 du,$$

where $\bar{R}(t)$ is given, depending on the coalescence mechanism and the rate-limiting stage, by one of the relationships (3.3)–(3.7). The expression for $P_n(u)$ was derived by Geguzin and Kaganovskii.[37]

This phase transition during coalescence may be complicated by the fact that the islands which have increased above the critical size may not undergo transition immediately but remain in a metastable phase because, for example, of the absence of a nucleus which might induce the phase transition in the island.[69] In this case we may have a system of closely spaced islands in a metastable state. The subsequent fate of this system and the coalescence kinetics change drastically at the moment when some of the islands undergo a transition due to some random event. Then, the difference between the chemical potentials $\Delta\mu_{ph} \approx q\Delta T/\tilde{T}$, between atoms in neighboring islands becomes important and it determines the directional flow of matter to the island which is now in an equilibrium phase state.

The problem of the coalescence of a system of islands which are in a metastable state deserves special consideration mainly because the difference between the chemical potentials $\Delta\mu_{ph}$ due to the differences between the phase states is usually (for $\Delta T/\tilde{T} \approx 10^{-1}$) much greater than the difference between the chemical potentials of the islands resulting from different radii of curvature of their surfaces ($\Delta\mu_{ph} \approx 10^4 \Delta\mu_R$[40]).

An important feature of this situation is that in the immediate vicinity of an island in the stable phase we may expect formation of a "courtyard" free of metastable islands and the kinetics of growth of this courtyard is governed by the same mechanism as the coalescence process.[45,40,70]

III. SYSTEM OF MOVING ISLANDS

By analogy with the movement of macroscopic inclusions in the interior of a crystal,[71] islands on the surface of a crystal may migrate as a whole under the action of a force acting directly on the islands, executing Borwnian motion or being exposed to external force fields. Such motion may influence greatly the mechanism and kinetics of the coalescence of islands and establishment of a continuous film. In this section we shall consider various specific situations under which we can expect motion of islands and we shall discuss the mechanisms of this motion as well as the relationships describing coalescence in a system of moving islands.

8. Mechanisms and kinetics of diffusive motion of islands

a) *Motion under the influence of external forces and Brownian movement.* In general, the velocity of an island and the force applied to it **F** are related by

$$\mathbf{v} = b\mathbf{F}, \tag{8.1}$$

where b is the mobility determined by the actual mechanism of transfer of mass needed to set the island in motion. In determining the mobility we have to distinguish two basically different situations: in one case an island moves on a mirror-smooth substrate, whose profile is not distorted by the island itself and the second is the case when an island partly "digs (diffuses) into the substrate"[56,72] and during its motion remains partly "immersed" in the substrate.

The motion on a mirror-smooth surface is a diffusive glide in which matter may move as a result of fluxes along the island–substrate interface or as a result of fluxes of volume or surface self-diffusion of the island material.

Diffusive boundary glide can be described by the boundary viscosity η, which is the coefficient of pro-

TABLE I.

Island–substrate system	Temperature range, °C	Investigation method	Range of D_S, cm²/sec	Q_S, kcal/mole	D_0, cm²/sec	Reference
Au — NaCl	370—450	From coalescence	10^{-13}—10^{-11}	52,0	$5 \cdot 10^4$	51
Ag — Ni	750—850	Ditto	$2 \cdot 10^{-8}$—10^{-7}	37,0	18	46
	700—850	Ditto	10^{-8}—10^{-6}	60,0	$4 \cdot 10^5$	46
	800	Ditto	$2 \cdot 10^{-5}$—$7 \cdot 10^{-5}$	—	—	59
	800	From growth of one-sided zone	$1,8 \cdot 10^{-4}$	—	—	59
Ni — W	1200—1300	From coalescence	$1 \cdot 10^{-5}$—$4 \cdot 10^{-5}$	30,0	$6 \cdot 10^{-1}$	47
Cr — Cu	1000	Ditto	$4 \cdot 10^{-6}$—$2 \cdot 10^{-5}$	—	—	59
	1000	From growth of two-sided zone	$3 \cdot 10^{-6}$—$9 \cdot 10^{-6}$	—	—	59
Cu — W	950	From coalescence	$7 \cdot 10^{-8}$	—	—	59
	950	From growth of one-sided zone	$8 \cdot 10^{-8}$	—	—	59

portionality between the tangential stress σ_t and the velocity gradient:[73]

$$\sigma_t = \eta \nabla v \approx \eta \frac{v}{\delta},$$

where δ is the thickness of the island–substrate boundary. Assuming approximately that $\sigma_t \approx F/R^2$, we obtain the following expression for the island mobility:

$$b_\eta = \frac{\delta}{R^2 \eta}.$$

The viscosity is governed largely by the properties of the interface layer. If the latter is sufficiently amorphous, the viscosity is given by[74] $\eta^0 \approx kT/D_{if}\delta$, where D_{it} is the diffusion coefficient of the island material in the interface layer. In this case, we find that

$$b_{if} = \frac{D_{if}}{kT}\left(\frac{\delta}{R}\right)^2. \tag{8.2}$$

It follows that the rate of diffusive interface glide of an island is given by Eqs. (8.1) and (8.2).

If the interface layer is not completely amorphous, the expression for b_{if} should depend on the real structure of the interface and this may vary with time. Various specific structures of interface layers are discussed extensively in the literature.[75-77]

We can easily obtain expressions for the mobility of an island in those cases when the transfer of mass is due to the surface (b_S) or volume (b_V) self-diffusion[71,78-81]

$$b_S \approx \frac{D'_S}{kT}\left(\frac{a}{R}\right)^4, \qquad b_V \approx \frac{D'_V}{kT}\left(\frac{a}{R}\right)^3. \tag{8.3}$$

where D'_S and D'_V are the surface and volume self-diffusion coefficients of the island material.

Numerical estimates of the value of b_{if} are practically impossible to obtain because of the absence of data on the diffusion coefficients along the island–substrate interface. Estimates of b_S and b_V can be found, for example, in the book by Geguzin and Krivoglaz.[71] By way of example, we shall give an estimate of b_S for copper islands of $R \approx 3 \times 10^{-7}$ cm size. At $T = 400\,°C$, we have $D'_S \approx 5 \times 10^{-8}$ cm^2/sec[82] and $b_S \approx 70$ cm·sec^{-1}·dyn^{-1}. It is convenient to use this estimate in calculating the time τ during which an island with a charge q_1 interacts with an active center located at a distance l from the island and carrying a charge q_2. We can easily show that $\tau \approx l^3/3 b_S q_1 q_2$. For $q_1 \approx q_2 \approx e$ and $l \approx 10^{-6}$ cm, we find that $\tau \approx 10^{-2}$ sec.

The motion of islands which are "immersed" in the substrate should be governed by the diffusion fluxes of the substrate material under conditions such that the required gradient of the chemical potential of the substrate atoms is due to the force applied to the island. If we assume that the shape of a depression under an island during its diffusive motion adjusts to the island shape, the process in question is qualitatively similar to the motion of a boat which is towed in water.

A consistent solution of the problem of the motion of a partly "immersed" island meets with serious mathematical difficulties. However, we can obtain estimates of the mobilities assuming that the motion of an island is similar to that of an inclusion in the bulk of a sample

(the immersed part of the island) under the action of external forces. The relevant estimates have been obtained earlier[71] and they can be described by the following expressions:

1) fluxes in the interior of the substrate,

$$b'_V \approx \frac{D_V}{kT}\left(\frac{a}{R}\right)^3, \tag{8.4}$$

where D_V is the volume self-diffusion coefficient of the substrate atom;

2) fluxes along the island–substrate interface,

$$b'_{if} \approx \frac{D_{if}}{kT}\left(\frac{a}{R}\right)^4; \tag{8.5}$$

3) fluxes of the substrate material via the interior of the island,

$$b''_V \approx \frac{D''_V c}{kT}\left(\frac{a}{R}\right)^3, \tag{8.6}$$

where D''_V and c are the diffusion coefficient and the solubility of the substrate material in the island material.

The above expressions for the mobilities govern also the rate of Brownian migration of islands as a whole. If we substitute in Eqs. (8.2)–(8.6) the value $b = D_B/kT$, we can estimate the coefficient of Brownian migration of an island, D_B, which should be used in the determination of the mean-square displacement r^2 in a time t:

$$r^2 = 4D_B t. \tag{8.7}$$

The coefficient of Brownian diffusion should be related to the corresponding atomic diffusion coefficient. However, there may be no direct relationship because the fluctuating force which sets an island in motion destroys an imperfect (patchy) contact between an island and its substrate. Apparently this is the situation which was observed in the well-known experiments of Kern et al.[75,76,83-85] who established that the effective viscosity and effective activation energy were influenced by the linear dimensions of the islands (see also Trusov and Kholmyanskii[86]).

We may also find that random migration of an island as a whole is not associated with thermal fluctuations but occurs under the action of a randomly varying (in magnitude and direction) external force resulting from electrostatic or elastic interaction between islands. In this case the "Brownian" diffusion coefficient found experimentally from the mean-square displacement in a given time [see Eq. (8.7)] depends not only on the actual mobility of an island but also on the applied force. In fact, we shall assume (for simplicity) that a constant force F acts on an island for a time interval τ and then its direction changes in a random manner. During the time τ the island is displaced through a distance $l \approx (D_B/kT)F_\tau$ and, therefore, the experimentally determined coefficient is related to the true Brownian coefficient by

$$D_B^{exp} = \frac{r^2}{4t} = \frac{l^2}{4\tau} = \frac{lF}{kT} D_B. \tag{8.8}$$

It follows from Eq. (8.8) that in the case of diffusion under the action of a fluctuating external force the experimentally determined "Brownian" diffusion coefficient is greater than the true value by a factor equal to

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the ratio of the work done by external forces during an "elementary event" (l is regarded as an elementary jump) to the thermal energy.

It follows that in an analysis of the experimental results we have to distinguish "free" migration under the action of thermal fluctuations from migration under the action of random forces causing displacements proportional to these forces.

It is worth drawing attention to the fact that random migration under the action of such forces is a relaxation process and, consequently, its velocity should tend to zero with time. This is indeed observed experimentally.[75,76,83-85]

Many experimental observations of Brownian migration[34,42,43,87,88] are really due to random forces of electrostatic or elastic origin. For example, Skofronick and Phillips[42] observed in a film of gold islands on graphite individual gold islands whose size was an order of magnitude greater than the average radius, and found that these left behind twisted paths free of gold. We observed similar behavior also in the case of silver films on LiF (Fig. 11). Formation of such paths is possible as a result of merging of moving islands with those at rest or those moving much more slowly than the ones under consideration. Since the paths form behind large islands, it is clear that their motion is not due to thermal fluctuations but due to random external forces. Otherwise, the larger islands would have moved more slowly than the smaller ones and their paths would have been filled with small islands.

Kern et al.[75,76,83-85] determined the Brownian migration coefficients of islands from the broadening (with time) of an abrupt boundary between a region filled with islands and a free surface (Fig. 12). They calculated D_B from the distribution curves on the assumption that each island moved independently of the others.

However, other results[90-92] indicated that islands interacted actively with one another via elastic stress fields whose existence was demonstrated experimentally in studies of the formation of dislocation (sintering) rosettes in the area of contact between an island and a crystalline substrate.[93] A possibility of the interaction between separate islands via the elastic stress fields created by them in the substrate was pointed out also by Indenbom,[119] who considered the influence of the elastic interaction on the epitaxial phenomena. Islands migrated under the influence of elastic forces and became dis-
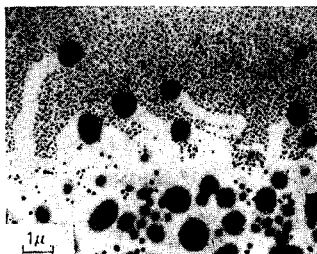

FIG. 11. Paths resulting from Brownian migration of silver islands on the surface of LiF ($T = 400°$C applied for $t = 45$ min).
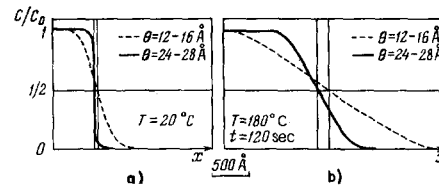

FIG. 12. Distribution of moving islands near the boundary of an island film of Al on the (100) face of KCl before (a) and after (b) annealing at $T = 180°$C for 120 sec.[84]

tributed on the surface in a somewhat ordered manner, as indicated by the radial distribution of the islands (Fig. 13a) with maxima at distances which were multiplets of a characteristic length. The island-size distribution was not affected (Fig. 13b). These results indicated that the energy of the elastic interaction between the islands at the investigated temperatures was much greater than kT, so that the experimentally determined coefficient D_B^{exp} was considerably greater than the true value. One could, therefore, predict a strong dependence of the coefficient D_B^{exp} on the density of the islands: the migration of the islands should be enhanced by an increase in the density.

It should be stressed that the picture of the Brownian migration of islands is not yet clear and experimental papers appear sporadically in which electron micrographs obtained in situ either support[94,120] or are in conflict[34,121] with this type of migration, which may be due to differences in experimental conditions and in investigated systems.

b) *Motion of islands in external force fields*. As before, we must distinguish the cases when an island is on a mirror-smooth surface and when it is partly "immersed" in the substrate.

The motion of an island on a mirror-smooth surface may be a consequence of directional fluxes of adatoms which move in an external force field and are adsorbed or emitted, respectively, by the front or rear surface of an island which then moves against the flux. In the case of a hemispherical island, we can describe the balance of matter during the motion of an island by $(\pi/2)R^2 dx = 2J_s \omega R \, dt$, i.e.,
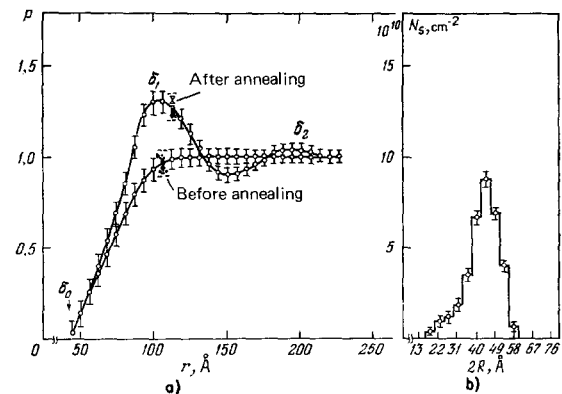
$$v = \frac{4\omega}{\pi R} J_B, \tag{8.9}$$

FIG. 13. Radial distribution function of islands $P(r)$ (a) and histogram of the island-size distribution (b) before and after annealing.[90]

where J_S is the surface flux governed by the gradient of the chemical potential of adatoms in an external field. The fluxes have been calculated[71] in the case of temperature $J_{S,T}$ and electric $J_{S,E}$ fields:

$$J_{S,T} = -\frac{D_S N_0}{T}\,\alpha_S \nabla_S T, \tag{8.10}$$

$$J_{S,E} = -\frac{D_S N_0}{kT}\,eZ_S E_S, \tag{8.11}$$

where $\alpha_S = Q_S^*/kT$ is the surface thermal diffusion ratio; Q_S^* is the heat of transfer on the surface, which in the case of the adatom diffusion mechanism is equal to the sum of the energies of formation and migration of an adatom; eZ_S is the effective charge of an adatom; $\nabla_S T$ and E_S are the temperature gradient on the surface and the surface component of the electric field. The velocities of interest to use are given by Eqs. (8.9)–(8.11). In general, the kinetics may be governed by the processes of acquisition and emission of adatoms by islands, i.e., by the boundary kinetics. Usually, the diffusion coefficient D_S should be replaced by the combined kinetic coefficient $\tilde{D}_S = D_S \beta_S a^2 R/(D_S + \beta_S a^2 R)$.

If an island is partly "immersed" in the substrate, its motion is governed by fluxes of two types: of adatoms of the island material along the substrate and of substrate atoms in a surface layer whose depth is of the order of the depth of immersion of the island. A consistent analysis of the problem of the velocity of an island in this case is difficult to carry out. In the limiting case when the motion of an island is governed by the mobility of its immersed part which-being an internal inclusion-appears to carry that part of the island which projects above the surface, we can use the expressions for the velocity of internal inclusions;[71] in the present case the application of such expressions can only give estimates.

A specific feature of the motion of an island immersed in the substrate, which distinguishes it from an internal inclusion, is that during its motion an island rotates about an axis perpendicular to the direction of an external field and lying in the plane of the surface. This effect is due to the fact that part of the immersion surface with the normal making an angle θ to the direction of motion travels at a velocity $v = v_0 \cos\theta$, where v_0 is the velocity of the island.[71] In this case the island experiences a torque which is due to the fact that parts of the front surface of the depression under the island move away from the center of the island and parts of the rear surface toward the center.

The motion of islands in external fields has been observed experimentally in a situation when the islands were immersed in the substrate forming characteristic tracks in it during their motion.

The motion of liquid islands ($R \approx 10^{-3}$ cm) of a germanium–gold alloy on the surface of germanium was investigated experimentally[95,96] under the action of a temperature gradient (Fig. 14); the motion was due to the diffusion of the substrate atoms via the interior of the island. It was found that in the case of islands of $R < 3 \times 10^{-3}$ cm dimensions the rate-limiting stage is the interface kinetics, indicated by the experimentally ob-
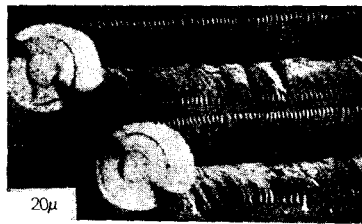

FIG. 14. Motion of germanium–gold alloy islands on the surface of germanium in a temperature gradient field.[96]

served linear dependence of the velocity on the radius.[71,97] However, in the $R > 3 \times 10^{-3}$ cm case the diffusion takes place via the interior of the island. If we know the characteristic size $\tilde{R}$ at which there is a change in the rate-limiting stage, we can estimate the specific interface flux: $\beta' \approx D/\omega R$. For $D \approx 10^{-5}$ cm^2/sec, $\omega \approx 10^{-23}$ cm^3, and $R \approx 3 \times 10^{-3}$ cm, we find that $\beta' \approx 3 \times 10^{20}$ cm^{-2}/sec^{-1}, which is in good agreement with estimates of β' deduced from other experiments.[98]

The motion of gold islands on the surface of NaCl in an external electric field was studied by Geguzin et al.[99] Islands of $R \approx 10^{-4}$ cm radius migrated at a velocity proportional to the field intensity but independent of the island size (Fig. 15), whereas islands of $R \gtrsim 10^{-3}$ cm radius traveled at a velocity inversely proportional to the radius. This motion could be regarded as diffusive migration of a depression in the substrate crystal under the island. This was why rotation of the island was observed during its motion (Fig. 16b). The motion of small islands was rate-limited by the volume diffusion fluxes and that of large islands by the diffusion along the island–substrate interface.[100]

Islands moving in an electric field (Fig. 16b) could gradually become "immersed" into the substrate. This effect was a quadratic function of the field and it resembled deformation of an inclusion at right-angles to the field.[70,101] In the absence of the field but under otherwise identical conditions there was practically no immersion effect (Fig. 16a).

An interesting case of spontaneous motion of Mo islands on a graphite surface was observed by Matthews and Jenkins.[102] Since a eutectic was formed at the island–substrate interface, rotation of the islands was a consequence of the tendency to increase the surface along which the contact melting took place.
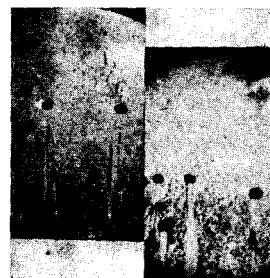

FIG. 15. Motion of Au islands on the (100) face of NaCl in an external electric field[99] ($T = 620°$C, $E = 110$ V/cm, magnification ×300, reproduced here at ×213).
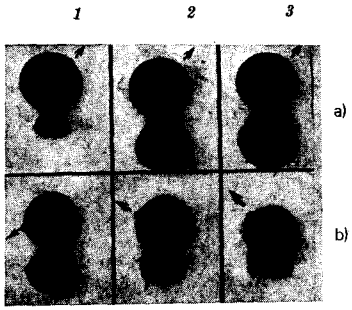
FIG. 16. "Immersion" and rotation of Au islands during their motion on the surface of NaCl.[99] Field E (V/cm): a) 0; b) 260. $T = 600°$C applied for different times t (h): 1) 0; 2) 1.2; 3) 3. Arrows identify reference points demonstrating rotation in the direction of the field. Magnification ×150, reproduced here at ×107.

9. Drag of islands by moving steps

When evaporation or condensation of the substrate material takes place or when matter is redistributed between regions with different local curvatures, steps on the surface of the substrate must move and interact with the islands encountered in their path. This interaction may result in two situations: either parts of a step between two islands may break through obstacles or a step pinned by the obstacles may move only together with islands. Clearly, both these situations may occur, depending on the ratio of the excess chemical potential $\Delta\mu$ responsible for the motion of the step and the value of $\Delta\mu_p$ which represents the pinning of a step which has come into contact with obstacles. Since $\Delta\mu_p = 2\gamma_2\omega/l$ (l is the average distance between the islands), the first situation occurs for $l > 2\gamma_2\omega/\Delta\mu$, and the second for $l < 2\gamma_2\omega/\Delta\mu$.

It should be noted that even when $l < 2\gamma_2\omega/\Delta\mu$, the breaking of a step through obstacles may still occur as a result of thermal-fluctuation-induced unpinning from obstacles which is a process resembling thermal-fluctuation-induced detachment of dislocations from obstacles in the bulk of a crystal.[103,104] Thus, the combined motion of a step with its obstacles is accompanied by the fluctuation-induced loss of the coupling between the step and the obstacles (islands).

In the process of combined motion of an island and a step of height h, the latter exerts a force $F_0 \approx (hl/\omega)\Delta\mu$, which determines the motion of the island.[3] The self-consistent velocity $\tilde{v}$ of the motion of a system consisting of a step and the islands situated on it can be estimated[105] by equating the velocities of the step and of the islands

$$\tilde{v} = bF_0 = b_s F_s^*,$$

where $F_s^* = F_s - n_0 F_0$; $F_s = (h/\omega)\Delta\mu$ is the force acting on a step of unit length; $n_0 = 1/l$; b and b_s are, respectively, the mobilities of an island ($[b] = $ sec/g) and of a step ($[b_s] = $ cm/sec/g^{-1}). Elementary transformations give

$$\tilde{v} = F_s b_s \frac{1}{1+m}, \quad m = \frac{n_0 b_s}{b}. \tag{9.1}$$

[3]We can easily show that if $\Delta\mu > (2R/a)\,\Delta\gamma\omega/l$, where $\Delta\gamma = \gamma_1 + \gamma_2 - \gamma_{12}$, the detachment of a step from an obstacle occurs definitely and not as a result of probable fluctuations.
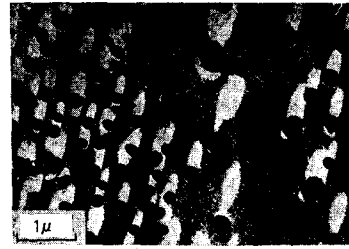

FIG. 17. Drag of Au islands by steps moving during evaporation of an LiF crystal.[105] The sagging of steps is evidence of their pinning by islands. The shape of the shadows shows that there are pedestals under the islands from which steps have become detached.

The values of b have been found earlier [see Eqs. (8.2)–(8.6)]; the values of b_s depend strongly on the rate-limiting stage which restricts the motion of a step during condensation or evaporation. In particular, when this stage is the migration of adatoms on the surface of the substrate crystal,[11,106] we have

$$b_s \approx \frac{2D_a'\xi_0'}{kT}\frac{a^4}{\lambda_s h^2},$$

where λ_s is the surface diffusion path of an adatom of the substrate material; ξ_0' is the equilibrium concentration of such adatoms; D_a' is the self-diffusion coefficient of these adatoms.

The process of breakthrough of parts of a step between islands is accompanied by bending around islands. Consequently, in the process of evaporation a pedestal of height which is a multiple of h should form under the island and during condensation an island should become correspondingly immersed in the substrate.

The predicted effects were observed experimentally[105,107] by electron-microscopic studies of gold island films on the surfaces of alkali halide single crystals. The islands acted as obstacles to the motion of steps and they moved in a directional manner during evaporation of the substrate crystal, as indicated by the sag of the steps between the obstacles (Fig. 17). The moving steps dragged the islands hindering their motion so that a zone free of gold appeared behind the moving steps. In the process of combined motion of steps and islands the latter coalesced and became larger (see Sec. II). Formation of pedestals under the islands could be deduced clearly from the shape of the shadow appearing when a sample with an island film was examined by the shadow technique at more advanced stages of evaporation. The shadow was weaker near the island base (Fig. 17).

Geguzin et al.[89] observed the interaction between monatomic steps moving on the surface of a KCl crystal in the course of its evaporation and the decorating gold islands with an average radius of ≈ 40 Å. Evaporation of KCl under isothermal conditions was followed for some time by the decoration of steps with gold; then, the evaporation was continued under identical conditions but in the presence of gold islands on the surface. The positions of the islands during the second evaporation changed by an amount which increased with increasing temperature and duration of evaporation (Fig. 18). Changes in the island positions accompanied
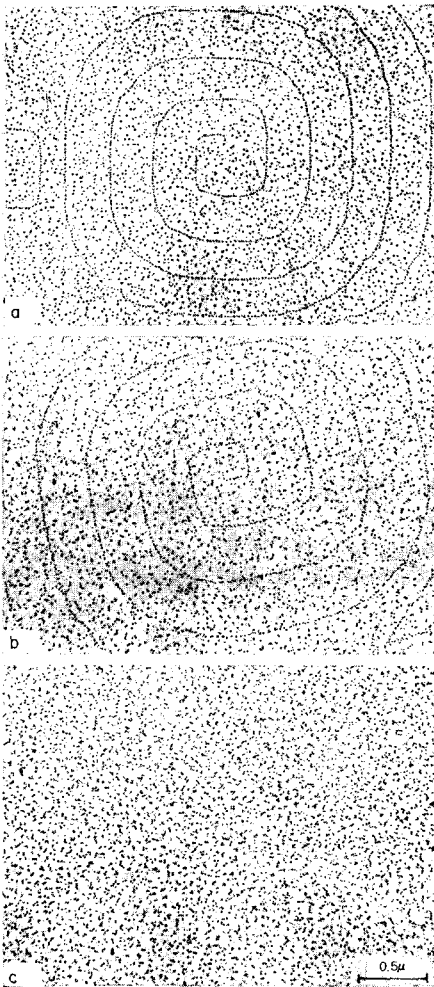
FIG. 18. Evaporation spirals on the surface of a KCl crystal:[89] a) decoration after evaporation at $T = 340°$ C for 30 min; b) after decoration of the spiral the sample was subjected to evaporation for another 30 min at the same temperature; c) after decoration the crystal was subjected to evaporation for 15 min at $T = 375°$ C.

by formation of groups indicated that they were dragged by moving steps. In these experiments the gold islands moved under the action of a drag force $F \approx 2\gamma_2 a$. Measurements of the average velocity v of the islands yielded the diffusion coefficient D_B, which determined the migration of islands as a whole. The estimates obtained[89] gave $v \approx 10^{-8}$ cm/sec at $T = 340$ °C for $F \approx 2 \times 10^{-5}$ dyn and hence it was found from Eq. (8.1) that $D_B \approx 10^{-17}$ cm^2/sec.

10. "Dispersion hardening" of the surface

The drag exerted by islands on the natural motion of steps should slow down all the processes whose velocity is governed by the step velocity. In particular, the mass transfer needed to heal surface defects[108,109] or to form a natural face of a crystal[110] should slow down. Moreoever, there should be also a slowing down of mass transfer in the evaporation or growth of a crystal from the vapor phase, when a reduction in the step velocity hinders the emission or acquisition of adatoms by the step. By analogy with the hardening (in the mechanical sense) influence of particles dispersed in the
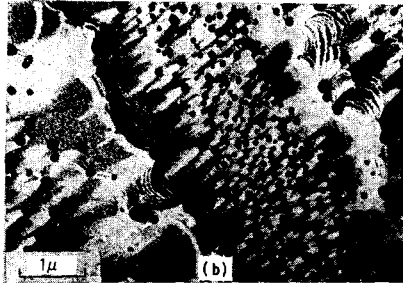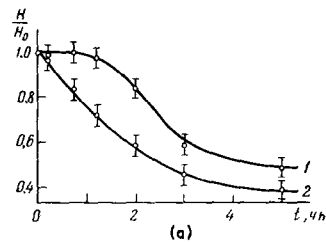

FIG. 19. a) Relative change of the depth of the scratches healed during evaporation of an LiF crystal with an Au island film (1) and without such a film (2); $T = 600°$ C. b) Electron photo-micrograph of a scratch on the surface of LiF with an island film.[112] The steps at the edges of this scratch interact actively with islands.

bulk, which hinder the motion of dislocations, we shall use the term "dispersion hardening" of a surface in relation to evaporation and condensation for the hindering of the motion of steps.

The slow down of the step velocity resulting in "dispersion hardening" may be associated either with the drag due to islands moving together with the steps (Sec. 9) or with the need to break through immobile obstacles.

This process is qualitatively similar to the pinning of steps by impurity atoms[111] except that the island mobility is always much less than that of an impurity atom.

The results of two experiments confirmed the occurrence of "dispersion hardening" of a surface. In one of them[112] a study was made of the change of the depth of a scratch on the surface of an LiF single crystal in the presence or absence of an island $(\overline{R} \approx 10^{-6}$ cm) gold film on the surface (Fig. 19a). Healing of scratches on a surface covered with an island film was found to be much slower than on a free surface. An electron-microscopic study revealed the pinning of steps by islands (Fig. 19b).

In another experiment,[113] the process of evaporation was investigated by electron microscopy as follows. An NaCl crystal whose natural cleavage face had points of emergence of screw dislocation was subjected to evaporation of a constant temperature in two stages of the same duration. During the first stage, when the surface was free of an island film, a step-which during evaporation formed a spiral around the screw dislocation-traveled a distance tens of times greater than during the second stage prior to which a gold island film was depostied on the surface. (Fig. 20a). The positions of steps during evaporation of a crystal was determined by the double decoration method.[114,115]
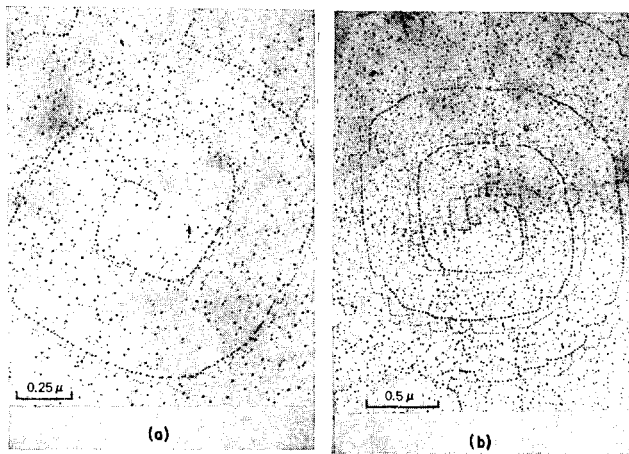
FIG. 20. Successive stages of the breakthrough of steps forming a spiral through pinning gold islands at $T = 320°C$.[113] "Free" evaporation time 15 min; evaporation time with an island film in place (min): a) 15; b) 25.

The breakthrough of steps through a chain of obstacles should in this experiment depend strongly on the ratio of the critical radius of two-dimensional nuclei $r*$ to the average distance between the obstacles. During the earliest stage of evaporation when the step has not yet broken through the obstacles, the density of adatoms in the surface region between two steps decreases strongly during the adatom lifetime τ and $r*$ decreases so much that the breakthrough begins between practically any pair of neighboring obstacles so that a system of half-loops of different radii appears along each step. Since the segments that break through are the sources of adatoms, the value of $r*$ increases and is governed now by the average curvature of the loops that have broken through. This begins the process of matched diffusive coalescence: loops of small radii disappear and those with large radii grow so that steps break through a chain of islands and close behind them (Fig. 20b).

Geguzin et al.[113] analyzed the conditions under which the breakthrough of steps through island obstacles must be accompanied by loop coalescence. They showed that this approach provides a description of the observed "dispersion hardening."

11. Coalescence in a two-dimensional system of moving islands

a) *Coalescence during motion in an external force field and during Brownian movement.* The problem of the kinetics of coalescence in a two-dimensional system of moving islands was discussed by Botvinko and Krivoglaz[116] (see also the monograph by Geguzin and Krivoglaz[71]). Botvinko and Krivoglaz[116] considered a set of islands moving in a directed manner at a velocity which was some function of their dimensions. Assuming that the coalescence of islands was limited by their velocity and not by the rate of coalescence of the islands that have already come in contact and that the velocity of diffusive motion depended strongly on the radii of the islands, for example, $|dv/dl| \approx v/R$, (this, in particular, occurs in the mechanism of motion governed by surface fluxes), Botvinko and Krivoglaz[116] obtained the following

estimate for the time of doubling of the characteristic size of an island

$$\tau_m \approx \frac{\bar{R}}{s_0\bar{v}},$$ (11.1)

where $\bar{v}$ is the velocity of an island with the most probable value of the radius $\bar{R}$ and s_0 is the initial area occupied by the islands per unit surface area of the substrate.

In addition to the process of coalescence during motion there is a competing process of ordinary diffusive coalescence described by Eqs. (3.5)–(3.7). If we compare, for example, Eqs. (11.1) and (3.5) we can show that in many real situations (high surface densities of large islands and high island velocities) the coalescence in the collision regime may be faster.

In the absence of external forces we may expect to observe coalescence of islands moving under Brownian migration conditions. The time for doubling the characteristic size of the islands is now given by[71]

$$\tau_B \approx \frac{R^2}{s_0 D_B},$$

where D_B depends on the island migration mechanism and is given by Eqs. (8.2)–(8.6).

We can easily show that coalescence in the Brownian regime may be noticeable (against the background of the usual diffusive coalescence) only in the case of very small islands present with a high density, i.e., at the very earliest stage of coalescence of a highly disperse island film.

An interesting case of the coalescence of silver islands on the surface of NaCl single crystals was studied by Dussaulcy et al.,[117] who observed a system of islands of ≈ 20 Å linear size in a field of $\sim 10^3$ V/cm, which created a dipole moment in the islands. The coalescence process was a consequence of the dipole–dipole interaction between the islands.

In considering coalescence in the collision regime it was assumed that islands coalesce every time they come into direct contact. However, in actual fact closely spaced islands may experience diffusive repulsion, which should be observed in the case when the concentration of adatoms between islands in the immediate neighborhood of them is higher than the concentration averaged over the whole system. In this case the overlap of the diffusion fields of adatoms of islands that have come close together increases the concentration of the adatoms between the islands and, consequently, their chemical potential; moreover, the concentration and chemical potential become dependent on the distance between the islands increasing on reduction of this distance. The latter circumstance implies the existence of a repulsive ("osmotic") force. An estimate shows that in the case of two islands of the same size the maximum value of this force is

$$F_m \approx \frac{\gamma_1 \omega}{2R^2}.$$

In particular, this force may prevent merging of very tiny islands moving under Brownian migration conditions when the force bringing them into collision is $F_B \approx kT/a$.
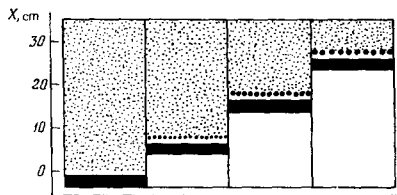
FIG. 21. Successive stages of coalescence in the "sweep" regime revealed by a model experiment.[118]

If we compare F_m and F_B we can demonstrate that islands of size $R \approx \sqrt{\gamma_1 \omega a / kT} \approx 10^{-7}$ cm should not merge.

b) *Coalescence under "sweep" conditions*. In contrast to the above case, when coalescence is due to the dependence of the velocity on the island size, we may also expect coalescence when some of the islands move at the same velocity and encounter other islands at rest. In particular, this may occur when islands are dragged by a moving step.

For a certain relationship between the velocity of a step during evaporation or condensation of the substrate and constants of the islands (such as their size, surface tension, and self-diffusion coefficient) a step may drag all the islands it encounters producing a sweep effect. The islands colliding in the course of the "sweep" may coalesce.

The problem of coalescence under sweep conditions[118] is characterized by the dimensionless time $t^* = (v_m/\bar{R})\tau$, where $\bar{R}$ is the average size of the colliding islands; v_m is the velocity of motion of the sweeping step; t^* is the time for diffusive coalescence of the islands. For $t^* \ll 1$ the true coalescence, i.e., an increase in the size as a result of collisions, does take place. However, for $t^* \gg 1$ the velocity of this motion is considerably greater than the rate of coalescence and, consequently, coalescence does not occur but islands accumulate in front of the sweeping step. In the most realistic case when the merging of islands is due to the surface self-diffusion mechanism (for $\bar{R} \lesssim 10^{-5}$ cm), the value of τ is given by Eq. (2.2). The conditions for coalescence can be described by the inequality

$$\bar{R}^3 v_m < \frac{\gamma_1 D_s}{kT} a^4.$$

If the constants are given reasonable values ($kT \approx 10^{-13}$ erg, $\gamma_1 = 10^3$ erg/cm^2, $a \approx 3 \times 10^{-8}$ cm, $D_s \approx 10^{-9}$ cm^2/sec), we can easily show that the coalescence of islands with $\bar{R} \approx 10^{-6}$ cm occurs if $v_m < 10^{-2}$ cm/sec.

Geguzin *et al.*[118] simulated the process of coalescence under sweep conditions. They studied changes in the size of identical circular coin-like islands swept by a plane ruler. Figure 21 shows a typical sequence of photographs corresponding to various stages of coalescence of a system of islands under sweep conditions when the ratio of the initial radius of the island to the average distance between them was $\varkappa = 0.33$. These experiments established the importance of collisions between islands which moved together with the ruler and whose size increased with time.

In a real experiment coalescence in the sweep case was observed[112] at evaporation or condensation nuclei
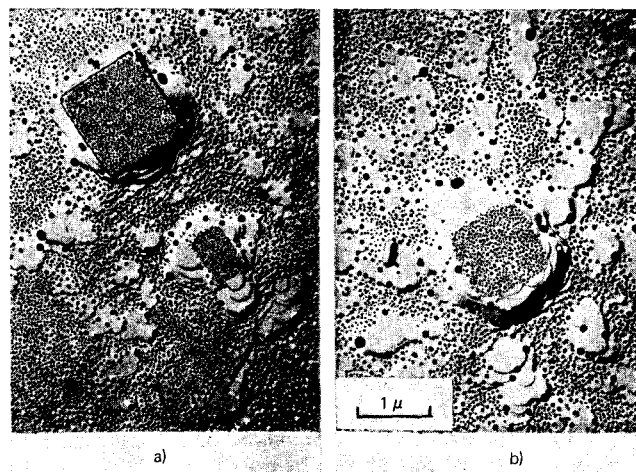

FIG. 22. Coalescence in the sweep regime in a condensation nucleus on an LiF crystal with an Au island film ($T = 600°$C, $t = 30$ min, magnification $\times 12\,000$, reproduced here at $\times 8520$).

on an LiF crystal, whose surface carried a system of gold islands of $\bar{R} \approx 10^{-5}$ cm radius with an average distance $\varkappa > 0.25$. During evaporation or condensation of LiF, steps on its surface moved at a velocity $v_g \approx 10^{-7}$ cm/sec and, therefore, the colliding islands definitely had a chance to merge by diffusion (Fig. 22).

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