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Theory of the nucleation of multicomponent precipitates

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The nucleation kinetics of multicomponent precipitates is studied. For this, asymptotic solutions of the corresponding stationary Fokker-Planck equation are derived and analyzed. The nucleation flux in composition space $\{\vec{n}\}$ is determined by the reaction rates R of the constituent components (kinetic barrier) and the formation free enthalpy $G(\vec{n})$ of the precipitates (energetic barrier). If the kinetic barrier is small compared with the energetic one, the nucleation flux goes across the saddle point of $G(\vec{n})$. For significantly different reaction rates the nucleation flux is bent into the directions of the rapidly reacting components, and the kinetic barrier is controlled by the *fastest* component i for which $\partial^2G/\partial n_i^2<0$. If the kinetic and energetic barriers are comparable, the nucleation flux can go across a ridge in the direction of a rapidly reacting component. In this case the nucleation barrier is governed by a balance of the kinetic and the energetic barriers. The condition for this is in approximate agreement with the one suggested by Stauffer and Kiang. As the simplest example for binary nucleation the formation of ideal gas bubbles under gas and vacancy supersaturation is considered to illustrate and test the most important results of the theory.

I. INTRODUCTION

In a supersaturated solid solution—as well as in a supersaturated vapor—nucleation of particles of a new phase usually occurs in a heterogeneous mode, i.e., at inhomogeneities such as dislocations, grain boundaries, and interfaces, or at impurities. Often nucleation is assisted by both matrix inhomogeneities and impurities. Since above the temperature at which nucleation of new phases starts all impurities become mobile, the new phases are usually new solid solutions or compounds. Thus we are faced with the problem of nucleation of multicomponent phases.

The kinetics of multicomponent nucleation was first considered by Reiss[1] who assumed that nucleation goes across the saddle point in the formation free enthalpy G of the particles of the new phase, following the steepest descent of G in the composition space. Based on a general multicluster coordinate nucleation theory,[2] Stauffer[3] and Kremer[4] showed that both the free enthalpy G and the reaction rates R of the constituents of the new phase determine the direction of the nucleation flux in the composition space. The limiting behavior of binary saddle-point nucleation for significantly different reaction rates (concentrations of the species) has been discussed by Mirabel and Clavelin.[5] Even earlier, Stauffer and Kiang[6] had suggested that—if in the binary case the reaction rates of the two constituents differ significantly—a nucleation path following the coordinate of the fast-reaction component across the ridge of G can be more favorable (i.e., it can result in a higher nucleation rate) than the saddle-point path.

In the present paper a general theory of nucleation of multicomponent precipitates is developed. First, a short derivation of the rate of nucleation across a saddle point is presented. The general expression for saddle-point nucleation is discussed for the case of significantly different reaction rates of the constituents. Then nucleation across a ridge in the direction of the fast-reaction components is analyzed.

Though the procedure presented is more general, we have diffusion-controlled nucleation of multicomponent precipitates in solids in mind. As the simplest example for binary nucleation we shall consider the formation of gas bubbles in a monatomic matrix containing dissolved gas and lattice vacancies in supersaturation (precipitation of gas atoms and lattice vacancies).

II. BASIC APPROXIMATIONS

For the derivation of the basic equation three important approximations are used:

(1) Concerning possible cluster configurations, consideration is restricted to clusters of (or around) equilibrium shape such that the only coordinates remaining are the numbers n_i of particles i consti-

tuting the clusters which may be summarized in a composition vector $\vec{\mathrm{n}}$.

(2) By considering the particle numbers to be continuous variables, the system of rate equations describing clustering kinetics is approximated by the corresponding Fokker-Planck equation.

(3) In confining the treatment to low cluster concentrations the clusters are considered to form an ideal solution.

With these approximations the temporal change of the cluster concentrations $c(\vec{\mathrm{n}})$ may be written as[2]

$$\frac{\partial c(\vec{\mathrm{n}})}{\partial t}=-\frac{\partial \vec{\mathrm{J}}}{\partial \vec{\mathrm{n}}}$$
$$=\frac{\partial}{\partial \vec{\mathrm{n}}}\underline{R}(n)e^{-\beta G(\vec{\mathrm{n}})}\frac{\partial}{\partial \vec{\mathrm{n}}}e^{+\beta G(\vec{\mathrm{n}})}c(\vec{\mathrm{n}}) . \tag{1}$$

Here, $\vec{\mathrm{J}}(\vec{\mathrm{n}})$ is the cluster current density in composition space. $G(\vec{\mathrm{n}})$ is the formation free enthalpy of the clusters which, because of the positive contribution of the interface between the clusters and the matrix, establishes a nucleation barrier; $\beta=1/kT$, where k is Boltzmann's constant and T is the absolute temperature. $\underline{R}(\vec{\mathrm{n}})$ is the generally strongly anisotropic matrix of the second moments of the cluster reaction rates.

If in a solid only single particles are diffusing between the matrix and the clusters the elements $R_i(\vec{\mathrm{n}})$ of $R_{ij}(\vec{\mathrm{n}})=R_i(\vec{\mathrm{n}})\delta_{ij}$ are given by[7]

$$R_i(\vec{\mathrm{n}})=4\pi c_i(\vec{\mathrm{n}})D_i r(\vec{\mathrm{n}}) , \tag{2}$$

where $c_i(\vec{\mathrm{n}})$ is the equilibrium concentration of particle i at the surface of a cluster with radius $r(\vec{\mathrm{n}})$ while D_i is the diffusion coefficient of particle i. Thus R_i is proportional to the permeation coefficient c_iD_i, and accordingly its activation free enthalpy consists of a solution and a diffusion free enthalpy.

Equation (1) must be completed by appropriate boundary conditions. Since small clusters may be assumed to be in thermal equilibrium and infinitely large clusters do not exist we take, respectively,

$$c(|\vec{\mathrm{n}}|\to 0)=c_0e^{-\beta G(\vec{\mathrm{n}})} \text{ and } c(|\vec{\mathrm{n}}|\to\infty)=0 , \tag{3}$$

where c_0 is the concentration of potential nucleation sites.

Thus Eq. (1), together with the boundary conditions (3), describe anisotropic and inhomogeneous diffusion subject to the field $G(\vec{\mathrm{n}})$ in the composition space. In the following we restrict our considerations to the stationary case $\partial c(\vec{\mathrm{n}})/\partial t=0$.

III. NUCLEATION ACROSS A SADDLE POINT

If the reaction rates of the particles constituting the new phase are large or comparable in magnitude, nucleation occurs across the lowest part of the barrier, i.e., across the saddle point $\vec{\mathrm{n}}^*$ of G where $\partial G/\partial\vec{\mathrm{n}}=0$ and $\underline{G}\equiv\partial^2G/\partial\vec{\mathrm{n}}^2$ has one negative eigenvalue and, otherwise, positive ones. (The detailed conditions for saddle-point nucleation will be given later.) Assuming that only the immediate vicinity of $\vec{\mathrm{n}}^*$ contributes to nucleation we expand G at $\vec{\mathrm{n}}^*$ up to second-order terms:

$$G\approx G^*+\tfrac{1}{2}\Delta\vec{\mathrm{n}}\cdot\underline{G}^*\cdot\Delta\vec{\mathrm{n}} ,\quad \Delta\vec{\mathrm{n}}=\vec{\mathrm{n}}-\vec{\mathrm{n}}^* , \tag{4}$$

where the asterisk indicates values at $\vec{\mathrm{n}}=\vec{\mathrm{n}}^*$. For sufficiently smooth $G(\vec{\mathrm{n}})$ this is justified if $\beta G^*\gg 1$.

Since $\underline{R}(\vec{\mathrm{n}})$ is slowly varying compared with the exponentials in Eq. (1), it may be set constant: $\underline{R}(\vec{\mathrm{n}})\approx\underline{R}(\vec{\mathrm{n}}^*)\equiv\underline{R}^*$. Using this we can remove the anisotropy of Eq. (1) by transforming $\vec{\mathrm{n}}$, $\vec{\mathrm{J}}$, and c into new variables $\vec{v}$, $\vec{\iota}$ and ζ, respectively:

$$\Delta\vec{\mathrm{n}}=(\underline{R}^*)^{1/2}\cdot\vec{v},\quad \vec{\mathrm{J}}=(\underline{R}^*)^{1/2}\cdot\vec{\iota}/(\det\underline{R}^*)^{1/2} ,$$
$$c=\zeta/(\det\underline{R}^*)^{1/2} ,$$

which in the stationary case leads to

$$\frac{\partial}{\partial\vec{v}}\exp(-\beta\vec{v}\cdot\underline{\Gamma}\cdot\vec{v}/2)\frac{\partial}{\partial\vec{v}}\exp(+\beta\vec{v}\cdot\underline{\Gamma}\cdot\vec{v}/2)\zeta=0 \tag{5}$$

with

$$\underline{\Gamma}=(\underline{R}^*)^{1/2}\cdot\underline{G}^*\cdot(\underline{R}^*)^{1/2} .$$

This is the general form of a transformation introduced by Feder *et al.*[8]

In the principle axes system of $\underline{\Gamma}$ Eq. (5) becomes separable, and thus the problem reduces to the well-known one-dimensional problem for single-component nucleation. In the transformed system nucleation goes in the direction of the eigenvector belonging to the negative eigenvalue of $\underline{\Gamma}$, while in the directions perpendicular to the latter one, $\exp(+\beta G)c$ is constant.

Using the boundary conditions (3) we find for the region close to the saddle point

$$c=c_0\exp[-\beta G(\vec{\mathrm{n}})]\tfrac{1}{2}\mathrm{erfc}(\sqrt{\beta|\lambda|/2}\xi) ,$$
$$\vec{\mathrm{J}}=\sqrt{\beta|\lambda|/(2\pi)}(\underline{R}^*)^{1/2}\cdot\vec{\mathrm{v}} \tag{6}$$
$$\times c_0\exp[-\beta G(\vec{\mathrm{n}})+\tfrac{1}{2}\beta\lambda\xi^2] ,$$

where λ is the negative eigenvalue of $\underline{\Gamma}$ (or equally of $\underline{R}\cdot\underline{G}$), $\vec{\mathrm{v}}=\partial\xi/\partial\vec{v}$, is the corresponding eigenvector $\underline{\Gamma}\cdot\vec{\mathrm{v}}=\lambda\vec{\mathrm{v}}$, and ξ is the coordinate in the direction of $\vec{v}$ in the transformed system. $\vec{J}$ is an eigenvector of $\underline{R}^*\cdot\underline{G}^*$ and thus is bent off the direction of steepest descent toward the directions of the components with the highest reaction rates.

The nucleation rate I, i.e., the temporal change of the concentration of stably growing precipitates, is obtained by integrating $\vec{J}$ over a surface in the composition space, most simply over a plane through $\vec{n}^*$ and perpendicular to $\vec{v}$. The final result is

$$I=\frac{\beta|\lambda|/(2\pi)}{\sqrt{\det[\beta\underline{G}^*/(2\pi)]}}c_0e^{-\beta G^*} . \tag{7}$$

This formula is the explicit version of results derived earlier.[2–4]

As in one-component nucleation the nucleation rate is proportional to the equilibrium cluster density $c_0\exp(-\beta G^*)$, and to the reaction rates at the saddle point. But in multicomponent nucleation the reaction rates (contained in λ) are coupled with the second derivatives of G. The latter ones together with those in the determinant in the denominator of Eq. (7) take fluctuations between the subcritical and the supercritical regions (reducing the nucleation rate), as well as the available configuration space at the saddle point (enhancing the nucleation rate), into account. In binary nucleation this "Zeldovich factor" is of the order of 1.

The activation free enthalpy G_N of nucleation consists of a kinetic part g, i.e., of that of the reaction matrix, and an energetic part G: $G_N=g+G$. It becomes especially transparent for the limiting case of significantly different reaction rates.

To illustrate the limiting behavior of saddle-point nucleation for significantly different reaction rates we first consider binary nucleation (generalizing earlier discussions[5]). What we need is the negative eigenvalue λ of $\underline{R}^*\cdot\underline{G}^*$ and the corresponding eigenvector determining the direction of $\vec{J}$.

Taking a coordinate system in which the reaction matrix $\underline{R}$ is diagonal we have $\underline{R}\cdot\underline{G}=\{R_{ii}G_{ij}\}$. Choosing $R_{11}\gg R_{22}$ and assuming that the elements of $\underline{G}$ are comparable in magnitude we meet two different cases indicated by the small figures inserted into Fig. 1:

(a) $G^*_{11}<0$, resulting in

$$\vec{J}/J\rightarrow\vec{e}_1,\ \ \lambda\rightarrow R^*_{11}G^*_{11} .$$

$\vec{J}$ is bent into the direction $\vec{e}_1$ of the fast component 1. The kinetic factor in the nucleation rate is controlled by the fast component 1 (activation free enthalpy g_1) and the activation free enthalpy of nucleation is

$$G_N=g_1+G^* . \tag{8a}$$

(b) $G^*_{11}>0$, resulting in

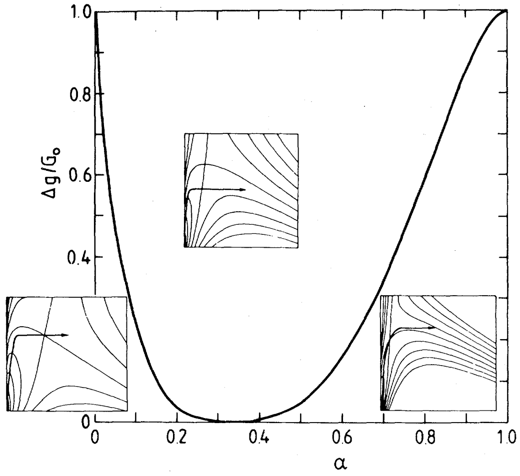

FIG. 1. Regions of saddle-point and ridge nucleation for bubble formation under vacancy and gas supersaturation with a small gas reaction rate, $R_2\ll R_1$ (see Sec. V). The coordinates are the difference in the activation free enthalpies of the gas and vacancy reaction rates, $\Delta g=g_2-g_1$, normalized to $G_0=G^*$ ($p=0$), and the supersaturation ratio $\alpha=p/(p+\sigma)$. Nucleation is of ridge type above and of saddle-point type below the limiting curve (heavy line of the main figure). The type of nucleation in each region is indicated by the small inserted figures showing contour maps of the formation free enthalpy of the bubble embryos (thin lines) and the nucleation paths (medium thick lines with arrows) in the composition plane (horizontal and vertical coordinates define the numbers of vacancies and gas atoms, respectively).

$$\vec{e}_1\cdot\underline{G}^*\cdot\vec{J}\rightarrow 0,\ \ \lambda\rightarrow R^*_{22}(\det\underline{G}^*)/G^*_{11} .$$

$\vec{J}$ follows the line of equilibrium with respect to component 1, $\partial G/\partial n_1=0$, passing the saddle point. The kinetic factor is controlled by the slow component 2 (activation free enthalpy g_2) and

$$G_N=g_2+G^* . \tag{8b}$$

The transition between the two cases occurs in the narrow range in which G^*_{11} is so small that the magnitude of $R^*_{11}G^*_{11}$ becomes comparable with those of the other elements of $\underline{R}^*\cdot\underline{G}^*$.

According to the meaning of these results the limiting behavior of the whole flux line can be defined as follows: It traces along the equilibrium line $\partial G/\partial n_1=0$, unless it either reaches the coordinate n^*_2 of a saddle point with $G^*_{11}<0$, or it reaches, after having passed a saddle point with $G^*_{11}>0$, a point $G_{11}=0$ of unstable growth with respect to component 1. At either of these points it bends over into the direction 1 (see Fig. 1).

The extension to more than two components is straightforward. If all reaction rates are significantly different the limiting flux line follows the line of equilibrium with respect to all components but the slowest one, s, unless it reaches either the saddle-point coordinate n_s^* or, after having passed the saddle point, eventually a point $G_{ii}=0$ of unstable growth with respect to one component i, and there bends off into the corresponding planes of constant n_s. As a result of this the dimension of the problem is reduced by 1, etc. The kinetic factor in the nucleation rate is controlled by the fastest component j for which $G_{jj}<0$.

IV. NUCLEATION ACROSS A RIDGE

If one reaction rate is essentially smaller than the other ones the flux line can turn into the directions of the fast-reacting components and pass a ridge *before* the saddle-point coordinate of the slowly reacting component is reached (see the small middle figure inserted into Fig. 1).

An asymptotic expression for this case is obtained by considering the continuous leakage of clusters from the flux in the "valley" defined by $G_i \equiv \partial G/\partial n_i = 0$, $G_{ii}>0$, and $i \in \{f\}$, due to nucleation in the direction of the fast-reacting components f. To illustrate the approximations we again start with the binary case and choose $R_{11} \gg R_{22}$. For small numbers n_2 the flux is strongly concentrated in the "valley" defined by $G_1=0, G_{11}>0$, if the barrier in the direction 1 is high. After a quadratic expansion of G, integration of Eq. (1) over the valley yields the total cluster current

$$I_2(n_2)=\int J_2 dn_1 = -\left[\frac{2\pi}{\beta G_{11}^{v}}\right]^{1/2} R_{22}^{v} e^{-\beta G^{v}} \frac{d}{dn_2} e^{\beta G^{v}} c^{v} , \tag{9a}$$

where the superscript v indicates values in the valley. Since $R_{11} \gg R_{22}$, the cluster leakage from the valley may be described by a nucleation current in the easy direction 1, i.e., by a one-component nucleation at constant n_2:

$$J_1(n_2)=\left[\frac{\beta | G_{11}^{r} |}{2\pi}\right]^{1/2} R_{11}^{r} e^{-\beta \Delta G} c^{v} . \tag{9b}$$

Here, r indicates values on the ridge defined by $G_1=0, G_{11}<0$. $\Delta G = G^r - G^v$ is the nucleation barrier in the direction 1. Approximation (9) implies that the flux line bends off sharply into the direction 1, i.e., that the region in which J_1 is comparable with J_2 is small compared with the width of J_2, which is fulfilled if $\beta \Delta G \gg 1$.

The current in the valley and the leakage across the ridge are coupled via the requirement of cluster number conservation (continuity)

$$\frac{d}{dn_2} I_2 + J_1 = 0 . \tag{10}$$

Hence in the stationary binary case our leakage approximation defined by Eqs. (12a) and (12b) has reduced the basic partial differential equation (1) to an ordinary differential equation.

Next we derive an asymptotic solution of Eq. (10). Assuming that the leakage by nucleation in the direction 1 occurs in a sufficiently narrow interval δn_2 around a presently unknown "nucleation coordinate" $\hat{n}_2$, we expand G linearly around $\hat{n}_2$ and set the slowly varying preexponentials in Eqs. (9a) and (9b) equal to their values at $n_2=\hat{n}_2$. Introducing the new coordinates

$$x = C(\hat{R}_{11}^{r}/\hat{R}_{22}^{v})^{1/2} \exp(-\beta \Delta G/2) , \tag{11a}$$

with

$$C = -\sqrt{2/(\pi\beta)}\, | \hat{G}_{11}^{r} \hat{G}_{11}^{v} |^{1/4} / \Delta \hat{G}_2$$

and

$$z = \exp(\beta G^{v}/2) c^{v} , \tag{11b}$$

Eq. (10) transforms into the differential equation for the modified Bessel functions

$$x^2 z'' + x z' - (x^2 + m^2) z = 0 \tag{12}$$

with

$$0 < m = -\hat{G}_2^{v} / \Delta \hat{G}_2 < 1 \quad \text{for } \hat{n}_2 < n_2^* .$$

The solution fulfilling the boundary condition $c^v \rightarrow 0$ for $n_2 \rightarrow \infty$ is the modified Bessel function $K_m(x)$. The other integration constant is obtained from the boundary condition $c^v \rightarrow c_0 \exp(-\beta G^v)$ for $n_2 \rightarrow 0$ $(x \rightarrow 0)$. The final result is

$$c^{v} = \frac{2}{\Gamma(m)} \left[\frac{\hat{x}}{2}\right]^{m} K_m(x) \exp[-\beta(\hat{G}^{v} + G^{v})/2] c_0 , \tag{13}$$

where $\hat{x}$ is the value of x at $n_2=\hat{n}_2$ and Γ is the Γ function.

Now we define the "nucleation coordinate" $\hat{n}_2$ as the n_2 value at which the leakage current J_1 is maximum. This condition results in the transcendental equation

$$xK_{m-1}(x)=2(1-m)K_m(x)\ . \tag{14}$$

In Fig. 2 the solution $x=\hat{x}$ is plotted as a function of m. Note that at the boundaries $m\rightarrow 0$ and $m\rightarrow 1$ nucleation goes across a saddle point where our linear expansion of G with respect to n_2 becomes inadequate. Sufficiently off the saddle point, $\hat{x}$ is of the order of 1. Considering that the factor C in Eq. (11a) is of the order of 1 or somewhat smaller we arrive at the approximate condition

$$\beta\Delta\hat{G}\approx\ln(\hat{R}^r_{11}/\hat{R}^v_{22})\approx\beta\Delta g\equiv\beta(g_2-g_1)\ . \tag{15}$$

This result confirms a supposition of Stauffer and Kiang.[6] Ridge nucleation is rate controlling if Eq. (15) is fulfilled before the saddle point is reached, i.e., if

$$\hat{n}_2<n_2^*\ \text{or}\ \Delta G^*\equiv\Delta G(n_2^*)<\Delta g\ . \tag{16}$$

If $\hat{n}_2>n_2^*$ nucleation goes first across the saddle point and afterwards across the ridge. In this case nucleation across the saddle point is rate controlling.

The rate of nucleation across the ridge for $\hat{n}_2<n_2^*$ is given by the total current I_2 in the valley for $n_2\rightarrow 0$ ($x\rightarrow 0$):

$$I=c_0\,|\,\Delta\hat{G}_2\,|\,(2\pi\beta/\hat{G}^v_{11})^{1/2}\times\frac{\Gamma(1-m)}{\Gamma(m)}\left[\frac{\hat{x}}{2}\right]^{2m}\hat{R}^v_{22}e^{-\beta\hat{G}^v}\ . \tag{17}$$

The activation free enthalpy G_N of nucleation is

$$G_N=g_2+\hat{G}^v=g_1+\hat{G}^r\ , \tag{18}$$

where Eq. (15) has been used.

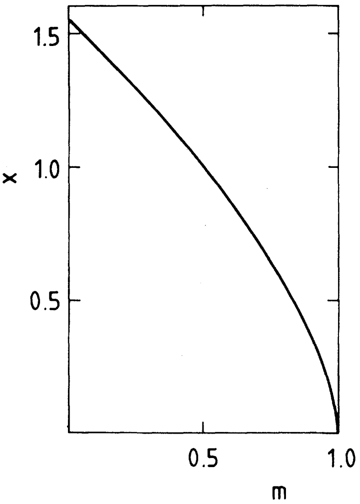

FIG. 2. Solution $x=\hat{x}$ of Eq. (14) as a function of m (see the text).

The approximations used in deriving these results, namely that the flux line bends off sharply into the direction 1, and that leakage across the ridge occurs in a sufficiently narrow interval, are justified if

$$\beta\Delta\hat{G}\approx\ln(\hat{R}^r_{11}/\hat{R}^v_{22})\gg 1\ . \tag{19}$$

Finally, we sketch the extension to more than two components. If the reaction rate of one component is significantly smaller than of the other ones the flux first follows the valley defined by the equilibrium with respect to the latter ones. The leakage may be described as nucleation in the (reduced) composition space of the fast components. By the same procedure the once reduced space can be further reduced, etc.

V. AN EXAMPLE FOR BINARY NUCLEATION: NUCLEATION OF GAS BUBBLES UNDER VACANCY SUPERSATURATION

The most simple binary example is the nucleation of gas bubbles in a monatomic matrix containing solved gas and vacancies in supersaturation (precipitation of gas atoms and lattice vacancies). If for this case the "capillarity approximation" and the ideal gas law are used, all approximations introduced above can be given in explicit analytical form. Here, we confine ourselves to the discussion of the *regions* of saddle-point and ridge nucleation and of the *activation free enthalpy* G_N of nucleation.

Within the capillarity approximation the formation free enthalpy of a spherical bubble of radius r, surface $S=4\pi r^2$, and volume $V=4\pi r^3/3$ containing n_1 vacancies of volume Ω and n_2 ideally behaving gas atoms is[9]

$$G=\gamma S-(\tilde{p}+\sigma)V+n_2kT\ln(\tilde{p}/p)\ , \tag{20}$$

with

$$S=(36\pi)^{1/3}(n_1\Omega)^{2/3}\ \text{and}\ V=n_1\Omega\ .$$

Here, γ is the surface free energy of the solid, σ is a (real or effective) hydrostatic external stress related to a relative change of the vacancy concentration (vacancy supersaturation) $\Delta C_V/C_V\approx\beta\sigma\Omega$, while $\tilde{p}=n_2kT/V$ is the actual gas pressure in the bubble and p is the equilibrium gas pressure corresponding to the gas concentration in the matrix.

The saddle-point coordinates are

$$n_1^*=\frac{4\pi}{3\Omega}\left[\frac{2\gamma}{p+\sigma}\right]^3,\quad n_2^*=\frac{p\Omega}{kT}n_1^*\ , \tag{21a}$$

and the corresponding free enthalpy

$$G^* = \frac{16\pi}{3} \frac{\gamma^3}{(p+\sigma)^2} \, . \tag{21b}$$

Since the direction of the nucleation flux $\vec{J}$ at the saddle point is determined by $\underline{R}^* \cdot \underline{G}^*$ we must know the properties of $\underline{G}^*$. Of course, $\det \underline{G}^* < 0$, but also $G_{22}^* > 0$ for *all* $0 < \alpha \equiv p/(p+\sigma) < 1$, while $G_{11}^* < 0$ for $0 < \alpha < \frac{1}{3}$ and $G_{11}^* > 0$ for $\frac{1}{3} < \alpha < 1$ (see the right and left small figures inserted into Fig. 1).

The reaction matrix $\underline{R}$ is diagonal if the gas atoms are absorbed and emitted as interstitial atoms independently of the vacancies. If the gas atoms diffuse via the vacancy mechanism, n_1 in Eq. (20) must be substituted by $n_1 + n_2$ to make $\underline{R}$ diagonal. According to Eq. (2) the reaction rates of the vacancies and the gas atoms are proportional to the corresponding permeation coefficients, i.e., in the case of vacancies proportional to the self-diffusion coefficient of the matrix. Usually, both quantities differ distinctly in magnitude.

For significantly different reaction rates of the vacancies and the gas atoms two main cases can be distinguished:

(1) The reaction rate of the gas atoms is much larger than of the vacancies, $R_2 \gg R_1$ (e.g., H in Nb). Then, since $G_{22} > 0$ everywhere, only subcase (b) of saddle-point nucleation described in Sec. III is possible. Thus during nucleation the gas pressure in the bubble embryos remains in equilibrium with the gas concentration in the matrix, i.e., the nucleation flux follows a straight line defined by $\tilde{p} = p$ $(G_2 = 0)$. The kinetic factor in the nucleation rate is controlled by the slow-reacting vacancies and the activation free enthalpy of nucleation is $G_N = g_1 + G$.

(2) The reaction rate of the gas atoms is much smaller than that of the vacancies, $R_2 \ll R_1$ (e.g., irradiation-induced He in metals). Then, since G allows positive and negative G_{11} and G_{11}^* ($G_{11} > 0$ for small n_1 and $G_{11} < 0$ for large n_1), both subcases (a) and (b) of nucleation across the saddle point, as well as nucleation across the ridge in the direction of the rapidly reacting vacancies, are possible. In all subcases the nucleation flux first follows the line of equilibrium with respect to the vacancies, $G_1 = 0$ $(p = 2\gamma/r)$, and then turns over into the direction of the rapidly reacting vacancies as soon as the condition for this is fulfilled (see Fig. 1).

Thus nucleation goes across the saddle point if in correspondence with Eq. (16), $\hat{n}_2 > n_2^*$, $\Delta G^* > \Delta g$. The two subspaces are as follows: (a) low gas supersaturation, $0 < \alpha < \frac{1}{3}$, $G_{11}^* < 0$. The nucleation flux turns over into the direction of the vacancies as soon as the saddle-point coordinate n_2^* is reached (left small figure inserted into Fig. 1). The kinetic factor in the nucleation rate is controlled by the vacancies and $G_N = g_1 + G^*$. (b) high gas supersaturation, $\frac{1}{3} < \alpha < 1$, $G_{11}^* > 0$. The line of equilibrium $G_1 = 0$ passes the saddle point (right small figure inserted into Fig. 1). The kinetic factor in the nucleation rate is controlled by the gas atoms and $G_N = g_2 + G^*$.

The nucleation flux turns over into the direction of the rapidly reacting vacancies and passes the ridge *before* the saddle-point coordinate n_2^* is reached if Eq. (16), $\hat{n}_2 < n_2^*$, $\Delta G^* < \Delta g$, is fulfilled (middle small figure inserted into Fig. 1). Kinetics and energetics of nucleation are coupled and $G_N = g_2 + \hat{G}^v = g_1 + \hat{G}^r$.

The transition from nucleation across the saddle point to nucleation across the ridge occurs at $\hat{n}_2 = n_2^*$, $\Delta G(\alpha) = \Delta g$. In Fig. 1 the corresponding $\Delta g(\alpha)/G_0$ line is shown where $G_0 = G^*$ $(p=0)$ is the free enthalpy barrier without gas.

The behavior of the nucleation rate around the transition line may be taken as an indication of the quality of the approximations introduced for ridge nucleation. For this the activation free enthalpy of nucleation in excess of that of the reaction rate of the rapidly reacting vacancies (both normalized to G_0) is plotted in Fig. 3 versus α for various $\Delta g/G_0$. The curves right and left of each pair of black dots belong to nucleation across a saddle point with $G_{11}^* > 0$ and $G_{11}^* < 0$, respectively, while the curves between the black dots belong to nucleation across the ridge. The smooth transitions of the curves from the regions of saddle-point nucleation to that

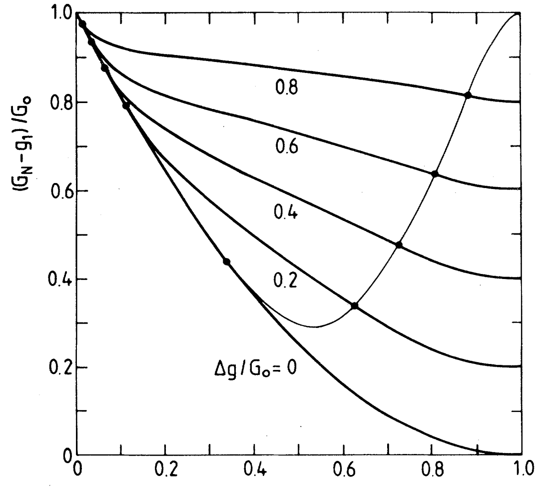

FIG. 3. Normalized excess activation free enthalpy of nucleation $(G_N - g_1)/G_0$ vs α for various $\Delta g/G_0$. The black dots mark the transitions from saddle-point to ridge nucleation (see text).

of ridge nucleation indicate that the approximations used for ridge nucleation are reasonable.

VI. SUMMARY AND CONCLUSIONS

In this paper asymptotic expressions for the rate of nucleation of multicomponent precipitates are derived and discussed. The derivations are based on three fundamental approximations: The particle clusters are considered to form an ideal solution (low concentration), the cluster coordinates are restricted to the numbers n_i of particles constituting the cluster, and the system of rate equations describing cluster kinetics is approximated by a Fokker-Planck equation (large critical clusters). Furthermore, it is assumed that the free enthalpy of formation $G(\vec{n})$ of the clusters establishes a nucleation barrier which is sufficiently smooth and high (large compared with kT). Apart from these conditions, in the general results $G(\vec{n})$ remains unspecified, in particular, the classical "capillarity approximation" need not be used.

Two essentially different types of nucleation are found: nucleation across a saddle point of $G(\vec{n})$ if the kinetic barrier is small compared with the energetic one, and nucleation across a ridge of $G(\vec{n})$ if the kinetic and energetic barriers are comparable and the reaction rates are significantly different. The latter type provides a continuous transition between homogeneous n-component and heterogeneous $(n-1)$-component nucleation.

For saddle-point nucleation only the quadratic approximation of $G(\vec{n})$ is needed in addition to the approximations mentioned above since the stationary Fokker-Planck equation can be solved exactly for a quadratic barrier. For ridge nucleation, approximations concerning the nucleation path are needed in addition to the expansion of $G(\vec{n})$ around the "nucleation points" in the valley and on the ridge. The derivation of the higher-order asymptotic terms (e.g., by a more accurate consideration of the flux direction on the ridge) is straightforward but tedious.

Therefore, other methods to check or to improve the approximations used for ridge nucleation are desirable. A heuristic check consists of considering the results of an application, e.g., to the nucleation of gas bubbles under gas and vacancy supersaturation. For this case the smooth behavior of the activation free enthalpy of nucleation at the transition indicates that the ridge approximations are reasonable. Another possibility is a numerical study of nucleation across a special ridge of simple analytical form (e.g., with only one cubic term). A method which allows improvements of the approximations consists of the variational principle related to the stationary Fokker-Planck equation resulting in the principle of maximum nucleation rate. Finally, it should be emphasized that the transition from saddle-point to ridge nucleation is not a rare but a rather common phenomenon in nucleation kinetics.

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