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KINETICS OF DIFFUSIVE DECOMPOSITION OF SUPERSATURATED SOLID SOLUTIONS

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The kinetics of the diffusive process of formation of grains of a new phase in a supersaturated solid solution is studied at a late stage of the process (coalescence of the grains). The exact asymptotic solution of the problem is obtained and investigated. The asymptotic distribution function is derived, the asymptotic number and average size of the grains are determined and the process of establishment of the asymptotic laws is analyzed. As an example of application of the theory, the mechanism of sintering is considered.

1. INTRODUCTION. STATEMENT OF THE PROBLEM

DURING the decomposition of a supersaturated solid solution, two stages must be distinguished in the diffusive process of formation of grains of a new phase. In the first stage there occur the fluctuating formation of nucleation centers of the new phase and their growth directly out of the supersaturated solution. In the second stage, when the grains are fairly large and the degree of supersaturation becomes extremely small, the principal process is coalescence: large grains "devour" small grains (the larger grains grow by the dissolution of smaller grains). In this second stage new nuclei would have to be of macroscopic size; thus their formation is practically excluded.

In the present paper we consider the kinetics of grain growth (coalescence) in the later stage. Other writers[1-4] have considered a problem of this type without arriving at a correct solution. Todes[4] has made the most thorough study of the question and has stated correctly that the asymptotic process for long times is independent of the initial conditions (the initial grain size distribution). He also correctly determined the order of magnitude of the rate of decrease of the number of grains with time. However, his quantitative solutions contain logarithmic divergences without physical meaning, which show that his reasoning is incorrect and also throw doubt on those of his qualitative results which are actually correct. The extremely peculiar behavior of the exact solution and the entire analysis which will be given below permit us to understand the origin of Todes' erroneous solution.

In stating the problem we shall, for simplicity, neglect anisotropy and assume the grains to be spherical. Allowance for nonspherical shapes would only change some numerical constants in the equations which follow. The equilibrium concentration C_R at the surface of a grain has the following usual relation to its radius R:

$$C_R = C_\infty + \alpha / R, \tag{1}$$

where C_∞ is the concentration of a saturated solution and α is associated with the interphase surface tension, with $\alpha = (\sigma/kT) V C_\infty$ (V is the volume of an atom of the solute).

Assuming the degree of supersaturation $\Delta = C - C_\infty$ to be small, i.e., $\Delta \ll 1$, and neglecting the "interaction" between grains (which is permissible because the grain diameter is small compared with the intergranular separation), we obtain for the diffusion flux of the dissolved substance per unit of grain surface the expression[*]

$$j = D \left.\frac{\partial C}{\partial R}\right|_{r=R} = \frac{D}{R}(C - C_R) = \frac{D}{R}\left(\Delta - \frac{\alpha}{R}\right)$$

and thus for the change of grain radius with time[†]

$$\frac{dR}{dt} = \frac{D}{R}\left(\Delta - \frac{\alpha}{R}\right). \tag{2}$$

Thus for each value of the supersaturation Δ there exists a critical radius $R_{cr} = \alpha\Delta$ at which the

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[*] The expression given for the flux corresponds to a stationary value of the gradient $\partial C/\partial r$ on the grain boundary. It is easily seen that this is permissible when the initial supersaturation is amall, $\Delta_0 \ll 1$.

[†] We note that if the grains are nonspherical but preserve similarity of their shapes while growing during the later stage (a similarity associated with the anisotropy α), Eq. (2) and all subsequent quantitative results remain valid. Then R signifies $(3V/4\pi)^{1/3}$, V being the grain volume, and α and D differ from their previous values by only a numerical factor which takes the grain shape into account.

grain is in equilibrium with the solution; when $R > R_{cr}$ the grain grows while when $R < R_{cr}$ it dissolves. This is the evident cause of the "devouring" of small grains by large grains. Δ and R_{cr} vary with time.

We shall hereafter use the dimensionless quantities $\rho = R/R_{cr}$, $t' = t/T$, ($R_{cr0} = \alpha/\Delta_0$, $T = R^3_{cr0}/\alpha\Delta$, Δ_0 is the initial supersaturation, R_{cr0} is the initial critical radius). Omitting the prime in t', we obtain

$$d\rho^3/dt = 3(\rho/x - 1), \tag{3}$$

where $x(t)$ is the dimensionless critical radius and $x(0) = 1$.

Introducing a grain-size distribution function $f(\rho, t)$ and regarding $v_\rho = d\rho/dt$ as the rate of grain travel in the space of grain sizes, we can write down the equations for the unknown functions $f(\rho, t)$ and $x(t)$. The first of these is the continuity equation in grain-size space:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \rho}(f v_\rho) = 0, \tag{4}$$

while the second equation is the law of conservation of matter:

$$Q_0 = \Delta_0 + q_0 = \Delta + q, \quad q = \frac{4\pi}{3} R^3_{cr0} \int_0^\infty f \rho^3 \, d\rho$$

or, with $x = \Delta_0/\Delta$,

$$1 = \frac{\Delta_0}{Q_0 x} + \varkappa \int_0^\infty f \rho^3 \, d\rho, \quad \varkappa = 4\pi R^3_{cr0}/3Q_0. \tag{5}$$

In this equation Q_0 is the total initial supersaturation, including the initial volume of matter q_0 in the grains. In (5) f is normalized to unit volume: $n = \int_0^\infty f \, d\rho$ is the number of grains per unit volume.

Our problem thus becomes the asymptotic solution of (4) and (5) for a given initial condition $f(\rho, 0) = f_0(\rho)$.

2. ASYMPTOTIC VARIATION OF CRITICAL SIZES

To solve our problem we must first determine the asymptotic variation of critical sizes $x(t)$ [or of the supersaturation $\Delta(t) = \Delta_0/x(t)$, which amounts to the same thing]. The motion of the point ρ which represents a grain radius on the axis of sizes, as determined by the equation of motion (3), presents the following picture: The points located to the left of $x(t)$ are accelerated toward the left and disappear upon reaching the coordinate origin (complete dissolution of the grain). The points which are originally to the right of $x(t)$ move to the right (the grains grow), but as the supersaturation diminishes the critical size $x(t)$ increases and successively "overtakes" points moving to the right, after which these points begin to move in the opposite direction and also "disappear" at the origin. This movement is always orderly; the original order of position of the points is preserved.

Both the form of Eq. (3) and the physical meaning of $x(t)$ suggest that for the independent variable in Eqs. (3), (4), and (5) we take instead of the grain radius ρ the relative radius (with respect to the critical radius)

$$u = \rho/x(t). \tag{6}$$

Since for $t \to \infty$ the supersaturation $\Delta \to 0$, we have $x(t) \to \infty$. Thus $x(t)$ can be used to compute time.* The "equation of motion" (3) acquires a canonical form when "time" is represented by the quantity

$$\tau = \ln x^3. \tag{7}$$

Insertion of (6) and (7) into (3) gives

$$du^3/d\tau = \gamma(u - 1) - u^3, \tag{8}$$

$$\gamma = \gamma(\tau) = 3dt/dx^3. \tag{9}$$

If $u(v, \tau)$ denotes the solution of (8) for the initial condition $u|_{\tau=0} = v$ and we consider that $\rho(v, \tau) = xu(v, \tau)$, $x(0) = 1$, and $\tau|_{t=0} = 0$, the total quantity q of matter in the grains can be expressed through the initial distribution function $f_0(\rho)$ as follows:

$$q = \varkappa Q_0 \int_{v_0(\tau)}^\infty f_0(v) x^3(\tau) u^3(v, \tau) \, dv. \tag{10}$$

Here $v_0(\tau)$, the solution of the equation $u(v_0(\tau), \tau) = 0$, is the lower limit of the original sizes of grains which had not dissolved up to the time τ. Noting that $x^3 = e^\tau$, we can write (5) as

$$1 - e^{-\tau/3} = \varkappa e^\tau \int_{v_0(\tau)}^\infty f_0(v) u^3(v, \tau) \, dv. \tag{11}$$

Equations (8) and (11) form a complete system. These equations can be used to determine the unknown function $\gamma(\tau) = 3dt/dx^3$ and thus ultimately $x(t)$.

Three possibilities exist for the asymptotic behavior of $\gamma(\tau)$ as $\tau \to \infty$: (1) $\gamma(\tau) \to \infty$; (2) $\gamma(\tau) \to$ const; (3) $\gamma(\tau) \to 0$. We shall begin

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*A formal exception is the case in which the initial distribution is a δ function [$f_0 = A\delta(\rho - \rho_0)$] or a sum of δ functions. In this case $x(t) \to$ const and the common size ρ assumes an equilibrium value. But the case is also unstable since even an extremely small spread of the initial distribution leads to $x(t) \to \infty$.

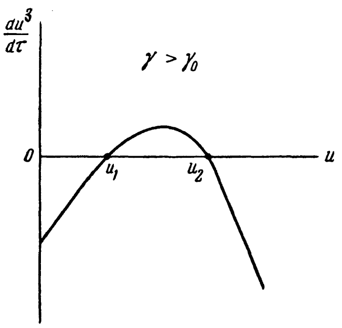

FIG. 1

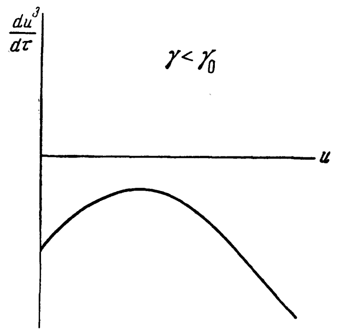

FIG. 2

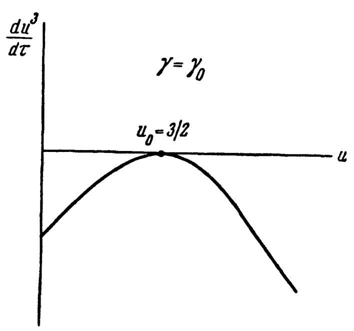

FIG. 3

our analysis with the case γ = const. Depending on the value of γ, the curve of the velocity $du^3/d\tau$ as a function of u can be tangent to the horizontal axis (for $\gamma = \gamma_0 = 27/4$), lie below this axis (for $\gamma < \gamma_0$), or have a positive section (for $\gamma > \gamma_0$) (Figs. 1, 2, 3).

(a) When $\gamma > \gamma_0$ all points that lie to the left of u_1 move toward the left and disappear when they reach the coordinate origin. All points that lie to the right of u_1 move to the point u_2, approaching it asymptotically from either the left or right. Therefore for $\tau \to \infty$ the integral in the right member of (11) approaches the constant value

$$I_0 = u_2^3 \int_{u_1}^{\infty} f_0(v)\, dv,$$

and the combined volume q of the grains, which is also in the right member, increases as e^τ,

$$q = \varkappa I_0 e^{\tau} \to \infty, \tag{12}$$

so that Eq. (11) is not satisfied. When we take into account the fact that a constant value $\gamma > \gamma_0$ is reached only asymptotically, the foregoing description remains unchanged: we need only shift the time origin and let $f_0(v)$ refer to the time when $\gamma(\tau)$ is close to its asymptotic value.

(b) When $\gamma < \gamma_0$ all points move to the left and reach the origin in a finite time. It follows from (8) that at the time τ all grains have been dissolved whose original sizes were smaller than $v_0(\tau)$. These sizes are determined from the equation

$$\int_0^{v_0(\tau)} \frac{3u^2\, du}{u^3 - \gamma(u-1)} = \tau.$$

When $\tau \gg 1$ we have $v_0(\tau) = e^{\tau/3}$. Therefore the combined volume of the grains will be determined from the "tail" of the original distribution $f_0(v)$:

$$q(\tau) = \varkappa e^{\tau} \int_{e^{\tau/3}}^{\infty} f_0(v)\, u^3(v, \tau)\, dv \sim \varkappa \int_{e^{\tau/3}}^{\infty} f_0(v)\, v^3\, dv \to 0 \tag{13}$$

[since $u(v, \tau) \sim ve^{\tau/3}$].* Thus in this case $q(\tau)$ approaches zero and Eq. (11) again lacks a solution.

When $\gamma \to \infty$ and $\gamma \to 0$ the reasoning for $\gamma > \gamma_0$ and $\gamma < \gamma_0$ is even more fully justified. Thus we need only investigate the case $\gamma(\tau) \to \gamma_0 = 27/4$. We note first that for the exact equality $\gamma = \gamma_0$ all points that lie to the right of the point of tangency $u_0 = 3/2$ move to the left but cannot pass through u_0 and "stick" at this point. Therefore, just as for $\gamma > \gamma_0$, Eq. (11) cannot be satisfied [$q(\tau) \sim e^{\tau} \to \infty$ for $\tau \to \infty$]. This means that $\gamma(\tau)$ must approach γ_0 from below; thus

$$\gamma(\tau) = \gamma_0 (1 - \varepsilon^2(\tau)). \tag{14}$$

The points that arrive at u_0 from the right "filter" more and more slowly through the "blocking".point $u_0 = 3/2$ at a rate that depends on the value of $\epsilon(\tau)$, which like $\gamma(\tau)$ must be obtained from (11) and the equation of motion (8):

$$\frac{du^3}{d\tau} = -\left(u - \frac{3}{2}\right)^2 (u+3) - \frac{1}{2}\gamma_0 \varepsilon^2(\tau), \tag{15}$$

where $\epsilon(\tau) \to 0$ for $\tau \to \infty$. Near $u_0 = 3/2$ this equation becomes

$$\frac{du}{d\tau} = -\frac{2}{3}\left(u - \frac{3}{2}\right)^2 - \frac{1}{2}\varepsilon^2(\tau). \tag{16}$$

With the introduction of the new function $z = (u - 3/2)/\epsilon$ it can be written as

$$\frac{3}{2}\frac{dz}{\varepsilon d\tau} = -z^2 - \frac{3}{4} + \frac{3}{2} z \frac{d(1/\varepsilon)}{d\tau}.$$

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*The exact value of $u(v, \tau)$ is the solution of

$$R(u) = R(v)\, e^{-\tau/3}, \qquad R(u) = \exp\left[\int_0^u \frac{u^2\, du}{u^3 - \gamma(u-1)}\right],$$

$R(0) = 1$, $R(v) = v$ for $v \gg 1$; therefore for $v \gg 1$ we have $v = R(u)e^{\tau/3}$ and the correct asymptotic expression for q is

$$q(\tau) \sim \varkappa x^4 \int_1^{\infty} f_0(xR)\, u^3(R)\, dR; \qquad x = e^{\tau/3}.$$

For $u \gg 1$, $R \approx u$ and we obtain (13).

A similar study shows that asymptotically

$$\frac{d(1/\varepsilon)}{d\tau} \to \frac{2}{\sqrt{3}}, \qquad \varepsilon^2 \to \frac{3}{4\tau^2}. \tag{17}$$

At the same time we have

$$\frac{3}{2}\frac{dz}{d\ln\tau} \to -\left(z - \frac{\sqrt{3}}{2}\right)^2,$$

which means that the velocity $dz/d\ln\tau$ vanishes asymptotically at the "blocking" point $z_0 = \sqrt{3/2}$.

Thus for sufficiently large τ the improved value of $\gamma(\tau)$ will be

$$\gamma(\tau) = \gamma_0(1 - 3/4\,\tau^2), \tag{18}$$

and the more precise location of the "blocking" point on the axis will be

$$u = {}^3/_2 + z_0\varepsilon(\tau) = {}^3/_2 + 3/4\,\tau. \tag{19}$$

Continuing the same line of reasoning, we obtain an asymptotic expansion for $\gamma(\tau)$:*

$$3\frac{dt}{dx^3} = \gamma(\tau) = \gamma_0\left[1 - \frac{3}{4\tau^2}\left(1 + \frac{1}{(\ln\tau)^2}(1 + \ldots)\right]\right., \tag{20}$$

and accordingly

$$x^3 = \frac{4}{9}t\left(1 + \frac{3}{4(\ln t)^2}(1 + \ldots)\right). \tag{21}$$

This expansion can be terminated at any term that is followed by a relatively small term. Thus the basic approximation $\gamma(\tau) = \gamma_0$, and accordingly $x^3 = {}^4/_9\,t$, is valid if $\tau^2 = (\ln t)^2 \gg 1$.

An interesting property of the expansions (20) and (21) is the fact that although the corrections to γ_0 decrease rapidly in magnitude as τ increases and the first approximation (21) becomes increasingly accurate the behavior of the solution near the blocking point is determined by these corrections.

In the entire region outside the vicinity of $u_0 = {}^3/_2$ the velocity $du/d\tau$ is given by

$$\frac{du}{d\tau} = -g(u); \qquad g(u) = \left(u - \frac{3}{2}\right)^2(u + 3)/3u^2. \tag{22}$$

3. ASYMPTOTIC DISTRIBUTION FUNCTION

In accordance with the preceding section, the distribution function will also be obtained in terms of the new variables u and τ. When expressed in terms of the relative size $u = \rho/x$ the distribution function $\varphi(u, \tau)$ has the following obvious relation to $f(\rho, t)$:

$$\varphi(u, \tau)\,du = f(\rho, t)\,d\rho = xf(\rho, t)\,du,$$

whence

$$f = \varphi(u, \tau)/x.$$

Except in the vicinity of u_0, when $\tau \gg 1$ the continuity equation for $\varphi(u, \tau)$ is given by

$$\frac{\partial\varphi}{\partial\tau} - \frac{\partial\varphi g(u)}{\partial u} = 0. \tag{23}$$

The solution of this equation to the left of u_0 is

$$\varphi = \chi(\tau + \psi)/g(u),$$

where

$$\psi = \int_0^u \frac{du}{g(u)} = \frac{4}{3}\ln(u + 3) + \frac{5}{3}\ln\left(\frac{3}{2} - u\right) + \frac{1}{1 - 2u/3} - \ln\frac{3^3 e}{2^{5/3}},$$

and χ is an arbitrary function still to be determined.

It follows from the analysis (given in the previous section) of the equation of motion (8) or (15) and thus of the characteristics of Eq. (23) that the vicinity of the point u_0 is to be regarded as a sink for all points $u > u_0$ and a source for the region $u < u_0$; for $u < u_0$ the sink is the coordinate origin $u = 0$. Moving from right to left all points pass through the vicinity of u_0 and remain there longer the later they arrive.

The distribution function to the right of u_0 for $\tau \to \infty$ is given by an infinitely distant portion of the "tail" of the original distribution, and its integral contribution to both the absolute and relative expressions rapidly approaches zero (Appendix, Sec. 1). It will be shown below that the relative contribution from the vicinity of u_0 also approaches zero as $\tau \to \infty$ (Appendix, Sec. 2). Thus the predominant contribution to matter conservation comes from grains with $u < u_0$. It follows that this conservation law can be used as an integral equation to determine the asymptotic behavior of the distribution function in zero approximation for $u < u_0$. (For $u > u_0$ the distribution function vanishes in this approximation.) From the foregoing considerations, by inserting the solution of (23) into the law of mass conservation we obtain an asymptotic equation for χ:

$$1 = \varkappa e^{\tau}\int_0^{3/2}\chi(\tau + \psi)\frac{u^3}{g(u)}\,du. \tag{24}$$

From this equation it is easy to determine $\chi(\tau + \psi)$ and thus $\varphi(u, \tau)$:

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*$\gamma(\tau)$ can be written formally as $\gamma(\tau) = \gamma_0(1 - {}^3\!/_4\,w(\tau))$, where $w(\tau)$ satisfies the functional equation $w(z) = z^{-2} + (1 + w(\ln z))$ when $z > 1$.

$$\chi(\tau+\psi) = Ae^{-\tau-\psi}, \qquad (25)$$

$$\varphi(u,\tau) = Ae^{-\tau-\psi}\frac{1}{g(u)} = \frac{3^4 e}{2^{5/3}}Ae^{-\tau}\frac{u^2\exp[-1/(1-2u/3)]}{(u+3)^{7/3}(3/2-u)^{11/3}},$$

where

$$A = \left[\varkappa\int_0^{3/2} e^{-\psi}\frac{u^3}{g(u)}du\right]^{-1} = \frac{3Q_0}{4\pi R^3_{\mathbf{cr0}}1.11} \approx 0.22\frac{Q_0}{R^3_{\mathbf{cr0}}}. \qquad (26)$$

We thus see that the asymptotic behavior of the distribution function for $u < u_0$ is independent of the form of the original distribution function.*

According to (25) the number of particles per unit volume is given by

$$n(\tau) = \int_0^{3/2}\varphi(u,\tau)\,du = Ae^{-\tau} = \left(\frac{3}{2}\right)^{4/3}\frac{A}{t}. \qquad (27)$$

Let $P(u)du$ be the probability that the size of a particle is between u and $u + du$. Then

$$\varphi(u,\tau) = n(\tau)P(u), \qquad (28)$$

where

$$P(u) = \begin{cases} \dfrac{3^4 e}{2^{5/3}}\dfrac{u^2\exp[-1/(1-2u/3)]}{(u+3)^{7/3}(3/2-u)^{11/3}}, & u < u_0 = 3/2; \\ 0 & u > u_0 = 3/2. \end{cases} \qquad (29)$$

This probability can be expressed conveniently with a different relative variable obtained by introducing the maximum size:

$$\rho_m = 3x/2, \quad v = \rho/\rho_m = u/u_m = 2u/3.$$

Then

$$P(u)\,du = P_1(v)\,dv, \quad P(u) = 2P_1(v)/3;$$

$$P_1(v) = \begin{cases} 2^{7/3}ev^2\exp[-1/(1-v)]/(v+2)^{7/3}(1-v)^{11/3}, & v < 1; \\ 0 & , v > 1. \end{cases}$$

Thus these formulas completely determine the asymptotic size and time distributions of the particles.† $P(u)$ is plotted in Fig. 4.

We now note that

$$\int_0^{3/2} e^{-\psi}\frac{u-1}{g(u)}du = \int_0^{\infty} e^{-\psi}(u(\psi)-1)\,d\psi = e^{-\psi}u^3(\psi)\Big|_0^{\infty} = 0. \qquad (30)$$

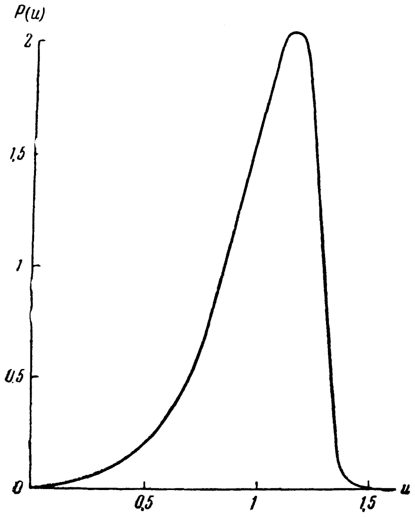

FIG. 4

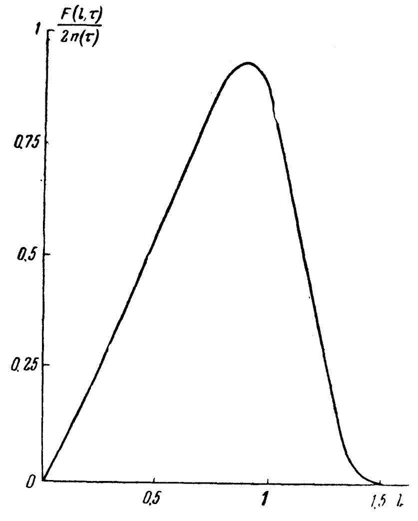

FIG. 5

We have used here the relation

$$du^3/d\psi = u^3 - 4(u-1)/27. \qquad (31)$$

This indicates that $\bar{u} = 1$; it thus follows that

$$\bar{\rho} = \bar{u}x = x(\tau). \qquad (32)$$

In order to obtain the distribution over absolute values of the radius ρ we need only replace u by ρ/x in (25) and divide by x, for which

$$x^3 = 4t/9. \qquad (33)$$

Considering that, according to (32), $\mu = R/\overline{R}$ and returning to the original dimensional quantities, we obtain

$$\begin{gathered} f(R,t) = n(t)P(R/\overline{R})/\overline{R}, \\ n(t) = \beta Q_0/\overline{R}^3 = B/t, \quad \beta \approx 0.22, \quad B \approx 1/2D\alpha, \\ \overline{R}^3 = 4D\alpha t/9, \end{gathered} \qquad (34)$$

where $P(u)$ is given by (28). The supersaturation at a given time is given by

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*It should be noted that the distribution given by Todes corresponds in form to the case $\gamma < \gamma_0$ of the present scheme. Our discussion makes it clear that such a distribution can never arise and that the case $\gamma < \gamma_0$ is meaningless. This accounts for the divergence of the integrals in Todes' equations.

†For measurements performed by means of a grain-size classifier it is easily shown that the distribution $\Phi(r,\tau)$ over the sizes r of the openings is given by

$$F(l,\tau)\,dl = \Phi(r,\tau)\,dr, \qquad \Phi(r,\tau) = x^{-1}F(r/x(\tau)\ \ \tau),$$

$$F(l,\tau) = 2x(\tau)\int_l^{3/2}\frac{\varphi(u,\tau)\,du}{\sqrt{(u/l)^2-1}}, \qquad l = \frac{r}{x(\tau)}, \qquad r = \frac{R}{R_{\mathbf{cr0}}}$$

$$\Delta(t) = \frac{\Delta_0}{x(t)} = \left(\frac{3}{2}\right)^{2/3} \Delta_0 \left(\frac{T}{t}\right)^{1/3} = \lambda t^{-1/3}, \quad \lambda = \left(\frac{3}{2}\right)^{2/3} \left(\frac{\alpha^2}{D}\right)^{1/3} \tag{35}$$

Finally, we shall discuss the limits of applicability of the formulas which have been derived. The preceding analysis shows that the asymptotic expressions are valid subject to the condition

$$\tau^2 = (3 \ln x)^2 = 9 \left(\ln \frac{\bar R}{R_{\mathrm{cr}0}}\right)^2 \gg 1; \quad \bar R \gg R_{\mathrm{cr}0}.$$

Here $R_{\mathrm{cr}0} = \alpha/\Delta_0$ is the initial critical radius for the coalescence process (Δ_0 is the initial degree of supersaturation). We must also take it into account that if the initial average grain size is of the order of the critical size ($\bar R_0 \sim R_{\mathrm{cr}0}$), this size will enter into the calculation performed above. But if $\bar R_0 \gg R_{\mathrm{cr}0}$ the grains will grow directly from the solution in the first stage. This process will continue until the degree of saturation drops to the point where the average size is of the order of the critical size $\bar R_1 \sim R_{\mathrm{cr}1}$), after which coalescence will generally begin. This size must then be used as the initial size, with its magnitude determined essentially by both the initial degree of supersaturation and the initial number of nuclei (if the latter can be regarded as fixed).

Thus with initial supersaturation Δ_0 and initial number n_0 of grains, and with $\bar R_0 \gg R_{\mathrm{cr}0} = \alpha/\Delta_0$, growth from the solution will continue up to the size

$$\tfrac{4}{3}\pi \bar R_1^3 \approx \Delta_0 / n_0,$$

and in the initial stage

$$\frac{d\bar R^2}{dt} = 2D\left(\Delta_0 - \frac{4\pi}{3}\bar R^3 n_0\right) = 2D\Delta_0\left(1 - (\bar R / R_{\mathrm{cr}1})^3\right). \tag{36}$$

$t_1 \sim \bar R_1^2/D\Delta_0$ is the duration of the first stage.

The characteristic time of the first portion of the second stage (coalescence) is

$$t_0 \sim \bar R_1^3 / D\alpha \sim t_1 \bar R_1 / R_{\mathrm{cr}0};$$

in our case $\bar R_1 \gg R_{\mathrm{cr}0}$, that is, $t_0 \gg t_1$. The dependence of the average size on time in this case is plotted in Fig. 6.

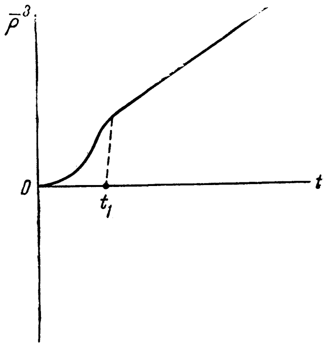

FIG. 6

4. PRESENCE OF A BOUNDARY. THEORY OF SINTERING

In the preceding sections we have investigated coalescence in infinite space. Thus the problem did not involve macroscopic diffusive flow of the solute. The situation changes when spatial uniformity is absent, the most important case being the presence of a boundary between the solution and a different phase. When this second phase is the pure solute (or, more generally, the phase for which we are investigating the grain growth), we get on this boundary $\Delta_{z=0} = 0$, which produces macroscopic diffusive flow to the boundary.

An important special case occurs when the part of solute atoms is played by vacancies and the part of the grains is played by pores which result from the coagulation of vacancies in a crystal that is "supersaturated with vacancies." When a free surface exists in such a crystal, two competing processes will occur: far from the boundary — the growth of pores (vacuum crystals) and their coalescence according to the scheme developed previously; near the boundary — the dissolution of pores and the diffusion of vacancies to the boundary (which can be regarded as a pore of infinitely large radius). Sintering is associated with this process of pore expulsion.

We shall discuss henceforth this specific process although all results will, of course, also apply to the more general case of a supersaturated solution.

For a half-space, Eq. (3) for grain growth and Eq. (4) for the distribution function [or the equivalent Eqs. (8) and (10)] will be retained. But instead of the conservation law $Q_0 = \Delta + q$, which corresponds to (5) [or (11) respectively], we must write a diffusion equation. Then each point z is a source (or sink) of strength dq/dt, $q = q(z, t)$ resulting from dissolution of the pores. Thus the exact system of equations will be

$$\frac{\partial(\Delta + q)}{\partial t} = D\frac{\partial^2 \Delta}{\partial z^2}, \quad \Delta|_{z=0} = 0; \tag{37}$$

$$q = \varkappa x^3 \int_{v(\tau)}^{\infty} f_0(v)\, u^3(v, \tau)\, dv, \quad x = \Delta_0/\Delta(z, t), \tag{38}$$

where $u(v, \tau)$ satisfies (8) and is itself determined by the function $\Delta(z, t)$.

The analysis in Sec. 2 has shown the peculiar "stability" of the asymptotic law found for the variation of supersaturation (35),

$$\Delta = \lambda t^{-1/3},$$

which means that the slightest retardation of the asymptotic reduction of supersaturation results in the infinite growth of grains ($q \rightarrow \infty$) and is thus impossible. On the other hand, even a slight acceleration of the asymptotic reduction of supersaturation leads relatively rapidly to complete dissolution of the grains ($q \rightarrow 0$). Therefore the asymptotic process of sintering must be the following. Three sharply separated regions are present:

(a) The region most distant from the boundary ($z_2 < z < \infty$), which is not affected by the boundary and where, as in the case of infinite space, supersaturation is given by Eq. (35).

(b) The region $z_1 < z < z_2$, where dissolution of pores (grains) occurs.

(c) The region $0 < z < z_1$, where pores are already completely absent and purely diffusive expulsion of vacancies occurs. The boundaries of these regions $z_1(t)$ and $z_2(t)$ move deeper into the specimen so that the "crust," which is free of pores, is continuously thickening. Strictly speaking, Eqs. (37) and (38) may be solved only for the intermediate region $z_1 < z < z_2$. But, as will be shown below, $(z_2 - z_1)/z_2 \ll 1$. Therefore in first approximation we set $(z_1 + z_2)/2 = \xi$, and replacing this region by the corresponding boundary condition, we determine the position of the boundary $\xi(t)$ and the variation of the concentration in the surface layer $0 < z < \xi$ (in the crust). Thus

$$\frac{\partial \Delta}{\partial t} = D \frac{\partial^2 \Delta}{\partial z^2}; \tag{39}$$

$$\Delta \Big|_{z=0} = 0; \quad \Delta \Big|_{z=\zeta} = \lambda t^{-1/3}; \quad D \frac{\partial \Delta}{\partial z}\Big|_{z=\zeta} = Q_0 \frac{d\zeta}{dt}. \tag{40}$$

The last condition replaces the transition region and expresses the fact that the boundary $\xi(t)$ is a source of strength $Q_0 d\xi/dt$ (since to the right practically all excess vacancies are within pores). The solution of (38) together with the boundary condition ($\Delta|_{z=0} = 0$) will be obtained in the form $\Delta = \sum_{n=1}^{\infty} \alpha_n(t) z^n$; we then obtain from (39)

$$\Delta = \sum_{n=0}^{\infty} \frac{\hat{p}^n \alpha_1(t)}{(2n+1)!} z^{2n+1}, \quad \hat{p} = \frac{1}{D} \frac{d}{dt}.$$

Before satisfying the other two boundary conditions, we note that $\alpha_1(t)$ is an asymptotically decreasing function of time (since it represents flow on the boundary $z = 0$, $\alpha_1(t) = D \partial\Delta/\partial z|_{z=0}$).

We shall therefore obtain α_1 asymptotically in the form $\alpha_1 = B/t^s$, $s > 0$. Then we have from (39)

$$\Delta = B \frac{z}{t^s} \sum_{n=0}^{\infty} (-1)^n \left(\frac{z^2}{Dt}\right)^n \frac{s(s+1)\ldots(s+n)}{(2n+1)!} \tag{41}$$

As will be shown below, $\xi^2(t)$ varies asymptotically more slowly than t ($\xi^2(t)/t \rightarrow 0$ for $t \rightarrow \infty$). Thus the main term of the asymptotic expression is that with $n = 0$:

$$\Delta = Bz / t^s \equiv \alpha_1 z. \tag{42}$$

Inserting (41) into (39), we have

$$\alpha_1 \zeta = \lambda t^{-1/3}, \qquad \alpha_1 = \frac{Q_0}{D} \frac{d\zeta}{dt}.$$

As a result we obtain

$$\zeta = \sqrt{3}\,(3/2)^{2/3} \bar{R}/Q_0^{1/2} = m\,(D\alpha t)^{1/3}/Q_0^{1/2}; \; m = (3/2)^{1/3}\sqrt{3} \approx 2;$$

$$\Delta = \lambda t^{-1/3} z / \zeta = \frac{m}{3} Q_0^{1/2} \frac{\alpha^{1/3} z}{(Dt)^{2/3}}. \tag{43}$$

The relative width of the intermediate region now remains to be determined. According to (43)

$$\delta\zeta / \zeta = \delta t / 3t = T_d(t) / 3t, \tag{44}$$

where T_d is the time of dissolution of the largest grains present at the boundary at time t, $R_{max} = 3R_{cr}/2$. In region I the critical radius as a function of time is

$$R_{cr}^3 \sim t^2.$$

A simple calculation shows that in the equation of motion (8) $\gamma = 3dt/dx^3 \leq 27/8 < \gamma_0$. From this equation we obtain the time of dissolution of the largest grains ($u_0 = 3/2$), $T_d(t) \approx t/3$. This gives for the relative width

$$\delta\zeta / \zeta \approx 1/9.$$

We note that

$$\delta\zeta / \bar{R} = 1/3\, Q_0^{1/2} \gg 1. \tag{45}$$

Moreover,

$$\delta\zeta / l \approx Q_0^{1/3} / 3Q_0^{1/2} = 1/3\, Q_0^{1/2} \gg 1, \tag{46}$$

where l is the average distance between grains. The inequalities (45) and (46) denote that $d\xi \gg l \gg \bar{R}$, which means that the width of the intermediate region is considerably larger than the average separation of the pores and the average size of the pores (grains), while at the same time it is considerably smaller than the first region (the crust). This also justifies all assumptions which we made in order to obtain the asymptotic expressions.

The periods of time for which the asymptotic formula (43) can be used are the same as for the asymptotic expression for coalescence in infinite space.

A special situation occurs when we take into account the finite size of a specimen instead of only a single boundary. For example, for a plate of thickness a there exist three characteristic times: the time for diffusive escape of vacancies at the surface of the plate ($T_0 \sim a^2/D$), the time for growth of pores from the solution ($T_1 \sim \overline{R}_1^2/D\Delta_0$, see page 336), and the characteristic time for coalescence ($T_{co} \sim \overline{R}^3/D\alpha$)

In order to make the foregoing "crust-forming" sintering mechanism possible, the diffusive escape time T_0 must be considerably longer than T_{co}, that is, $a^2 \gg \overline{R}_1^3/\alpha$, and the average size of the pores which enter into this inequality must be in accord with the development of the coalescence process, $\overline{R} \gg R_1$. In the other limiting case $T_0 \ll T_1$ the vacancies escape without forming pores. In the intermediate case $a^2 \sim R_1^3/\alpha$ the kinetics of the process is determined by factors associated with the initial distribution and is not of a general character.

The method which has been proposed here can be applied to a number of similar problems, which will be investigated separately.

APPENDIX

Determination of the Distribution Function for $u > u_0$ in the Vicinity of the Point u_0

1. We shall determine the distribution function for $u > u_0$. Introducing $\psi = \int du/g(u)$ we note that $g(u) \rightarrow u/3$, $u \rightarrow e^{\psi/3}$ for $u \rightarrow \infty$, that is,

$$ux^{1/3} \rightarrow \exp[(\tau + \psi)/3]. \tag{A.1}$$

In addition, the solution on the right for $u \rightarrow \infty$ must be determined by the initial distribution function:

$$\chi(\tau + \psi) \rightarrow f_0(ux^{1/3})\, x^{1/3} g(u), \tag{A.2}$$

where f_0 is the initial distribution over ρ. From this condition we determine the distribution for $u > u_0$:

$$\chi(\tau + \psi) = f_0(z)\, z/3, \quad z = e^{(\tau+\psi)/3} \tag{A.3}$$

or

$$\varphi(u, \tau) = f_0(z)\, z/3\, g(u). \tag{A.4}$$

$f_0(z)$ varies at least more rapidly than z^{-4} (which is necessary for the existence of $\int_0^\infty f_0(z) z^3 dz$), and usually is an exponential function of z. Hence the probability density for $u > u_0$ in zero approximation vanishes:

$$P(u, \tau) = \varphi(u, \tau)/n(\tau)$$
$$= \frac{1}{3A} f_0(z) z^4 \frac{e^{-\psi}}{g(u)} \rightarrow 0 \text{ for } z \rightarrow \infty. \tag{A.5}$$

The probability density for $u < u_0$ is known to be finite.

2. We shall show that the integral contribution from the vicinity of the point is negligibly small for $\tau \rightarrow \infty$. The amount of matter in this vicinity is given by

$$q_\delta = x^3 \int_{u_0-\delta}^{u_0+\delta} \varphi u^3 du = u_0^3 e^\tau n_\delta(\tau), \tag{A.6}$$

$$n_\delta(\tau) = \int_{u_0-\delta}^{u_0+\delta} \varphi du, \quad 1 \gg \delta \gg \varepsilon(\tau). \tag{A.7}$$

From the equation of continuity we obtain

$$\frac{dn_\delta}{d\tau} = \varphi g(u) \Big|_{u_0-\delta}^{u_0+\delta} = Ae^{-\tau} e^{-\psi(u_0-\delta)} = Ae^{-\tau} \exp(-3/2\,\delta) \tag{A.8}$$

(the flow to the right is determined for $\tau \rightarrow \infty$ by the infinitely distant tail of the distribution and can thus be neglected),

$$n_\delta = Ae^{-\tau} \exp(-3/2\delta) + B;$$
$$q_\delta = A \exp(-3/2\,\delta) + Be^\tau. \tag{A.9}$$

It is evident that $B = 0$, since matter must be conserved. We finally obtain the quantity of matter in the vicinity of u_0 for $\tau \rightarrow \infty$:

$$q_\delta = A \exp(-3/2\,\delta) \rightarrow 0, \quad \delta \rightarrow 0. \tag{A.10}$$

3. We shall show how a more accurate expression for the distribution function is obtained in the vicinity of the point $u_0 = 3/2$. The continuity equation in the vicinity of this point is

$$\frac{\partial \varphi}{\partial \tau} + \frac{\partial}{\partial u} \varphi g(u) = 0, \quad g(u)$$
$$= -\frac{2}{3}\left[\left(u - \frac{3}{2}\right)^2 + \varepsilon^2(\tau)\right], \quad \varepsilon(\tau) = 3/4\,\tau. \tag{A.11}$$

Introducing the notation

$$z = \frac{2}{3}\left(u - \frac{3}{2}\right)\tau, \quad f(z, \tau)\, dz = \varphi(u, \tau)\, du. \tag{A.12}$$

we obtain

$$\frac{\partial f}{\partial \ln \tau} - \frac{\partial}{\partial z} f g(z) = 0, \quad g(z) = \left(z - \frac{1}{2}\right)^2. \tag{A.13}$$

The solution of this equation is

$$f = f\left(\ln\left[\tau \exp \int \frac{dz}{g(z)}\right]\right). \tag{A.14}$$

We now note that

$$\tau + \int_0^u \frac{du}{g(u)} \rightarrow \tau \exp \int \frac{dz}{g(z)}, \quad \frac{1}{g(z)} \rightarrow \frac{2}{3}\,\frac{\tau^2}{g(z)} \exp \int \frac{dz}{g(z)},$$

$$1 \gg \left| u - \frac{3}{2} \right| \gg \varepsilon(\tau). \qquad \text{(A.15)}$$

In actuality

$$\tau + \int_0^u \frac{du}{g(u)} = \tau\left(1 - 1 \Big/ \frac{2}{3}\left(u - \frac{3}{2}\right)\tau\right) = \tau\left(1 - \frac{1}{z}\right)$$

$$= \tau \exp \int \frac{dz}{g(z)}; \; z \gg 1. \qquad \text{(A.16)}$$

Also, for such values of u we must obtain the previous distribution function in zero approximation:

$$f\,\frac{dz}{du} \rightarrow \frac{A}{{}^2/_3\,(u - {}^3/_2)^2} \exp\left\{ -\left(\tau - \frac{1}{{}^2/_3\,(u - {}^3/_2)}\right)\right\}, \; z \gg 1. \qquad \text{(A.17)}$$

Hence we obtain immediately

$$f = A\,\frac{\tau}{g(z)} \exp\left[\int \frac{dz}{g(z)} - \tau \exp \int \frac{dz}{g(z)}\right]. \qquad \text{(A.18)}$$

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PROJECTION OPERATORS IN THE THEORY OF ELEMENTARY PARTICLES

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Minimal polynomials in the matrices occurring in relativistic wave equations and the spin matrices are used to construct projection matrices, which are dyads describing arbitrary possible states of a free particle of arbitrary spin. The fundamental physical quantities (energy and momentum, charge and current, transition probabilities) are expressed directly in terms of these projection operators in an invariant way (independent of the choice of basis for the representation). Thus the calculation of various effects for particles of any spin is reduced to the computation of the traces of certain combinations of matrices. As examples of the application of the method we obtain the general conditions for definiteness of the energy and charge for particles with a single mass and give a simple derivation of the general commutation relations for particles of arbitrary spin.

IN various calculations relating to particles with spin one needs to find the free-field wave functions, which are solutions of the first order equations

$$(\gamma_k \nabla_k + \varkappa)\psi = 0,$$

where $x_4 = it$, $c = h = 1$, and the γ_k are square matrices. For plane waves $\psi \sim e^{ipx}$, corresponding to the four-momentum $p = (p_k)$, these equations take the form

$$(ip_k\gamma_k + \varkappa)\psi = 0. \qquad (1)$$

We use the notation $\hat{p} = ip_k\gamma_k$. As has been shown in reference 1, the minimal equation for the matrix p in the general case has the form

$$P(\hat{p}) = \hat{p}^n(\hat{p}^2 + \lambda_1^2 p^2)(\hat{p}^2 + \lambda_2^2 p^2) \ldots (\hat{p}^2 + \lambda_q^2 p^2) = 0, \qquad (2)$$

where λ_l ($l = 1, 2, \ldots q$) are distinct nonvanishing eigenvalues of the matrix γ_4. To each value $\pm\lambda_l$ there corresponds a set of states of the particle.

Since $p^2 = -m^2$ and $\lambda_l = \kappa/m_l$, where $m_l^2 = -p^{(l)2}$, we can write instead of Eq. (2)