

THE KINETICS OF PRECIPITATION FROM SUPERSATURATED SOLID SOLUTIONS*

I. M. LIFSHITZ and V. V. SLYOZOV

Physico-Technical Institute, Kharkov, U.S.S.R.

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Abstract—An analysis is made of the process whereby diffusion effects can cause the precipitation of grains of a second phase in a supersaturated solid solution. The kinetics of this type of grain growth are examined in detail. Some grains grow, only to be later dissolved; others increase in size and incorporate further grains that they encounter in so doing. This latter phenomenon of coalescence is discussed in a new "kinetic" approximation. Formulae are given for the asymptotic grain size distribution, for the number of grains per unit volume and for the supersaturation as a function of time. The effects of anisotropy, strain, crystalline order and the finite size of the specimen are allowed for. It is pointed out that for a material that can be said to be "supersaturated with vacancies", the discussion can be applied to the vacancies as solute "atoms" which cluster together to form internal cavities. The practical case of a real, finite crystal is here important, because the vacancies can in general also escape to the surface. A special analysis is made of this example, and the results are applied to the theory of sintering.

1. FORMULATION OF THE PROBLEM

In a supersaturated solid solution, diffusion effects may bring about the formation of grains of a new phase. Two stages of this process may be distinguished. In the first, concentration fluctuations produce nuclei of the new phase, which grow directly from the supersaturated medium. The second stage may be considered to begin when the grains thus formed have reached an appreciable size and the degree of supersaturation of the matrix has become very slight. In such circumstances the determining process is that of coalescence, i.e. the growth of large grains of the new phase by the incorporation of small ones. Fluctuation effects play a negligible part in the second stage, as new nuclei, to be of any importance, would need to be of macroscopic proportions.

The kinetics of this coalescence process are considered in what follows. Some years ago, TODES^(1,2) discussed a similar phenomenon and correctly arrived at various qualitative conclusions.† Unfortunately his quantitative argument is in error

and the results contain meaningless logarithmic divergencies. A satisfactory solution was first given in our paper of 1958,⁽⁴⁾ in which the mode of arrival of the system at the asymptotic distribution of grain sizes was analysed in detail. The results of this earlier study are rederived herein by a rather different method, using the more accurate "kinetic approximation" which allows the stability of the asymptotic solutions to be examined. We also consider the effect on coalescence of various factors such as anisotropy and internal strain.

In the first instance we shall simplify matters by ignoring anisotropy and considering the grains to be spherical. The actual shape of real grains may be taken into account by adjusting certain numerical constants in the relevant formulae.

Fundamental equations

If C_∞ is the concentration of the saturated solution, and $\alpha = (2\sigma/kT)vC_\infty$ is a parameter containing the inter-phase surface tension σ and the atomic volume v of the solute, the equilibrium concentration C_R at the boundary of a grain is related to the grain radius by the usual formula:

$$C_R = C_\infty + \frac{\alpha}{R}. \quad (1)$$

* Translated by R. D. LOWDE.

† A similar problem has also been considered by GREENWOOD⁽³⁾ but not to the same extent.

The degree of supersaturation is small, so that $C - C_\infty = \Delta \ll 1$, and for the present we may ignore the interaction between grains since their dimensions are small compared with the mean distance between them. Then the diffusion current of solute across the grain boundary is given, per unit area, by*

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

The radius R of the grain therefore varies with time as†

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

Thus for every value Δ of the supersaturation there exists a critical radius $R_c = \alpha/\Delta$ with which a grain is in equilibrium with the solution. If $R > R_c$ the grain grows, if $R < R_c$ it dissolves. This obvious mechanism also explains why large grains can "devour" small ones by incorporation. Both Δ and R_c themselves vary with time.

Writing Δ_0 for the initial supersaturation, $R_{c0} = \alpha/\Delta_0$ for the initial critical radius, and $T = R_{c0}^3/\alpha\mathcal{D}$, we now go over to dimensionless reduced magnitudes

$$\rho = \frac{R}{R_{c0}}, \quad t' = \frac{t}{T}.$$

Dropping the prime on t , we obtain

$$\frac{d\rho^3}{dt} = 3 \left(\frac{\rho}{x} - 1 \right), \quad (3)$$

in which $x(t)$ is a dimensionless critical radius such that $x(0) = 1$. We now introduce a function $f(\rho^3, t)$ which within a factor $\frac{4}{3}\pi$ is the volume distribution function of the grains, and the rate $V_R = d\rho^3/dt$ of growth of the grains in dimension

* The equation contains the stationary value $\partial C/\partial r$ of the concentration gradient at the grain boundary. It is easily shown that this procedure is valid if the initial supersaturation is small ($\Delta_0 \ll 1$).

† If the grains are aspherical, but in the later stages of the process grow in such a way as to preserve their shape due to an anisotropy in α , then equation (2) and all quantitative deductions from it remain correct so long as R is interpreted as $(3V/4\pi)^{1/3}$, with V the grain volume, and α , α and \mathcal{D} are modified to the extent of numerical factors depending on the shape in question.

space. The unknown functions $f(\rho^3, t)$ and $x(t)$ may be determined as follows: from the equation of continuity in dimension space,

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial \rho^3} (f v_\rho) = 0, \quad (4)$$

while from the conservation of matter

$$Q_0 = \Delta_0 + q_0 = \Delta + q.$$

Q_0 is the total initial supersaturation, making allowance through a term q_0 for the volume of material initially in the grains. We have

$$q = \frac{4}{3}\pi R_{c0}^3 \int_0^\infty f \rho^3 d\rho^3.$$

Bearing in mind that $x = \Delta_0/\Delta$, it follows that

$$\left. \begin{aligned} 1 &= \frac{\Delta_0}{Q_0} \frac{1}{x} + \kappa \int_0^\infty f \rho^3 d\rho^3, \\ \kappa &= \frac{4}{3}\pi R_{c0}^3 Q_0^{-1}. \end{aligned} \right\} \quad (5)$$

A normalization to unit volume has here been performed, so that

$$n = \int_0^\infty f d\rho^3$$

is the number of grains per unit volume. It follows that the distribution function $F(\rho, t)$ over the dimension ρ is related to $f(\rho^3, t)$ by

$$F(\rho, t) d\rho = f(\rho^3, t) d\rho^3,$$

i.e.

$$F(\rho, t) = 3\rho^2 f(\rho^3, t).$$

2. TIME VARIATION OF THE CRITICAL DIMENSIONS AND THE ASYMPTOTIC FORM OF THE DISTRIBUTION FUNCTION IN HYDRODYNAMIC APPROXIMATION

Along an axis in dimension space representing grain volume, the point ρ^3 (which apart from a factor $\frac{4}{3}\pi$ is the volume of some given grain) moves according to the following prescription. Points to the left of $x^3(t)$ accelerate to the left, until on reaching the origin they fall out of consideration, the grain having completely dissolved. Points initially to the right of $x^3(t)$ accelerate at first to the

right; but as the degree of supersaturation falls, $x^3(t)$ increases and successively overtakes points that in the first instance were to the right of it. After being overtaken, such points begin to move in the opposite direction and finally also disappear into the origin. The motion is throughout regular in the sense that the initial order of a set of points is preserved.

Canonical form of the equations

Both the form of equation (3) and the physical meaning of $x(t)$ suggest that it would be more natural to express equations (3)–(5) in terms of a reduced volume

$$z = \frac{\rho^3}{x^3(t)}, \quad x(0) = 1 \quad (6)$$

that compares ρ^3 with the critical volume x^3 . Moreover, as $t \rightarrow \infty$, $\Delta \rightarrow 0$, so that $x(t) \rightarrow \infty$; thus $x(t)$ may be used as a measure of time. It now appears that (3), (4) and (5) take on canonical form if time is introduced through the variable

$$\tau = \ln x^3(t) \quad (7)$$

and a new volume distribution function ϕ is employed such that

$$\phi(z, \tau) dz = f(\rho^3, t) d\rho^3. \quad (8)$$

Using (6), (7) and (8), equations (3), (4) and (5) become respectively

$$\frac{\partial \phi}{\partial \tau} + \frac{\partial}{\partial z} \phi v(z, \gamma) = 0, \quad (9)$$

$$\left. \begin{aligned} \frac{dz}{d\tau} &= v(z, \gamma) = (z^{1/3} - 1)\gamma(\tau) - z, \\ \gamma(\tau) &= 3 \frac{dt}{dx^3}; \end{aligned} \right\} \quad (10)$$

$$\left. \begin{aligned} 1 &= \frac{\Delta_0}{Q_0} e^{-\tau/3} + \kappa e^\tau \int_0^\infty \phi(z, \tau) z dz, \\ \phi|_{\tau=0} &= f_0(z), \quad z|_{\tau=0} = \rho^3. \end{aligned} \right\} \quad (11)$$

If the solution of (10) under the initial condition $z|_{\tau=0} = y$ be written $z(y, \tau)$, then (11) may be

expressed in terms of the initial distribution function $f_0(z)$ thus:

$$1 - \frac{\Delta_0}{Q_0} e^{-\tau/3} = \kappa e^\tau \int_{y_0(\tau)}^\infty f_0(y) z(y, \tau) dy. \quad (12)$$

Here $y_0(\tau)$ is the solution of $z[y_0(\tau), \tau] = 0$, i.e. the lower limit of the range of starting volumes appropriate to grains that are still undissolved at time τ .

The asymptotic solution

As it will be shown that $\phi(z, \tau)$ is asymptotically independent of $f_0(y)$, the unknown functions are now $\phi(z, \tau)$ and $\gamma(\tau)$.

The supersaturation $\Delta(t)$ decreases monotonically with time, and therefore $1/x(t)$ does the same. There are therefore only three possibilities for the asymptotic behaviour of $\gamma(\tau)$ as $\tau \rightarrow \infty$, viz. $\gamma(\tau) \rightarrow \infty$, 0 or constant. We shall show that the first two do not apply.

(i) $\gamma(\tau) \rightarrow \infty$ as $\tau \rightarrow \infty$. In this case, $x^3(t)$ varies more slowly than t . The ultimate number of grains per unit volume is associated with a rate $dz/d\tau > 0$, which implies

$$\int_0^\infty \phi(z, \tau) z dz > \text{const.} \quad (13)$$

The amount of matter in grain form at $\tau \rightarrow \infty$ will therefore be

$$q > \text{const.} e^\tau \xrightarrow{\tau \rightarrow \infty} \infty,$$

so that (11) is not satisfied.

(ii) $\gamma(\tau) \rightarrow 0$ as $\tau \rightarrow \infty$, i.e. $x^3(t)$ varies more quickly than t . At sufficiently large times the solution of (10) in this case is

$$\frac{dz}{d\tau} = (z^{1/3} - 1)\gamma - z \approx -\gamma(\tau) - z,$$

$$z = ye^{-\tau} - e^{-\tau} \int_0^\tau e^{\tau'} \gamma(\tau') d\tau'.$$

From the condition $z[y_0(\tau), \tau] = 0$,

$$y_0(\tau) = \int_0^\tau e^{\tau'} \gamma(\tau') d\tau' = 3t(\tau);$$

the amount of matter in grain form at $\tau \rightarrow \infty$ is

$$q = e^{\tau} \int_{\gamma_0(\tau)}^{\infty} f_0(y) z(y, \tau) dy \leq \int_{3t}^{\infty} f_0(y) y dy \xrightarrow[\tau \rightarrow \infty]{z(\tau) \rightarrow \infty} 0.$$

Thus equation (12) cannot be satisfied [nor indeed equation (11)].

It follows that $\gamma(\tau)$ must tend asymptotically to some constant value γ_0 , and this we now proceed to determine, together with the asymptotic form of $\phi(z, \tau)$. We first remark that at such times as $\gamma(t)$ may be put constant in equation (9), the general solution of (9) is

$$\phi(z, \tau) = \chi(\tau + \psi) \frac{1}{g(z, \gamma)},$$

with

$$g(z, \gamma) = -v(z, \gamma), \quad \psi = \int_0^z g^{-1}(z, \gamma) dz,$$

and χ an arbitrary function. Substituting this result into (11) it will be seen that if the first part is to be asymptotically time-independent, χ must have the form

$$\chi(\tau + \psi) = A e^{-(\tau + \psi)}.$$

Thus $\phi(z, \tau)$ must tend asymptotically to

$$\phi(z, \tau) = e^{-\tau} \Phi(z, \gamma).$$

So far we have examined only the asymptotic dependence of ϕ on τ . We now turn to the determination of γ , for which we write out the asymptotic forms of equations (9)-(11):

$$-\Phi + v(z, \gamma) \frac{d\Phi}{dz} + \Phi \frac{dv}{dz} = 0; \quad (15)$$

$$\frac{dz}{d\tau} = v(z, \tau) = (z^{1/3} - 1)\gamma - z, \text{ with } \gamma = \text{const}; \quad (16)$$

$$1 = \kappa \int_0^{\infty} \Phi z dz. \quad (17)$$

Examination of equation (15) shows that to satisfy (17), $\Phi(z, \gamma)$ can be different from zero only in the

ultimate phase of change of z ; for otherwise

$$\int_0^{\infty} \Phi z dz$$

would be logarithmically divergent, irrespective of the detailed nature of Φ . For such a solution to exist and to be continuous and finite over the whole range of changing z , it would appear sufficient that Φ and its first derivative go to zero at some point $z = z_0$ and beyond this point join onto a constant zero. Solutions of this type can formally be found, and correspond to values of $\gamma > \gamma_0$.

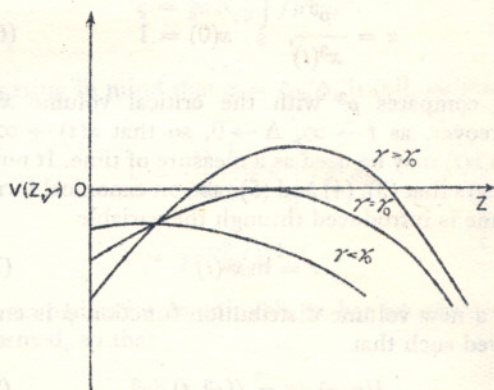


FIG. 1.

However, in Section 3 it will be shown that these solutions are unstable when the encounters between different grains are taken into account. It turns out that the only stable solution is that for which $\Phi(z, \gamma)$ and all its derivatives go to zero at z_0 , so that to the right of z_0 the solution is identically zero. Further inspection of equation (15) now shows that the stable solution corresponds to a value of $\gamma = \gamma_0$ such that the rate of change $v(z, \gamma_0)$ has a second order zero at $z = z_0$. Using, therefore, the conditions

$$v(z, \gamma_0) = 0,$$

$$\left. \frac{dv}{dz} \right|_{z=z_0} = 0,$$

we find

$$\gamma = \gamma_0 = \frac{27}{4}; \quad z_0 = \frac{27}{8} = \frac{\gamma_0}{2}.$$

The present results may be interpreted in the light of Fig. 1, which shows $v(z, \gamma)$ as a function of z for various values of γ . If $\gamma < \gamma_0$, the representative points of all grains move to the left and disappear into the origin. The grains in existence at any given time comprise asymptotically a volume distribution in the form of an infinitely long "tail" to the initial distribution function, falling off with z faster than z^{-2} ; therefore, the total amount of material in grain form tends to zero:

$$q \sim \int_{y_0(\tau)}^{\infty} \frac{1}{y^{(2+\alpha)}} y dy \xrightarrow[\tau \rightarrow \infty]{y_0(\tau) \rightarrow \infty} 0$$

instead of to a constant value. If on the other hand $\gamma > \gamma_0$, all grains to the right of a point z_1 move towards the point z_2 , with the result* that

$$\begin{aligned} q &\sim e^{\tau} \int_{z_1}^{\infty} f_0(y) z(y, \tau) dy \\ &\sim e^{\tau} \int_{z_1}^{\infty} f_0(y) z_2 dy \\ &\sim \text{const.} e^{\tau} \xrightarrow[\tau \rightarrow \infty]{} \infty, \\ [z(y, \tau) \xrightarrow[\tau \rightarrow \infty]{} z_2, \quad y > z_1] \end{aligned} \quad (18)$$

this again contradicting the conditions of the problem. Thus only the case $\gamma = \gamma_0$ remains valid.

$\Phi(z, \gamma_0)$ has the form

$$\Phi(z, \gamma_0) = \begin{cases} A e^{-\psi(z, \gamma_0)} \frac{1}{g(z, \gamma_0)}, & z \leq z_0 = \frac{27}{8} \\ 0, & z \geq z_0 = \frac{27}{8} \end{cases} \quad (19)$$

in which

$$g(z, \gamma_0) = -v(z, \gamma_0) \geq 0; \quad (20)$$

* Even if $\Phi(z, \gamma_0) = 0$ for $z \geq z_1$ at the outset, the encounters between grains treated in Section 3 produce grains in the region $z > z_1$, to which this conclusion then applies.

$$\begin{aligned} \psi &= \int_0^z \frac{dz}{g(z, \gamma_0)} = \frac{4}{3} \ln(z^{1/3} + 3) + \frac{5}{3} \ln\left(\frac{3}{2} - z^{1/3}\right) + \\ &\quad + (1 - \frac{2}{3} z^{1/3})^{-1} - \ln(3^3 2^{-5/2} e); \end{aligned} \quad (21)$$

$$A = \frac{\kappa^{-1}}{\int_0^{z_0} e^{-\psi} \frac{z dz}{g(z, \gamma_0)}} = \frac{3Q_0}{4\pi R_{c0}^3 (1.11)} \doteq 0.22 \frac{Q_0}{R_{c0}^3}.$$

Higher approximations

From a general point of view, we have found $\phi(z, \tau)$ and $\gamma(\tau)$ only in the zero approximation, this being the most interesting in practice. More accurate expressions for these quantities are derived in the appendices. Here we remark only that in the accurate equation $\gamma = \gamma_0$, all points lying to the right of the point of contact $z_0 = \frac{27}{8}$ and moving to the left are found to be unable to pass across z_0 ; they are, so to speak, "caught" there with the result that the quantity of matter

$$q \sim e^{\tau} \xrightarrow[\tau \rightarrow \infty]{} \infty$$

and equation (11) cannot be satisfied. The conclusion is that $\gamma(\tau)$ tends to γ_0 from below:

$$\gamma(\tau) = \gamma_0 [1 - \epsilon^2(\tau)], \quad \epsilon^2(\tau) \xrightarrow[\tau \rightarrow \infty]{} 0.$$

It follows that the "leakage" across z_0 of points approaching z_0 from the right takes place more and more slowly with the passage of time, the exact rate depending on ϵ^2 , which like $\gamma(\tau)$ itself must be determined from equation (11) and the equation of motion (10).

In the next approximation, $\phi(z, \tau)$ is not zero to the right of the "blocking" point z_0 , but is some function governed by the initial distribution function $f_0(z)$. However, as $\tau \rightarrow \infty$, it is increasingly dominated by its infinitely long tail and its total contribution in equation (11) tends to zero. We now see that in the region of the blocking point z_0 , every initial distribution function is transformed into a unique universal function, z_0 becoming a sink for points with $z > z_0$ and a source for points with $z < z_0$. (The latter set of points have their sink at the origin.)

The results summarised

The basic results of this section may now be written out explicitly. The complete volume distribution function has the form

$$\phi(z, \gamma_0) = \begin{cases} A e^{-\tau} \frac{e^{-\psi}}{g(z, \gamma_0)} = n(\tau) p(z, \gamma_0), & z \leq z_0 \\ 0, & z \geq z_0 \end{cases} \quad (22)$$

where

$$n(\tau) = \int_0^{\infty} \phi(z, \tau) dz = A e^{-\tau} \quad (23)$$

is the number of grains per unit volume, and

$$p(z, \gamma_0) = \begin{cases} \frac{e^{-\psi}}{g(z, \gamma_0)} = 3^{3/2-5/3} e \cdot (z^{1/3} + 3)^{-7/3} (\frac{3}{2} - z^{1/3})^{-11/3} \exp - (1 - \frac{2}{3} z^{1/3})^{-1}, & z \leq z_0 \\ 0; & z \geq z_0 \end{cases}$$

$$\left(\int_0^{\infty} p(z, \gamma_0) dz = \int_0^{z_0} p(z, \gamma_0) dz = 1 \right) \quad (24)$$

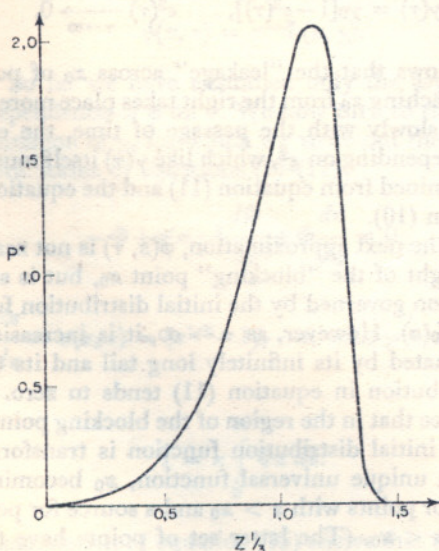


FIG. 2.

is the probability that a grain shall have a reduced volume between z and $z+dz$. Fig. 2 shows $p^*(z^{1/3}, \gamma_0) = p(z, \gamma_0) \cdot (dz/dz^{1/3})$, the probability that a grain has mean dimension between $z^{1/3} = (R/x)$ and $(R/x) + d(R/x)$, as a function of $z^{1/3}$.

Further, from the fact that

$$\frac{dz}{d\psi} = z - \gamma_0(z^{1/3} - 1)$$

we find

$$z^{1/3} - 1 = \int_0^{z_0} e^{-\psi} \frac{z^{1/3} - 1}{g(z, \gamma_0)} dz = [\gamma_0^{-1} e^{-\psi} z]_0^{z_0} = 0, \quad (25)$$

from which it follows that

$$\bar{\rho} = z^{1/3} x = x(t). \quad (26)$$

To obtain the distribution function relating to the absolute dimension ρ of the grains, we need only replace z in (22) by $[\rho^3/x^3(t)]$ and divide by

$$x^3(t) = \frac{4}{9} t. \quad (27)$$

Inserting the original parameters, and remembering that according to (26), $z = R^3/\bar{R}^3$, we obtain

$$\left. \begin{aligned} f(R^3, t) &= n(t) p(R/\bar{R}) \bar{R}^{-3}, \\ n(t) &= \beta Q_0 \bar{R}^{-3} = \mathcal{B} t^{-1}, \text{ with} \\ \beta &\doteq 0.22, \mathcal{B} \doteq (2\mathcal{D}\alpha)^{-1}, \\ \bar{R}^3 &= \frac{4}{9} \mathcal{D}\alpha t. \end{aligned} \right\} \quad (28)$$

If measurements are to be made on a section of the material it is convenient to transform the volume distribution function $\Phi(z, \tau)$ into a distribution function over the apparent dimension r of the grains as revealed on the surface of the section.

Writing $l = (r/x)$, this latter function is defined by

$$F(l, \tau) dl = \Phi(r, \tau) dr; \quad \Phi(r, \tau) = \frac{1}{x} F\left(\frac{r}{x}, \tau\right)$$

and is easily shown to be

$$F(l, \tau) = 2 \int_0^{27/8} \phi(z, \tau) \left[\left(\frac{z^{1/3}}{l} \right)^2 - 1 \right]^{-1/2} dz$$

(see Fig. 3).

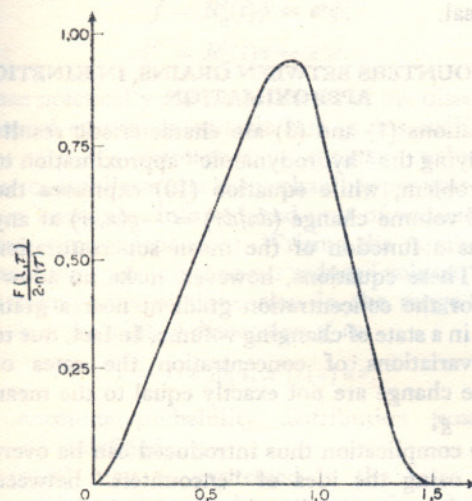


FIG. 3.

The degree of supersaturation at time t is given by

$$\Delta(t) = \frac{\Delta_0}{x(t)} = \left(\frac{2}{3} \right)^{2/3} \Delta_0 \cdot \left(\frac{T}{t} \right)^{1/3} = \lambda t^{-1/3}, \quad (29)$$

with

$$\lambda = \left(\frac{2}{3} \right)^{2/3} (\alpha^2 / \mathcal{D})^{1/3}.$$

Range of validity of the formulae

The above formulae completely determine the asymptotic distribution as a function of grain dimension and time. As shown in the appendix, they are valid when

$$1 \ll \tau^2 = (\ln x^3)^2 = 9[\ln(\bar{R}/R_{c0})]^2, \quad \bar{R} \gg R_{c0}.$$

In this inequality, $R_{c0} = \alpha/\Delta_0$ is the initial critical radius for coalescence, corresponding to the starting supersaturation Δ_0 . It will be realised that

if at the outset the mean grain dimensions are of the order of the critical size ($\bar{R}_0 \sim R_{c0}$), then this latter dimension must appear in the condition. However, if $\bar{R}_0 \gg R_{c0}$, then the first stage of development consists in a growth of grains directly from the solution, which goes on until the degree of supersaturation has so fallen that the critical radius has caught up with the mean grain size ($\bar{R}_1 \sim R_{c1}$); thereafter, strictly speaking, coalescence supervenes. In this case, R_{c1} plays the part of an initial dimension. The critical size is governed not only by the initial supersaturation, but also by

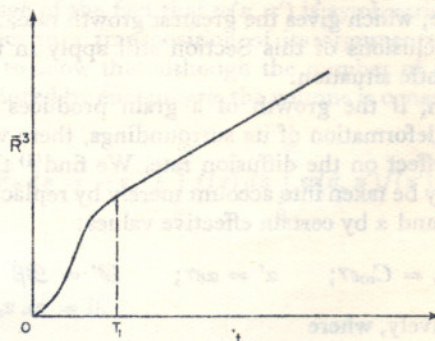


FIG. 4.

the number of grain nuclei (where this can be considered a fixed quantity). Thus if there are to begin with n_0 nuclei, and $\bar{R}_0 \gg R_{c0} = \alpha/\Delta_0$, growth from the solution takes place until

$$\frac{4}{3} \pi \bar{R}_1^3 \approx \frac{\Delta_0}{n_0}.$$

In this first stage,

$$\frac{d\bar{R}^2}{dt} = 2\mathcal{D}(\Delta_0 - \frac{4}{3}\pi n_0 \bar{R}^3) = 2\mathcal{D}\Delta_0 \left[1 - \left(\frac{\bar{R}}{R_{c1}} \right)^2 \right],$$

and this development occupies a time

$$t_1 \sim \bar{R}_1^2 / \mathcal{D}\Delta_0.$$

The initial processes of the second stage (coalescence) have a characteristic time

$$t_0 \sim \bar{R}_1^3 / \mathcal{D}\alpha \sim t_1(\bar{R}_1/R_{c0})$$

when, as in the situation discussed, $\bar{R}_1 \gg R_{c0}$, i.e. $t_0 \gg t_1$. Fig. 4 shows schematically the mean dimensions as a function of time for this case.

Influence of other effects

We have so far ignored a number of second-order effects such as that of grain shape, crystalline order, and the elastic strain that results from a difference between the specific volumes of the grains and the matrix. These matters are examined in detail in a companion paper in the *Journal of Solid State Physics*,⁽⁵⁾ in which we show that the qualitative conclusions of the present study are unaffected.

For instance, if the grains initially have a variety of shapes, we find that at sufficiently great times the only shape to survive is the most favourable one, which gives the greatest growth rate. All the conclusions of this Section still apply in the asymptotic situation.

Again, if the growth of a grain produces an elastic deformation of its surroundings, there will be an effect on the diffusion rate. We find⁽⁴⁾ that this may be taken into account merely by replacing C_∞ , \mathcal{D} and α by certain effective values:

$$C'_\infty = C_\infty e^\gamma; \quad \alpha' = \alpha e^\gamma; \quad \mathcal{D}' = \mathcal{D}\beta$$

respectively, where

$$\gamma = (kT)^{-1} \left(\mathcal{E}_{II} - \mathcal{E}_I - \left[\frac{\partial \mathcal{E}_I}{\partial C} \right]_{c=0} \right);$$

$$\beta^{-1} = \int_0^1 e^{px} dx;$$

$$p = \frac{(1+\sigma) \left[\frac{\partial \mathcal{E}_I}{\partial C} \right]_{c=0}}{3[(1+\sigma) + 2n(1-\sigma)]} \frac{V}{kT} \left(\frac{\Delta V}{V} \right)^2.$$

Here \mathcal{E}_I is the elastic energy per atom in the grain, \mathcal{E}_{II} the same quantity in the surroundings; E is Young's modulus, and $n = E_I/E_{II}$; σ is Poisson's ratio; V is the volume per atom in the grain, and ΔV the difference between the volumes per atom of the grain and the surrounding medium.

The possibility of order in the atomic arrangement we allow for in the case where the energy required to jump an atom from one sublattice to the other is rather large, so that there can be said to exist two essentially unrelated diffusion fluxes. The flux of particles to the grain is then treated exactly

as above, except that \mathcal{D} is further replaced by

$$\mathcal{D}_{\text{eff}} = \frac{2\mathcal{D}_1\mathcal{D}_2}{\mathcal{D}_1 + \mathcal{D}_2},$$

the suffixes 1 and 2 referring to the individual sublattices separately.

These second-order effects, therefore, call for no more than a re-expression of certain parameters in the theory. They do not alter the asymptotic grain size distribution function or influence its stability; our present solution, therefore, is universal.

3. ENCOUNTERS BETWEEN GRAINS, IN KINETIC APPROXIMATION

Equations (1) and (3) are characteristic results of applying the "hydrodynamic" approximation to our problem, while equation (10) expresses the rate of volume change $(dz/d\tau) = -g(z, \tau)$ at any time as a function of the mean supersaturation $\Delta(\tau)$. These equations, however, make no allowance for the concentration gradient near a grain that is in a state of changing volume. In fact, due to local variations of concentration the rates of volume change are not exactly equal to the mean value $-g$.

The complication thus introduced can be overcome, using the idea of "encounters" between grains. An encounter is a situation in which two or more grains find themselves separated by a distance that is less than their mean linear dimension, and either unite directly or at least undergo a diffusion interaction. The discussion may be said to introduce a "kinetic approximation".

In the treatment of Section 2, the stable asymptotic volume distribution was derived by an argument which revolved round the leaking of representative points z across a blocking point $z_0 = \frac{2}{3}$. Now encounters have the effect of carrying representative points across this barrier, and so the whole problem of their influence on the asymptotic distribution must be examined closely. This is true even if the over-all supersaturation is small and encounters are a rare phenomenon.

Treatment of encounters

In the ordinary physical space of the material we take the origin of coordinates in the middle of some chosen grain and use a reduced position

vector $\zeta = r/R_c(t)$. Although the centres of the other grains are fixed in the lattice, the fact that $R_c(t) \rightarrow \infty$ means that in reduced coordinates all grains draw closer together and move radially towards the selected one. Of course, the majority of the grains disappear before reaching the origin and do not have encounters.

We also employ a reduced distribution function f and a reduced grain density \mathcal{N} which refer to a unit of volume such that $\zeta^3 = 1$. They are related to the earlier quantities ϕ and n through:

$$f = R_c^3(t)\phi = e^{\tau}\phi,$$

$$\mathcal{N} = R_c^3(t)n = e^{\tau}n.$$

Since practically the whole excess of the dissolved material eventually collects into grains such that $n \sim e^{-\tau}$, \mathcal{N} approaches a constant value as $t \rightarrow \infty$. It follows that the probability per unit time of an encounter in a reduced unit of volume becomes time-independent. Writing the number of encounters, per unit time per reduced volume unit, between grains of dimension in the range z to $z+dz$ and grains of dimension z' as

$$\nu = f(z')p(z, z')f(z)dz,$$

an encounter-probability distribution function $p(z, z')$ is defined.

$p(z, z')$ may be expressed in the form $p = w(z, z')/\tau_e$, with τ_e a characteristic time for encounters, and $w(z, z')$ a reduced volume centred around a grain z , over which the interaction with one of the grains z' may be held to occur. It is not difficult to show that to order of magnitude, $w \approx z+z'$, i.e. is given by the over-all reduced volume of the two grains. τ_e must be of the order of unity, inasmuch as all the parameters are of the order of unity both in the initial condition $z|_{\tau=0} = z_0$ and in the equation

$$\frac{dz}{d\tau} \approx -\gamma - z$$

that describes the dissolution of the lesser grain.

When two grains meet, the greater of them absorbs the lesser, and their total volume is approximately conserved. A certain fraction of the material may in fact go back into solution, but it will be obvious that nothing is essentially changed if we ignore this detail. For if the effects of encounters are to be allowed for, the first approximate

equality in (18) must contain a term corresponding to the total "encounter integral"

$$\mathcal{J}_e = \tau_e^{-1} \left[\frac{1}{2} \int_0^z w(z-z', z') f(z-z') f(z') dz' - \int_0^\infty f(z) \int_0^\infty w(z, z') f(z') dz' \right]. \quad (30)$$

(The factor $\frac{1}{2}$ is necessary, because without it each encounter would be reckoned twice.) Taking advantage of the fact that $w(z, z')$ is symmetric with respect to a transposition of its arguments, it is easy to show that although the number of grains is reduced by encounters, the volume is conserved:

$$\int_0^\infty \mathcal{J}_e dz = -\tau_e^{-1} \frac{1}{2} \int_0^\infty f(z) dz \int_0^\infty w(z, z') f(z') dz';$$

$$\int_0^\infty \mathcal{J}_e z dz = 0.$$

The distribution function

Returning for the moment to equation (17), it will be observed that f is dependent on the small parameter $1/x$. To bring out more clearly its dependence on the small parameter Q_0 we introduce the function

$$\Phi = xf.$$

Using this variable, a complete set of equations controlling the system can now be written out with full allowance for encounters. The equations have the asymptotic form:

$$\frac{d}{dz} \Phi_g(z, \gamma) + \Phi = -\mathcal{J}_e$$

$$= -\frac{3Q_0}{4\pi} \tau_e^{-1} \left[\frac{1}{2} \int_0^z w(z-z', z') \Phi(z-z') \Phi(z') dz' - \int_0^\infty w(z, z') \Phi(z') dz' \right], \quad (31)$$

$$1 = \int_0^{\infty} \Phi x \, dx, \quad \gamma = \text{const.} \quad (32)$$

They may be solved by successive approximation, using the fact that \mathcal{J}_e is small.

At this point we may usefully notice that both from the analysis of Section 2 and directly from physical arguments one must expect that the new considerations reduce γ below γ_0 . For in the terms of the earlier discussion, grains that are carried

so that for $(3\gamma_0)^{-2} + \gamma_0 > \gamma > \gamma_0$ a solution of the type mentioned is possible; it is, however, unstable in respect of the first term in equation (31), since in the next higher approximation it is

$$\Phi(z, \gamma) = \frac{e^{-\psi}}{g(z, \gamma)} \left\{ c - \int \mathcal{J}_e[f(z', \gamma)] e^{\psi} dz' \right\}$$

and diverges at $z = z_2$. This also shows that (19) is the only stable solution of (15).

Taking, therefore, (19) as the zero-order solution, the encounter integral becomes

$$\mathcal{J}_e[\Phi] \approx \mathcal{J}_e[\Phi_0(z, \gamma_0)] = \frac{3Q_0}{4\pi} \tau_e^{-1} \mathcal{J}_0(z), \quad (33)$$

$$\mathcal{J}_0(z) = \begin{cases} \frac{1}{2} \int_0^z w(z-z', z') \Phi_0(z-z') \Phi_0(z') \, dz' - \Phi_0(z) \int_0^{\infty} w(z, z') \Phi_0(z') \, dz', & z \leq 2z_0 \\ 0, & z > 2z_0 \end{cases}$$

$$\Phi_0 \equiv \Phi_0(z, \gamma_0).$$

across the barrier-point z_0 by encounters have a non-zero probability of leaking back, and this implies $\gamma < \gamma_0$. We shall now show that the zero-order approximation is equivalent to taking the solution of (31) without the first part and with $\gamma = \gamma_0$, and that this is equation (19). Indeed, the solution of the homogeneous equation with $\gamma < \gamma_0$ does not satisfy (32), as

$$\int_0^{\infty} \Phi x \, dx$$

is then logarithmically divergent.

If $\gamma > \gamma_0$, a solution may be constructed that is continuous and has a continuous first derivative over the whole range of z , and which is different from zero only for $z < z_1$. $g(z, \gamma) = 0$ for $z = z_1$ and $z_2, z_2 > z_1$, otherwise

$$\int_0^{\infty} \Phi x \, dx$$

will diverge at z_2 . In the neighbourhood of $z = z_1$, $\Phi(z, \gamma)$ behaves like

$$(z - z_1)^{-(\partial g / \partial z)_{z=z_1} + 1} = (z - z_1)^{-(1/2)\gamma_0^{-1}(\gamma - \gamma_0)^{-1} + 1},$$

The method of successive approximation must consist in refining the value of

$$\frac{d}{dz} \Phi_1 g_1 + \Phi_1 = -\mathcal{J}_e[\Phi_0],$$

$$1 = \int_0^{\infty} \Phi_1 x \, dx.$$

In general this will lead to

$$\frac{d}{dz} \Phi_n g_n + \Phi_n = -\mathcal{J}_e[\Phi_{n-1}],$$

$$1 = \int_0^{\infty} \Phi_n x \, dx,$$

$$g_n = g(z, \gamma^n), \quad (34)$$

so that

$$\Phi_1 = \frac{e^{-\psi}}{g(z, \gamma_0)} \left\{ c + \int_z^{2z_0} \mathcal{J}_e[\Phi_0(z, \gamma_0)] e^{\psi} dz \right\};$$

the convergence of

$$\int_0^{\infty} \Phi x \, dx$$

requires $c = 0$. A refined value of γ is found from the condition

$$\int_0^{\infty} \Phi z \, dz = 1.$$

The desired solution of (34) is accordingly

$$\Phi(z, \gamma) = \begin{cases} e^{-\psi} g^{-1} \int_z^{2z_0} \mathcal{J}_0[\Phi_0(z', \gamma_0)] e^{\psi} dz', & z \leq 2z_0 \\ 0, & z > 2z_0 \end{cases} \quad (35)$$

$$\psi = \int_0^z g^{-1}(z, \gamma_0) dz.$$

(35) may be confirmed without difficulty if one remembers that $f(z, \gamma)$ and its first derivative go to zero at $z = 2z_0$, so that the first equation in (34) is satisfied over the whole range of z .

Explicitly, we have shown that in first approximation

$$\Phi = \begin{cases} \frac{3Q_0}{4\pi} \tau_e^{-1} e^{\Delta} A e^{-\psi} g^{-1}, & z < z_0 \\ A = \int_{z_0}^{2z_0} e^{\psi^*} \mathcal{J}_0(z') dz'; & z_0 < z < 2z_0 \\ \frac{3Q_0}{4\pi} \tau_e^{-1} e^{-\psi^*} g^{-1} \int_z^{2z_0} e^{\psi^*} \mathcal{J}_0(z') dz'; & z > 2z_0 \\ 0, & \end{cases} \quad (36)$$

These formulae take into account the fact that where $\Delta\gamma \ll 1$, ψ increases sharply in the neighbourhood of z_0 and thereafter varies smoothly, with $\psi^*(z, \gamma) = \psi(z, \gamma_0)$; in this condition $\Delta = \frac{3}{2}\pi(\frac{2}{3}\Delta\gamma/\gamma_0)^{-1/2}$. It follows that where $z > z_0$, $f(z) \sim Q_0$. There is, of course, a smooth transition between the two regions $z < z_0$ and $z > z_0$.

The next approximation to the distribution function may be obtained by substituting (36) back into the encounter integral; by iteration, the distribution function can be determined to any desired accuracy.

Dependence on the initial supersaturation

It is interesting to see that if in each interval $nz_0 < z < (n+1)z_0$ we retain only the terms in the lowest power of Q_0 , the solution may be written

$$f(z) = Q_0^{z/z_0} \cdot \phi(z). \quad (37)$$

$\phi(z)$ in (37) can be determined within each interval; for instance, in the range $0 \leq z \leq 2z_0$ we determined it above. Physically, this type of dependence on Q_0 may be traced to the fact that the number of grains of magnitude z is continually augmented by the agglomeration of smaller grains having total volume $z_a + z_b = z$.

The form of (37) makes it apparent that to an

order of accuracy Q_0 , the principal contribution in equation (34a) comes from the distribution function in the region $z < z_0$. Using this fact, we can determine the asymptotic dependence of $\Delta\gamma$ on Q_0 as follows:

$$1 = \frac{3Q_0}{4\pi} \tau_e^{-1} A e^{\Delta} \int_0^{z_0} e^{-\psi} \frac{z}{g(z, \gamma)} dz. \quad (38)$$

Now because $\gamma = \gamma_0 - \Delta\gamma$ differs little from γ_0 , (38) may be rewritten

$$1 = \frac{3Q_0}{4\pi} \tau_e^{-1} A e^{\Delta} \int_0^{z_0} e^{-\psi} \frac{z}{g(z, \gamma_0)} dz, \quad (39)$$

whence

$$\frac{\Delta\gamma}{\gamma_0} = 12\pi^2 \left[2 \ln \frac{4\pi}{3Q_0} - \ln p \right]^{-2} \approx \frac{3\pi^2}{(\ln Q_0)^2} \quad (40)$$

with

$$p = A \tau_e^{-1} \int_0^{z_0} e^{-\psi} \frac{z}{g(z, \gamma_0)} dz \approx 1.$$

4. THE EFFECT OF CRYSTAL BOUNDARIES, AND THE THEORY OF SINTERING

The supersaturated crystal studied in Sections 1-3 was by implication unrestricted in size, and therefore contained no gross diffusion currents on a macroscopic scale. If we now remove the condition of over-all spatial uniformity, the problem is altered. The most important practical example of this more complicated situation is provided by an interphase boundary between the solution and some other phase, which might be, for instance, a crystal of pure solute, or more generally perhaps a crystal of the same phase whose precipitation is being considered. At such a boundary, the supersaturation $\Delta|_{l=0} = 0$ and macroscopic diffusion currents exist.

Vacancies.

An important special case is that of a crystal supersaturated with vacancies, in which our discussion can be applied to the vacancies as solute "atoms" which cluster together to form cavities playing the part of our grains. If such a crystal has

free surface, two competing processes will take place. Far from the surface, cavities will grow and coalesce according to the scheme developed in the earlier sections; on the other hand, near the border the cavities will tend to dissolve and the vacancies to diffuse to the surface. (The surface can be regarded as a cavity of infinite radius.) This dislodgment of cavities is also connected with the phenomenon of sintering.

In the remainder of this section we often refer expressly to the particular example of vacancy diffusion, although it is to be understood that the results are equally applicable to the more general case of a supersaturated solution.

Allowance for the crystal surface

Consider the situation in a half-space. Equation (3) for the grain growth and the distribution function (4) will still apply, and so will their equivalents (9) and (10). However, the conservation law $Q_0 = \Delta + q$ that underlies equations (5) and (12) must be replaced by a diffusion equation. Each point of coordinate l is now a source or sink of intensity $\partial q / \partial t$, and q is now $q(l, t)$ because the cavities are on the whole dissolving. The complete set of equations is properly

$$\frac{\partial}{\partial t}(\Delta + q) = \mathcal{D} \frac{\partial^2 \Delta}{\partial l^2}, \quad \Delta|_{l=0} = 0, \quad (41)$$

$$q = \kappa x^3(\tau) \int_{y_0(\tau)}^{\infty} f_0(y) z(y, \tau) dy, \quad (42)$$

$$z[y_0(\tau), \tau] = 0, \quad x = \frac{\Delta_0}{\Delta(l, t)};$$

in which $z(y, t)$ satisfies (10) and itself determines the form of $\Delta(l, t)$.

It will be remembered from Section 2 that the analysis led to a unique law for the decay of supersaturation [equation (29)]:

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

This means in principle that if the asymptotic fall of the supersaturation were to be in some way retarded, however slightly, a process of limitless grain growth would set in and $q \rightarrow \infty$. Alternatively, an indefinitely small artificial increase in the rate of decay below the $t^{-1/3}$ law must fairly

quickly result in the total dissolution of all grains ($g \rightarrow 0$). The mechanism of sintering is obviously related to this fact, and at least asymptotically must admit of the following discussion.

Reduction of the problem

There are, asymptotically, three fairly sharply defined regions in a supersaturated half-space:

(a) the farthest from the boundary, in a range $l_2 < l < \infty$. Here the influence of the boundary is negligible, and as with an infinite medium the supersaturation is given by (29);

(b) a region $l_1 < l < l_2$ in which the cavities (grains) have a general tendency to dissolve; and

(c) the region $0 < l < l_1$ in which there are no cavities (grains) at all, but an over-all diffusion of vacancies to the side.

The limiting distances $l_1(t)$ and $l_2(t)$ are situated well inside the crystal, and the skin layer that is free from cavities thickens continually.

Strictly speaking, equations (41) and (42) should be applied only to the intermediate region $l_1 < l < l_2$. However, it will be shown below that $(l_2 - l_1)/l \ll 1$. For a first approximation we shall accordingly, consider an average depth $\zeta(t) = \frac{1}{2}(l_1 + l_2)$, and by imposing some suitable boundary condition at ζ shall evaluate its magnitude and the vacancy concentration in the surface layer $0 < l < \zeta(t)$. For this purpose the intermediate region may effectively be replaced by a source of strength $Q_0(d\zeta/dt)$ at ζ , beyond which all the excess vacancies may be said to be in the cavities. Then we may say:

$$\frac{\partial \Delta}{\partial t} = \mathcal{D} \frac{\partial^2 \Delta}{\partial l^2}; \quad (43)$$

$$\Delta|_{l=0} = 0, \quad \Delta|_{l=\zeta(t)} = \lambda t^{-1/3};$$

$$\mathcal{D} \frac{\partial \Delta}{\partial l} \Big|_{l=\zeta(t)} = Q_0 \frac{d\zeta}{dt}. \quad (44)$$

A solution of (38) is now required subject to the condition $\Delta|_{l=0} = 0$. On seeking it in the form

$$\Delta = \sum_{n=1}^{\infty} \alpha_n(t) l^n,$$

(39) gives

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

Before imposing the other two boundary conditions it is helpful to notice that $\alpha_1(t)$ is the flux of particles at the surface:

$$\alpha_1(t) = \mathcal{D} \frac{\partial \Delta}{\partial l} \Big|_{l=0}.$$

Asymptotically, therefore, it must be a decreasing function of time, which suggests using the asymptotic form $\alpha_1(t) = B/t^s$, ($s > 0$). Application of (42) now yields

$$\Delta = B \frac{l}{t^s} \sum_{n=0}^{\infty} (-1)^n \left(\frac{l^2}{\mathcal{D}t} \right)^n \frac{s(s+1) \dots (s+n)}{(2n+1)!}. \quad (45)$$

As will appear shortly, $\zeta^2(t)$ is $o(t)$, that is to say

$$\zeta^2(t)/t \xrightarrow{t \rightarrow \infty} 0.$$

It follows that at large t the principal term in (45) is that with $n = 0$;

$$\Delta = \frac{Bl}{t^s} = \alpha_1(t) \cdot l. \quad (46)$$

Substituting now (41) into (39) we find

$$\alpha_1 \zeta = \lambda t^{-1/3},$$

$$\alpha_1 = \frac{Q_0}{\mathcal{D}} \frac{d\zeta}{dt},$$

and therefore

$$\zeta = 3^{1/2} \left(\frac{3}{2} \right)^{2/3} \frac{\bar{R}}{Q_0^{1/2}} = m \frac{(\mathcal{D} \alpha t)^{1/3}}{Q_0^{1/2}};$$

$$\Delta = \lambda t^{-1/3} l / \zeta = \frac{1}{2} m Q_0^{1/2} \alpha_1^{1/3} l (\mathcal{D} t)^{-2/3};$$

$$m = 3^{1/2} \left(\frac{3}{2} \right)^{1/3} \div 2. \quad (47)$$

Orders of magnitude

It remains to determine the width of the intermediate region. By (43),

$$\frac{\delta \zeta}{\zeta} = \frac{\delta t}{3t} = \frac{T_d(t)}{3t},$$

where T_d is the time required to dissolve the largest grain to be found on the boundary at time t . Now $R_{\max} = \frac{2}{3}R_0$, and $R^3 \sim t^2$. A simple calculation shows that in the equation of motion (10), $\gamma = 3(dt/dx^3) \leq \frac{2}{3} < \gamma_0$. The largest grain has $x_0 = \frac{2}{3}t$, and we deduce that it dissolves in a time $T_d \div \frac{1}{3}t$. Thus

$$\frac{\delta\zeta}{\zeta} \approx \frac{1}{9}.$$

By the same token,

$$\frac{\delta\zeta}{\bar{R}} = \frac{1}{3Q_0^{1/2}} \gg 1 \quad (49)$$

and

$$\frac{\delta\zeta}{L} = \frac{1}{3Q_0^{1/6}} \gg 1, \quad (50)$$

with L the mean distance between grains. Consequently

$$\delta\zeta \gg L \gg \bar{R}.$$

Although, therefore, the intermediate region is much thinner than the surface layer its width is considerably greater than both the mean cavity size and the mean distance between cavities (grains). The assumptions we made for equations (43) and (44) are therefore justified *post facto*.

The characteristic times associated with equation (47) are the same as those for the asymptotic equations describing coalescence in an infinite medium.

A further restriction

If the discussion for a half-space is now taken over to a specimen of finite size, as of course in practice, it must be realized that there is another condition to satisfy. For example, consider a plate-shaped layer of thickness a . Three characteristic times may be defined: that for the escape of vacancies to the surface, $T_0 \sim a^2/D$; that for the growth of cavities from solution, $T_1 \sim \bar{R}_1^2/D\Delta_0$ (as shown in Section 2); and the characteristic time for coalescence, $T_c \sim \bar{R}^3/D\alpha$. For our picture to apply, T_0 must necessarily be much greater than T_c , so that $a^2 \gg \bar{R}_1^3/\alpha$; the inequality is written in this form because the mean cavity dimensions must be those appropriate to the situation after coalescence has set in, i.e. $\bar{R} \gg \bar{R}_1$. In the opposite

limiting case, when $T_0 \ll T_1$, the vacancies are lost to the surface before cavities can be formed with any appreciable probability. In the intermediate situation where $a^2 \sim \bar{R}_1^3/\alpha$, the exact course of events will be heavily influenced by the initial distribution function and is not amenable to a general discussion.

5. SUMMARY

1. An investigation is made of the way in which, in a supersaturated solid solution, grains of a new phase grow as the result of diffusion processes. The final stage of the process is examined in particular. A critical dimension α is determined such that large grains having dimension $\rho > \alpha$ grow at the expense of small ones with $\rho < \alpha$.

2. At large times t the critical dimension α tends asymptotically to depend on time as $t^{1/3}$. The degree of supersaturation correspondingly falls as $t^{-1/3}$ and the number of grains as t^{-1} .

3. A detailed picture of the law of grain growth is provided by the distribution function of grain dimensions. With the passage of time this distribution approaches a certain universal function [equations (22–24)] irrespective of the initial distribution. This function is remarkable in that the tail of the distribution towards infinity has disappeared, leaving a maximum grain size one-and-a-half times the critical dimension ($\rho_{\max} = \frac{3}{2}\alpha$).

4. The effects of anisotropy and of the non-spherical nature of the original grain nuclei, like the effect of internal strain set up during the decay of the supersaturated solution, can all be taken into account simply by the use of "effective" parameters in place of certain quantities in the expression for the critical size. The form of the distribution function is unaffected by these considerations.

5. The process herein demonstrated for the coalescence of grains can also be applied to the study of "crust sintering". Each microscopic cavity in a specimen before sintering may be regarded as a crystal composed of vacancies. The cavities near the surface tend to dissolve as a result of their vacancies moving outwards to the boundary of the specimen, while in the depth of the material a process of coalescence goes forward essentially as in an infinite medium. The thickness of the "crust" increases with time as $\zeta \sim t^{1/3}$ [equation (47)].

APPENDIX 1. AN ACCURATE EXPRESSION FOR THE ASYMPTOTIC BEHAVIOUR OF $\gamma(\tau)$

As shown in Section 2, $\gamma(\tau) < \gamma_0$, so that we may write it

$$\gamma(\tau) = \gamma_0[1 - \epsilon^2(\tau)].$$

$\epsilon(\tau)$ may be determined from the equation of motion (10):

$$\begin{aligned} \frac{dz}{d\tau} &= (z^{1/3} - 1)\gamma(\tau) - z \\ &= -(z^{1/3} - \frac{3}{2})^2(z^{1/3} + 3) - \frac{1}{2}\gamma_0\epsilon^2(\tau). \end{aligned}$$

The latter term on the right has been so written because it is important only near $z = z_0 = \frac{27}{8}$. Put now for convenience $z = u^3$. Near $z = z_0$ or $u = u_0 = \frac{3}{2}$ the equation becomes

$$\frac{du}{d\tau} = -\frac{2}{3}(u - \frac{3}{2})^2 - \frac{1}{2}\epsilon^2(\tau).$$

Changing variable to $y = (u - \frac{3}{2})/\epsilon(\tau)$ we may write this:

$$\frac{3}{2} \frac{dy}{d\tau} = -y^2 - \frac{3}{4} + \frac{3}{2}y \frac{d\left(\frac{1}{\epsilon}\right)}{d\tau}.$$

For the same reasons as those given in the text, the existence of a stable solution requires that in this approximation there should be a "blocking" point on the z axis and that the rate of change of z should have a second order zero at this point. This yields

$$\frac{d\left(\frac{1}{\epsilon}\right)}{d\tau} \rightarrow \frac{2}{\sqrt{(3)}}, \quad \epsilon^2(\tau) \rightarrow \frac{3}{4\tau^2}, \quad \tau \rightarrow \infty;$$

from which

$$\frac{3}{2} \frac{dy}{d \ln \tau} \rightarrow [y - \frac{1}{2}\sqrt{(3)}]^2.$$

Evidently $dy/d\tau$ does have a second order zero at the blocking point $y = y_0 = \frac{1}{2}\sqrt{3}$.

It is now apparent that at sufficiently great times,

$$\gamma(\tau) = \gamma_0(1 - \frac{3}{4}\tau^{-2}).$$

The expression for the blocking point has been refined to

$$z_0^{1/3} = \frac{3}{2} + \frac{1}{2}\sqrt{(3)}\epsilon(\tau) = \frac{3}{2} + \frac{3}{4}\tau^{-1}.$$

By continuing with this procedure, an asymptotically accurate expansion for $\gamma(\tau)$ can be derived:

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

D

and correspondingly

$$x^3 = \frac{4}{3}t \left[1 + \frac{3}{4(\ln t)^2} (1 + \dots) \right].$$

The expansions may be broken off at any point at which the succeeding term is sufficiently small; in particular, the basic approximations $\gamma(\tau) = \gamma_0$ and $x^3 = (4/3)t$ are justified if

$$\tau^2 = (\ln x^3)^2 = (\ln \frac{4}{3}t)^2 \gg 1.$$

The fractional correction to γ_0 decreases swiftly with time, so that the first approximation becomes more and more accurate. It is a rather curious fact that the behaviour of the solution near the blocking point nevertheless continues to depend on just this correction.

APPENDIX 2. THE DISTRIBUTION FUNCTION IN THE REGION $z > z_0$, AND IN THE NEIGHBOURHOOD OF z_0

(i) Introduce the variable

$$\psi = \int \frac{dz}{g(z)},$$

and notice that as $z \rightarrow \infty$, $g(z) \rightarrow z$ and $z \rightarrow e^\psi$, i.e. $zx^3 \rightarrow e^{\tau+\psi}$. The form of the distribution function to the right of z_0 must be related to the initial distribution $f_0(\rho^3)$ over ρ^3 :

$$\chi(\tau + \psi) \rightarrow f_0(\rho^3)g(\rho^3) \rightarrow f_0(zx^3)zx^2.$$

This being the case, we may determine the distribution function for $z > z_0$ from

$$\chi(\tau + \psi) \rightarrow f_0(e^{\tau+\psi})e^{\tau+\psi},$$

or,

$$\phi(z, \tau) = f_0(e^{\tau+\psi})e^{\tau+\psi}g^{-1}(z).$$

Because

$$\int_0^\infty f_0(z)z dz$$

exists, $f_0(z)$ falls off certainly faster than z^{-2} , and in fact normally is exponential in z . It follows that in the zero-order approximation, the volume probability density to the right of z_0 is zero. For

$$\begin{aligned} p(z, \tau) &= \frac{\phi(z, \tau)}{n(\tau)} = f_0(e^{\tau+\psi})e^{2(\tau+\psi)}e^{-\psi}g^{-1}(z) \\ &= f_0(p)p^2e^{-\psi}g^{-1}(z) \rightarrow 0 \\ (p &= e^{\tau+\psi} \xrightarrow{\tau \rightarrow \infty} \infty). \end{aligned}$$

Of course, the probability density is non-zero to the left of z_0 .

(ii) To derive a more accurate distribution function in the vicinity of $z = z_0 = \frac{1}{2}$.

Write again for convenience $z = u^3$. Near z_0 the equation of continuity may be expressed as

$$\begin{aligned}\frac{\partial \phi}{\partial \tau} + \frac{\partial}{\partial u} \phi g(u) &= 0; \\ g(u) &= -\frac{2}{3}(u - \frac{1}{2})^2 - \frac{1}{2}\epsilon^2(\tau), \\ \epsilon^2(\tau) &= \frac{2}{3}\tau^{-2}.\end{aligned}$$

Changing the variable to

$$y = \frac{2}{3}(u - \frac{1}{2})\tau,$$

yields

$$\phi(u, \tau) du = f(y, \ln \tau) dy$$

$$\frac{\partial f}{\partial \ln \tau} - \frac{\partial}{\partial y} f g(y) = 0,$$

$$g(y) = (y - \frac{1}{2})^2.$$

The solution must be of the form

$$f \equiv f[\ln(\tau e^{\int g^{-1}(y) dy})].$$

We now observe that

$$\tau + \int_0^u g^{-1}(u) du \rightarrow \tau e^{\int g^{-1}(y) dy}$$

and

$$g^{-1}(u) \rightarrow \frac{2}{3}g^{-1}(y)\tau^2 e^{\int g^{-1}(y) dy},$$

given that $1 \gg |u - \frac{1}{2}| \gg \epsilon^2(\tau)$. In fact

$$\begin{aligned}\tau + \int_0^u g^{-1}(u) du &= \tau \{1 - [\frac{2}{3}(u - \frac{1}{2})\tau]^{-1}\} \\ &= \tau(1 - y^{-1}) = \tau e^{\int g^{-1}(y) dy}.\end{aligned}$$

Moreover at the same point $u = z^{1/3}$ the original distribution function must be given in zero order approximation by

$$f \frac{dy}{du} \rightarrow \frac{A}{\frac{2}{3}(u - \frac{1}{2})^2} \exp \{-\tau - [\frac{2}{3}(u - \frac{1}{2})\tau]^{-1}\},$$

from which we at once obtain

$$f = A g^{-1}(y) \tau e^{\int g^{-1}(y) dy} e^{-\tau} \exp \int g^{-1}(y) dy.$$

(iii) To show that as $\tau \rightarrow \infty$, the integral contribution from the neighbourhood of z_0 becomes negligibly small.

The quantity of material accounted for in this region is

$$q_\delta = x^3 \int_{z_0 - \delta}^{z_0 + \delta} \phi x dx = x_0 e^\tau n_\delta(\tau);$$

$$n_\delta(\tau) = \int_{z_0 - \delta}^{z_0 + \delta} \phi dz, \quad 1 \gg \delta \gg \epsilon(\tau).$$

Now from the equation of continuity,

$$\begin{aligned}\frac{dn_\delta}{d\tau} &= \phi(z, \tau) g(z) \Big|_{z_0 - \delta}^{z_0 + \delta} \\ &= A e^{-\tau} e^{-\psi(z_0 - \delta)} = A e^{-\tau} e^{-3/2 \delta^{-1/2}},\end{aligned}$$

because to the right of z_0 the distribution is in the form of an infinitely long drawn out tail, which may be ignored. Thus

$$n_\delta = A e^{-\tau} e^{-(3/2) \delta^{-1/2}} + B,$$

$$q_\delta = A e^{-(3/2) \delta^{-1/2}} + B e^\tau.$$

Evidently B must be zero, since matter must be conserved. Consequently the amount of material represented in the vicinity of z_0 as $\tau \rightarrow \infty$ is

$$q_\delta = A e^{-(3/2) \delta^{-1/2}} \xrightarrow{\delta \rightarrow 0} 0.$$

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