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INTERFACE AREA, EDGE LENGTH, AND NUMBER OF VERTICES IN CRYSTAL AGGREGATES WITH RANDOM NUCLEATION

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Summary

The interface area, edge length, and numbers of faces, edges and vertices in an aggregate consisting of a large number of crystals are calculated for two models. In the first ("cell model") the crystals start to grow simultaneously and isotropically from nuclei distributed at random. In the second ("Johnson-Mehl") model the nuclei appear at different moments, the rate of nucleation being constant. Corresponding calculations are made for plane sections of the aggregates and for two-dimensional aggregates. For the one-dimensional case the size-distribution curves are calculated. From a discussion of the results it is concluded that in the two- and three-dimensional cell models the crystals are less equiaxial than in the Johnson-Mehl models.

Résumé

Pour deux modèles d'un agrégat comprenant un grand nombre de cristaux on donne un calcul de l'aire total des limites de grains, de la longueur totale des arêtes et des nombres de facettes, d'arêtes et de sommets. Dans le premier("modèle à cellules"), les cristaux se développent simultanément et d'une manière isotrope à partir de germes disposés au hasard. Dans le second (modèle de "Johnson-Mehl"), les germes apparaissent à des instants différents, la vitesse de germination étant constante. Des calculs correspondants sont effectués pour des sections planes des agrégats et pour des agrégats à deux dimensions. Pour un agrégat à une dimension on déduit des courbes de répartition des longueurs. La discussion des résultats aboutit à la conclusion que dans les modèles de cellules à deux et à trois dimensions, les cristaux sont moins équiaxes que dans les modèles de Johnson-Mehl.

Zusammenfassung

Der Artikel gibt eine Berechnung der gesamten Kristallgrenzoberfläche, der Kantenlänge und der Anzahl Flächen, Kanten und Eckpunkte in einem aus einer großen Zahl von Kristallen bestehenden Aggregat für zwei Modelle. Im ersten ("Zellenmodell") erfolgt das Wachstum der Kristalle gleichzeitig und isotrop von statistisch verteilten Keimen aus. Im zweiten ("Johnson-Mehl") Modell entstehen die Keime in verschiedenen Augenblicken, wobei die Geschwindigkeit der Keimbildung konstant ist. Es werden entsprechende Berechnungen angestellt für ebene Schnitte der Aggregate und für zweidimensionale Aggregate. Für den eindimensionalen Fall werden die Größenverteilungskurven berechnet. Eine Erörterung der Ergebnisse führt zu dem Schluß, daß in den zwei- und dreidimensionalen Zellenmodellen die Kristalle weniger gleichachsig sind als in den „Johnson-Mehl"-Modellen.

1. The cell model

Because of the growing interest in the quantitative treatment of crystal boundaries, edges, etc. (cf. [1]) and [2])) it appears worth while to make some calculations on an aggregate with random nucleation.

We first consider the simplest model, which we shall call the *cell model*: each volume element belongs to that crystal whose nucleus is nearest. This amounts to all crystals starting to grow at the same time and with the same velocity in all directions. The spatial distribution of the nuclei is random; the probability that a small volume element δV contains a nucleus is called $n\ \delta V$. Thus the probability that there is no nucleus in a certain volume V is

$$\lim_{\delta V \to 0} (1 - n\delta V)^{V/\delta V} = e^{-nV}. \tag{1}$$

The mean crystal volume n^{-1} will alternatively be called b^3. Disturbing effects by the boundaries of the aggregate are eliminated by assuming its dimensions to be very large compared with b.

We begin by calculating the mean *surface area* of one crystal. The complications caused by the mutual impingement of the adjacent crystals are circumvented by solving the problem in two steps. First we consider the bisecting planes between the nucleus of our selected crystal and *all* other nuclei, irrespective of whether these "mathematical" interfaces are partly real physical boundaries or are cancelled by other crystals. By this mathematical non-interference the statistical problem is kept free from correlation difficulties.

The number of bisecting planes passing the nucleus at a distance between x and $x + \mathrm{d}x$ is equal to the number of nuclei inside a spherical shell of radius $2x$ and thickness $2\ \mathrm{d}x$. Thus in the average

$$32\ \pi n x^2 \mathrm{d}x \tag{2}$$

planes pass at a distance between x and $x + \mathrm{d}x$. What is the area of these planes that is contained in a spherical shell of radius r (again with centre in the selected nucleus) and thickness $\mathrm{d}r$? For one plane, passing at a distance $x < r$, this is $(\mathrm{d}/\mathrm{d}r)\{\pi(r^2 - x^2)\}\ \mathrm{d}r = 2\pi r \mathrm{d}r$. The total is $64\ \pi^2 n r \mathrm{d}r \int_0^r x^2\ \mathrm{d}x$. The "mathematical" surface area of the "central" crystal lying between r and $r + \mathrm{d}r$ from the nucleus is thus in the average

$$\tfrac{64}{3}\ \pi^2 n r^4 \mathrm{d}r. \tag{3}$$

We can now take the second step in our calculation, because the probability that an element of mathematical surface area at a distance r from the nucleus will be part of a real physical boundary of the "central"

crystal is determined solely by r. We draw a sphere of radius r around the surface element; it passes through two nuclei. The condition that the element is real, is equivalent to the condition that this sphere contains no (other) nuclei. As the volume in question is $\frac{4}{3}\pi r^3$, the probability that the condition is fulfilled is given (cf. eq. (1)) by

$$e^{-4/3\pi nr^3}. \tag{4}$$

It is independent of the incidental value of the "mathematical" area, between r and $r + \mathrm{d}r$, of the interface between the two crystals in question; multiplication of the average value thus yields the statistical *real* surface area of a crystal, between r and $r + \mathrm{d}r$: $\frac{64}{3}\pi^2 nr^4 e^{-4/3\pi nr^3}\mathrm{d}r$. By integrating from 0 to ∞ one obtains *)

$$\left(\frac{256\pi}{3}\right)^{1/3}\Gamma(\tfrac{5}{3})n^{-2/3} = 5{\cdot}821n^{-2/3}$$

for the mean surface area of a crystal. The total interface area **) (each interface being counted only once) per unit volume is obtained by multiplying by $\frac{1}{2}n$, yielding $2{\cdot}91n^{1/3}$.

We now calculate the *length* of the *edges*, where three crystals meet. We first find the number of "mathematical" edges passing at a distance $<z$ from one nucleus. Consider two other arbitrary nuclei, at distances $2x$ and $2y$ from the first nucleus. Draw a sphere of radius z around it. When x and y are both $<z$ the two bisecting planes *may* intersect inside the sphere.

Fig. 1 lies in the plane going through the three nuclei. N is the "central" nucleus, M the second one; the direction of NM in space can of course be taken as a fixed reference line. $MA = NA = x$; the bisecting plane passes vertically through BAC. The third nucleus lies somewhere on a circle of radius $2y$ around N and thus the second bisecting plane must pass vertically through a tangent to the circle of radius y which is drawn in the figure. The intersection of this tangent with BAC is the point where the edge passes vertically through the plane of the paper. When the third nucleus lies in about the same direction (from N) as M, the tangent runs nearly parallel to BAC and their point of intersection lies outside the circle of radius z. In the figure the limiting case is depicted, where the tangent DC ***) and BAC just intersect *on* the circle. The angle between the two directions thus has to be greater than $\angle MND$

*) $\Gamma(w) = \int_0^\infty x^{w-1}e^{-x}\mathrm{d}x$.

**) In view of the large number of crystals in the aggregate, it would appear unnecessary to consider an ensemble of aggregates.

***) and FB respectively; the figure is symmetrical with respect to MN.

to yield an edge passing at a distance $<z$ from N. But when it becomes greater than $\angle MNE$, the point of intersection again comes out of the circle. We call $x/z = \cos\varphi$ and $y/z = \cos\psi$. So $\angle MND = \varphi - \psi$ and $\angle MNE = \varphi + \psi$.

The possible directions from N to the third nucleus are completely random in space, and correspond to the radii of the sphere formed when the circle of radius y is rotated about MN as axis. Then the probability that the edge passes at a distance $<z$ from the "central" nucleus is equal to the fraction of this sphere surface lying between the circles described by D and E. This fraction is $\frac{1}{2}\{\cos(\varphi - \psi) - \cos(\varphi + \psi)\} = \sin\varphi \sin\psi$.

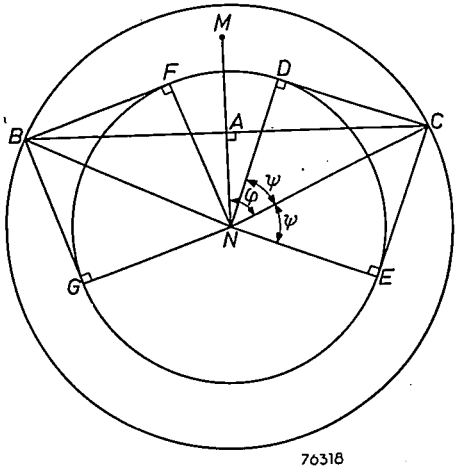

Fig. 1. Figure used for deriving the probability that two randomly oriented planes at distances x and y from the point N intersect each other at a distance $<z$ from N. The plane of the paper is at right angles to both planes. $NA = x$, $ND = y$, $NC = z$. CD, CE, BF and BG give the limiting cases, where the two planes intersect each other just at a distance z from N.

In fig. 1 we have taken $\varphi > \psi (x < y)$; a rather similar figure is obtained for the case $x > y$, the resulting probability being again $\sin\varphi \sin\psi$. Obviously the randomness of the system is not affected by choosing the shorter of the two lines connecting N with the other nuclei as fixed reference axis.

There are on the average $32\pi n z^2 \cos^2\varphi \, dz\cos\varphi$ bisecting planes (cf. expression (2)) passing N at a distance between x and $x + dx$, and $32\pi n z^2 \cos^2\psi \, dz\cos\psi$ that pass at a distance between y and $y + dy$. Multiplying these expressions together and by $\sin\varphi \sin\psi$ yields $1024\pi^2 n^2 z^6 \cos^2\varphi \sin^2\varphi \cos^2\psi \sin^2\psi d\varphi d\psi$ edges. The total number of ("mathematical") edges passing the nucleus at a distance $<z$ is obtained by integrating over both φ and ψ from 0 to $\frac{1}{2}\pi$ and dividing by 2 to avoid each edge being counted twice.

As $\int_0^{1/2\pi} \cos^2\varphi \sin^2\varphi d\varphi = \pi/16$, this becomes $2\pi^4 n^2 z^6$. Differentiation with respect to z yields

$$12\pi^4 n^2 z^5 dz \tag{5}$$

for the *number* of "mathematical" edges of a crystal passing its nucleus at a distance between z and $z + dz$.

We now want the "mathematical" edge length of a crystal contained in a spherical shell of radius r around the nucleus and thickness dr. One edge passing at a distance $z<r$ runs for a distance $2\sqrt{r^2 - z^2}$ inside the sphere, and thus $2rdr/\sqrt{r^2 - z^2}$ of it lies inside the shell. Multiplication by expression (5) and integration with respect to z, from 0 to r, yields the average "mathematical" edge length lying between r and $r + dr$ from the nucleus:

$$24\,\pi^4 n^2 r dr \int_0^r \frac{z^5}{\sqrt{r^2 - z^2}}\, dz = \tfrac{64}{5}\pi^4 n^2 r^6 dr. \tag{6}$$

The probability that one such edge element is physically real is again given by the factor (4). Integrating

$\frac{64}{5}\pi^4 n^2 r^6 e^{-4/3\pi n r^3} dr$ from 0 to ∞ yields $(4\pi)^{5/3} 3^{1/3} 5^{-1} \Gamma(\frac{4}{3}) n^{-1/3} = 17{\cdot}50 n^{-1/3}$

for the mean real edge length of one crystal. The total edge length per unit volume (each edge being counted only once) $= 5{\cdot}83\ n^{2/3}$.

To calculate the *number* of *vertices*, where four crystals meet, we first find the number of "mathematical" vertices of one crystal, lying at a distance $<r$ from its nucleus. This is done by calculating the number of intersections of the mathematical edges with the mathematical boundary planes (whose densities we know already). In each edge the "central" crystal meets two others; each plane stands for an interface between the "central" crystal and a fourth. Clearly the result will have to be divided by 3, to avoid each vertex being counted three times.

We begin by finding the probability that a plane and an edge, at distances x and z respectively from the nucleus, intersect each other inside a sphere of radius r around the nucleus. This can only happen when x and z are smaller than r; then we call $x = r\cos\gamma$ and $z = r\cos\beta$.

Fig. 2 shows the sphere. One of its diametric planes is the plane of the paper, which has been chosen in the following way. It is the plane common to the perpendicular (of length x) from the "central" nucleus N to the bisecting plane, and to the perpendicular NC to the edge. (These perpendiculars intersect the sphere in A and P respectively.) This edge can then have any direction through C at right angles to NC. The plane of the possible edges and the bisecting plane make a certain angle α with each

other. They meet the sphere in circles, and when these circles intersect, as in the figure, the edge and the plane may intersect each other inside the sphere, namely when the edge is inside the sector 2λ (which is bisected by the plane of the paper). The probability that this is the case, for a given α, equals

$$\left.\begin{array}{rl} & 2\lambda/\pi \text{ for } 2\lambda < \pi, \\ & 1 \quad \text{for } 2\lambda = \pi, \\ \text{and} \quad & (2\pi - 2\lambda)/\pi \text{ for } 2\lambda > \pi. \end{array}\right\} \tag{7}$$

The relation between λ, α, β and γ is found from the spherical triangle PAB, and is

$$\cos\gamma = \cos\lambda \sin\beta \sin\alpha + \cos\beta \cos\alpha. \tag{8}$$

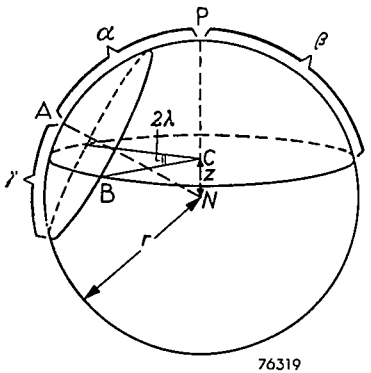

Fig. 2. Figure used for deriving the probability that a plane and an edge which have distances x and z, respectively, from the point N and are randomly oriented with respect to each other, intersect at a distance $<r$ from N. The sphere of radius r around N intersects the plane in a circle with pole distance γ. The edge passes through C and must lie in a plane at a distance z from N; when it is inside the sector 2λ the point of intersection lies inside the sphere.

We now calculate the number of intersections of our edge with *all* boundary planes, thus varying α (between 0 and π) and γ (between 0 and $\frac{1}{2}\pi$). As all directions in space have equal probability, the chance that the angle between the two circles in fig. 2 lies between α and $\alpha + \mathrm{d}\alpha$ is given by $\frac{1}{2}\sin\alpha\, \mathrm{d}\alpha$. According to expression (2), in the average $32\pi n x^2 \mathrm{d}x$ boundary planes have a distance between x and $x + \mathrm{d}x$ from N. Substituting $x = r\cos\gamma$, the number of planes with parameters between γ and $\gamma + \mathrm{d}\gamma$ and between α and $\alpha + \mathrm{d}\alpha$ becomes

$$16\pi n r^3 \cos^2\gamma \sin\alpha\, \mathrm{d}(-\cos\gamma)\mathrm{d}\alpha. \tag{9}$$

This expression must be multiplied by the probability given by (7)

and integrated over γ and α. Calling for convenience $\cos\lambda = u$, (7) is transformed into

$$\left.\begin{array}{l} \dfrac{2 \arccos u}{\pi} \text{ for } u>0, \\ \dfrac{2\pi - 2 \arccos u}{\pi} \text{ for } u<0. \end{array}\right\} \tag{10}$$

We substitute $u \sin\beta\sin\alpha + \cos\beta\cos\alpha$ for $\cos\gamma$ (cf. (8)) in (9), multiply by (10) and integrate over u (from 1 to 0 and then further to -1) and over α. The integration with respect to u yields:

$$32\, nr^3 \sin\alpha d\alpha \left\{ \int_0^1 (u\sin\beta\sin\alpha + \cos\beta\cos\alpha)^2 \sin\beta\sin\alpha \arccos u \, du + \right.$$
$$\left. + \int_{-1}^0 (u \sin\beta\sin\alpha + \cos\beta\cos\alpha)^2 \sin\beta\sin\alpha \, (\pi - \arccos u) \, du \right\}.$$

As $\pi - \arccos u = \arccos(-u)$, the sum of the two integrals can be written as

$$\sin\beta\sin\alpha \int_0^1 \left\{(u \sin\beta\sin\alpha + \cos\beta\cos\alpha)^2 + (-u \sin\beta\sin\alpha + \cos\beta\cos\alpha)^2\right\} \arccos u \, du$$
$$= 2 \sin\beta \sin\alpha \int_0^1 (u^2\sin^2\beta\sin^2\alpha + \cos^2\beta\cos^2\alpha) \arccos u \, du =$$
$$= 2 \sin\beta\sin\alpha \, (\tfrac{2}{3} \sin^2\beta\sin^2\alpha + \cos^2\beta\cos^2\alpha$$

This expression is multiplied by $32nr^3\sin\alpha d\alpha$ and integrated over α, between 0 and $\frac{1}{2}\pi$*). One obtains

$$64\, nr^3 \sin\beta \int_0^{1/2\pi} (\tfrac{2}{3} \sin^2\beta\sin^4\alpha + \cos^2\beta\cos^2\alpha\sin^2\alpha) \, d\alpha = 4\pi nr^3 \, (\sin\beta - \tfrac{1}{3} \sin^3\beta) \qquad (1$$

for the number of intersections — at a distance $<r$ from N — given by one edge passing at a distance $r \cos\beta$ from N.

The number of edges with distance between z and $z + dz$ (cf. expression (5)) is $12\pi^4n^2z^5dz = 12\pi^4n^2r^6\cos^5\beta d(\cos\beta)$. Multiplying this by expression (11), one obtains $48\pi^5n^3r^9 \, (-\sin^2\beta + \frac{1}{3} \sin^4\beta)\cos^5\beta d\beta$, which on integrating over β from $\frac{1}{2}\pi$ to 0 yields $\frac{1024}{315} \, \pi^5n^3r^9$ intersections. As said earlier, we must divide by 3 to get the "mathematical" vertices of a crystal at a distance $<r$ from its nucleus. Differentiating with respect to r one obtains

$$\tfrac{1024}{105} \, \pi^5n^3r^8dr \tag{12}$$

*) In our integration over u we have admitted values of $\gamma > \frac{1}{2}\pi$. Varying γ between 0 and π, and α between 0 and $\frac{1}{2}\pi$ is equivalent to the opposite procedure, which for the derivation of (9) is somewhat more convenient.

for the number of these vertices that lie between r and $r + \mathrm{d}r$ from the nucleus. The probability that such a vertex is real is again given by the factor (4). Integrating the product with respect to r, from 0 to ∞, one obtains

$$\tfrac{1024}{105}\,\pi^5 n^3 \int_0^\infty r^8 e^{-4/3\pi n r^3}\mathrm{d}r = \tfrac{96}{35}\,\pi^2 = 27{\cdot}07$$

for the average number of vertices of one crystal.

The average *number of edges* of one crystal is $\frac{3}{2}$ times this number $= \frac{144}{35}\pi^2$. From Euler's theorem we get the average *number of faces* (boundary planes) of one crystal:

$$\tfrac{48}{35}\,\pi^2 + 2 = 15{\cdot}54.$$

This is the mean number of neighbours of a crystal. The total numbers of vertices, edges and boundary planes per unit volume are found by multiplying the requisite numbers by $\frac{1}{4}n$, $\frac{1}{3}n$ and $\frac{1}{2}n$ respectively. The average length of an edge and the average area of a crystal face are now also known.

For use in the next section we write the "mathematical" interface area, edge length and vertex number between r and $r + \mathrm{d}r$ from all nuclei, per unit volume, in a special way. When each element is counted only once, we can write *)

(for interfaces): $$\frac{(4\pi n r^2 \mathrm{d}r)^2/2}{\frac{3}{4}\,\mathrm{d}r}, \tag{13a}$$

(for edges): $$\frac{(4\pi n r^2 \mathrm{d}r)^3/6}{(5/2\pi)\ (\mathrm{d}r)^2}, \tag{13b}$$

(for vertices): $$\frac{(4\pi n r^2 \mathrm{d}r)^4/24}{(35/8\pi)\ (\mathrm{d}r)^3}. \tag{13c}$$

In the numerators of these expressions, $4\pi n r^2 \mathrm{d}r$ is the total "mathematical" crystal volume (per unit volume) between r and $r + \mathrm{d}r$: it stands for the probability that an arbitrary point lies between r and $r + \mathrm{d}r$ from some nucleus. Its second, third and fourth powers divided by the permutational factors 2!, 3! and 4! stand for the probability that this is the case for 2, 3 or 4 nuclei at the same time. For example, to each vertex there corresponds a small volume element containing all points whose distances to the four nuclei involved lie between r and $r + \mathrm{d}r$, without having to be precisely equal. It is the volume common to four thin spherical shells. In the limit, for $\mathrm{d}r$ nearing zero, the volume element is bounded

*) Cf expressions (3), (6) and (12) multiplied by $\frac{1}{2}n$, $\frac{1}{3}n$ and $\frac{1}{4}n$ respectively.

by 4 pairs of parallel planes; each pair, with mutual distance dr, is at right angles to the direction from the vertex to one of the four nuclei. Clearly the volume of such an element is $p(\mathrm{d}r)^3$, where p is a dimensionless factor depending only on the angles between the four directions. As all four directions are mutually independent and completely random, integration over all directions should yield the average value of p, which is also obtained by dividing the total volume of the elements, $(4\pi nr^2\mathrm{d}r)^4/24$, by the number of vertices (both per unit volume of the aggregate). Obviously $\bar{p} = 35/8\pi$.

Each *edge* element lying between r and $r + \mathrm{d}r$ from three nuclei is a body diagonal of a small parallelopiped, formed by three pairs of planes at right angles to the directions to the nuclei. This parallelopiped contains all points for which the distances to the three nuclei lie between r and $r + \mathrm{d}r$. Its volume and the length of the diagonal are proportional to $(\mathrm{d}r)^3$ and to dr respectively; both proportionality factors are determined by the three directions. Integration over all directions thus should yield firstly the total volume of the parallelopipeds, which — per unit volume — is given by the numerator of (13 b), and secondly the total length of the edge elements, which — again per unit volume — is equal to $\frac{1}{3}n$ times expression (6). One obtains then, by division, the denominator of (13b).

The volume lying between r and $r + \mathrm{d}r$ from *two* nuclei is a "torus" obtained by rotating a small rhomb about the axis through the two nuclei. The narrow ring described by the diagonal of the rhomb at right angles to the axis constitutes the portion of the interface lying between r and $r + \mathrm{d}r$ from the nuclei. To obtain infinitesimal elements with defined directions to the two nuclei such a "torus" has to be divided in to a great number of small sectors. Integration over all directions yields the total area of the interface elements and the total volume of the "torus" elements. By division one thus obtains the denominator of (13 a).

The object of writing down (13) will become clear in the next section.

2. The Johnson-Mehl model

In many practical cases the *Johnson-Mehl model* [3]) is more appropriate than the "cell model" examined in the preceding section. The difference with the latter consists in the nuclei starting to grow at different times, the rate of nucleation being constant: the probability that in a small uncrystallized volume element dV during a small time dt a nucleus will be born is called here $\alpha\,\mathrm{d}V\,\mathrm{d}t$. The linear velocity of growth (isotropic) is v. The constants α and v have dimensions $\mathrm{cm}^{-3}\mathrm{sec}^{-1}$ and $\mathrm{cm\ sec}^{-1}$ respectively. Johnson and Mehl showed that the fraction of material not yet crystallized, as a function of time, is given by

$$e^{-1/3\pi\alpha v^3 t^4}, \tag{14}$$

where t is the time elapsed since the start of the crystallization process. The derivation is given in an appendix not attached to the paper published, but its essential points can be gleaned from the authors' answer to the discussion.

The number of crystals formed per unit volume is obtained by integrating $\alpha e^{-1/3\pi a v^3 t^4} dt$ from 0 to ∞, yielding

$$\left(\frac{3}{\pi}\right)^{1/4} \Gamma\left(\tfrac{5}{4}\right) \left(\frac{\alpha}{v}\right)^{3/4} = 0{\cdot}8960 \left(\frac{\alpha}{v}\right)^{3/4}. \qquad (15)$$

A short elegant derivation was given by Evans [4]), using Poisson's formula. A third way will be given here; it is easy and presents the opportunity to emphasize an essential point (cf. next foot-note).

Consider an arbitrary point at time t. It will still be uncrystallized when the following condition is fulfilled for all times T between 0 and t: Between T and $T + dT$ no nucleus must be formed inside a sphere of radius $v(t-T)$ around the point in question *). The probability, for one value of T is, $e^{-4/3\pi v^3 (t-T)^3 a dT}$ (compare eq. (1)), when the condition is known to be fulfilled for all smaller values of T, so that the sphere is still completely uncrystallized. Considering all values of T, starting with 0 and ending with t, we get the probability that the point is not crystallized at time t by multiplying all these factors, thus by integrating the exponent, yielding $e^{-1/3\pi a v^3 t^4}$ again.

We now proceed to calculate the interface area, edge length and number of vertices for the Johnson-Mehl model. Again we start by considering the "mathematical" interfaces, etc.; all mutual obstruction is ignored, not only for the crystals really born, but also for those that would have been born if their birth place had not already been crystallized. Thus "mathematically" nuclei are formed at a constant rate everywhere **).

The crystal boundaries in this model are hyperboloids of revolution with the two nuclei as foci. The area of the narrow ring formed between t

*) That these conditions are not only sufficient, but also necessary, is due to the spherical growth of the crystals. This excludes the possibility that the crystallization of the point is retarded by impingement. When a crystal is prevented from attaining the point, then the obstructing crystal (or that obstructing this one, etc.) can only attain the point earlier, not later. This is *not* true when the crystals are growing as ellipsoids, cubes, etc., with varying orientations. In that case the crystallization is not strictly given by the generalized formula

$$1 - \exp\left(-\tfrac{1}{3}\pi a \overline{v^3} t^4\right)$$

(where v^3 has been averaged over all directions), contrary to what can be gathered from a remark by Evans [4]) concerning the analogous two-dimensional case. Even when all orientations are parallel the obstructive effect can operate, when the crystals show dendritic growth.

**) This artifice preserves randomness and so cuts out correlation difficulties. It was used already by Johnson and Mehl in their derivation of formula (14).

and $t + \mathrm{d}t$ on such an interface can be calculated as a function of the times of birth of the two nuclei involved, and of their distance. Triple integration then yields

$$\tfrac{8}{2}\tfrac{2}{7}\,\pi^2\alpha^2v^5t^6\mathrm{d}t \tag{16}$$

for the "mathematical" interface area formed between t and $t + \mathrm{d}t$ per unit volume. It would be difficult to calculate the edge length and number of vertices in this way. However, with the help of the considerations at the end of section 1 things are rather easier. The total "mathematical" crystal volume (per unit volume of the aggregate) as a function of time is

$$\int_0^t \tfrac{4}{3}\pi v^3(t-T)^3\alpha\mathrm{d}T = \tfrac{1}{3}\pi\alpha v^3t^4.$$

Thus the "mathematical" crystal volume formed between t and $t + \mathrm{d}t$ (per unit volume) is $\frac{4}{3}\pi\alpha v^3t^3\mathrm{d}t$. This is the probability that an arbitrary point is crossed between t and $t + \mathrm{d}t$ by one of the growing spheres. The probability that during this interval the point is crossed by j spheres is equal to

$$(\tfrac{4}{3}\pi\alpha v^3t^3\mathrm{d}t)^j/j! \tag{17}$$

This expression is to be compared with the numerators of (13): its stands for the total volume (per unit volume of the aggregate) of "torus" elements ($j = 2$), parallelopipeds ($j = 3$) and eight-faced volume elements around the vertices ($j = 4$), as described at the end of section 1. To obtain the "mathematical" interface area, edge length and number of vertices (per unit volume) one must obviously divide (17) by

$$f_j(v\mathrm{d}t)^{j-1}, \tag{18}$$

where f_j is a dimensionless factor. Now the values of f_j are equal to the numerical factors in the denominators of (13): $f_2 = \frac{3}{4}$, $f_3 = 5/2\pi$ and $f_4 = 35/8\pi$. The point is that both in the "cell model" and in the Johnson-Mehl model the distribution of the directions from, say, a "mathematical" vertex to the nuclei is completely isotropic. For one combination of directions the shape of the element in question is the same *); for $\mathrm{d}r = v\mathrm{d}t$ this is also the case for its volume and thus the average volume for all combinations of directions is the same for the two models. In the case of edge elements, for one combination of the three directions the parallelopipeds *and* their diagonals are the same for both models, when $\mathrm{d}r = v\mathrm{d}t$. The discussion is least easy for $j = 2$, due to the fact that in the Johnson-Mehl model a complete "torus" is obtained by rotating the infinitesimal rhomb about an axis which is not at right angles to the diagonal. However,

*) In the limit $\mathrm{d}t \to 0$ the *lengths* of the vectors to the nuclei have no influence!

in this case we have an independent check: substitution of $f_2 = \frac{3}{4}$ yields (16)*).

Instead of substituting the values of f_j from (13) into (17) divided by (18), we can also find (16) and the analogous expressions for the edge length (20) and vertex number (21) by substituting

$$\left.\begin{array}{l} r \longrightarrow vt \\ n \longrightarrow \frac{1}{3}at \end{array}\right\} \tag{19}$$

directly into the corresponding expressions for the "cell model" (cf. last foot-note in section 1). This was pointed out to the author by Dr Wise of this laboratory. Indeed, viewed from the points that at time t are attained by one or more growing "mathematical" spheres, the Johnson-Mehl model is effectively the same as a "cell model" with a concentration of nuclei equal to $\frac{1}{3}at$.

Per unit volume we find for the "mathematical" edge length formed between t and $t + \mathrm{d}t$:

$$\tfrac{6\,4}{4\,0\,5}\,\pi^4\alpha^3v^7t^9\mathrm{d}t \tag{20}$$

and for the number of "mathematical" vertices formed between t and $t + \mathrm{d}t$:

$$\tfrac{2\,5\,6}{8\,5\,0\,5}\,\pi^5\alpha^4v^9t^{12}\mathrm{d}t\,. \tag{21}$$

In reality a point is crystallized only by the first crystal attaining it. The factor necessary to convert the "mathematical" values into real ones is equal to the probability that an *arbitrary* point is not yet crystallized at time t, thus $e^{-1/3\pi\alpha v^3t^4}$. The fact that it is known that 2, 3 or 4 crystals are on the verge of attaining the point in question ("mathematically") has no influence.

Thus we find

$\tfrac{3\,2}{2\,7}\,\pi^2\alpha^2v^5t^6e^{-1/3\pi\alpha v^3t^4}\,\mathrm{d}t$ for the interface area,

$\tfrac{6\,4}{4\,0\,5}\,\pi^4\alpha^3v^7t^9e^{-1/3\pi\alpha v^3t^4}\,\mathrm{d}t$ for the edge length, and

$\tfrac{2\,5\,6}{8\,5\,0\,5}\,\pi^5\alpha^4v^9t^{12}e^{-1/3\pi\alpha v^3t^4}\,\mathrm{d}t$ for the number of vertices

formed *between t and $t + \mathrm{d}t$*, per unit volume**). Each interface, etc., has been counted only once. Integrating t from 0 to ∞ one finds:
for the total interface area per unit volume:

*) Another check on the method described is obtained in the two-dimensional case, for the number of three-crystal junctions (cf. second foot-note in section 3).

**) The rates of formation of crystallized volume, interface area, edge length and number of vertices are maximal when the uncrystallized volume fraction is $e^{-3/4}$, $e^{-3/2}$, $e^{-9/4}$ and e^{-3} respectively. When the nuclei start to grow simultaneously ("cell model"), these fractions are $e^{-2/3}$, $e^{-4/3}$, e^{-2} and $e^{-8/3}$ respectively.

$$\frac{8\pi^{1/4}}{3^{5/4}}\left(\frac{a}{v}\right)^{1/4}\Gamma(\tfrac{7}{4}) = 2{\cdot}479\left(\frac{a}{v}\right)^{1/4}, \tag{22a}$$

for the total edge length per unit volume:

$$\frac{4\pi^2}{5\sqrt{3}}\left(\frac{a}{v}\right)^{1/2} = 4{\cdot}559\left(\frac{a}{v}\right)^{1/2}, \tag{22b}$$

for the total number of vertices per unit volume:

$$\frac{4{\cdot}3^{1/4}.\,\pi^{7/4}}{7}\left(\frac{a}{v}\right)^{3/4}\Gamma(\tfrac{5}{4}) = 5{\cdot}053\left(\frac{a}{v}\right)^{3/4}. \tag{22c}$$

The *number of edges* ending in two vertices is twice the number of vertices, but the total number of edges is somewhat greater, as in this model there is the possibility of an isolated edge closed in itself; a crystal bounded by only two other crystals has such an edge. The number of interfaces cannot be given exactly either.

In Table I the various numerical quantities are expressed per crystal (elimininating a/v in (22) with (15)); now for instance each edge is counted for each of its three crystals. It is noteworthy that the average number of vertices of a crystal is $16\pi^2/7$, thus $\frac{5}{6}$ of that found for the cell model. The numerical quantities of that model are also incorporated in Table I, and for comparison also those of a cell model with the nuclei situated on a body-centered cubic lattice. In this non-random model the crystals are cube-octahedrons of equal size; each has 6 square faces and 8 regular hexagonal faces (see[2]), fig. 19).

In section 4 some of the numerical quantities will be discussed and compared with experimental results obtained in alloys.

TABLE I

Mean characteristic quantities for one crystal (mean volume b^3)

	Cell model	Johnson-Mehl model	Cube-octahedron model
Number of faces	15·54	>13·28	14
Number of edges	40·61	>33·84	36
Number of vertices	27·07	22·56	24
Surface area	5·821 b^2	5·143 b^2	5·315 b^2
Edge length	17·50 b	14·71 b	16·04 b
"Full neighbours"	8	7	14

As an example of an average quantity which is quite sensitive to randomness, the mean number of "full neighbours" of a crystal is given in the bottom line of the table. We call two crystals "full neighbours" when, growing, they meet head-on, not retarded by obstruction. The numbers 8 and 7 are found easily by calculating the number of "mathematical" meeting points that are physically real. From the table it is seen that for the cell model nearly half of the perpendiculars drawn from a nucleus of a crystal onto its faces do not have their feet in the real part of the face in question.

3. Plane sections and two-dimensional aggregates

In practice a three-dimensional aggregate has mostly to be judged by inspection of plane sections. As can be easily shown (cf. [8])), the total boundary length of the crystal sections per unit area is equal to $\pi/4$ times the interface area per unit volume, and the number of corners (where three crystal sections meet) per unit area is equal to half the edge length per unit volume. This is true for each section through an aggregate with random crystallization (if a great number of crystals are cut, of course) and for an ensemble of random sections through an ordered aggregate like the cube-octahedron model.

In a section through the cell model the crystal boundaries and crystal sections are respectively $\frac{3}{2}$ and $\frac{1}{2}$ times as numerous as the polygon corners *). For the Johnson-Mehl model these ratios must be somewhat greater because of the occurrence of closed boundaries due to interfaces sectioned without any of their edges being cut. The number of crystal sections per unit area is found to be $>1{\cdot}140\ (a/v)^{1/2}$; Johnson and Mehl themselves [3]) found $1{\cdot}01\ (a/v)^{1/2}$ by an approximate analysis. Calling the average crystal volume b^3, the mean crystal section area is $<0{\cdot}816\ b^2$ and for the cell model $= 0{\cdot}686\ b^2$.

Scheil and Wurst [5]) have measured areas of crystal sections in a piece of Armco iron cooled slowly from above the transition point. The specimen was polished repeatedly, about 8 microns being removed each time. So about 1400 crystal sections in all were measured. By integrating over the depth, the volumes of 68 crystals were determined. The distribution curves of these volumes and section areas themselves are not given in the paper, but those of the radii of spheres and circles having the same volume and area respectively. By graphical integration (using curve 1 in their fig. 4 and curve 2 in fig. 5) the author found $0{\cdot}80\ b^2$ for the mean crystal section area.

*) For a group of an infinite number of polygons the number of sides is equal to the sum of the numbers of polygons and corners, which follows directly from Euler's theorem (cf. [2])).

For the two-dimensional case (crystals grown in a very thin strip) calculations were made on the same lines as for the three-dimensional case. With m nuclei per unit area one finds $4/\sqrt{m}$ for the mean perimeter of a crystal in the "cell model". For the Johnson-Mehl model, with β nuclei formed per unit area and unit time, the uncrystallized fraction is $e^{-1/3\pi\beta v^2 t^3}$ and the number of crystals per unit area $(3/\pi)^{1/3}\,\Gamma(\frac{4}{3})\,(\beta/v)^{2/3}$ (cf. [4])). For the total length of the grain boundaries, per unit area, we find $2(3/\pi)^{2/3}\,\Gamma(\frac{5}{3})\,(\beta/v)^{1/3}$.

For both models the mean number of boundaries of a crystal was calculated to be 6*). This result follows directly from Euler's theorem (cf. first foot-note of this section) and thus constitutes only a check on the method of calculation. For the average number of "full neighbours" one finds 4, again for both models. Consequently, in half of the corners three boundaries have converged, while in the other half two boundaries have met, whereupon the third has started to grow. When a thin layer of a nearly pure liquid crystallizes and the impurities are insoluble in the solid state, in certain circumstances these will be concentrated in corners where three crystals (and boundaries) converge. When the nucleation is random (one of the two models discussed), these impurity pockets are just equal in number to the nuclei.

In Table II the numerical quantities calculated for the two random two-dimensional models are compared with those of the most obvious

TABLE II

Mean characteristic quantities for one crystal or crystal section (mean area c^2)

	Perimeter	Boundaries	"Full neighbours"
Cell model (2 dim.)	$4\ c$	6	4
Johnson-Mehl model (2 dim.)	$3{\cdot}734\ c$	6 **)	4
Honeycomb	$3{\cdot}722\ c$	6	6
Section through 3-dim. cell model	$3{\cdot}786\ c$	6	
Section through 3-dim. J.-M. model	$<3{\cdot}648\ c$	<6	
Mean of random sections through cube-octah. model	$3{\cdot}611\ c$	6	

*) For the Johnson-Mehl model the method treated in Section 2 (cf. expression (17)) was used. The transformation $n \rightarrow \frac{1}{3}at$ in (19) here becomes $m \rightarrow \frac{1}{2}\beta t$. For the grain-boundary length this method was also used. The two-dimensional analogue of the calculation of (16) is impeded by the appearance of elliptic integrals.

**) The mean number of neighbours is <6, as in this model two crystals may have more than one common boundary, their "mathematical" boundary being interrupted by smaller crystal(s).

non-random model (a honeycomb of regular hexagons) and the plane sections through the three-dimensional models given in Table I.

4. Discussion on numerical data and crystal form

From Table I it is seen that the numerical quantities for the cell model are greater than those for the cube-octahedron model and these again (to a lesser extent) are greater than those for the Johnson-Mehl model *). The first comparison is in contradiction with a statement in [2]), saying that the numbers of faces, edges and vertices for the cube-octahedron model are the greatest possible in crystal aggregates. This statement, however, has been retracted afterwards [9]) [10]).

Suppose we start from the cube-octahedron model and let one crystal absorb one of its neighbours. When the mutual interface was a hexagon, 6 vertices and 7 faces are lost (12 faces become pairwise identical and may be thought to be smoothed out), so that the mean numbers in question do not change by the loss of one crystal. But when the mutual interface was a square, only 4 vertices and 5 faces are lost, and so the mean numbers of the aggregate can be increased to more than 6 and 7 respectively.

Apparently this surpassing is due to a marked deviation from the equiaxial crystal form. When a crystal absorbs all its 14 neighbours in the cube-octahedron model, forming one big "equiaxial" crystal, the number of faces lost is 110, which is more than 7 times the number of crystals lost, viz. 14. Thus in this case the mean numbers for the remaining aggregate are less than 7 faces and 6 vertices. We may draw the following somewhat indefinite conclusions for aggregates in general:

The average numbers of interfaces, edges and vertices per crystal will *decrease* with increasing spread in the size distribution of the crystals; they will *increase* with increasing deviation from equiaxial crystal form. It is readily seen that the interface area of an aggregate with constant volume and constant number of crystals is also decreased for a wider size distribution and increased for oblong forms. As in the process of coalescing two adjacent cube-octahedrons (see above) the size distribution is affected at the same time as the crystal form, we think that in general the latter of the two factors can be regarded as the most important one.

Comparing the data for the cell model and the Johnson-Mehl model in Table I we are inclined therefore to attribute the systematic differences

*) Disregarding the number of "full neighbours" for the cube-octahedron model, which is high because of the ordered nature of this model. Although the number of faces and edges for the Johnson-Mehl model are not exactly known, it is to be expected that they do not reach 14 and 36 respectively, as the number of isolated closed edges (cf. paragraph immediately after expressions (22)) will be small.

to a more equiaxial average crystal form in the latter model. This difference in form is plausible when we consider a model that can be regarded as a modification of the cell model in the direction of the Johnson-Mehl model: Let only half of the nuclei start growing at $t = 0$ and the other half after a certain, not too long, time in the volume not yet crystallized. It looks obvious that the irregularities entailed by the random distribution of the former nuclei will be mitigated more by the crystals growing from the latter nuclei than when these would have started also at $t = 0$ from nuclei distributed completely at random. This expectation is supported by calculations for the one-dimensional models (section 5).

In the two-dimensional case (cf. Table II) the mean crystal perimeter shows differences in the same direction: it is greater for the cell model than for the Johnson-Mehl model, and the same applies for plane sections through three-dimensional aggregates. Comparing these sections with the two-dimensional aggregates, we see that the latter have the greatest mean perimeter, both for the cell model and the Johnson-Mehl model. This is natural enough, as the distribution of nuclei over a range of distances from a plane will have a similar influence as their distribution over a range of starting times. In practice, when the models treated are usually more or less crude approximations, one will still expect crystal sections in an aggregate to be rather more equiaxial than crystals grown in a thin strip under equal circumstances.

Experimentally, faces, edges and vertices in alloy aggregates have been counted in 1919 by Desch [6]) and recently by Williams and Smith [7]) *). Desch examined crystals obtained by disintegrating a β-brass aggregate by immersion in mercury. He found 14·50 faces and 24·85 vertices per crystal in the average. Williams and Smith experimented with an alloy of aluminium with a small concentration of tin, which had been worked, annealed above the eutectic temperature and quenched. By this procedure Sn assembles along the crystal edges. Using stereoscopic microradiography 91 contiguous crystals were examined, yielding in the average 12·48 faces and 20·9 vertices per crystal.

5. Size-distribution curves for the one-dimensional case

We end with the one-dimensional case: a wire which is very thin compared with the average crystal length. For the *Johnson-Mehl model* we call the probability that in a small uncrystallized length element dx during a small time dt a nucleus will be born $\gamma\, dx\, dt$. The velocity of growth is again called v. The crystallized fraction as a function of time

*) For some other measurements, in non-metallic aggregates, cf. [2]).

(corresponding to (14) for the three-dimensional case) is easily found to be

$$e^{-\gamma v t^2}. \tag{23}$$

The number of nuclei born between t and $t + \mathrm{d}t$, per unit length, is thus

$$\gamma e^{-\gamma v t^2}\,\mathrm{d}t \tag{24}$$

and the mean crystal length

$$\bar{L} = 2\sqrt{\frac{v}{\pi\gamma}}. \tag{25}$$

Here, with only one dimension, we need not be content with this average, but can calculate the probability distribution of crystal lengths.

From each nucleus two "branches" start growing in opposite directions. The probability that an arbitrary branch which is growing at time t will stop doing so (by meeting another) in the next small time interval $\mathrm{d}t$ is equal to the probability that an arbitrary uncrystallized point will crystallize in this interval $\mathrm{d}t$, viz.

$$2\gamma v t\,\mathrm{d}t. \tag{26}$$

The factor 2 in (26) is a result of the double relative velocity of the meeting branches in the former case and the double chance of invasion from both sides in the latter case. Integration of (26) yields (23) in the latter case, while the probability that a branch started at time T is still growing at time t is found to be

$$e^{-\gamma v(t^2-T^2)}. \tag{27}$$

Differentiation with respect to t leads to the probability that the final length attained by a branch started at T lies between p and $p + \mathrm{d}p$:

$$2\gamma(p/v + T)\, e^{-(\gamma/v)(p^2+2vTp)}\,\mathrm{d}p. \tag{28}$$

For the two branches starting from one nucleus at T these probabilities are not interdependent. Simple combination thus gives the probability that the crystal consisting of them has a length between L and $L + \mathrm{d}L$:

$$4\frac{\gamma^2}{v^2}\, e^{-(\gamma/v)(L^2+2vTL)}\,\mathrm{d}L \int_0^L (p + vT)\,(L - p + vT)\, e^{-2(\gamma/v)(p^2-Lp)}\,\mathrm{d}p. \tag{29}$$

Putting the dimensionless quantity

$$L\sqrt{\frac{\gamma}{2v}} = u, \tag{30}$$

(29) reduces to

$$\left[2\sqrt{\pi}\left\{(u + \sqrt{2\gamma v}\,T)^2 - \tfrac{1}{2}\right\}\operatorname{erf} u + 2ue^{-u^2}\right] e^{-u^2-2\sqrt{2\gamma v}\,Tu}\,\mathrm{d}u. \tag{31}$$

The probability that an arbitrary nucleus has been born between T and $T + \mathrm{d}T$ (cf. (24) and (25)) is

$$2\sqrt{\frac{v}{\pi\gamma}}\,\gamma e^{-\gamma v T^2}\mathrm{d}T.$$

Multiplication by (31) and integration with respect to T from 0 to ∞ yields the probability that an arbitrary crystal has a reduced length between u and $u + \mathrm{d}u$ (cf. (30)):

$$\{2u + \sqrt{\pi}\,(2u^2 + 1)\,e^{u^2}\,\mathrm{erf}\,u\}\,\{1 - \mathrm{erf}(u\sqrt{2})\}\,\mathrm{d}u. \qquad (32)$$

This size-distribution curve is represented in fig. 3, where the average crystal length (corresponding to $u = \sqrt{2/\pi}$) is taken as unit.

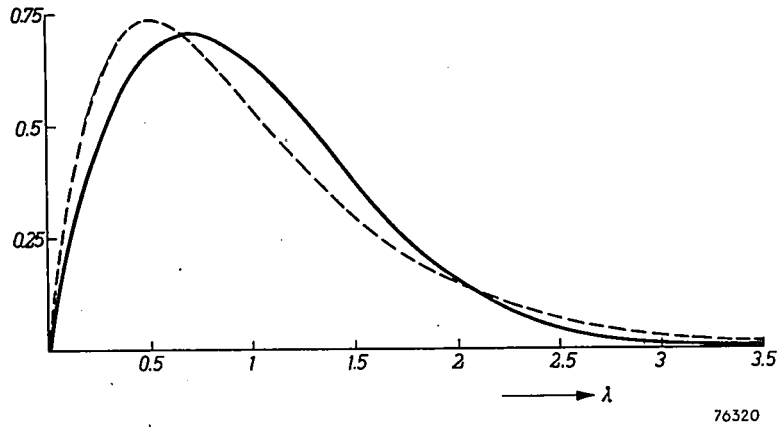

Fig. 3. Normalized frequency of relative crystal lengths λ (mean length as unit). Full curve: one-dimensional Johnson-Mehl model. Dashed curve: one-dimensional cell model.

For the *cell model* things are easier. The probability that a crystal has a length between λ and $\lambda + \mathrm{d}\lambda$ (mean length as unit) is found to be $4\lambda e^{-2\lambda}\mathrm{d}\lambda$.

From fig. 3 it is seen that this model has a wider spread than the Johnson-Mehl model: below 0·65 and above 2·1 times the mean length the frequency is largest for the cell model.

In fig. 4 the size-distribution curves of the crystal *branches* are drawn. Their equations are simply $e^{-\lambda}$ for the cell model and $(2/\pi)\,e^{-\lambda^2/\pi}$ for the Johnson-Mehl model, $\lambda = 1$ pertaining to the mean length of a branch. In fig. 5 the statistical distribution of nucleus locations in the crystals is given. For the cell model all positions have equal probability, but for the Johnson-Mehl model there is a marked preference for the central part

of the crystal, owing to the smaller spread in branch length for this model. Calling the position coordinate x (varying between $-\frac{1}{2}$ and $+\frac{1}{2}$ at the crystal ends) the equation for this curve is

$$\frac{\sqrt{2}}{(1+4x^2)^{3/2}}. \tag{33}$$

We use these figures for considerations regarding the two-and three-

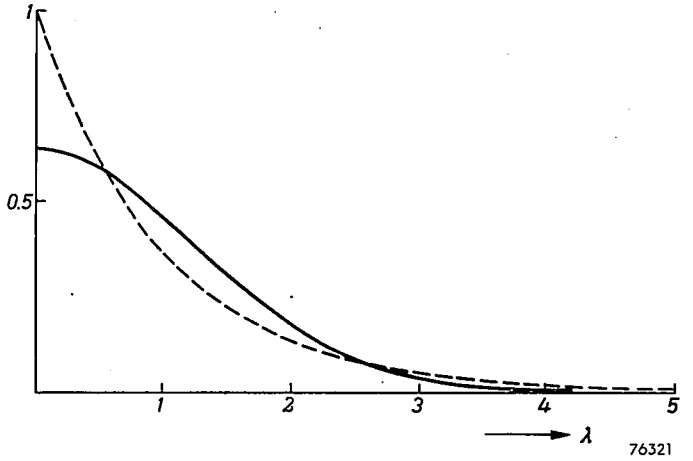

Fig. 4. Normalized frequency of relative lengths of *branches* (crystal parts at one side of nucleus); mean branch length as unit. Full curve: one-dimensional Johnson-Mehl model. Dashed curve: one-dimensional cell model.

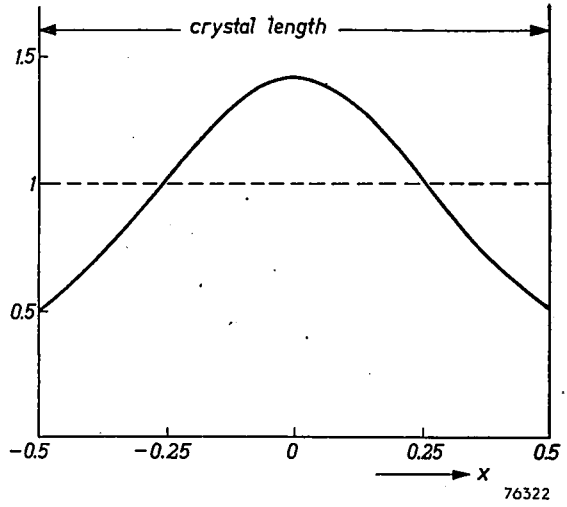

Fig. 5. Normalized frequency of location of nucleus in the crystal. Full curve: one-dimen sional Johnson-Mehl model (cf. (33)). Dashed: one-dimensional cell model.

dimensional models. From figs 4 and 5 we may safely predict that in these cases the cell model gives rise to less equiaxial crystals than the Johnson-Mehl model. This will result in larger values of average crystal perimeter, interface area, number of faces, etc. (cf. section 4), for the cell model. On the other hand, from figs 3 and 4 we must expect this model to have a wider spread in crystal size for more than one dimension too, and this tends to change the values mentioned above in the other direction. Now the spread in size diminishes when going over from single branches (fig. 4) to complete crystals (fig. 3), and presumably is still smaller (and, taken absolutely, less different for the two models) in the more-dimensional cases. Furthermore, from the process of coalescing two adjacent crystals in the cube-octahedron model (cf. section 4) it appeared that at least the numbers of faces, edges and vertices are — crudely speaking — more sensitive to form than to spread in size. Therefore we think that the results for the one-dimensional case are in harmony with the systematic differences between cell model and Johnson-Mehl model shown by Tables I and II, and confirm the conclusion in section 4 that in the Johnson-Mehl model the crystals are more equiaxial. Its numerical quantities in Table I are also surpassed by those of the cube-octahedron model, thanks, evidently, to the total absence of spread in crystal size for that model.

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Eindhoven, April 1953

REFERENCES

1) C. S. Smith, Trans. A.I.M.M.E. **175**, 15-51, 1948.
2) C. S. Smith, "Metal Interfaces", Seminar A.S.M., 65-113, 1951.
3) W. A. Johnson and R. F. Mehl, Trans. A.I.M.M.E. **135**, 416-458, 1939.
4) U. R. Evans, Trans. Faraday Soc. **41**, 365-374, 1945.
5) E. Scheil and H. Wurst, Z. Metallk. **28**, 340-343, 1936.
6) C. H. Desch, J. Inst. Metals **22**, 241-263, 1919; cf. ref 2), Table III.
7) W. M. Williams and C. S. Smith, J. Metals **4**, 755-765, 1952.
8) C. S. Smith and L. Guttman, J. Metals **5**, 81-87, 1953.
9) C. S. Smith, Acta Metallurgica **1**, 295-300, 1953.
10) J. L. Meijering, Acta Metallurgica, in the press.