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Alfred Seeger

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I. Diffusion Problems Associated with the Growth of Crystals from Dilute Solution

By Alfred Seege*  
H. H. Wills Physical Laboratory, University of Bristol†  
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Summary

Crystals growing from solutions with plane faces must have considerable supersaturation at some parts of the surface. A supersaturation number $\sigma$ is introduced to give a measure of the maximum supersaturation. For two-dimensional growth in very dilute solutions a general method for evaluating $\sigma$ is given; it is applied to the growth of regular polygons, to the growth of a step on a surface, and to growth on the edge of a plate. For three-dimensional growth only a rough estimate for the supersaturation occurring with regular polyhedra can be given; it is estimated that the maximum supersaturation on the surface of a cube or regular octahedron is between 0.25 and 0.4 of the concentration difference between the vertices and infinity.

§1. Introduction

It is known that crystals can grow from solutions with plane faces. We consider here only those cases in which there is no particularly large surface mobility for solute atoms, and in which the solution is dilute, and the diffusion coefficient independent of concentration. Then at any

* On leave from Technische Hochschule, Stuttgart, Institut für theoretisch und angewandte Physik.
† Communicated by F. C. Frank.
moment the flux of matter or the normal gradient of concentration has to be constant all over a face. This condition is the only one at the crystal surface that is required to specify the mathematical solution of the diffusion problem. This means that the concentration itself will not be uniform at a given face. All over a growing face, however, there must be at least a slight supersaturation; therefore a considerable supersaturation will occur on parts of the faces, especially near corners and vertices. This conclusion is in agreement with experimental observations on growth of square or rectangular crystals between plates from NaClO₃ solutions (Berg 1938, Bunn 1949, Humphreys-Owen 1949). It is presumably this excess of supersaturation at crystal corners which in certain circumstances causes dendritic rather than polyhedral growth; it is therefore very desirable to estimate how this supersaturation excess depends upon crystal geometry.

The fact of growth in plane faces (plane means here only macroscopically plane, not plane on a molecular scale), in spite of a certain amount of supersaturation, is in accordance with the view (Burton, Cabrera and Frank 1951) that below a certain supersaturation crystals can grow only by the screw dislocation mechanism and not by a nucleation process at the surface.

This paper is concerned with theoretical investigation of the diffusion problem and the supersaturation conditions at the crystal surface. This would be a very difficult task for three-dimensional growth and for non-dilute solutions. The problem, however, is tractable for two-dimensional growth in a simple shape at very small concentrations. The latter condition ensures (together with the reasonable assumption that surface migration is unimportant) that the flux has to be constant over any face, and that the growth rate is slow, so that the whole problem can be treated statically. This should give good results for the problem of the advancing step, because the characteristic length of this problem, the step-height $a$, does not exceed a few hundred ångströms, and is small compared with the ratio of diffusion-coefficient $D$ and growth-rate $v$ in a typical experiment. In the case, however, of regular polygons ($a=$length of a side) growing in two dimensions it will be more difficult to satisfy the condition $a \ll D/v$, and our treatment is to be regarded as giving the limiting case for very dilute solutions.

We cannot use any of the present observations on two-dimensional growth for comparison with the theory, because the conditions were not sufficiently symmetric and the solutions were far from being dilute. However, it is hoped that future experiments at moderate concentrations and under well-defined conditions will supplement the theory in finding the general dependence of supersaturation conditions on concentration and growth rate.

In §4 we give a few remarks on three-dimensional growth. They are meant only to give a very rough idea about the supersaturation conditions that are to be expected in three-dimensional growth of polyhedra.
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§ 2. General Method for Two-Dimensional Growth

The assumptions made in §1 permit the application of the methods of the theory of functions. The mathematical problem is to find the concentration \( c \), satisfying the two-dimensional potential equation \( \nabla^2 c = 0 \), to which the diffusion equation reduces, subject to the flux conditions stated above.

Two steps are involved in the solution of this problem. Firstly we consider the plane in which the two-dimensional crystal lies as a complex plane \( w = u + iv \), and we map the exterior of the crystal by a conformal transformation on the upper half of a complex plane \( z = x + iy \). During this transformation the concentration \( c \) remains invariant, the normal gradient at the surface, however, is changed. Secondly we solve the potential problem in the \( x-y \)-plane by means of Fourier integrals.

For a crystal with polygonal shape this can be done quite generally. The integrals involved can be evaluated only in simple cases. We are not, however, very much interested in the determination of the concentration \( c(u, v) \) everywhere in the exterior of the crystal, but mainly in the supersaturation conditions at the crystal surface, especially in the largest supersaturation that occurs in a certain mode of growth. This can be characterized by a single number, the supersaturation-number \( \sigma \), which we define as the difference between the highest and the lowest concentration at the crystal surface, divided by the integral of the normal gradient of the concentration, taken over the trace of the crystal surface in the \( w \)-plane. We shall evaluate \( \sigma \) for several crystal shapes.

According to the Schwarz–Christoffel transformation the interior of the polygon shown in fig. 1 in the \( w \)-plane is mapped on the upper half of the \( z \)-plane by a mapping function

\[
\omega = \phi(z) \quad . . . . . . . . \quad (1)
\]

which satisfies

\[
\frac{d\omega}{dz} = \psi(z) = \mu(z-z_1)^{\beta_1-1} \ldots (z-z_n)^{\beta_n-1}, \quad . . . . \quad (2)
\]

or

\[
\omega = \phi(z) = \int_0^z \psi(t) \, dt + \mu. \quad . . . . . \quad (3)
\]

\( z_1, \ldots, z_n \), being points on the real \( z \)-axis, are the images of the corners of the polygon. It is mainly the difficulty in finding the \( z_i \) for a given polygon that limits the present method either to very symmetrical cases or polygons with only few corners.

The normal derivative \( (\partial c/\partial y)_{y=0} = G(x) \) at the boundary in the \( z \)-plane can be expressed in terms of \( \partial c/\partial n \) and \( \psi(x) \) according to the formula

\[
\frac{\partial c}{\partial y} = \frac{\partial c}{\partial n} \frac{\partial n}{\partial y'} + \ldots . \quad . . . . . . . . \quad (4)
\]

and is therefore known. The general solution of the potential equation \( \nabla^2 c = 0 \) with the right behaviour at infinity is given by

\[
c(x, y) = \int_{-\infty}^{\infty} g(k)e^{ikx} e^{-|k|\nu dk} \quad . . . . . \quad (5)
\]
From

\[ G(x) = - \int_{-\infty}^{\infty} g(k) \frac{1}{k} e^{i k x} \, dk \]  

(6)

\( g(k) \) is determined by

\[ g(k) = - \frac{1}{2 \pi} \int_{-\infty}^{\infty} G(x) e^{-i k x} \, dx \]  

(7)

The equations (3), (5) and (7) contain the solution of the problem, and practical applications are solely a question of evaluating these integrals.

§ 3. EXAMPLES

(i) Regular Polygons (fig. 2 (a))

By symmetry it is sufficient to consider the polygon ABCD with the interior angles \( \alpha_1 = \alpha_2 = \pi \left( \frac{1}{2} + \frac{1}{n} \right) \) if the regular polygon has \( n \) corners. The upper half of the \( z \)-plane (fig. 2 (b)) is mapped on the interior of ABCD by

\[ w = \mu \int_0^\infty (1 - t^2)^{(1/n - 1/2)} \, dt \]  

(8)

The factor \( \mu \) is to be determined from the fact that \( z = -1 \) should correspond to \( w = -\frac{1}{2}a \), \( z = 1 \) should correspond to \( w = \frac{1}{2}a \) (\( a \) being the length of a side of the regular polyhedron). Using the formula (Groebner–Hofreiter 1950)

\[ \int_0^1 x^{\lambda-1}(1-x)^{\kappa-1} \, dx = B(\lambda, \kappa) = \Gamma(\kappa)\Gamma(\lambda)/\Gamma(\kappa+\lambda), \]  

we obtain

\[ a = \mu B \left( \frac{1}{2}, \frac{1}{2} + \frac{1}{n} \right) \]  

(10)
The region within ABCD of fig. 2 (a) is mapped upon the region $y > 0$ of fig. 2 (b).
Let the concentration gradient at the boundary of the regular polyhedron be $\frac{\partial c}{\partial n} = q$. Then the boundary conditions in the $z$-plane are given by

$$G(x) = \begin{cases} 0 & |x| > 1, \\ q \mu (1 - x^2)^{(1/n - 1/2)} & |x| > 1. \end{cases}$$

(11)

Due to the symmetry of $G(x)$ we may write the general solution for $c(x, y)$ as

$$c(x, y) = 2 \int_0^\infty g(k) \cos kx e^{-ky} dk,$$

(12)

where

$$g(k) = -\frac{1}{\pi k} \int_0^\infty G(\xi) \cos k\xi d\xi.$$

(13)

It is a mathematical convenience to introduce the complex function $c(z)$, whose real part is the physically significant concentration $c(x, y) = \Re c(z)$. Then

$$c(z) = -\frac{2}{\pi} \int_0^\infty \int_0^\infty \cos k\xi e^{ikz} G(\xi) d\xi dk.$$

(14)

In order to obtain known functions we consider $dc(z)/dz$, interchange the order of integration, and use the formula

$$\int_0^\infty \cos k\xi e^{ikz} dk = -\frac{iz}{z^2 - \xi^2},$$

(15)

which holds for $y > 0$.

This gives

$$\frac{dc(z)}{dz} = -\frac{2}{\pi} \int_0^\infty G(\xi) \frac{z}{z^2 - \xi^2} d\xi,$$

(16)

and (apart from an unessential additive constant)

$$c(z) = \frac{1}{\pi} \int_0^\infty G(\xi) \ln (z^2 - \xi^2) d\xi.$$

(17)

Using eqn. (11), eqn. (16) becomes

$$\frac{dc(z)}{dz} = -\frac{2q\mu}{\pi} \int_0^1 (1 - \xi^2)^{(1/n - 1/2)} \frac{z}{\xi^2 - z^2} d\xi.$$

(18)

This integral can be evaluated in terms of the hypergeometric function

$$F(a, b, c, z) = \frac{\Gamma(c)}{\Gamma(b)\Gamma(c-b)} \int_0^1 t^{b-1}(1-t)^{c-b-1}(1-tz)^{-a} dt.$$

(19)

The result is

$$\frac{dc(z)}{dz} = \frac{q\mu}{\pi z} B \left( \frac{1}{2}, \frac{1}{2} + n \right) F \left( 1, \frac{1}{2}; 1 + \frac{1}{n}; \frac{1}{z^2} \right).$$

(20)

By analytic continuation this holds not only for $y > 0$, but also for $y = 0$. We did not succeed in expressing $c(z)$ in terms of well-investigated functions. It is, however, possible to express the minimum concentration $c(0)$ at $w = 0$ and the maximum concentration $c(1)$ at $w = \frac{1}{2}a$ in terms of the logarithmic derivative of the factorial

$$\Psi(z) = \frac{d \ln \Gamma(z)}{dz} = \frac{d \ln \Gamma(z+1)}{dz}.$$
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by using the formula (Groebner–Hofreiter 1950)

\[ \int_0^1 x^{\lambda-1}(1-x)^{\lambda-1} \ln(1-x) \, dx = B(\kappa, \lambda)[\Psi(\lambda-1) - \Psi(\kappa+\lambda-1)]. \]

This gives

\[ c(1) = \frac{q\mu}{2\pi} B \left( \frac{1}{2}, \frac{1}{2} + \frac{1}{n} \right) \left[ \Psi \left( -\frac{1}{2} + \frac{1}{n} \right) - \Psi \left( \frac{1}{2} \right) \right] \quad \text{... (23)} \]

and

\[ c(0) = \frac{q\mu}{2\pi} B \left( \frac{1}{2}, \frac{1}{2} + \frac{1}{n} \right) \left[ \Psi \left( -\frac{1}{2} \right) - \Psi \left( \frac{1}{2} \right) \right] \quad \text{... ...} \quad \text{... (24)} \]

The saturation number is

\[ \sigma = \frac{c(1) - c(0)}{nq\alpha} = \frac{1}{2\pi n} \left[ \Psi \left( -\frac{1}{2} + \frac{1}{n} \right) - \Psi \left( -\frac{1}{2} \right) \right] \quad \text{... ...} \quad \text{... (25)} \]

An approximately valid formula for large \( n \) is obtained from the leading term,

\[ \sigma = \pi/4n^2, \quad \text{... ... ... ...} \quad \text{... (26)} \]

of the Taylor expansion in powers of \( 1/n \). It gives values for \( \sigma \) (in table 1 given as \( \sigma_2 \)) which are too large, the correction term being of the order \( 1/n^3 \).

Another upper bound for \( \sigma \) was suggested by F. C. Frank. If the concentration field were that of a line-sink of unit strength (so having circular symmetry despite the polygonal form of the crystal boundary), giving

\[ c = (1/2\pi) \ln r \quad \text{... ... ... ...} \quad \text{... (27)} \]

the supersaturation number would be

\[ \sigma = -(1/2\pi) \ln \cos \left( \pi/n \right). \quad \text{... ... ... ...} \quad \text{... (28)} \]

The actual value for \( \sigma \) (which we give in table 1 as \( \sigma_1 \)) must be between 0 and the value given by eqn. (28). For large \( n \) eqn. (28) reduces to eqn. (26), the next term being of the order \( 1/n^3 \).

We refer to the approximation that gives eqn. (28) as the ‘circle-approximation’; corresponding values of \( \sigma \) appear in table 1 as \( \sigma_2 \). The corresponding ‘sphere-approximation’ may be applied to regular polyhedra and will be dealt with in §4.

Table 1

<table>
<thead>
<tr>
<th>( n )</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_1 )</td>
<td>0.111</td>
<td>0.0570</td>
<td>0.0349</td>
<td>0.0171</td>
<td>0.0101</td>
<td>0.00674</td>
<td>0.00177</td>
</tr>
<tr>
<td>( \sigma_2 )</td>
<td>\infty</td>
<td>0.1103</td>
<td>0.0551</td>
<td>0.0229</td>
<td>0.0126</td>
<td>0.00798</td>
<td>0.00198</td>
</tr>
<tr>
<td>( \sigma_3 )</td>
<td>0.196</td>
<td>0.0822</td>
<td>0.0492</td>
<td>0.0218</td>
<td>0.0123</td>
<td>0.00785</td>
<td>0.00196</td>
</tr>
</tbody>
</table>

As it is difficult to give the concentration along one of the faces of the polygons by evaluation of eqns. (8) or (17), we shall now derive a simple interpolation formula for the concentration along the faces. We denote
this concentration as a function of \( u \) by \( C(u) \), and we express \( C(u) \) by an interpolation formula giving the correct value for \( \sigma \) and for \( dC(u)/du \) at \( u = \frac{1}{2}a \) (which we denote by \( C'(\frac{1}{2}a) \)). Such an interpolation formula is

\[
C(u) - C(0) = \{2C(\frac{1}{2}a) - 2C(0) + \frac{1}{4}aC'(\frac{1}{2}a)\}(\frac{2u}{a})^2
+ \{\frac{1}{4}aC'(\frac{1}{2}a) - C(\frac{1}{2}a) + C(0)\}(\frac{2u}{a})^4. \tag{29}
\]

In order to evaluate \( C'(\frac{1}{2}a) \) we apply to eqn. (20) the formula

\[
F(a, b; c; z) = \frac{\Gamma(c)\Gamma(c-a-b)}{\Gamma(c-a)\Gamma(c-b)} F(a, b; a+b-c+1; 1-z)
+ (1-z)^{a-b} \frac{\Gamma(c)\Gamma(a+b-c)}{\Gamma(a)\Gamma(b)} F(c-a, c-b; c-a-b+1; 1-z). \tag{30}
\]

and proceed then to the limit \( u = \frac{1}{2}a \) (\( z = 1 \)) in the equation for \( C'(u) \). This gives after some calculation

\[
C'(\frac{1}{2}a) = \frac{q}{\pi} \frac{\Gamma\left(\frac{1}{2} + \frac{1}{n}\right) \Gamma\left(\frac{1}{2} - \frac{1}{n}\right)}{\Gamma(1)} = \frac{q}{\cos(\pi/n)}. \tag{31}
\]

Our interpolation formula (31) becomes now

\[
\frac{C(u) - C(0)}{qa} = \left\{2\sigma n - \frac{1}{4 \cos(\pi/n)}\right\}(\frac{2u}{a})^2 + \left\{-\sigma n + \frac{1}{4 \cos(\pi/n)}\right\}(\frac{2u}{a})^4.
\]

\[
\ldots \ldots \tag{32}
\]

This method can of course be extended to include higher derivatives, for instance \( \frac{d^2C}{du^2} \) at the centre of an edge.

(ii) **Growth of Steps on Crystal Surfaces**

Crystals showing growth-spirals grow in steps of a step-height equal to the Burgers vector of the screw-dislocation which forms the axes of the spiral. One does not know anything about the actual shape of the step. We assume here that it is a plane, but we do not make any assumptions about the angle \( \gamma \) (see fig. 3). We can treat this problem along the lines indicated in §2. We introduce a complex variable \( w = u + iv \) as shown in fig. 3. The mapping function of the (degenerate) polygon formed by the trace of the crystal surface on the \( z \)-plane is

\[
w = \mu \int_0^z \left(\frac{1+t}{1-t}\right)^{\gamma/n} \frac{dt}{t} + \mu. \tag{33}
\]

From the condition that the distance between \( A \) and \( B \) is equal to \( a \), \( \mu \) is determined by

\[
a = \mu \int_{-1}^{1} \left(\frac{1+t}{1-t}\right)^{\gamma/n} \frac{dt}{t} = \frac{2\mu \gamma}{\sin \gamma}. \tag{34}
\]

The function \( (\partial c/\partial y)_{y=0} = G(x) \) is, if the normal gradient of the concentration along the step is denoted by \( q \),

\[
G(x) = \begin{cases} 0 & |x| > 1, \\ q \mu \{(1+x)/(1-x)\}^{\gamma/n} & |x| \leq 1. \end{cases} \tag{35}
\]
By calculations similar to those in the first example one finds for the concentration
\[ c(x, y) = R c(z) = \frac{q\mu}{\pi} R \int_{-1}^{+1} \ln(z - \xi) \left(\frac{1 + \xi}{1 - \xi}\right)^{\gamma/n} d\xi. \]  
(36)
The difference \( \Delta c \) between the concentrations at \( z = -1 \) and \( z = 1 \) is given by
\[ \Delta c = \frac{q\mu}{\pi} \int_{-1}^{+1} \left(\frac{1 + \xi}{1 - \xi}\right)^{\gamma/n} \ln\left(\frac{1 + \xi}{1 - \xi}\right) d\xi = qa \left(\frac{1}{\gamma} - \cot\gamma\right), \]  
(37)
and the saturation number is
\[ \sigma = \frac{\Delta c}{qa} = \frac{1}{\gamma} - \cot\gamma = \frac{1}{3} \gamma + \frac{1}{45} \gamma^3 + \frac{2}{945} \gamma^5 + \ldots. \]  
(38)
\( \sigma \) is plotted as a function of \( \gamma \) in fig. 4. A remarkable feature is that \( \sigma \) is approximately a linear function of \( \gamma \) for small \( \gamma \) but that it rises sharply if the angle becomes an obtuse one.

We should mention that the problem solved in this example also provides the solution for a crystal growing in the shape shown in fig. 5.

Fig. 3

Coordinates for a stepped crystal surface.

§ 4. THREE-DIMENSIONAL GROWTH OF REGULAR POLYHEDRA

Quantitative observations during growth of crystals suitable for checking the theory are most likely to be made for two-dimensional growth. For natural growth of crystals, however, the growth in three dimensions is most important. The simplest cases of growth in polyhedral shape are growth in the form of a cube or of a regular octahedron. These cases cannot be treated exactly even under the idealized conditions which we introduced into the earlier parts of this paper. These idealizations allow one to replace the diffusion problem by a problem of heat conduction; we have to find the temperature outside a solid body with zero thermal conductivity and with a uniform distribution of heat sinks on
Dependence of the supersaturation range at a step upon its steepness, $\gamma$.

Another crystal form to which the step solution applies.
its surface. In this heat-conduction problem we can ask for the solution of this problem not only for octahedron, cube and tetrahedron (these are the only regular solids that are possible growth shapes of crystals), but also for icosahedron, dodecahedron and for the dihedra. These dihedra (Klein 1924) are improper regular solids with zero volume; they consist of two regular polygons as the only faces.

We shall apply the sphere-approximation to the proper regular polyhedra, and we may expect from the results in §3 that this will give an overestimate for $\sigma$ of about 10 to 20% for the icosahedron and the dodecahedron. On the other hand we can solve the heat-conduction problem accurately in a simple way for one of the dihedra, namely the limiting case of a large number of corners, the circular disk. So we get for the sequence of regular solids two numerical values for the saturation number comparatively accurately, and we may interpolate for the other regular solids. (We continue to give the discussion in terms of concentration rather than in terms of temperature.)

We denote the radius of the circumscribed sphere of the regular polyhedra by $R_1$, the radius of the inscribed sphere by $R_2$, and the length of the edges by $d$. In order to get a dimensionless quantity for the supersaturation number $\sigma$ we adopt a definition slightly different from the one used in two dimensions. We define $\sigma/R_1$ as the difference between the maximum and the minimum concentration divided by the integral of the normal gradient of concentration, taken over the whole surface.

The concentration field of a unit point-sink is given by

$$c = -1/4\pi r.$$  \hspace{1cm} (39)

In the sphere-approximation we assume this to be the concentration also in the presence of the solid. The supersaturation number is then given by

$$\sigma = (1/4\pi)(-1 + R_1/R_2).$$  \hspace{1cm} (40)

In table 2 we give a list for $R_1$, $R_2$ (Buerklen-Ringleb 1936) and for $\sigma$, calculated from eqn. (40).

For the circular disk the sphere-approximation would give an infinite supersaturation number. We can, however, solve this problem exactly. If $\rho$, $z$, $\phi$ are cylindrical polar coordinates, $\rho = R_1$, $z = 0$ correspond to the circumference of the disk, and $q$ is equal to $|\partial c/\partial z|$ on the disk, then the concentration is given by

$$c(\rho, z) = -qR_1 \int_0^\infty J_0(\lambda \rho) J_1(\lambda R_1) e^{-i\lambda} d\lambda/\lambda.$$  \hspace{1cm} (41)

$J_\nu$ is the Bessel function of order $\nu$. The minimum concentration at the centre of the disk is

$$c(0, 0) = -qR_1 \int_0^\infty J_1(\lambda R_1) d\lambda/\lambda = -qR_1;$$  \hspace{1cm} (42)
the maximum concentration at the circumference is

\[ c(R_1, 0) = -q R_1 \int_0^\infty J_0(\lambda R_1) J_1(\lambda R_1) \, d\lambda / \lambda = -2q R_1 / \pi. \ldots \] (43)

The supersaturation number is

\[ \sigma = \frac{1}{2\pi} - \frac{1}{\pi^2} = 0.0579. \ldots \ldots \ldots \ldots \] (44)

This is less than the value of \( \sigma \) in table 2 for the tetrahedron, cube and octahedron. Comparing with \( n=2 \) in two dimensions one would expect the proper solids to have smaller supersaturation numbers than an improper one. This shows that we have to reduce these values of \( \sigma \) to a considerable extent. We think that it might be a good estimate to assume that \( \sigma \) is between 0.025 or 0.03 for cube and octahedron, and between 0.03 and 0.04 for the tetrahedron.

Table 2

<table>
<thead>
<tr>
<th>Solid</th>
<th>( R_1/d )</th>
<th>( R_2/d )</th>
<th>( R_1/R_2 )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Icosahedron</td>
<td>( \sqrt[4]{2(5+\sqrt{5})} )</td>
<td>( \sqrt[4]{3(1+\sqrt{5})} )</td>
<td>1.258</td>
<td>0.0205</td>
</tr>
<tr>
<td>Dodecahedron</td>
<td>( \sqrt{2} )</td>
<td>( \sqrt[6]{6} )</td>
<td>1.258</td>
<td>0.0205</td>
</tr>
<tr>
<td>Octahedron</td>
<td>( \sqrt{3} )</td>
<td>( \sqrt[6]{6} )</td>
<td>1.732</td>
<td>0.0587</td>
</tr>
<tr>
<td>Cube</td>
<td>( \sqrt[4]{6} )</td>
<td>( \sqrt[6]{6} )</td>
<td>2.000</td>
<td>0.0796</td>
</tr>
<tr>
<td>Tetrahedron</td>
<td>( \sqrt[4]{2(7+3\sqrt{5})/6} )</td>
<td>( \sqrt[4]{(5+22\sqrt{5})/5} )</td>
<td>1.732</td>
<td>0.0587</td>
</tr>
</tbody>
</table>

In three dimensions it is possible to relate the concentration difference \( \Delta_1 c \) between infinity and the surface of the crystal to the supersaturation \( \Delta c \) at the surface. If the concentration field were really that given by eqn. (39), and if \( \Delta_1 c \) were taken at the vertices of the solid, this relation would be

\[ \Delta c = 4\pi \sigma \Delta_1 c. \ldots \ldots \ldots \ldots \] (45)

In the case of the disk the corresponding relation is

\[ c = 0.571 \Delta_1 c, \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \] (46)

if \( \Delta_1 c \) is taken between the edge of the disk and infinity, and

\[ c = 0.364 \Delta_1 c, \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \] (47)

if \( \Delta_1 c \) is taken between the centre of the disk and infinity.

For the disk the numerical factor \( 4\pi \sigma \) in eqn. (45) would be 1.23 times the correct factor given by eqn. (46), so that both give the same order of magnitude. A rough estimate for a cube and a regular octahedron would be that under symmetrical conditions \( \Delta c \) is between 25\% and 40\% of \( \Delta_1 c \).
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