

The Growth of Crystals and the Equilibrium Structure of their Surfaces

W. K. Burton, N. Cabrera and F. C. Frank

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THE GROWTH OF CRYSTALS AND THE EQUILIBRIUM STRUCTURE OF THEIR SURFACES

BY W. K. BURTON*, N. CABRERA AND F. C. FRANK

H. H. Wills Physical Laboratory, University of Bristol

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Parts I and II deal with the theory of crystal growth, parts III and IV with the form (on the atomic scale) of a crystal surface in equilibrium with the vapour. In part I we calculate the rate of advance of monomolecular *steps* (i.e. the edges of incomplete monomolecular layers of the crystal) as a function of supersaturation in the vapour and the mean concentration of *kinks* in the steps. We show that in most cases of growth from the vapour the rate of advance of steps will be independent of their crystallographic orientation, so that a growing closed step will be circular. We also find the rate of advance for parallel sequences of steps, and the dependence of rate of advance upon the curvature of the step.

In part II we find the resulting rate of growth and the steepness of the growth cones or growth pyramids when the persistence of steps is due to the presence of dislocations. The cases in which several or many dislocations are involved are analysed in some detail; it is shown that they will commonly differ little from the case of a single dislocation. The rate of growth of a surface containing dislocations is shown to be proportional to the square of the supersaturation for low values and to the first power for high values of the latter. Volmer & Schultze's (1931) observations on the rate of growth of iodine crystals from the vapour can be explained in this way. The application of the same ideas to growth of crystals from solution is briefly discussed.

Part III deals with the equilibrium structure of steps, especially the statistics of kinks in steps, as dependent on temperature, binding energy parameters, and crystallographic orientation. The shape and size of a two-dimensional nucleus (i.e. an 'island' of new monolayer of crystal on a completed layer) in unstable equilibrium with a given supersaturation at a given temperature is obtained, whence a corrected activation energy for two-dimensional nucleation is evaluated. At moderately low supersaturations this is so large that a *perfect* crystal would have no observable growth rate. For a crystal face containing two screw dislocations of opposite sense, joined by a step, the activation energy is still very large when their distance apart is less than the diameter of the corresponding critical nucleus; but for any greater separation it is zero.

Part IV treats as a 'co-operative phenomenon' the temperature dependence of the structure of the surface of a perfect crystal, free from steps at absolute zero. It is shown that such a surface remains practically flat (save for single adsorbed molecules and vacant surface sites) until a transition temperature is reached, at which the roughness of the surface increases very rapidly ('*surface melting*'). Assuming that the molecules in the surface are all in one or other of two levels, the results of Onsager (1944) for two-dimensional ferromagnets can be applied with little change. The transition temperature is of the order of, or higher than, the melting-point for crystal faces with nearest neighbour interactions in both directions (e.g. (100) faces of simple cubic or (111) or (100) faces of face-centred cubic crystals). When the interactions are of second nearest neighbour type in one direction (e.g. (110) faces of s.c. or f.c.c. crystals), the transition temperature is lower and corresponds to a surface melting of second nearest neighbour bonds. The error introduced by the assumed restriction to two available levels is investigated by a generalization of Bethe's method (1935) to larger numbers of levels. This method gives an anomalous result for the two-level problem. The calculated transition temperature decreases substantially on going from two to three levels, but remains practically the same for larger numbers.

Note on authorship. Although at all times a constant interchange of ideas took place between all three authors, the principal contributions of one of us (F.C.F.) are to part II of this paper. Part IV, and all the calculations in parts I and III, are due exclusively to W.K.B. and N.C.

A THEORY OF GROWTH OF REAL CRYSTALS

PART I. MOVEMENT OF STEPS ON A CRYSTAL SURFACE

1. *Introduction*

The theory of growth of perfect crystals has been developed extensively during the past thirty years, especially by the work of Volmer (1939), Stranski (1928, 1934), and Becker & Döring (1935). The essential ideas were put forward earlier by Gibbs (1878).

According to this theory, when all surfaces of high index (stepped surfaces) have disappeared, the crystal will continue to grow by two-dimensional nucleation of new molecular layers on the surfaces of low index (saturated surfaces). As in all nucleation processes, the probability for the formation of these two-dimensional nuclei is a very sensitive function of the supersaturation. This probability is quite negligible below a certain critical supersaturation and increases very rapidly above it. Assuming reasonable values for the edge energy of the two-dimensional nuclei, one recognizes that this critical supersaturation should be of the order of 50 %. At the supersaturations at which real crystals grow (1 % and even lower) the probability of formation of nuclei should be, according to this theory, absolutely negligible (Burton, Cabrera & Frank 1949; Burton & Cabrera 1949, cf. also part III).

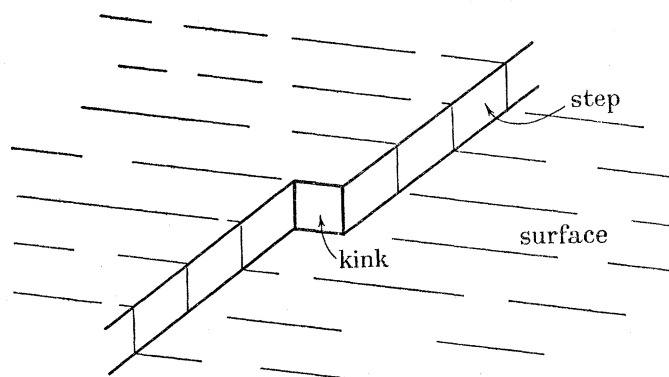


FIGURE 1. The presence of a kink in a step on a crystal surface.

Recently, Frenkel (1945) pointed out that the structure of a perfect crystal surface above the absolute zero of temperature would have a certain roughness produced by thermal fluctuations. He discussed the structure of a monomolecular *step* and proved that it will contain a high concentration of *kinks*, illustrated in figure 1, and introduced before by Kossel (1927) and Stranski (1928). Burton & Cabrera (1949, cf. also part III) have shown that the concentration of *kinks* is even larger than was supposed by Frenkel; this result is very important from the point of view of the rate of advance of the steps, which will be developed in part I of this paper. On the other hand, Frenkel generalized this idea to the formation of steps in a perfect crystal surface, but Burton & Cabrera (1949, cf. also part IV) have shown that steps will not be created by thermodynamical fluctuations in a low-index crystal surface, unless, perhaps, close to the melting-point; therefore the steps required for growth can only be produced, on a perfect crystal surface, under a highly supersaturated environment.

We conclude that the growth of crystals under low supersaturations can only be explained by recognizing that the crystals which grow are *not* perfect, and that their imperfections (in particular, dislocations terminating in the surface with a screw component) will provide the steps required for growth, making two-dimensional nucleation unnecessary. This idea, introduced by Frank (Burton *et al.* 1949; Frank 1949) will be developed in this paper, and we shall see that it explains most of the features of crystal growth at low supersaturations.

This theory of growth of real crystals assumes the existence of dislocations in them, but does not depend critically on their concentration. The study of crystal growth should perhaps also explain the formation of dislocations which, as in the case of steps in a crystal surface, cannot be due to thermodynamical fluctuations. Several mechanisms can be visualized for

the formation of new dislocations during growth (Frank 1949), but no detailed theory has yet been formulated.

2. *Mobility of adsorbed molecules on a crystal surface*

We know that in general a crystal surface in contact with its vapour will contain a certain concentration n_s per cm^2 of adsorbed, essentially mobile molecules. Under equilibrium conditions, the concentration n_{s0} of adsorbed molecules will be given by a formula of the type

$$n_{s0} = n_0 \exp(-W_s/kT), \quad (1)$$

where W_s is the energy of evaporation from the kinks on to the surface; n_0 contains entropy factors, but in simple cases will be of the order of the number per cm^2 of molecular positions on the surface.

The process of growth of a crystal surface *with* steps will be the result of three separate processes: (i) exchange of molecules between adsorbed layer and vapour, (ii) diffusion of adsorbed molecules towards the steps and exchange with them, and (iii) perhaps also diffusion of adsorbed molecules in the edge of the steps toward the kinks and exchange with them.

In order to discuss the role of the diffusion on the surface we must introduce the *mean displacement* x_s of adsorbed molecules. This can be defined in quite general terms by Einstein's formula:

$$x_s^2 = D_s \tau_s, \quad (2)$$

where D_s is the diffusion coefficient and τ_s the mean life of an adsorbed molecule before being evaporated again into the vapour. For simple molecules we can write

$$D_s = a^2 \nu' \exp(-U_s/kT), \quad (3)$$

and
$$1/\tau_s = \nu \exp(-W'_s/kT), \quad (4)$$

where U_s is the activation energy between two neighbouring equilibrium positions on the surface, distant a from each other, and W'_s the evaporation energy from the surface to the vapour. The frequency factors ν' and ν would both be of the order of the atomic frequency of vibration ($\nu \sim 10^{13} \text{sec}^{-1}$) in the case of monatomic substances, but they will be different in the case of more complicated molecules. Using (3) and (4), (2) becomes

$$x_s = a \exp\{(W'_s - U_s)/2kT\}, \quad (5)$$

assuming $\nu' \sim \nu$. The condition for the diffusion on the surface to play an important role is that $x_s > a$, and therefore from (5), $W'_s > U_s$. This is probably always the case; then x_s can be much larger than a and increases rapidly as the temperature decreases.

In order to have an idea of the values that we can expect for x_s , let us consider, for instance, a (1, 1, 1) close-packed surface of a face-centred cubic crystal. By simple considerations regarding the interaction ϕ between nearest neighbours only, $W'_s = 3\phi$, i.e. half the total evaporation energy $W = W_s + W'_s$; while $U_s \sim \phi = \frac{1}{8}W$. However, fuller calculations carried out by Mackenzie (1950) using Lennard-Jones forces show that U_s is considerably smaller, about $\frac{1}{20}W$. Hence, in this case, (5) becomes

$$x_s \sim a \exp(3\phi/2kT) \sim 4 \times 10^2 a \quad (6)$$

for the typical value $\phi/kT \sim 4$.

It is interesting to notice that x_s will be a function of the crystal face considered, both W'_s and U_s being different for different faces. In general, x_s will be smallest for the closest packed surface, because W'_s increases more rapidly than U_s . For instance, for a (1, 0, 0) surface in a face-centred cubic (f.c.c.) crystal assuming nearest neighbour forces, $W'_s = 4\phi$ and U_s is probably still very small. Then

$$x_s \sim a \exp(2\phi/kT) \sim 3 \times 10^3 a.$$

3. Concentration of kinks in a step

Frenkel (1945) and Burton & Cabrera (1949, cf. also part III) have shown that these steps must always contain a large concentration of kinks. In the case of short-range intermolecular forces, we can briefly summarize in the following manner the results of the theory which have an important bearing on growth.

Let a close-packed crystallographic direction be taken as the x -axis, and consider a step which follows this axis in the mean, so that the surface is one molecule higher in the region $y \ll 0$ than in the region $y \gg 0$. Following the step along the direction of increasing x , points where y increases or decreases by a unit spacing a are called positive or negative kinks respectively. For this orientation, the step contains equal numbers of positive and negative kinks, and their total number is less than for any other orientation. Let $2n$ and q be the probabilities for having a kink or no kink, respectively, at a given site in the step. Then we must have

$$n/q = \exp(-w/kT), \quad 2n + q = 1,$$

where w is the energy necessary to form a kink. Hence the mean distance $x_0 = a/2n$ between kinks is

$$x_0 = \frac{1}{2}a\{\exp(w/kT) + 2\} \sim \frac{1}{2}a \exp(w/kT), \quad (7)$$

where a is the intermolecular distance in the direction of the step.

As the inclination θ of the step relative to a close-packed direction increases, the number of kinks increases. Let n_+ and n_- be the probabilities for having a positive or negative kink respectively.

As an approximation, we neglect the difference between q and unity. Then

$$2n = n_+ + n_-, \quad \theta = n_+ - n_-,$$

where n is the probability for having a kink of any kind and θ is assumed to be small. For any inclination, and from thermodynamical considerations,

$$n_+ n_- = \exp(-2w/kT).$$

Thus the mean distance $x_0(\theta)$ between kinks will now be

$$x_0(\theta) = x_0\{1 - \frac{1}{2}(x_0/a)^2 \theta^2\}, \quad (8)$$

assuming $\theta < a/x_0$ and x_0 is given by (7).

No detailed calculation of w has yet been made, but simple considerations suggest that w must be a small fraction of the evaporation energy. For instance, in a close-packed step in a (1, 1, 1) face of a f.c.c. crystal, with nearest neighbour interactions ϕ , it is easy to see that w is equal to a quarter of the energy necessary to move one molecule from a position in the

straight step to an adsorption position against the straight step, equal to 2ϕ ; hence $w = \frac{1}{2}\phi$ or $\frac{1}{12}W$, and the mean distance between kinks is, from (7),

$$x_0 = \frac{1}{2}a \exp(\phi/2kT) \sim 4a, \quad (9)$$

for the typical value $\phi/kT \sim 4$.

The concentration of kinks in the steps will remain practically unchanged even if the vapour is supersaturated. Hence the problem of the rate of advance of a step is reduced to a classical diffusion problem on the surface. The important ratio in this calculation is x_s/x_0 . From (5) and (7) this is approximately $2 \exp\{(\frac{1}{2}W'_s - \frac{1}{2}U_s - w)/kT\}$. With the estimates of W'_s , U_s and w which we have made above on the basis of the simple model of a close-packed homopolar crystal, this is about 10^2 . Thus it appears that we may generally assume $x_s \gg x_0$, in which case we can perform the diffusion calculation regarding the step as a continuous-line sink. It is an interesting corollary of this case that the rate of advance of a step is then independent of its crystallographic orientation. However, the estimate is uncertain for various reasons, such as the neglect of entropy factors, and we shall also examine the cases in which x_0 is comparable with or larger than x_s .

4. Rate of advance of a step

The supersaturation σ in the vapour is defined as

$$\sigma = \alpha - 1, \quad \alpha = p/p_0, \quad (10)$$

where p is the actual vapour pressure, p_0 the saturation value, and α will be called the saturation ratio. We assume σ to be constant above the surface. There will also be a supersaturation σ_s of adsorbed molecules on the surface (in general, dependent on position) defined by

$$\sigma_s = \alpha_s - 1, \quad \alpha_s = n_s/n_{s0}, \quad (11)$$

where n_s and n_{s0} are the actual and equilibrium concentration of adsorbed molecules respectively.

The equations governing the diffusion of adsorbed molecules towards the step are easily written down. The current on the surface will be

$$j_s = -D_s \text{grad } n_s = D_s n_{s0} \text{grad } \psi, \quad \psi = \sigma - \sigma_s, \quad (12)$$

where D_s is the diffusion coefficient of adsorbed molecules. There will also be a current j_v going from the vapour to the surface, which is easily seen to be

$$j_v = (\alpha - \alpha_s) n_{s0} / \tau_s = n_{s0} \psi / \tau_s, \quad (13)$$

where τ_s is the *mean life* of an adsorbed molecule on the surface, defined in §2.

Let us make the assumption (to be justified *a posteriori*) that the movement of the step can be neglected in the diffusion problem, so that the adsorbed molecules have a steady distribution on either side of the step which is practically the same as though the step were absorbing molecules without moving. Under these conditions ψ must satisfy the continuity equation

$$\text{div } j_s = j_v,$$

or using (6) and (7) and assuming D_s independent of direction in the surface

$$x_s^2 \nabla^2 \psi = \psi, \quad (14)$$

where x_s is the *mean displacement* of adsorbed molecules, defined in §2.

Now if we compare the typical values for x_s and x_0 estimated in (6) and (9) respectively, we see that in most cases, certainly for monatomic substances, $x_s \gg x_0$. Under these conditions, each molecule deposited from the vapour on the surface near the step will have a high probability to reach a kink in the step before being evaporated again into the vapour. Therefore the concentration of adsorbed molecules near the step will be controlled by evaporation from and condensation into the kinks. Then, provided this exchange is very rapid, the concentration near the step should be maintained equal to the equilibrium value, independently of the supersaturation existing in the vapour.

Thus, if we assume that $\sigma_s = 0$ near the step, and $\sigma_s = \sigma$ far from it, equation (14) has the simple solution

$$\psi = \sigma \exp(\mp y/x_s), \quad (15)$$

where y is the distance to the step, the minus sign being used for $y > 0$ and the plus sign for $y < 0$. Now the current j going into the step per cm. per sec. will be obtained from (12) using (15) and putting $y = 0$. The velocity of the step is then $v_\infty = j/n_0$, where $1/n_0$ is the area per molecular position; therefore

$$v_\infty = 2\sigma x_s \nu \exp(-W/kT), \quad (16)$$

where expressions (1) and (4) for n_{s0} and τ_s have been used, and $W = W_s + W'_s$ is the total evaporation energy. The factor 2 comes about because of the contribution from $y > 0$ and $y < 0$. The advance of the step is therefore owing to the molecules condensing from the vapour on a strip of width x_s at both sides of the step. This expression represents the maximum velocity of a step in a given direction, and if D_s and therefore x_s were independent of direction, then the velocity of the step would be independent of its orientation.

We can now justify our neglect of the motion of the step when treating the diffusion problem. This is permissible if the characteristic distance (D_s/v_∞) is great compared with the characteristic distance x_s . Now, from (3), (5) and (16),

$$v_\infty x_s / D_s = 2\sigma \exp(-W_s/kT) \sim 2\sigma \exp(-12) \ll 1.$$

We believe that (16) is correct, at least in the case of monatomic substances. In the case of molecular substances we must introduce two possible complications: (i) as Wyllie (1949) has pointed out the exchange between the kinks and the adsorbed layer might not be rapid enough to maintain $\sigma_s = 0$ near the kinks; (ii) the condition $x_s \gg x_0$ is perhaps not satisfied.

It is easy to see that (i) introduces a supplementary factor $\beta < 1$ in formula (16) given by

$$\beta = (1 + x_s \tau / a \tau_s)^{-1}, \quad (17)$$

where τ is the time of relaxation necessary to re-establish equilibrium near the step. The supersaturation near the step will then be $\sigma_s(0) = (1 - \beta)\sigma$; β will be smaller than 1, for instance, when the rotational entropy of the adsorbed molecules is much larger than that of the molecules in the solid. If condition $x_s \gg x_0$ is nevertheless satisfied, then v_∞ should still be independent of the orientation of the step.

On the other hand, if $x_s \gg x_0$ is not satisfied, the supersaturation near the step will not be constant, and will be a function of x_0 . The other extreme case, when $x_0 \gg x_s$, is easy to consider. It is then necessary to discuss the influence of the diffusion of adsorbed molecules in the edge of the step. If the contribution of the current via the edge is important, then this will help

to keep the supersaturation constant near the step, even if $x_0 \gg x_s$. The most unfavourable case would be when the current via the edge can be neglected altogether. Then, assuming D_s to be independent of direction, the required solution of (14), around an isolated kink on the step, is

$$\psi(r) = \beta\sigma \frac{K_0(r/x_s)}{K_0(a/x_s)},$$

where K_0 is the Bessel function of second kind with imaginary argument and order zero, and we assume that the supersaturation of adsorbed molecules is maintained equal to $(1-\beta)\sigma$ at a distance $r = a$ from the kink. The current going into every step is then easily calculated and the velocity of advance of the step is given by

$$v_\infty = \{2\sigma\beta x_s v \exp(-W/kT)\} \pi x_s/x_0 \ln(2x_s/\gamma a),$$

where we assume always $x_s > a$ and we use the approximate formulae

$$K_0(a/x_s) = \ln(2x_s/\gamma a), \quad K_1(a/x_s) = -x_s/a,$$

$\gamma = 1.78$ being Euler's constant. We may verify once again that, at least for sufficiently small supersaturations, we may neglect the motion of the kink in treating the corresponding diffusion problem. The criterion this time is $(v_{\text{kink}} x_s/D_s) \ll 1$, where $v_{\text{kink}} = v_\infty x_0/a$. Now by use of (3) and (5)

$$v_{\text{kink}} x_s/D_s = [2\pi\beta\sigma \exp\{-(W + \frac{1}{2}U_s - \frac{3}{2}W'_s)/kT\}] / \{\ln(2/\gamma) + (W'_s - U_s)/kT\}.$$

The exponential factor here remains considerably less than unity for any reasonable estimate of the energies, especially as the condition $x_0 > x_s$ is only likely to arise when U_s is unusually large or W'_s unusually small, though U_s can scarcely exceed W'_s so as to make the denominator small.

We see that apart from the factor β , the maximum velocity (16) is multiplied by another factor $c_0 < 1$, given by

$$c_0 = \pi x_s/x_0 \ln(2x_s/\gamma a). \quad (18)$$

In the general case, the velocity of advance of the step can also be represented by the general formula

$$v_\infty = 2\sigma x_s v \exp(-W/kT) \beta c_0, \quad (19)$$

where c_0 is between 1 and the value given by equation (18).

The calculation of c_0 in the general case is a difficult problem. The easiest way to solve it is to assume that *there is* a diffusion in the edge of the step and that it is important enough for the current going directly from the surface to the kinks to be neglected. In appendix A we treat along these lines the problem of a single step with equally spaced kinks.

The relative importance of the current diffusing in the edge of the step and that diffusing on the surface will be represented by the non-dimensional factor

$$D_e n_{e0}/D_s n_{s0} a,$$

where D_e and n_{e0} are the diffusion coefficient and the equilibrium concentration respectively of adsorbed molecules in the edge. This factor is equal to $(x_e/a)^2$, where x_e is the mean displacement of adsorbed molecules in the edge. Actually $x_e^2 = D_e \tau_e$, and by definition

$$\tau_e = n_{e0} a/D_s n_{s0} = (1/v) \exp\{(W'_e + U_s)/kT\};$$

therefore

$$x_e^2 = D_e n_{e0} a/D_s n_{s0} \sim a^2 \exp\{(W'_e + U_s - U_e)/kT\}, \quad (20)$$

where W'_e is the energy necessary to take an adsorbed molecule from the edge to the surface and U_e is the activation energy for diffusion in the edge.

It is clear that $D_s > D_e$; on the other hand, $n_{s0}a < n_{e0}$. If $x_e > a$, the current going into the kinks goes essentially via the edge and the point of view adopted above is justified. If, on the contrary, $x_e < a$, the important contribution is that due to direct condensation from the surface into the kinks. The case $x_e \sim a$ can also be interpreted as if the edge did not exist at all, since this would correspond to $W'_e = 0$, $U_e = U_s$, which implies also $x_e = a$. Hence the method of calculation suggested above should give for $x_e \sim a$ the same result as if the influence of diffusion in the edge were neglected altogether.

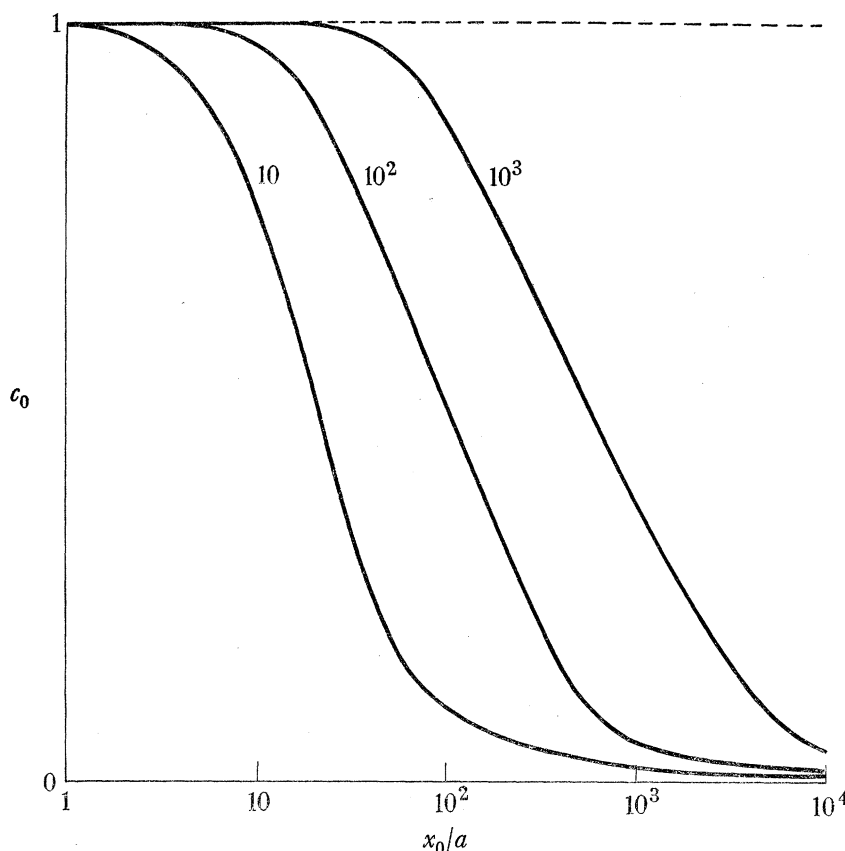


FIGURE 2. The factor c_0 as a function of x_0/a for the values of x_s/a indicated on the curves.

It is difficult in general to estimate x_e . In the particular case of a close-packed step in a (1, 1, 1) face of a f.c.c. crystal, with nearest neighbour interactions ϕ , we can estimate $W'_e = 2\phi$, $U_s \sim 0$, $U_e \sim 2\phi$, hence $x_e \sim a$. Assuming this to be the case, the general formula given in appendix A reduces to

$$1/c_0 = 1 + 2b \ln \left\{ (4bx_s/a) / (1 + (1 + b^2)^{1/2}) \right\}, \quad b = x_0/2\pi x_s, \quad (21)$$

which is represented in figure 2 as a function of x_0/a for several values of x_s/a . It is interesting to notice that if x_0 increases indefinitely in (21), then

$$c_0 = \pi x_s/x_0 \ln(4x_s/a),$$

which practically coincides with (18) as we should expect. We notice that c_0 differs appreciably from unity for $x_0 \geq x_s$.

In conclusion to this paragraph, and from the estimates of x_s and x_0 made in §§ 2 and 3, we deduce that in most cases of growth from the vapour *the rate of advance of the step must be practically independent of its orientation*. In some cases, perhaps, the factor c_0 in (19) could be smaller than 1 for the close-packed slowest steps, containing a minimum number of kinks. As the orientation of the step deviates from that of closest packing, c_0 will become rapidly equal to 1.

5. *Parallel sequence of steps*

Another interesting problem is that of the movement of a parallel sequence of steps separated by equal distances y_0 .

If we assume that the distance x_0 between kinks in every step satisfies the condition $x_0 \ll x_s$, and that near every step $\sigma_s = 0$, the solution of equation (14) is easily seen to be

$$\psi = \sigma \frac{\cosh(y/x_s)}{\cosh(y_0/2x_s)} \quad (22)$$

between two steps, where y is the distance from the mid-point between two steps. The current going into every step is again calculated from (12), using (22) and putting $y = \frac{1}{2}y_0$; the velocity of every step is then

$$v_\infty = 2\sigma x_s \nu \exp(-W/kT) \tanh(y_0/2x_s), \quad (23)$$

which reduces to (16) if $y_0 \rightarrow \infty$.

In the general case where (i) the interchange with the kinks is not rapid enough to maintain $\sigma_s = 0$ near the step and (ii) the condition $x_0 \ll x_s$ is not satisfied, we obtain again a general formula of the type

$$v_\infty = 2\sigma x_s \nu \exp(-W/kT) \tanh(y_0/2x_s) \beta c_0, \quad (24)$$

where $c_0 \leq 1$ is a function of x_0 and y_0 . The calculation of c_0 is now rather complicated.

In the particular case when $x_e \sim a$ in the edge of the steps, one can give for c_0 the approximated expression

$$\begin{aligned} 1/c_0 &= 1 + 2b \tanh(y_0/x_s) [\ln \{(4bx_s/a)/(1 + (1 + b^2)^{\frac{1}{2}})\} + (2x_s/y_0) \tan^{-1} b], \\ b &= x_0/2\pi x_s. \end{aligned} \quad (25)$$

For $y_0 \rightarrow \infty$ this expression reduces of course to (21). As y_0 decreases, c_0 in general will be nearer 1 than (21) is, as we should expect, but this does not mean that for a sufficiently small value of y_0 we shall get $c_0 = 1$, because of the second term in the parentheses in (25).

6. *The rate of advance of small closed step-lines*

We know that, given a certain supersaturation in the vapour, there will be a certain two-dimensional nucleus which is in unstable equilibrium with it. The shape and size of this *critical* nucleus are perfectly defined; its shape has been studied in detail in one special case, Burton *et al.* 1949; cf. also part III. It is interesting to notice at this point that the number of kinks per unit length in every position of the edge of the critical nucleus is the same as that in an infinite step having the same orientation.

If the nucleus is larger than the critical one it will grow. Then its shape will be determined essentially by the differences in velocity for the different orientations and *not* by thermo-

dynamical considerations. In particular, if the velocity is the same for all orientations, it will become circular. The study of the shape of a growing nucleus of large dimensions will be considered in detail by one of us (F. C. F.) in a later paper; here we are concerned with the absolute value of the velocity when the dimensions are not very different from those of the critical nucleus.

Let us consider first the case of independence of velocity on orientation, when the nucleus is circular. We shall consider afterwards what changes can be expected when the velocity depends on the orientation.

The mean evaporation from the nucleus to the surface will be a function of its dimensions. If its radius is ρ , and we define an edge energy of the nucleus equal to γ per molecule, the mean energy of evaporation will be

$$W_s(\rho) = W_s - (\gamma a/\rho),$$

where a is as usual the intermolecular distance.

Let σ be the supersaturation in the vapour; the nucleus will grow, but at every moment a steady distribution of adsorbed molecules will be formed provided the nucleus is not too small. The influence of the movement of the boundary on the diffusion problem can be neglected for the low supersaturations considered. The steady supersaturation in the surface will satisfy the continuity equation (14) which now becomes

$$x_s^2 \nabla^2 \psi(r) = \psi(r), \quad \psi(r) = \sigma - \sigma_s(r). \quad (26)$$

The solution of this equation is

$$\begin{aligned} \psi(r) &= \psi(\rho) \frac{I_0(r/x_s)}{I_0(\rho/x_s)} \quad (r < \rho), \\ \psi(r) &= \psi(\rho) \frac{K_0(r/x_s)}{K_0(\rho/x_s)} \quad (r > \rho), \end{aligned} \quad (27)$$

where I_0 and K_0 are the Bessel functions of first and second kind with imaginary argument. $\psi(\rho)$ is the value of ψ near the edge of the nucleus. If the interchange of molecules between the nucleus and the surface is rapid enough, the supersaturation $\sigma_s(\rho)$ near the edge of the nucleus will be maintained equal to that which would be in equilibrium with it. This supersaturation $\sigma_s(\rho)$ is given by

$$\sigma_s(\rho) = \frac{\exp[-W_s(\rho)/kT]}{\exp[-W_s/kT]} - 1 = \exp(\gamma a/\rho kT) - 1;$$

therefore
$$\psi(\rho) = \sigma - \sigma_s(\rho) = \sigma - [\exp(\gamma a/\rho kT) - 1]. \quad (28)$$

The current going into the nucleus is now

$$j = 2\pi\rho D_s n_{s0} (\partial\psi/\partial r)_{r=\rho} = 2\pi D_s n_{s0} \psi(\rho) / I_0(\rho/x_s) K_0(\rho/x_s),$$

where the formulae

$$I_0'(z) = I_1(z), \quad K_0'(z) = -K_1(z), \quad I_0(z) K_1(z) + I_1(z) K_0(z) = 1/z$$

have been used. The radial velocity, $v(\rho) = j(\rho)/2\pi\rho n_0$, is therefore

$$v(\rho) = x_s^2 v \exp(-W/kT) \psi(\rho) / \rho I_0(\rho/x_s) K_0(\rho/x_s), \quad (29)$$

where we have used the expressions for x_s , τ_s and n_{s0} , given by (2), (4) and (1). Current and velocity change sign when $\sigma_s(\rho_c) = \sigma$, which defines the critical nucleus to have a radius ρ_c given by

$$\rho_c = \gamma a / kT \ln \alpha, \quad \alpha = 1 + \sigma. \quad (30)$$

When $\rho > x_s$ we can use the approximation

$$I_0(\rho/x_s) K_0(\rho/x_s) = x_s/2\rho,$$

so that (29) becomes

$$v(\rho) = v_\infty(\alpha - \alpha^{\rho_c/\rho})/\sigma, \quad \alpha = 1 + \sigma, \quad (31)$$

or if σ is small,

$$v(\rho) = v_\infty(1 - \rho_c/\rho), \quad (32)$$

where v_∞ is the maximum velocity (16) of a straight step of any orientation, calculated in § 4. This formula will be valid down to $\rho = \rho_c$, provided the supersaturation is low enough for ρ_c to be larger than x_s , and $\ln \alpha \sim \sigma$. As σ increases and ρ_c decreases, $v(\rho)$ will be a more complicated function for $\rho \sim \rho_c$.

It is also interesting to consider the rate of advance of a sequence of concentric circles, distant y_0 from each other. The diffusion problem can also be solved in a similar way. The radial velocity of the circle of radius ρ turns out to be

$$v(\rho) = 2\sigma x_s v \exp(-W/kT) \tanh(y_0/2x_s) (1 - \rho_c/\rho), \quad (33)$$

when $\rho > x_s$, $y_0 \ll \rho$ and $\ln \alpha \sim \sigma$. We see that $v(\rho)$ is again of the general form (32), if v_∞ means now the velocity (23) corresponding to a sequence of parallel steps. We see therefore that the only change in the rate of advance of a large closed step of radius ρ , with respect to that of an infinite step is the factor $(1 - \rho_c/\rho)$. This is just what we should expect because the mean supersaturation near the edge of the nucleus is not zero, as in the case of the straight step, but $\sigma\rho_c/\rho$.

The same general formula (32) will apply also when (i) the interchange of molecules between nucleus and surface is not rapid, and (ii) the velocity depends on the orientation of the edge. Then the nucleus will not be a circle, but the close-packed slowest orientations of the edge will move according to (32) where v_∞ is now given by the general formula (24); ρ will be the normal distance from the edge to the centre of the nucleus and ρ_c that corresponding to the critical nucleus.

PART II. RATES OF GROWTH OF A CRYSTAL SURFACE

7. Introduction

In part I we have studied the movement of steps on a perfect crystal surface, without considering their origin. This information is sufficient to calculate the rates of growth of stepped surfaces (those of high index) where the steps exist because of the geometry of the surface; nevertheless, it is clear that these steps will disappear in any finite crystal, after a finite amount of growth which completes the body bounded by close-packed, unstepped surfaces circumscribed to the initial crystal.

Frank (1949) has shown that further growth of these surfaces must be attributed to the presence of steps associated with crystal defects, in particular dislocations having a component of displacement vector normal to the crystal face at which they emerge, 'screw dislocations'

for short, though they are not necessarily 'pure screw' dislocations. He has also shown that when the crystal is growing under a supersaturated environment, the step due to a dislocation winds itself in a spiral in such a way that a single screw dislocation sends out successive turns of steps (figure 3). If the step is due to a right- and left-handed pair of dislocations, they will send out closed loops (figure 4) provided their distance apart is greater than the diameter of a critical nucleus. In both cases the dislocations will form pyramids and the concentration of step lines thereon will be large and practically independent of the number of dislocations. This provides an interpretation of the pyramids of vicinal faces long recognized as a normal

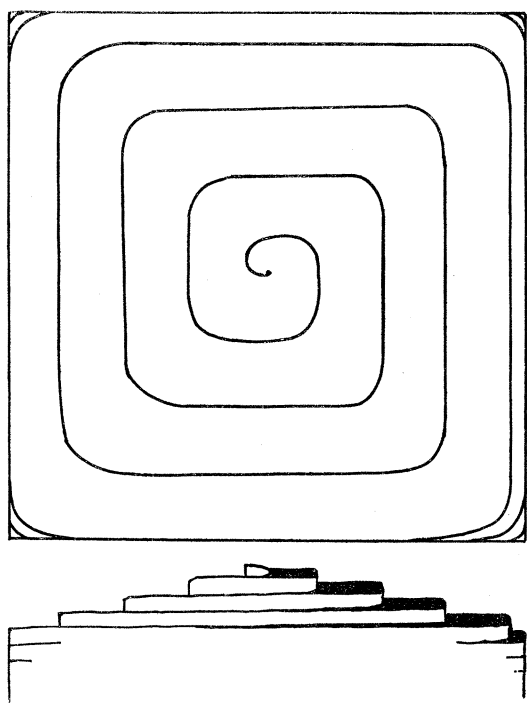


FIGURE 3. Growth pyramid due to a single screw dislocation.

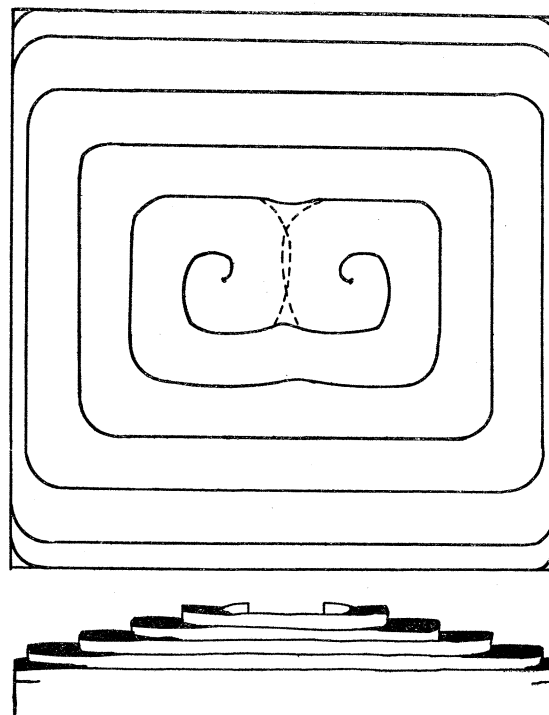


FIGURE 4. Growth pyramid due to a pair of dislocations.

feature of slow crystal growth (Miers 1903, 1904). In this part we shall study in more detail the mathematics of these pyramids (§§ 8, 9); once the rate at which these pyramids grow is known we shall apply the results to growth from the vapour using the formulae for rate of advance of steps deduced in I (§§ 10, 11). The application of the same ideas to growth from solution will also be considered briefly in § 12. The resulting topography of the crystal surface will be discussed by one of us in a later paper.

8. *The growth pyramid due to a single dislocation*

Let us first consider the spiral due to a single dislocation ending on an otherwise perfect crystal surface. We may suppose that, as new layers are added, the direction of the dislocation remains perpendicular to the surface, since this will usually minimize the elastic energy. If the rate of advance of a step is independent of its orientation (probably the case during growth from the vapour, see I) the growing spiral will form a low cone, but it will tend to form a pyramid when the rate of advance depends on the orientation (as is illustrated in figures 3 and 4). We consider first the case of a growing cone.

Following any increase in supersaturation, the step due to the dislocation will rapidly wind itself up into a spiral centred on the dislocation, until the curvature at the centre reaches the critical value $1/\rho_c$, at which curvature the rate of advance falls to zero; the whole spiral will then rotate steadily with stationary shape.

We know (I, formula (32)) that the normal rate of advance of a portion of spiral with radius of curvature ρ is given by

$$v(\rho) = v_\infty(1 - \rho_c/\rho), \quad (34)$$

provided the supersaturation is not too high. Now let $\theta(r)$ represent the rotating spiral, in (rotating) polar co-ordinates (r, θ) . The radius of curvature at a point r will be

$$\rho = (1 + r^2\theta'^2)^{\frac{1}{2}} / (2\theta' + r^2\theta'^3 + r\theta''), \quad (35)$$

θ' and θ'' being the derivatives of $\theta(r)$. If the angular velocity of the whole spiral is ω , the normal velocity at the point r is

$$v(r) = \omega r(1 + r^2\theta'^2)^{-\frac{1}{2}}. \quad (36)$$

We must now find $\theta(r)$ and ω from these three equations.

A good approximation is obtained by taking an Archimedean spiral

$$r = 2\rho_c\theta > 0, \quad (37)$$

which has the proper central curvature. ω is then given by

$$\omega = v_\infty/2\rho_c. \quad (38)$$

This approximation does not satisfy (34), especially for small r , but nevertheless gives a good approximation to ω .

A better approximation can be obtained in the following way: one obtains the solutions for small r (neglecting r^2) and for large r (neglecting $1/r^2$):

$$r \rightarrow 0: \quad \theta' = 1/2\rho_c - \omega r/3v_\infty\rho_c, \quad (39)$$

$$r \rightarrow \infty: \quad \theta' = (\omega/v_\infty)(1 + \rho_c/r). \quad (40)$$

Then, choosing a general expression of the form

$$\theta' = a + b/(1 + cr), \quad (41)$$

one determines, a , b , c and ω in such a way that (41) reduces to (39) and (40) for the proper ranges of r . We obtain in this way

$$\left. \begin{aligned} \theta &= \frac{3^{\frac{1}{2}}}{2(1+3^{\frac{1}{2}})} [r/\rho_c + \ln(1+r/3^{\frac{1}{2}}\rho_c)], \\ \omega &= 3^{\frac{1}{2}}v_\infty/2\rho_c(1+3^{\frac{1}{2}}) = 0.63v_\infty/2\rho_c. \end{aligned} \right\} \quad (42)$$

This solution satisfies (34) within a few units per cent of v_∞ for all values of ρ . The interesting point is that the value of ω obtained differs from (38) only by a factor close to 1, showing that ω is insensitive to the actual law of dependence of v on ρ in the range in which $\rho \sim \rho_c$. Even the crudest approximation to (34),

$$\rho = \rho_c: \quad v = 0; \quad \rho > \rho_c: \quad v = v_\infty,$$

(Frank 1949) gives an angular velocity only twice as large as (38), i.e. just over three times the best approximation (42).

In the rest of this part, the number of turns of the spiral per second, $\omega/2\pi$, will be called the *activity*. The actual rate of vertical growth R of the pyramid and therefore of the crystal will clearly be

$$R = \omega a/2\pi = n_0 \Omega v_\infty / 4\pi \rho_c, \quad (43)$$

where $a = n_0 \Omega$ is the height of a step (n_0 the number of molecular positions per cm.² in the surface, Ω the volume of a molecule), and we have used the approximation (38) for ω .

The distance y_0 between successive turns of the spiral for large r is given by

$$y_0 = 2\pi/\theta' = 4\pi\rho_c. \quad (44)$$

These formulae will also be approximately valid when there is an influence of the crystallographic orientation on the rate of advance of the steps. v_∞ is then the value corresponding to the slowest advancing orientation, and ρ_c half the dimension of the critical two-dimensional nucleus.

9. *The growth pyramids due to groups of dislocations*

9.1. *Topological considerations*

We now consider the interactions between the growth spirals centred on different dislocations. We have already considered the case of a pair of opposite sign, and seen that if they are closer together than a critical distance ($2\rho_c$ in the simple case) no growth occurs, while if they are further apart than this they send out successive closed loops of steps. It is obvious that if there are *two such pairs* these loops unite on meeting, and the number of steps passing any distant point in a given time is the same as if only one pair existed. The whole area may be formally divided into two areas by a locus of intersections of the two families, and one area may be considered to receive steps from the one centre, the other from the other centre.

Hence two similar pairs of dislocations of opposite sign, separated by a distance large compared with the separation in the pairs, have the same activity as one pair alone. Unless the separation between pairs is a visible distance, there will be no macroscopic distinction from the case of one pair.

If the two families of loops are circles growing at the same rate the locus of intersections is a hyperbola in the general case, and in the symmetrical case a straight line bisecting the line of centres. Consideration of the locus of intersections, though trivial in the present case, is useful for the treatment of more complex cases later. The conclusion remains valid if the loops are not circles, but, on account of dependence of growth rate on crystallographic orientation, are deformed into polygons. The same point applies in cases treated later.

We chose to start with the case of two opposed pairs as the simplest, since it can be topologically analyzed in terms of the locus of intersections of growing circles. When we consider *two simple dislocations*, instead of pairs, we have to consider the locus of intersections of spirals. If they are *of opposite sign*, a locus of intersections still divides the area into two parts which may be said to be fed with steps from each centre respectively. Of the possible loci of intersections, depending on the relative phase of rotation of the two spirals, the most important one is that which is symmetrical—the bisector of the line of centres. For in this case there is a possibility for an influence to be transmitted along each step from the point where turns of the two spirals meet, in to the respective centres, and there modify the rate of rotation. If

they meet nearer to the centre of one than the other, there is a tendency for the rate of rotation of the former to be increased. So, in time, the two become synchronized in phase and the locus of intersections is the symmetrical one. As shown in appendix B, the increase in rate of advance of the steps which is transmitted along the spirals from their meeting point to the neighbourhood of their dislocation centres produces a small increase in the rate of rotation of the spirals amounting probably at most to a few units per cent when the distance between dislocations is of the order of $3\rho_c$ and decreasing exponentially for larger distances. Then the activity of the pair is indistinguishable from the activity of one; at the same time there is no important topological difference from the case of growing circles.

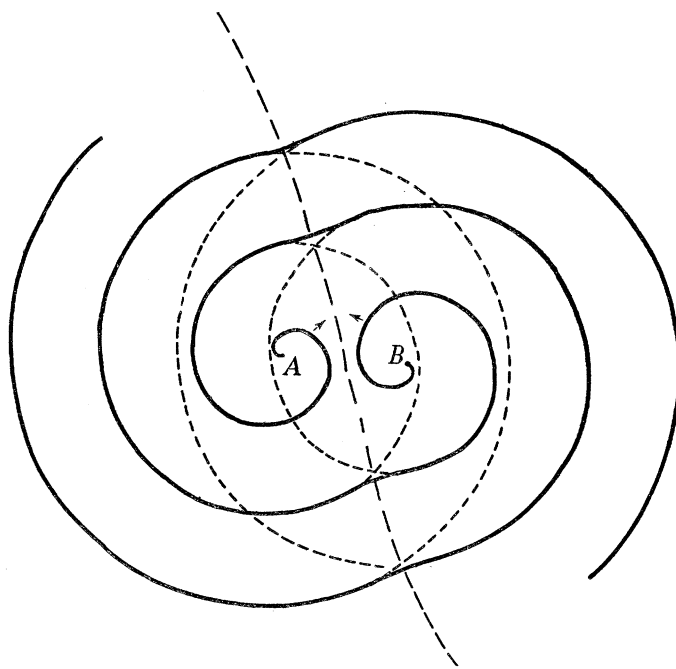


FIGURE 5. A pair of dislocations of like sign, separated by a distance $l = AB > 2\pi\rho_c$.

A pair of dislocations of like sign gives a more complex situation. If they are *far apart*, a locus of intersections still divides the area into two parts, which may be said to be fed with steps from each centre respectively. As before, there will be a tendency for the symmetrical case to establish itself. The locus of intersections is then no longer a straight line, but an S-shaped curve. If the spirals are represented by equation (37) and their centres are a distance l apart, the locus crosses the line of centres at an angle $\tan^{-1}(l/4\rho_c)$ and passes to infinity on asymptotes which make an angle $\cos^{-1}(2\pi\rho_c/l)$ with the line of centres (figure 5). The activity is still indistinguishable from that of one dislocation.

However, if the centres are *closer together* than half the radial separation between successive turns, i.e. than $2\pi\rho_c$, the spirals have no intersections except near the origin. The locus of intersections is now an S-shaped curve running from one centre to the other, and no longer divides the area into two (figure 6). In this case the turns of both spirals reach the whole of the area. In the limiting case in which the distance between dislocations l is much less than ρ_c we have effectively the complete Archimedean spiral $r = 2\rho_c\theta$, with the branches for both negative and positive r . Actually it still consists of a pair of spirals, which exchange centres on meeting, at every half-turn. If $l \ll \rho_c$ this shift of centres should scarcely affect the

rotation of the spirals, so that the activity of the pair should be *twice* the activity of a single dislocation. For small non-negligible values of l/ρ_c we may crudely estimate that the shift of centres imposes a delay corresponding to the time required for an unperturbed spiral to turn through an angle of the order of magnitude l/ρ_c , but we make no quantitative estimate

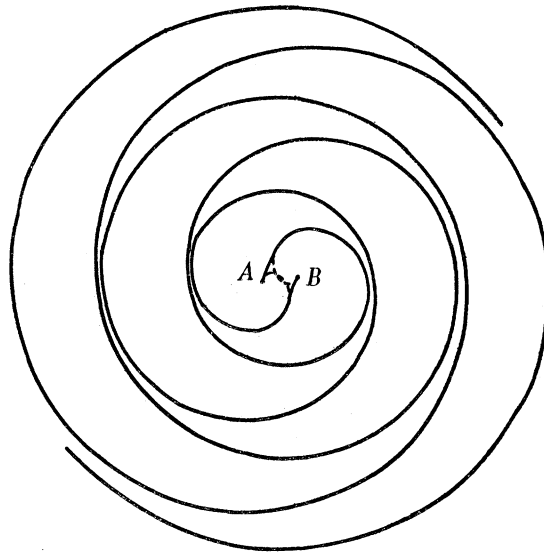


FIGURE 6. Pair of dislocations of like sign, at a distance $d < 2\pi\rho_c$.

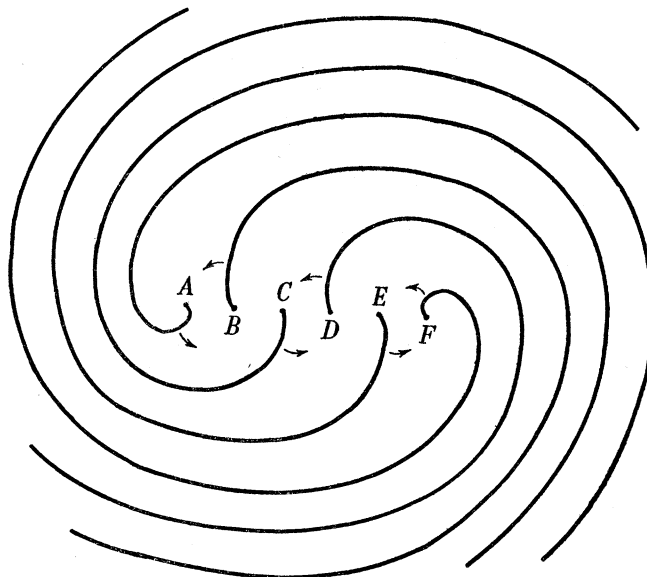


FIGURE 7. A group of dislocations of the same sign.

beyond saying that the activity of the pair now lies between 1 and 2 times the activity of a single dislocation.

A group of s dislocations of the same sign, each a distance smaller than $2\pi\rho_c$ from its next neighbour, will generate a spiral system of s branches. Supposing they are arranged in a line (the most likely arrangement, since groups of dislocations usually belong to 'mosaic', 'subgrain' or 'lineage' boundaries), and the length of the line is L , it is easy to see that each branch will take a time of the order of $2(L + 2\pi\rho_c)/v_\infty$ to execute a circuit round the group so that the resultant activity of the group is $s/(1 + L/2\pi\rho_c)$ times that of a single dislocation (figure 7).

If L is small compared with ρ_c , the activity of the group is s times that of a single dislocation; if L is large, and the average distance between dislocations is $\bar{l} = L/S$, the activity is $2\pi\rho_c/\bar{l}$ times that of a single dislocation.

In the more general case of a group of like dislocations not in a straight line, we may replace L in the above formula by $\frac{1}{2}P$, where P is the perimeter of the group. But in this case it may happen that the growth fronts have difficulty in penetrating into the group itself. The dislocation group will still promote growth outside it, but may develop a pit in the surface of the crystal.

In concluding this subsection we can say that the activity of a group of dislocations is in general greater than that of a dislocation alone by a factor ϵ , which in the case of a group of dislocations of the same sign can be as great as the number of dislocations contained in it.

In any case, the distance y_0 between steps produced by the group, far from it, will be given by their rate of advance v_∞ , divided by the number of steps passing a given point per sec.: $\omega/2\pi$. Therefore, using (38),

$$y_0 = 4\pi\rho_c/\epsilon. \quad (45)$$

We shall see in § 10 that in spite of the fact that the activity of a group can be several times greater than that of a single dislocation, the absolute value of the activity cannot surpass a certain maximum, the reason being that the rate of advance decreases when the distance between steps decreases.

9.2. General case

Suppose now we have *any distribution* whatever of dislocations in a crystal face, and a fixed degree of supersaturation σ , and consequently a fixed value of ρ_c (where σ and ρ_c may be slowly varying functions of position on the face). We now make a formal grouping of the dislocations. The first group consists of *inactive pairs*, all pairs of dislocations of opposite sign, closer together than $2\rho_c$. These have no activity by themselves, and their only effect, save in exceptional cases when they may possibly fence off a region of the crystal face, and inhibit growth there, is to impose a small delay on the passage of steps originating elsewhere, which to a first approximation may be disregarded. When a particular dislocation has two neighbours closer than $2\rho_c$, the pairing may be made arbitrarily, but in such a way that as many close pairs as possible are assigned to this class. We now take $2\pi\rho_c$ as the effective distance within which dislocations influence each other's activity, and by drawing imaginary lines connecting all dislocations closer together than this, divide all the remaining dislocations into groups, whose members influence each other's activity, but in which the groups are without influence upon each other. The number of these groups will increase with the supersaturation. Each group can be assigned a *strength* $s = 0, \pm 1, \pm 2, \dots$, according to the excess of right-handed over left-handed screws in the group. A group of strength 0 has an activity ϵ times that of a single dislocation, where ϵ is now approximately 1 and generally slightly greater (the inactive groups of this strength have already been put into a separate class). If the supersaturation is increased, so that ρ_c decreases, ϵ tends rapidly to 1. When it reaches 1 the group can be subdivided into two, of strengths s_1, s_2 , where $s_1 + s_2 = 0$. If the dislocations are in random arrangement, $|s_1|$ will seldom exceed 1 or 2, but it must be borne in mind that dislocations are likely to be in regular arrangements, as in mosaic or subgrain boundaries, in which case this conclusion does not necessarily follow.

Reduction of ρ_c will also transform some of the inactive pairs into active groups of strength 0.

Groups of strength $s \neq 0$ may have an activity up to $\epsilon = |s|$ times that of a single dislocation.

With increase of supersaturation, diminishing ρ_c , the groups of strength s subdivide into groups of strength s_1, s_2 , where $s_1 + s_2 = s$. Since s_1 and s_2 can be of opposite signs $|s_1|$ may be larger than s . But with increasing supersaturation the groups are ultimately all subdivided into single dislocations behaving independently.

At every stage prior to this, there is in general some group more active than the rest.

The resultant activity is always that of the most active independent group.

10. Rate of growth from the vapour

Let us first consider the simplest case of one screw dislocation in an otherwise perfect crystal surface. The rate of growth will then be given by (43), where v_∞ is the rate of advance of the steps, far from the centre of the spiral.

The value of v_∞ has been calculated in I, formula (24), that is to say,

$$v_\infty = 2\sigma x_s \nu \exp(-W/kT) \tanh(y_0/2x_s) \beta c_0(x_0, y_0), \quad (46)$$

where σ is the supersaturation, x_s the mean displacement of adsorbed molecules, ν a frequency factor, W the evaporation energy, y_0 the distance between successive turns of the spiral, β a factor taking account of the fact that perhaps the exchange of molecules between the step and the adsorbed layer is not rapid enough to maintain around them the equilibrium concentration of adsorbed molecules, and c_0 another factor, which is a function both of y_0 and of the distance x_0 between kinks in the steps, and given in general by formula (25), I. According to the estimates made in I for x_s and x_0 we expect the condition $x_s \gg x_0$ to be satisfied in most cases; then the factor c_0 is of the order of 1, and the rate of advance of the steps is independent of their orientation. In this case, using (46) and (44) for the distance y_0 between successive turns of the spiral, (43) becomes

$$R = \beta \Omega n_0 \nu \exp(-W/kT) (\sigma^2/\sigma_1) \tanh(\sigma_1/\sigma), \quad (47)$$

where

$$\sigma_1 = (2\pi\rho_c/x_s) \sigma = 2\pi\gamma a/kTx_s \quad (48)$$

(cf. I, equation (30)). For low supersaturations ($\sigma \ll \sigma_1$) we obtain the *parabolic law*

$$R = \beta \Omega n_0 \nu \exp(-W/kT) \sigma^2/\sigma_1. \quad (49)$$

For *high supersaturations* ($\sigma \gg \sigma_1$) (47) becomes the *linear law*

$$R_1 = \beta \Omega n_0 \sigma \nu \exp(-W/kT), \quad (50)$$

which corresponds to the case when x_s is larger than the distance between successive turns of the spiral. We see that there is a critical supersaturation σ_1 , given by (48), below which the rate of growth is essentially parabolic, and above which it is essentially linear. For the typical values $\gamma/kT \sim 4$, $x_s \sim 4 \times 10^2 a$ we obtain $\sigma_1 \sim 10^{-1}$. In figure 8 we plot the factor

$$R/R_1 = (\sigma/\sigma_1) \tanh(\sigma_1/\sigma)$$

as a function of σ/σ_1 (continuous curve).

In the case (an unusual one, we believe) when the condition $x_s \gg x_0$ is not satisfied, expression (47) has to be multiplied by the factor $c_0(\sigma/\sigma_1, b)$ given by (cf. I, formula 25)

$$c_0(\sigma/\sigma_1, b) = \{1 + 2b(A + B\sigma/\sigma_1) \tanh(\sigma_1/\sigma)\}^{-1},$$

where

$$b = x_0/2\pi x_s, \quad A = \ln [4bx_s/a(1 + (1 + b^2)^{\frac{1}{2}})], \quad B = \tan^{-1} b.$$

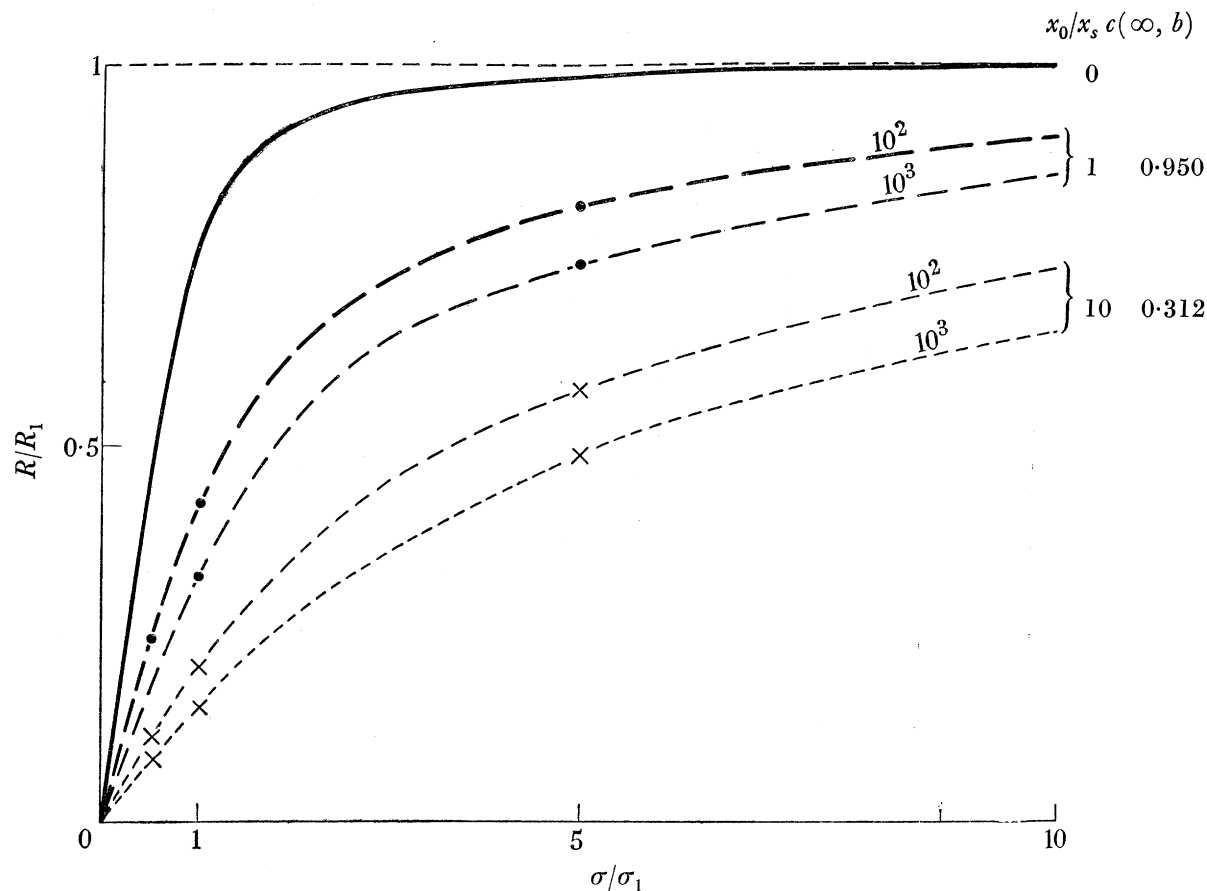


FIGURE 8. Correcting factor R/R_1 to the linear rate of growth as a function of σ/σ_1 . The numbers on the curves indicate the values of x_0/x_s .

For low supersaturations ($\sigma \ll \sigma_1$) the parabolic law (49) will be multiplied by the factor

$$c_0(0, b) = (1 + 2bA)^{-1};$$

for high supersaturations ($\sigma \gg \sigma_1$), the linear law (50) will be multiplied by

$$c_0(\infty, b) = (1 + 2Bb)^{-1},$$

which can be included in the unknown constant β . The factor $c_0(0, b)$ is always smaller than $c_0(\infty, b)$. The correcting factor $\{(\sigma/\sigma_1) \tanh(\sigma_1/\sigma)\} c_0(\sigma/\sigma_1, b)/c_0(\infty, b)$ is also represented in figure 8; for a given value of b , A is also a slowly varying function of x_s/a . We see that the influence of the factor c_0 is important for $x_0/x_s \geq 1$, which we do not think will usually occur. As x_0/x_s increases, the linear law is reached for higher values of σ/σ_1 .

Similar considerations apply to the rate of growth produced by a group of dislocations. If the group is a balanced one (equal number of right- and left-handed dislocations, strength $s = 0$) then there must be another critical supersaturation σ_2 below which no growth occurs

at all. σ_2 will be defined by the condition $2\rho_c = l$, where l is the maximum distance between pairs of dislocations actually coupled by a step; therefore

$$\sigma_2 = 2\gamma a/kTl. \quad (51)$$

For an unbalanced group (strength $s \neq 0$), or a balanced group above σ_2 , the rate of growth will be given by

$$R = \Omega n_0 \epsilon(\sigma) v_\infty / 4\pi\rho_c, \quad (52)$$

where the factor $\epsilon(\sigma)$ is of the order of magnitude 1 for a balanced group, but can be larger for an unbalanced group; in both cases $\epsilon(\sigma)$ tends ultimately to 1 when σ increases. Using (46) (assuming $c_0 = 1$) and (12) for the distance y_0 between steps, (52) becomes

$$R = \beta \Omega n_0 v \exp(-W/kT) \epsilon(\sigma) (\sigma^2/\sigma_1) \tanh[\sigma_1/\epsilon(\sigma) \sigma]. \quad (53)$$

We see from this expression that, however large $\epsilon(\sigma)$ is, R cannot surpass the linear law (50). On the other hand, R cannot be smaller than (47) for an unbalanced group, but it could become zero for a balanced group below the critical supersaturation σ_2 .

In the general case of an arbitrary distribution of dislocations in the crystal face we expect to have values for the rate of growth between that for a single dislocation (47) and the linear law (50), according to the distribution occurring in the particular crystal considered. A critical supersaturation σ_2 of the type (51) could occur in some random distributions of dislocations or a grouping of dislocations in balanced groups only; nevertheless, there is evidence showing that the dislocations are distributed in a very irregular way, and groups of dislocations of the same sign occur in mosaic or subgrain boundaries, in which case we do not expect critical supersaturations of the type (51) to occur.

11. Comparison with experiment

There are few quantitative measurements of the rate of growth of crystals from the vapour. The most interesting from our point of view are those of Volmer & Schultze (1931). These authors studied very carefully the growth from the vapour of naphthalene, white phosphorus and iodine crystals just below 0°C , under different supersaturations σ (from 10^{-3} to 10^{-1}). For all three substances they found a rate of growth proportional to the supersaturation. This linear law was valid for C_{10}H_8 and P_4 down to the lowest supersaturation used ($\sim 10^{-3}$), but for iodine the rate of growth becomes smaller than that given by the linear law when $\sigma < 10^{-2}$.

Let us first compare their linear law with (50) calculated in the preceding section for high supersaturations. This formula is actually the same as that used by Hertz (1882) and other authors (Volmer 1939; Wyllie 1949) for the growth of liquids and crystals from the vapour; it can be written also in the equivalent form

$$R = \beta \Omega p_0 (2\pi mkT)^{-\frac{1}{2}} \sigma, \quad (54)$$

as follows from the equality

$$n_0 v \exp(-W/kT) = p_0 (2\pi mkT)^{-\frac{1}{2}} \quad (55)$$

representing the balance between the current of evaporation and that of condensation at equilibrium. β in (54) is usually called the *condensation coefficient*, p_0 is the saturation pressure and m the mass of a molecule.

In table 1 we compare the experimental linear laws obtained by Volmer & Schultze (1931) with (54). The first column gives the average experimental value for R/σ . The supersaturation σ was obtained by maintaining a reservoir at 0°C and cooling the crystal under examination to a temperature $-\Delta T^\circ\text{C}$. Assuming that the vapour pressure between the two crystals is uniform, the supersaturation at the growing crystal is $\sigma = W\Delta T/kT^2$. The second column gives the theoretical values for $R/\beta\sigma$ from (54), taking for p_0 the values measured by Gillespie & Fraser (1936) for I_2 , by Centnerszwer (1913) for P_4 and by Andrews (1927) for C_{10}H_8 . The first row gives the Volmer-Schultze results for liquid Hg, for which careful measurement by Knudsen (1915) showed that $\beta = 1$. For all the three molecular crystals, $\beta < 1$.

TABLE 1. LINEAR RATES OF GROWTH R FROM THE VAPOUR AT 0°C , AS FUNCTIONS OF SUPERSATURATION

	R/σ (exp.) (cm./sec.)	$R/\beta\sigma$ (theor.) (cm./sec.)	β	W (eV)	ν (sec. ⁻¹)
Hg (liquid)	0.66×10^{-6}	0.6×10^{-6}	1.1	0.66	10^{13}
I_2	0.9×10^{-4}	3×10^{-4}	0.3	0.70	5×10^{16}
P_4	0.9×10^{-5}	0.8×10^{-4}	0.1	0.63	10^{15}
C_{10}H_8	0.8×10^{-4}	1.5×10^{-4}	0.5	0.79	10^{18}

The last two columns in table 1 give the values of W and ν deduced from (22). For Hg the frequency factor is of the order of the frequency of atomic vibrations, as we should expect; in the other cases ν is larger, due to the difference in rotational entropy between the crystal and the vapour.

Coming back to the deviations from the linear law, we notice first that P_4 and C_{10}H_8 follow the linear law to the lowest supersaturations observed. That means that σ_1 is smaller than 10^{-3} , and therefore, from (48), that $x_s > 10^4 a$. This is not surprising; in fact, the estimate of x_s/a made in I, equation (6), is valid for spherical molecules, for which the energy of evaporation W'_s of an adsorbed molecule was assumed to be of the order of $\frac{1}{2}W$; in the case of a flat molecule like C_{10}H_8 , we expect W'_s to be larger, and therefore x_s/a will also be larger.

Figure 9 gives the results (logarithmic scale for both axes) obtained by Volmer & Schultze on several I_2 crystals. The experimental rates of growth are not reproducible even for the same face of the same crystal; this is not unexpected on the basis of the present theory.

Assuming that the rate of advance of steps is independent of orientation ($x_s \gg x_0$), one can choose a value for $\sigma_1 \sim 0.2$ such that most of the experimental results are contained between the rate of growth (47) of a single dislocation (continuous line in figure 9) and the linear law (50) (broken line in figure 9). Taking $\sigma_1 \sim 0.2$ and $\gamma/kT \sim 4$, we deduce from (48), $x_s \sim 10^2 a$ for I_2 at 0°C , which is in reasonable agreement with what we should expect (cf. I, equation (6)).

Nevertheless, one notices that the experimental rates of growth for the lowest supersaturations are below the theoretical curve (47); in particular, the rate of growth at

$$\sigma = 3.8 \times 10^{-3} (\Delta T = 0^\circ.037)$$

is $< 10^{-3}$ times the rate of growth given by the linear law. The reduction given by formula (47) is only a factor $\sigma/\sigma_1 \sim 5 \times 10^{-2}$ with respect to the linear law. This fact could be explained in a number of ways:

(i) It is an obvious corollary to our view of crystal growth that it is susceptible to poisoning by traces of impurity, particularly at low supersaturations at which the number of

dislocations producing growth is smallest. From this point of view new measurements of the rate of growth would be very welcome.

(ii) There may be a critical supersaturation of the type (51) of the order of $\sigma_2 \sim 10^{-2}$, and therefore the dislocations are about 10^{-3} cm. apart; nevertheless, we are loath to draw this conclusion from such slight evidence.

(iii) Of course, it would be possible to choose a larger value for σ_1 , in order to explain the small rates of growth at the lowest supersaturations, but the corresponding value for $x_s \sim 6a$

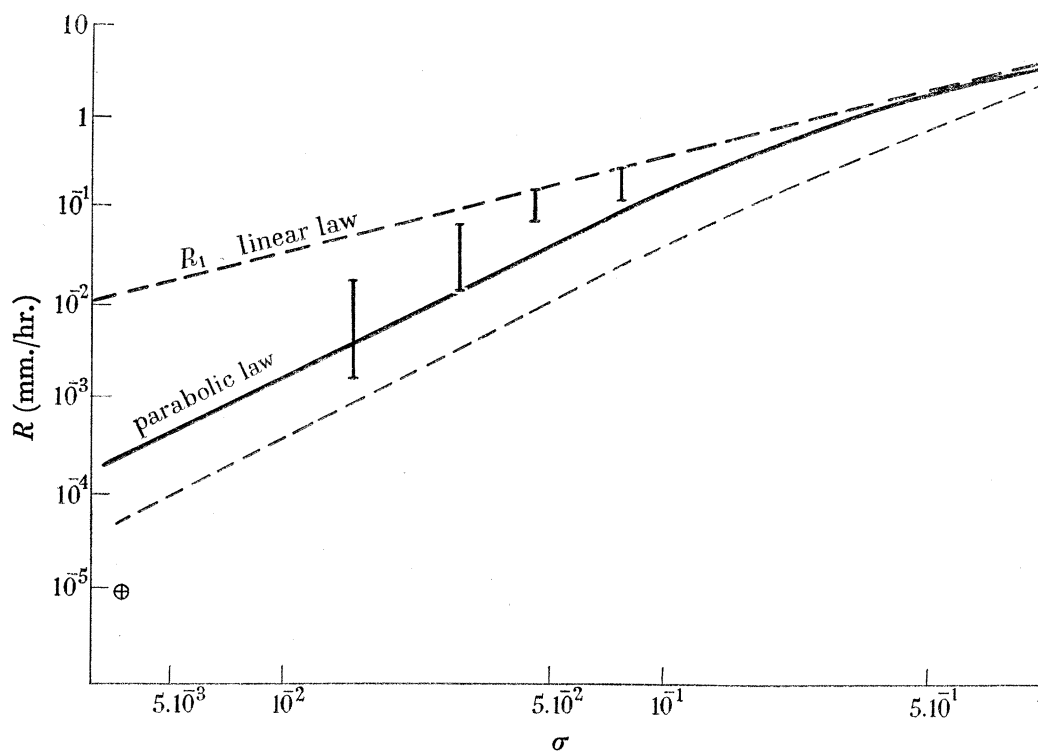


FIGURE 9. The rate of growth of I_2 crystals at 0° C as a function of σ (Volmer & Schultze 1931) in a logarithmic scale. The broken line is the Hertz law with a condensation coefficient $\beta = 0.3$. The continuous curve is the rate of growth of a single dislocation (formula (47)) with $x_s = 10^2 a$. The dotted curve is that of a single dislocation assuming $x_0 = 10$, $x_s = 10^3 a$.

would be too small. Another alternative is to suppose that the condition $x_s \gg x_0$ is not satisfied for I_2 . In order to decrease the number of degrees of freedom, let us assume that the condensation coefficient β is due only to the factor $c_0(\infty, b)$. That fixes $x_0/x_s \sim 10$. Assuming for $x_s \sim 10^2 a$, one obtains the dotted curve represented in figure 9. As we said before we do not think that a value $x_0/x_s \sim 10$ is actually possible. This point will be decided when the topography of a crystal grown from the vapour is observed. If, as we believe, $x_0 \ll x_s$ the steps must be circular, if $x_0 \gg x_s$ then they must follow the crystallographic orientation, as is observed in the case of growth from solution (Griffin 1950; Frank 1950).

We have been considering the rate of growth of macroscopic surfaces, for which the growth is due essentially to the molecules condensing from the vapour; in this case formula (54) represents the maximum rate of growth for a given surface. When the dimensions of the surface are small, diffusion of molecules from neighbouring surfaces can give an important contribution to its growth, and the rate of growth may be substantially greater than (54).

For instance, Volmer & Estermann (1921) studied the growth of small crystals of Hg at -63°C . The crystals had a plate shape, the thickness h was not observable but was estimated to be of the order of 10^2a . The rate of growth of the edges was estimated to be 10^3 times that given by (54). The ratio between the contribution to the growth from diffusion on the flat surface and directly from the vapour should be $2x_s/h$. Therefore we deduce $x_s \sim 10^5a$ for Hg at $T = 210^{\circ}\text{K}$, which agrees with the value that we should expect.

12. Growth from solution

We consider now, very briefly, the application of the preceding ideas to growth from solution. Although it is clear that from a qualitative point of view there is no essential difference between growth from the vapour and from solution, a quantitative theory of the rate of growth from solution is much more difficult.

First of all, we expect the rate of advance of a step in the crystal surface to be a definite function of the distance x_0 between kinks in the step, because although x_0 is always small, the diffusion of solute molecules towards the kinks, either through the solution, on the surface or in the edge of the step, is now much slower than on the free surface of a crystal. It is difficult to decide the relative importance of these three currents. For instance, the ratio between the current through the solution and on the surface will be represented by the factor $DN_0a/D_s n_{s0}$, where D and D_s are the diffusion coefficients and N_0 and n_{s0} the saturation concentrations in the solution and on the surface respectively; it is likely that $D > D_s$ but also $N_0a < n_{s0}$, therefore the factor above may be greater or smaller than 1. Nevertheless, for the time being and in order to simplify the problem, we shall suppose that the contributions from the diffusion on the surface and in the edge can be neglected. Even under these conditions we find another difficulty in the fact that neglect of the motion of the sinks is no longer generally justifiable.

Let us suppose we have a set of parallel steps, at distance y_0 from each other, in one of the close-packed crystallographic directions (for which x_0 , the distance between successive kinks, is a maximum). As an approximation the diffusion through the solution can be broken up as follows: At distances $r < x_0$ from each kink we have a hemispherical diffusion field around each kink (provided $D/v_{\text{kink}} \gg x_0$, otherwise the movement of the kink cannot be neglected) with the diffusion potential $(1 - a/r) \sigma(x_0)$, where $\sigma(x_0)$ is the supersaturation at a distance x_0 ; at distances r between x_0 and y_0 from each step we have a semi-cylindrical diffusion field around each step (provided $D/v_{\text{step}} \gg y_0$) with the diffusion potential

$$[\ln(y_0/x_0)]^{-1} [\sigma(x_0) \ln(y_0/r) + \sigma(y_0) \ln(r/x_0)],$$

where $\sigma(y_0)$ is the supersaturation at a distance y_0 ; and finally, at distances z from the crystal surface between y_0 and δ , the thickness of the unstirred layer at the surface of the crystal, we have a plane diffusion field with the diffusion potential $[(z - y_0) \sigma + (\delta - z) \sigma(y_0)] (\delta - y_0)^{-1}$, where σ is the supersaturation in the stirred solution. The latter diffusion potential applies in any case, but it would be improper to equate the flux calculated from its gradient to the rate of growth R of the crystal unless $D/R \gg \delta$. Usually D/v_{kink} , D/v_{step} and D/R are not very large unless both the concentration and the supersaturation in the solutions are small. We assume in the following considerations that this is the case.

Under these conditions and in terms of the supersaturation $\sigma(x_0)$ the rate of advance of every step is clearly

$$v_\infty = DN_0\Omega 2\pi\sigma(x_0)/x_0. \quad (56)$$

As v_∞ is proportional to the number of kinks per cm., $1/x_0$, the velocity of the step will increase appreciably as the inclination with respect to the close-packed slowest direction increases.

Equating the sum of the hemispherical fluxes going to all the kinks in the step to the semi-cylindrical flux, and equating also the sum of the semi-cylindrical fluxes going to all the steps in the surface to the plane flux, we eliminate $\sigma(y_0)$ and find

$$\sigma(x_0)/\sigma = [1 + 2\pi a(\delta - y_0)/x_0 y_0 + (2a/x_0) \ln(y_0/x_0)]^{-1}, \quad (57)$$

which, introduced in (56), gives v_∞ as a function of x_0 and y_0 . v_∞ will clearly increase when y_0 increases.

Applying now formulae (43) and (44) for the rate of growth R and the distance between steps y_0 of the growing pyramid, which will be approximately valid in our problem also, we obtain

$$R = DN_0\Omega a\sigma(x_0)/2x_0\rho_c, \quad (58)$$

where $2\rho_c = 2\gamma a/kT\sigma(x_0)$ is the dimension of the critical nucleus and $\sigma(x_0)$ is given by (57). For low supersaturations the third term in the bracket in (57) is the important one; then the rate of growth becomes parabolic. On the contrary, at high supersaturations, the second term in (57) is the important one, and the rate of growth becomes linear:

$$R_1 = DN_0\Omega\sigma/\delta. \quad (59)$$

The change-over from parabolic to linear occurs at a supersaturation σ_1 , roughly given by

$$\sigma_1 \sim \gamma x_0/kT\delta. \quad (60)$$

For reasonable values of γ and δ , $\sigma_1 \sim 10^{-3}$. Above σ_1 one should observe only the linear law (59); below σ_1 , all the rates of growth between (58) and (59) could be expected. As far as we know there is no experimental evidence for such a critical supersaturation.

On the other hand, we observe frequently (Bunn 1949; Humphreys-Owen 1949) that the rate of growth is substantially smaller than the linear law (59) would suggest; sometimes a crystal surface does not grow at all in spite of the fact that it is in contact with supersaturations as large as $\sigma \sim 0.1$. This could possibly be interpreted as being due to the absence of dislocations in the surface or to the presence of so many that the mean distance between them is smaller than $2\rho_c$. In this last case, the number of dislocations per sq.cm. would have to be of the order of 10^{12} cm.⁻², which is high. Moreover, in this case, the dislocations would have to be distributed in a peculiar way, with least density at the centre of each face; for otherwise the growth, when it did occur, would be most rapid at the corners, i.e. dendritic. We are more inclined to think that the number of dislocations involved is quite small, and that they are situated near the middle of the face. The changes in growth rate could be due to rearrangements of the dislocations or to the effect of impurities adsorbed on the steps. The required amount of such impurity is very small indeed. For example, if the number of dislocations per sq.cm. is as high as 10^8 , the number of atomic sites on the step-lines connecting them need not exceed 10^{-4} of all sites in the area.

EQUILIBRIUM STRUCTURE OF CRYSTAL SURFACES

PART III. STEPS AND TWO-DIMENSIONAL NUCLEI

13. *Introduction*

We begin with an outline of the theory to be developed in later sections. Some of the statements made in this outline receive their fuller justification later.

It is clear that a crystal will grow only if there are *steps* of monomolecular height in its surface, and growth will take place by the advance of these steps forming new molecular layers. The rate of advance of the steps will depend on their structure when in equilibrium with the vapour; hence the necessity for studying this structure as a preliminary to the study of crystal growth.

Frenkel (1945) has recently shown that such steps, when in equilibrium at temperatures above 0°K , will contain a number of *kinks* (cf. figure 11), i.e. molecular positions from which the energy necessary to take a molecule from the crystal to the vapour is equal to the evaporation energy W . This is true for intermolecular forces of a very general character, as has been shown by Kossel (1927) and Stranski (1928). According to Frenkel, the proportion of molecular positions in the step occupied by kinks is given by a formula of the type

$$e^{-w/kT}, \quad (61)$$

where w is the energy necessary for the formation of a kink in the step. Our first purpose in this part is to study in detail the structure of steps of any crystallographic direction and to estimate the value of w . The concentration of kinks turns out to be in general considerably larger than the concentration of adsorbed molecules in the edge of the step. We consider as a working model a Kossel crystal, a simple cubic structure with first and second nearest neighbour interactions. When the crystal is in real equilibrium with its vapour, a step in equilibrium must be in the mean straight but can have any crystallographic direction.

On the other hand, if the vapour is supersaturated, it is known that there is a two-dimensional nucleus (critical nucleus) which is in unstable equilibrium with the vapour. Our second purpose in this part is to calculate the shape, the dimensions and the total edge free energy of the critical nucleus in equilibrium with a given supersaturation at a given temperature, for the particular case of a $(0, 0, 1)$ surface of a Kossel crystal.

If one assumes that the crystal is perfect, its growth in a supersaturated environment requires the formation of nuclei of critical size, because it is only when they reach this size that they are able to grow freely forming a new molecular layer. It can be proved, on thermodynamical grounds, that the number of critical nuclei created per second must be proportional to $\exp(-A_0/kT)$, where A_0 is half the total edge free energy of a critical nucleus, which will also be called *activation energy for nucleation* (Volmer 1939; Becker & Döring 1935). In the calculation of A_0 , the previous authors neglected the configurational entropy, which amounts to supposing that the shape of the critical nucleus is the same as it would be at $T = 0^\circ\text{K}$. Under this assumption, and for the simple case of a $(0, 0, 1)$ surface in a Kossel crystal, the size of the critical (square) nucleus and the activation energy A_0 for nucleation are given by

$$kT \ln \alpha = \phi/l, \quad A_0 = \phi^2/kT \ln \alpha, \quad (62)$$

where α is the saturation ratio, defined as the ratio between the actual concentration in the vapour to the equilibrium value, ϕ the energy of interaction between nearest neighbours and

l^2 the number of molecules in the critical (square) nucleus. Taking account of the entropy factors, we show that the critical nucleus has essentially the same dimensions given in (62) but has rounded corners, which decreases A_0 only by a factor of the order of 0.8 in a typical case. We deduce therefore that the activation energy for nucleation is enormous for the values of α for which growth is observed ($\alpha \sim 1.01$; $A_0/kT \sim 3.6 \times 10^3$, for the typical value $\phi/kT \sim 6$), and consequently the observed growth at low supersaturations cannot be explained on the basis of a perfect crystal theory.

We believe that the observed rates of growth of crystals can only be explained by recognizing, as has been suggested by Frank (Burton *et al.* 1949; Frank 1949), that those crystals which grow are *not* perfect, and that their lattice imperfections (dislocations) provide steps on the crystal surface making the two-dimensional nucleation unnecessary. If the distance between a pair of dislocations producing a step in the surface is such that a critical nucleus can pass between them the step will grow freely. If that is not the case the step will require a certain activation energy for growth. Using our preceding results we calculate this activation energy, and we show that it is small only when the distance between dislocations is practically equal to the size of the critical nucleus.

In part IV we shall consider the problem of the equilibrium structure of a crystal surface not containing steps, in order to study whether thermal fluctuations are able to produce steps in the surface, in the same way that they produce kinks in a step. The answer will be *no*, provided the temperature is below a certain critical temperature, which for the more close-packed surfaces is of the order of or higher than the melting-point. The problem of the structure of a crystal surface is actually an example of a co-operative phenomenon.

14. *Equilibrium structure of a step*

By a step on a crystal surface we mean a connected line such that there is a difference of level equal to an intermolecular spacing between the two sides of the line.

If the crystal lattice contains no dislocations, then there can only be two varieties of step in the surface; either the step begins and ends on the boundary of the surface or it forms a closed loop on the surface itself (thus bounding a monomolecular elevation or depression on the surface). However, if dislocations are present, it is possible that a step can start on a surface and terminate on a boundary, or it can have both ends in the surface. If a step has an end in the surface, this end must be a place where a dislocation meets the surface with a screw component normal to the surface.

For the sake of simplicity we shall consider a crystal in contact with its vapour, but many of our conclusions will apply for other primary phases; also we shall assume the crystal to be very large compared with the range of molecular forces involved, that is, we shall speak of infinite crystals. We only consider, for simplicity, a (0, 0, 1) face of a simple cubic crystal with forces between molecules of the nearest neighbour or possibly the nearest and next nearest neighbour type. Finally, we neglect altogether the differences in frequency of vibration and rotational free energy of the molecules in different positions in the crystal surface.

If a crystal is then in stable equilibrium with its vapour (the vapour being neither super-saturated nor under-saturated), then it is fairly clear even at this stage (and we prove this later) that a step in equilibrium in the crystal surface will have a constant mean direction

(this direction not necessarily being along a crystallographic axis), and hence under these conditions no finite closed step can be in equilibrium. The latter will only be in equilibrium when the vapour is supersaturated or under-saturated. In this case the equilibrium is unstable. To avoid unnecessary circumlocutions we introduce here the saturation ratio α , defined as the actual vapour concentration divided by the vapour concentration under conditions of stable equilibrium with an infinite crystal surface. Summarizing, then, we expect to find steps of constant mean direction (straight steps) if $\alpha = 1$ and curved steps if $\alpha \neq 1$, the two possibilities being mutually exclusive.

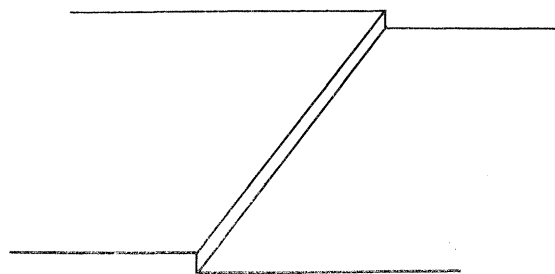
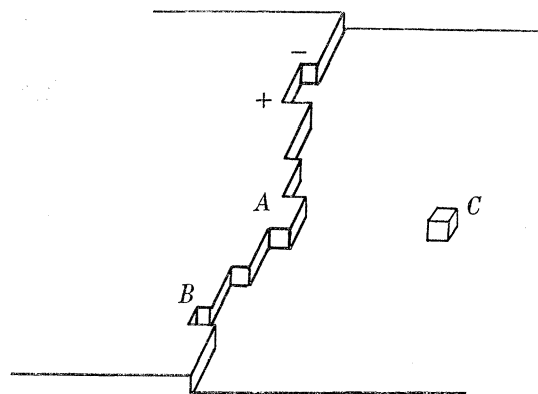
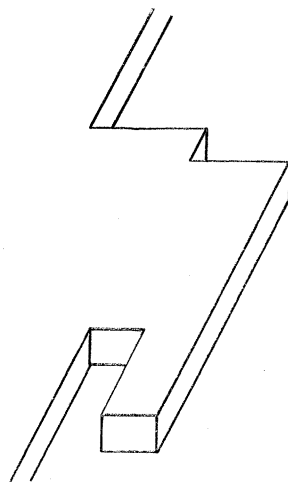
FIGURE 10. Step at $T = 0^\circ \text{K}$.FIGURE 11. Step at $T > 0^\circ \text{K}$.

FIGURE 12. Overhangs in a step.

Potential energy considerations show that at 0°K a step will tend to be as straight as possible. This is shown explicitly in § 14.1 (figure 10). As the temperature is raised, a number of kinks appear (+, -), separated by certain distances (figure 11); a certain number of adsorbed molecules (A), and a certain number of vacant step sites (B) also appear. A certain number of adsorbed molecules (C) also appear on the crystal surface proper. We shall see that the concentration of adsorbed molecules and vacant sites in the step is small compared with that of kinks. We require only the knowledge of the concentration of kinks to form a picture of the structure of the step. The representation of the step by kinks, even when we admit kinks of any height, is not capable as it stands of including such a feature as that depicted in

figure 12, which we call an ‘overhang’; to this extent our treatment will be slightly inaccurate. However, when the concentration of kinks is small, the concentration of overhangs will be negligible.

In what follows, our unit of length will always be the intermolecular spacing. We distinguish two types of kinks, which we call positive and negative, corresponding to a ‘jump’ and a ‘drop’ respectively at the point in question (figure 11). We use the symbol $n_{+r}(x)$ to denote the probability that there is a jump of amount r at a point whose co-ordinate is x . Similarly for $n_{-r}(x)$. We denote by $q(x)$ the probability that there is no jump of any kind at the point x . In the present case there are no geometrical constraints, i.e. at each point in a step, any of the various possibilities can occur independently of what there is at any of the other points. Hence the probability of the occurrence of a given configuration is equal to the product of the probabilities of occurrence of the individual situations which make up the configuration, and we may write as a normalization condition

$$q(x) + \sum_{r=1}^{\infty} \{n_{+r}(x) + n_{-r}(x)\} = 1. \quad (63)$$

We define the local mean direction of a step at a point x by the equation

$$h(x) = \tan \theta = \sum_{r=1}^{\infty} r \{n_{+r}(x) - n_{-r}(x)\} \quad (0 \leq h \leq 1), \quad (64)$$

where θ is the smallest angle between the step and the $[0, 1]$ direction. Our problem is now to evaluate the equilibrium values of $q(x)$, $n_{+r}(x)$ and $n_{-r}(x)$ as a function of the temperature T , and also of the first and second nearest neighbour interaction energies ϕ_1 and ϕ_2 .

It is possible to prove in a number of ways (see appendix C) that the probabilities n and q must satisfy the thermodynamical relations

$$g_{\pm r}(x) = \{g_{\pm}(x)\}^r \eta_2^{2(r-1)}, \quad (65)$$

$$g_+(x) g_-(x) = \eta_1^2, \quad (66)$$

$$g_{\pm}(x) = g_{\pm}(0) \alpha^{\mp x}, \quad (67)$$

where the g represent the relative probabilities

$$g_{\pm r}(x) = n_{\pm r}(x)/q(x); \quad (68)$$

we write g_{\pm} for $g_{\pm 1}$, and we use the notation

$$\eta_{1,2} = \exp(-\phi_{1,2}/2kT). \quad (69)$$

We see, from equation (67), that if $\alpha = 1$, and therefore the crystal is in thermodynamical equilibrium with its vapour, all the probabilities are independent of x , and therefore, from (64), the step will have a constant mean direction h . On the contrary, if $\alpha \neq 1$, the step will be curved; its local mean direction is then a function $h(x)$ of position in the step.

14.1. *Equilibrium structure of a straight step.* Let us now consider in more detail the structure of a straight step. Since there is now no dependence on x , we shall omit the variable from our notation. From (63), (65) and (66), using the notation (68), we obtain by summing a geometric series

$$g_+ + g_- = \frac{1 + \eta_1^2 \eta_2^4 - q[1 - \eta_1^2 \eta_2^2 (2 - \eta_2^2)]}{q + (1 - q) \eta_2^2}. \quad (70)$$

In the same way, for a given mean direction h of the step, using (64), (65) and (66), we obtain

$$g_+ - g_- = hq(1 - \eta_1^2 \eta_2^4) / [q + (1 - q) \eta_2^2]^2, \quad (71)$$

where we have also used (70) to eliminate $g_+ + g_-$.

From equations (66), (70) and (71) we can express q , n_+ and n_- as functions of η_1 , η_2 and h . Equations (65) then enable us to find n_{+r} and n_{-r} as functions of the same quantities, thus completing the solution of our problem. The general expressions are complicated and cumbersome, so we do not give them; instead, we consider some particular cases.

At $T = 0$, we get

$$q = 1 - h, \quad n_+ = h, \quad n_- = 0, \quad n_{\pm r} = 0 \quad (r \neq 1),$$

i.e. the step is as straight as it can be.

Before considering higher temperatures, let us see what typical values should be assigned to ϕ_1 and ϕ_2 . In our model, the evaporation energy per molecule is $W = 3\phi_1 + 6\phi_2$; assuming $W \sim 0.7$ eV (iodine for instance) and $\phi_2/\phi_1 \sim 0.2$, we have $\phi_1 \sim 0.15$ eV and $\phi_2 \sim 0.03$ eV. Thus at temperatures of the order of 300° K, we have $\eta_1 \sim 0.05$ and $\eta_2 \sim 0.6$. Accordingly, at these temperatures, it is reasonable to assume $\eta_2 \sim 1$, which amounts to neglecting the effect of second nearest neighbours. Under these conditions the solution to our problem becomes

$$\left. \begin{aligned} q &= [1 + \eta_1^2 - \{(1 + \eta_1^2)^2 - (1 - \eta_1^2)^2 (1 - h^2)\}^{1/2}] / (1 - \eta_1^2) (1 - h^2), \\ 2g_+ &= 1 + \eta_1^2 - q(1 - \eta_1^2) (1 - h), \\ 2g_- &= 1 + \eta_1^2 - q(1 - \eta_1^2) (1 + h). \end{aligned} \right\} \quad (72)$$

For $h = 0$, that is to say for the (0, 1) step, equations (66), (70) and (71) give

$$q = (1 - \eta_1^2 \eta_2^2) / (1 + 2\eta_1 - \eta_1 \eta_2^2), \quad n_+ = n_- = q\eta_1. \quad (73)$$

At low temperatures we get

$$q = 1 - 2\eta_1, \quad n_+ + n_- = 2\eta_1 = 2 \exp(-\phi_1/2kT). \quad (74)$$

The expression $n_+ + n_-$ now represents the proportion of step sites occupied by kinks from which the evaporation energy into the vapour is W . Thus, we obtain the same formula as Frenkel (1945) for the concentration of kinks, the energy of formation of those kinks being here $w = \frac{1}{2}\phi_1$. This value for w is, of course, equal to the increase in edge energy of the step by the formation of a kink. Since w is small, we shall have a considerable number of kinks; in fact, if $T \sim 300^\circ$ K, $\phi_1 \sim 0.15$ eV, we shall have one kink for every ten molecules in the step. The concentration of molecules diffusing in the edge of the step is much smaller than that of the kinks, being in fact proportional to η_1^2 which gives one diffusing molecule per 100 molecules in the step, if we use the above values for ϕ_1 and T .

As the inclination of the step increases ($h > 0$) with respect to the [0, 1] direction, the total number of kinks increases, because of the presence of kinks due to geometrical reasons; actually n_+ increases and n_- decreases in such a way that $n_+ + n_-$ increases. For h very small ($h < 2\eta_1$), and at low temperatures, one deduces

$$n_+ + n_- = 2\eta_1 \left[1 + \frac{h^2}{8\eta_1^2} \right]. \quad (75)$$

On the other hand, as we approach the $[1, 1]$ direction ($h = 1$), the positions in the step from which the evaporation energy is W , are no longer the kinks of height 1 (probability n_+), because of the influence of the second nearest neighbour bonds. Consequently the number of kinks with evaporation energy W reaches a maximum somewhere near $h = 1$, and decreases again being a minimum for the direction $[1, 1]$. Actually, for the $(1, 1)$ step at low temperatures at which η_1 and η_2 are small, we obtain

$$q = n_{+2} = \eta_2 = \exp(-\phi_2/2kT), \quad n_+ = 1 - 2\eta_2, \dots \quad (76)$$

Now the proportion of step sites from which the evaporation energy is W is represented by $q + n_{+2}$. We obtain again a formula of Frenkel type with an energy of formation $w = \frac{1}{2}\phi_2$ which is extremely small, much smaller than in the case of the $(0, 1)$ step. At higher temperatures, for which $\eta_2 \sim 1$, we obtain

$$q = \frac{1}{2} \frac{1 - \eta_1^2}{1 + \eta_1^2}, \quad n_+ = \frac{1}{4}(1 - \eta_1^2), \quad n_- = \frac{1 - \eta_1^2}{(1 + \eta_1^2)^2} \eta_1^2, \dots \quad (77)$$

It can now be seen why we have gone to the trouble of considering second nearest neighbours; we have done so in order to obtain the correct behaviour at low temperatures for the directions near $(1, 1)$. In fact for low temperatures (77) becomes

$$q = \frac{1}{2}, \quad n_+ = \frac{1}{4}, \quad n_- = 0, \quad n_{+r} = \left(\frac{1}{2}\right)^{r+1},$$

independent of temperature.

14.2. Free energy of steps

It is of interest to evaluate the configurational free energy of a straight step. Using standard methods ($S = k \ln W$, $F = U - TS$, etc., $W =$ number of ways in which kinks can be arranged in a step) we obtain the following general expression for the edge free energy per molecule:

$$F = \frac{1}{2}(\phi_1 + 2\phi_2) + \frac{1}{2}h\phi_1 + kT(\ln q + h \ln g_+), \quad (78)$$

where, of course, q and g_+ are functions of h . This expression is referred to the $[0, 1]$ direction; in order to obtain the free energy per unit length of the step itself, we must divide the expression by $(1 + h^2)^{\frac{1}{2}}$.

In the general case the extended form of (78) is exceedingly cumbersome, so we again consider some particular cases. For the $(0, 1)$ step at low temperatures the formula (78) gives

$$F_{01} = \frac{1}{2}(\phi_1 + 2\phi_2) - 2kT\eta_1; \quad (79)$$

under the same conditions the corresponding quantity for the $(1, 1)$ step is

$$F_{11} = \phi_1 + \phi_2 - 2kT \ln(1 + \eta_2). \quad (80)$$

The contribution of the entropy of the kinks to the edge free energy is small for the $(0, 1)$ step, but for the $(1, 1)$ step it is not negligible. In fact, at temperatures for which $\eta_2 \sim 1$, formula (80) gives $2kT \ln 2 \sim 0.07$, or a third of ϕ_1 .

At reasonable temperatures the free energy is always smaller for the $(0, 1)$ step than for any other, so we might conclude that steps other than the $(0, 1)$ steps are not in real equilibrium, and that there must be a tendency for these steps to change into $(0, 1)$ steps. If the

steps are infinite, this conclusion would be erroneous. Actually, every step is in equilibrium with the same vapour pressure. Moreover, although the (0, 1) step has the smallest free energy, there is no tendency for other steps to change their orientation, because even the smallest rotation of step requires the transport of an infinite amount of material.

Frenkel (1945) has treated the kinetical problem of the transformation of any step into a (0, 1) step, assuming that only the latter are present in equilibrium, on account of the higher energy of the former. He obtains in this way a time of relaxation independent of the length of the step. This result is clearly incorrect, because the processes allowing a finite step to change its orientation occur only at the corners; consequently the time required for this rotation increases with the length of the step.

15. *The two-dimensional nucleus: activation energy for nucleation*

We have seen in § 14 that if the saturation ratio α is unity then the equilibrium steps are in the mean straight. If $\alpha \neq 1$ we shall find that the equilibrium step forms a closed loop; if $\alpha > 1$ the step bounds a finite incomplete layer of molecules on the surface, in which case we speak of a two-dimensional nucleus, and if $\alpha < 1$ the step bounds a finite hole in an infinite incomplete layer.

The most obvious method for calculating the shape of an equilibrium nucleus would be to use the free-energy formulae and Wulff's theorem.* Although the use of Wulff's theorem is simple in principle, the details prove to be cumbersome. However, the results gleaned in § 14 enable us to find the shape directly.

We know that in general (see appendix C)

$$g_{\pm}(x) = g_{\pm}(0) \alpha^{\mp x}, \quad (67)$$

and to complete the explicit determination of g as a function of x it is necessary only to evaluate $g(0)$. So far we have not specified an origin for x ; let us now choose it to be the point where the local mean direction of the step is (0, 1). Then, by symmetry,

$$g_+(x) = g_-(-x).$$

Hence, using (66), we obtain $g_+(0) = g_-(0) = \eta_1$,

so that with (67) we get $g_{\pm}(x) = \eta_1 \alpha^{\mp x}$. (81)

Invoking once more the normalization condition (63) we obtain

$$q(x) = \frac{1 + (\eta_1 \eta_2^2)^2 - \eta_1 \eta_2^2 (\alpha^x + \alpha^{-x})}{1 - \eta_1^2 \eta_2^2 (2 - \eta_2^2) + \eta_1 (1 - \eta_2^2) (\alpha^x + \alpha^{-x})}, \quad (82)$$

using (65) and (81). It is now clear that our information on the structure of the step at every point x is complete.

15.1. *The shape of the equilibrium nucleus*

The local mean direction $h(x)$, and therefore the shape of a step in equilibrium with an external phase of saturation ratio α , is clearly obtained from (4), using (21) and (22). In Cartesian co-ordinates, the shape of the step is represented by the equation

$$y = \int_0^x h(x') dx',$$

* In appendix D we offer a new proof of a generalized Wulff's theorem, which will be used later in § 16.

where the origin is at a place where the local mean direction is $(0, 1)$ (see figure 13). Integrating, we find

$$y \ln \alpha = \ln \left\{ (1 - \eta_1 \eta_2^2 \alpha^x) (1 - \eta_1 \eta_2^2 \alpha^{-x}) / (1 - \eta_1 \eta_2^2)^2 \right\} - \frac{1}{2} \ln [H(x) H(-x) / \{H(0)\}^2], \quad (83)$$

where $H(x)$ is given by

$$H(x) = \{1 - \eta_1^2 \eta_2^2 (2 - \eta_2^2)\} \alpha^x + \eta_1 (1 - \eta_2^2) (\alpha^{2x} + 1).$$

The second term in (23) can be shown to be always small and negative; when $\eta_2 = 1$ it is zero.

The value of y in (83) becomes infinite when $x = \pm \frac{1}{2} l'$, where l' is given by

$$kT \ln \alpha = (\phi_1 + 2\phi_2) / l' \quad (\alpha > 1). \quad (84)$$

Thus (83) represents a finger-shaped figure (figure 13). It is interesting to note that l' coincides with the dimensions of the equilibrium or critical nucleus when a square shape is assumed [§ 13, formula (62)] and $\phi_2 \ll \phi_1$.

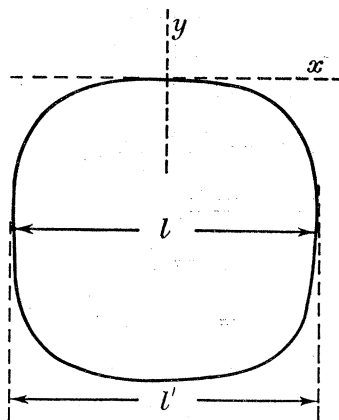


FIGURE 13. Step in equilibrium with supersaturated vapour ($\phi_1/kT \sim 6$).

If in (83) we replace α by its expression as a function of l' from (84), we see that y/l' is a function only of x/l' ; hence the shape of the step is independent of α . The value of α fixes the size of the figure. The shape is, of course, dependent on the temperature; at low temperatures the 'corners' become sharper and the 'edges' straighter. At temperatures for which $\eta_2 \sim 1$ the expression for the shape can be written in the form

$$y/l' = (kT/\phi_1) \ln \{1 - [\sinh(\phi_1 x/2kTl') / \sinh(\phi_1/4kT)]^2\}. \quad (85)$$

The figure we have obtained is not, of course, entirely correct, in the sense that we should have obtained a closed figure. The reason is the neglect of 'overhangs' (figure 12), which is not a good approximation when the inclination of the step is much greater than $\frac{1}{4}\pi$ with respect to the $(0, 1)$ direction taken as x -axis. Nevertheless, knowledge of the step shape in a range $\frac{1}{4}\pi$ enables us to state the complete shape, because of the square symmetry of the $(1, 0, 0)$ face of the simple cubic lattice. The diameter l of the nucleus obtained in this way (see figure 13) turns out to be given by

$$kT \ln \alpha = (\phi_1 + 2\phi_2 - 4kT\eta_1) / l, \quad (86)$$

to the first order in η_1 . The expression in parentheses is seen to be $2F_{01}$ (equation 79), F_{01} being the edge free energy per unit length of the $(0, 1)$ step. This is the result that we should

expect from a correct application of the Gibbs-Thomson formula (see appendix D), and it shows that the shape we have calculated is a good approximation. The difference between l given by (86) and l' given by (84) is practically negligible for ordinary temperatures.

The radius of curvature ρ of the nucleus at the corners when $\eta_2 \sim 1$, is easily shown to be given by

$$\rho/l = -\sqrt{2} (kT/\phi_1) \tanh^2(\phi_1/2kT). \quad (87)$$

The rounding of the corners at high temperatures is considerable. For the melting-point T_M , for which $kT_M/\phi_1 \sim 0.6$, the nucleus would have practically a circular shape. According to (87), the nucleus would become square at $T = 0^\circ \text{K}$. If second nearest neighbours are considered the nucleus would become an octagon.

15.2. *Activation energy for two-dimensional nucleation*

It is easy to show how the activation energy for nucleation A_0 is related to the total edge free energy F_0 of the critical nucleus. Let n be the number of molecules contained in a nucleus, then n will be variable and will have the value n_0 for the critical nucleus itself. Let us suppose that the shape of the nucleus does not change appreciably for values of n around n_0 . Then the increase in free energy by the formation of a nucleus containing n molecules will be

$$A = -nkT \ln \alpha + \beta n^{\frac{1}{2}},$$

where β is assumed to be a constant given by

$$F_0 = \beta n_0^{\frac{1}{2}}.$$

Now A has to be a maximum for $n = n_0$, because the critical nucleus is in unstable equilibrium with the vapour of saturation ratio α . This condition fixes the value of

$$n_0 = (\beta/2kT \ln \alpha)^2,$$

and the maximum of A is equal to

$$A_0 = n_0 kT \ln \alpha = \frac{1}{2} F_0. \quad (88)$$

The probability for the formation of a critical nucleus is then proportional to $\exp(-A_0/kT)$, and A_0 is called the *activation energy for two-dimensional nucleation*.

In the case of our (0, 0, 1) face in a simple cubic crystal we know that by an application of the Gibbs-Thomson formula (see appendix D) the dimension l of the two-dimensional critical nucleus is given by

$$kT \ln \alpha = 2F_{01}/l, \quad (86)$$

where F_{01} is the edge free energy per molecular position in the direction [0, 1]. The activation energy for two-dimensional nucleation can then be written in the form

$$A_0 = \frac{n_0 (2F_{01})^2}{l^2 kT \ln \alpha}. \quad (89)$$

Assuming that the critical nucleus is a square of size l and putting $F_{01} \sim \frac{1}{2}\phi_1$, we deduce the Becker-Döring expression

$$A_0 = \phi_1^2/kT \ln \alpha. \quad (62)$$

Formula (89) differs from (62) essentially by the factor n_0/l^2 , the ratio of the actual area of the nucleus to that of the square circumscribed on it. For the typical value $\phi_1/kT \sim 6$ we obtain graphically from figure 13 that $n_0/l^2 \sim 0.86$. This shows that the actual activation for

two-dimensional nucleation is reduced with respect to (62) only by a small factor, which is not sufficient to account for the observed growth rate at low supersaturations.

16. Steps produced by dislocations

As a final application of the generalized Wulff theorem (see appendix D) we evaluate the activation energy for nucleation in the presence of screw dislocations.

A real crystal is supposed not to have a perfect lattice, but to contain a number of lattice imperfections in the form of dislocations, and Frank (1949) has shown that when dislocations having a screw component normal to the surface terminate in the crystal surface, they ensure the permanent existence of steps in the surface during growth. Every dislocation is

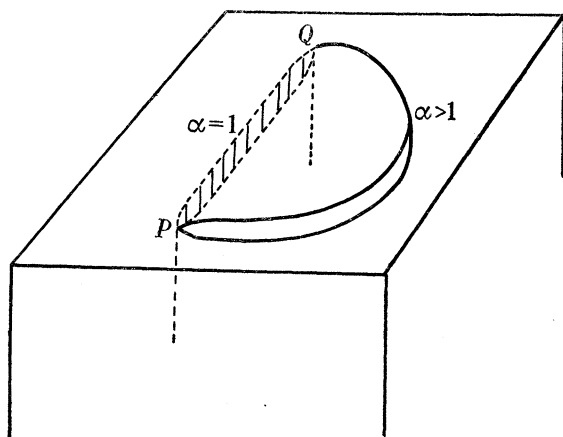


FIGURE 14. Step between two screw dislocations P and Q terminating in the surface.

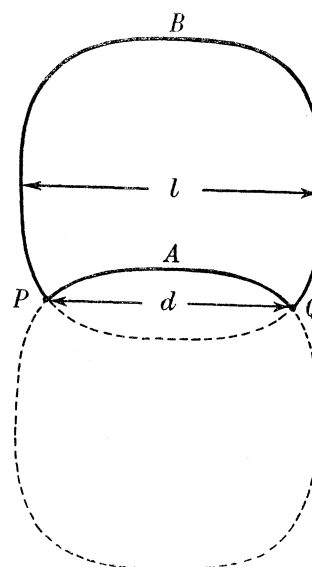


FIGURE 15. Equilibrium positions of a step between two dislocations P and Q : PAQ stable, PBQ unstable.

the origin of a step, which finishes usually in another dislocation of different sign. Therefore we must study the behaviour of a step between two screw dislocations of opposite sign. A picture of the surface in this case is shown in figure 14. We shall suppose for definiteness that the line joining the dislocations is in the $[0, 1]$ direction, and we let the distance between the dislocations be d (figure 15). In real equilibrium ($\alpha = 1$) the step will remain straight between the two dislocations (figure 14), having the structure of a piece of step $(0, 1)$. If $\alpha > 1$ the step will become curved (figure 14), and its shape, seen from above, under equilibrium conditions, is the same as part of the shape of a 'free' nucleus passing through the dislocations P, Q (figure 15). (Our calculations show in fact (appendix C) that the kink density at a point in a step depends only on conditions in the immediate neighbourhood of this point.) The diameter of this free nucleus will be l , given by (89) or approximately by (62). If $l > d$, there are two possible equilibrium positions: PAQ which is stable, and PBQ which is unstable. For growth we require the transition $PAQ \rightarrow PBQ$, and the activation energy A_d for this is half the edge free energy of the piece PBQ minus half the edge free energy of the piece PAQ . This quantity is easily evaluated graphically. To find the free energy of a piece of boundary we have merely to evaluate the area of the sector contained by

the piece and the lines joining its ends to the centre of the nucleus, as a function of d/l (see appendix D). This we have done for $\phi_1/kT \sim 6$, and figure 16 shows the ratio of A_d to the activation energy A_0 for ordinary nucleation. The curve has a vertical tangent at $l = d$, which means that we have to go to values of l very close to d in order to obtain a reasonably small value for the activation energy. Of course if $l < d$, the activation energy is zero. The dotted curve in figure 16 is obtained if we assume that the free equilibrium nucleus is a square.

Hence we conclude that given a certain saturation ratio α , and therefore a value l for the dimensions of the critical nucleus, all the steps connecting dislocations distant $d < l$ will not move at all, and those connecting dislocations distant $d > l$ will be able to move freely without requiring an activation energy.

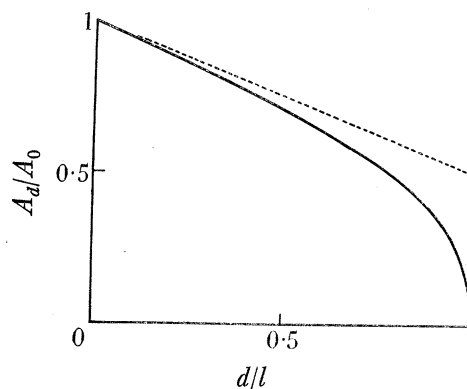


FIGURE 16. Activation energy A_d for the growth of a step between two dislocations a distance d apart.

PART IV. STRUCTURE OF A CRYSTAL SURFACE AS A CO-OPERATIVE PHENOMENON

17. Introduction

Following an idea put forward by Frenkel (1945), we discussed in part III the structure of the edge of an incomplete molecular layer on a crystal surface, which we call a 'step'. We found that such an edge contains in equilibrium at temperature T a large number of 'kinks'. The results of this part enable us to describe the structure at a temperature T of surfaces of high index, which contain steps even at the absolute zero of temperature. Frenkel appears also to have concluded that a surface of low index, and thus flat at the absolute zero, would acquire at a finite temperature a definite number of such steps. This we believe to be incorrect. We shall show in this part that the problem of the structure of a surface is different from that of a step, being actually a problem in co-operative phenomena. The result of our investigations is that a surface of low index will remain flat, and not acquire any steps, below a certain transition temperature; above this temperature the surface becomes essentially rough, a large number of steps appearing.

The problem of the structure of a step is actually one-dimensional; we were dealing with situations spread over a line. As we pointed out in §14, we could assign independent probabilities for the existence of given features (kinks) at each point in the step, i.e. the range of possible states at each point is independent of the states at all the other points. In the two-dimensional problem which concerns us, this is no longer the case. This can be seen in the following way.

We are interested in the difference of levels between neighbouring molecules. If two neighbouring molecules differ in level by r molecular spacings, we speak of a *jump* of magnitude r . It is clear that the number of places where jumps can occur is greater than the number of molecules in the surface; hence the probability of having a jump between two given molecules cannot be independent of the jumps occurring in all the other positions. Figure 17 shows a $(0, 0, 1)$ surface of a simple cubic crystal. At $T > 0$ the surface will contain a certain number of jumps or differences of levels. The levels of the molecules can of course be assigned independently; however, the jumps cannot. For suppose we trace out a closed path $ABCDEFA$ in the surface, then the magnitude of the jump at any point on the path must be uniquely fixed by the magnitudes of the jumps at the remaining points on the path.

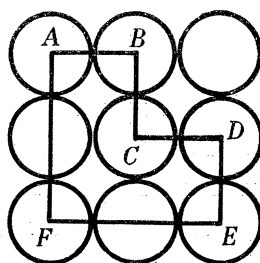


FIGURE 17

We shall consider the surface structure problem as solved when the surface potential energy at equilibrium is known as a function of temperature. For instance, if we consider a simple cubic model with nearest neighbour interactions ϕ , then a completely flat $(0, 0, 1)$ surface has a surface potential energy $\frac{1}{2}\phi$ per molecule. If, however, the surface contains a jump of magnitude r , then there will be an extra contribution to the surface potential energy of amount $\frac{1}{2}r\phi$. In general, we shall define the *surface roughness* s as $(U - U_0)/U_0$, where U_0 is the surface potential energy per molecule of the flat surface ($T = 0$) and U that of the actual surface; s is equal to the average number of bonds per molecule parallel to the surface.

In the case of a $(0, 0, 1)$ surface in a simple cubic crystal, mentioned above, the problem of finding $U - U_0$, which we call the configurational potential energy, is seen to be equivalent to finding the same quantity for a square lattice of units each capable of taking a range μ of states, such that the energy of interaction between two neighbouring units is a certain function $u(\mu, \mu')$ of their states. In the simple case considered we have

$$u(\mu, \mu') = \frac{1}{2}\phi |\mu - \mu'| \quad (\mu, \mu' = 0, \pm 1, \pm 2, \dots). \quad (90)$$

Our problem, then, is an example of the so-called standard problem of co-operative phenomena in crystal lattices; given a lattice composed of identical units, each capable of a number of states μ , such that the energy of interaction between neighbouring units i, j is a function of μ_i and μ_j , what is the partition function per unit of the lattice?

18. Co-operative phenomena in crystal lattices

It seems to be characteristic of co-operative problems that the thermodynamical functions are non-analytic functions of the temperature; they thus possess discontinuities or infinities

in themselves or in their derivatives. The temperature at which these singularities occur are called *transition temperatures*. But this result is by no means generally proved. It is conceivable that in certain cases there will be a critical region where some of the thermodynamical functions change very rapidly without having a singularity.

So far, only particular cases of the general co-operative problem in lattices have been completely solved: those in which μ is capable of two values only, and the lattice is two-dimensional. The partition function is completely known only in the case of a rectangular lattice with equal or different interactions in the two crystallographic directions (Onsager 1944; Onsager & Kaufmann 1946). In this case a single singularity is known to exist and its position is also known. Under the assumption that a single transition temperature exists for any symmetrical (equal interaction in all directions) two-dimensional lattice, its value is known (Wannier 1945), again with the limitation that μ is two-valued.

For our purpose, only the potential energy U is required. There are, in fact, several approximate methods for finding U , the best known of which is that due to Bethe (1935). These methods have been applied extensively (Wannier 1945) to the Ising model of a two-dimensional ferromagnet. However, the rigorous solution for a rectangular lattice, due to Onsager (1944, 1946), is qualitatively different from all the approximate solutions. In the approximate methods both the potential energy and the specific heat can be discontinuous functions of temperature; the correct treatment shows that both are continuous, but the specific heat has a logarithmic infinity at a temperature some 10% below that at which Bethe's method predicted a discontinuity. The reasons for this discrepancy have been discussed by Wannier (1945). These results have thrown considerable doubt on the predictions of approximate methods, especially when they predict a latent heat, i.e. that the potential energy is also discontinuous. Broadly speaking, it is characteristic of these approximations that the calculated quantities are evaluated more accurately on the low-temperature side of the transition temperature than on the high side.

The exact Onsager solution was applied to the case of a two-dimensional ferromagnet; the same solution could be applied with little change to an adsorbed monolayer on a perfectly flat crystal surface. It seems not unreasonable to suppose that the behaviour of a monolayer will be similar to that of the crystal surface itself. Such an interpretation means that we suppose that the molecules in the crystal surface are capable of two levels only. This means that if we include adsorbed molecules or nuclei in the model, holes are excluded. The two-level model of a crystal surface is undoubtedly an over-simplification, but it has the advantage that we shall be able to use the results of Onsager's treatment for several types of symmetrical and unsymmetrical surface lattices (§ 19). The generalization of Onsager's method to more than two levels seems to be very difficult; hence, in order to study how the transition temperature changes with the number of levels, we generalize Bethe's method to a many level problem in § 20.

19. *Two-level model of a crystal surface*

In appendix E we shall give a short mathematical account of the interpretation of Onsager's solution from the point of view of our problem. In this section we shall state the results and discuss their physical consequences.

In the case of a two-dimensional lattice with z nearest neighbours and equal interaction energy ϕ in all directions (symmetrical case), Wannier (1945) has shown that, assuming there is a transition temperature T_c , it will be given by the general formula

$$\text{gd } H_c = \pi/z, \quad H_c = \phi/2kT_c, \quad (91)$$

where gd is the Gudermannian function defined by

$$\text{gd } x \equiv 2 \tan^{-1} e^x - \frac{1}{2}\pi \equiv 2 \tan^{-1} (\tanh \frac{1}{2}x).$$

In the simplest case of a square lattice ($z = 4$), (91) becomes

$$\sinh H_c = 1,$$

or
$$\eta_c = e^{-H_c} = \sqrt{(2) - 1} \sim 0.41, \quad \frac{kT_c}{\phi} = (2 \ln \cot \frac{1}{8}\pi)^{-1} \sim 0.57. \quad (92)$$

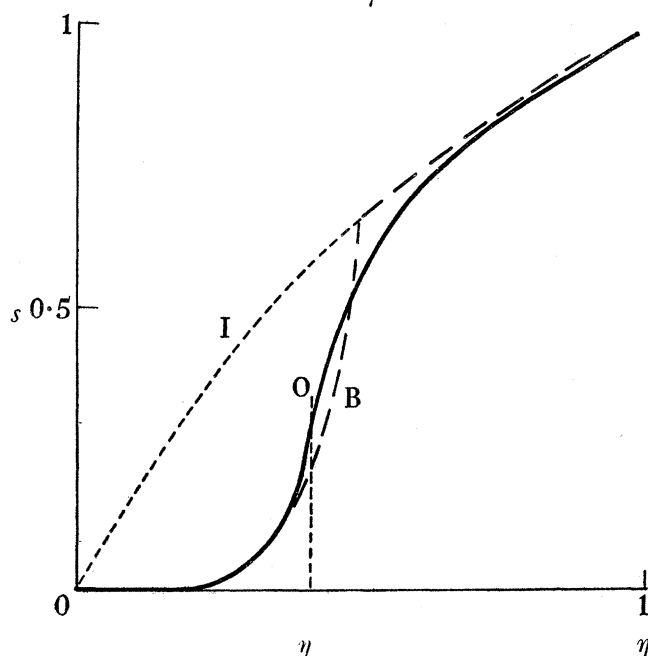


FIGURE 18. The surface roughness s of a square surface lattice as a function of η for a two-level model. O, Onsager's solution; B, Bethe's solution; I, assuming no geometrical constraints.

In this case Onsager and Onsager & Kaufmann have found the exact partition function of the lattice for all temperatures. The configurational potential energy per molecule $U - U_0$ or the surface roughness $s = 2(U - U_0)/\phi$ (see § 17) is found to be given by the formula

$$s = 1 - \frac{1}{2} \left(1 + \frac{2}{\pi} k_2 K_1 \right) \coth H, \quad (93)$$

where

$$K_1 = K(k_1) = \int_0^{\frac{1}{2}\pi} [1 - k_1^2 \sin^2 \omega]^{-\frac{1}{2}} d\omega$$

is the complete elliptic integral of the first kind, and

$$k_2 = 2 \tanh^2 H - 1, \quad k_1 = \frac{2 \sinh H}{\cosh^2 H}.$$

A graph of s against $\eta = \exp(-H) = \exp(-\phi/2kT)$ is given in figure 18. The curve possesses a vertical tangent at the transition temperature given by (92). For low temperatures or small η , (93) becomes

$$s = 4\eta^4. \quad (94)$$

This result shows that at low temperatures the jumps existing in the surface are due essentially to adsorbed molecules; in fact, the proportion of molecular positions on the surface occupied by adsorbed molecules is $\eta^4 = \exp(-2\phi/kT)$; as every adsorbed molecule has four horizontal bonds, the number of these bonds per molecule due to adsorbed molecules turns out to be equal to (94). In an actual crystal surface there will also be vacant surface sites in number equal to that of adsorbed molecules, therefore s should be $8\eta^4$; the reason why (94) is only half of that is, clearly, the assumption of a two-level model. In fact there will also be on the crystal surface nuclei of adsorbed molecules and holes consisting of more than one vacant surface site, but their concentration will be very small at low temperatures. Provided that is so, they can be considered as independent entities, and their concentration is proportional to η^6 for nuclei (or holes) of two adsorbed molecules (or vacant surface sites) and to higher powers of η for greater nuclei (or holes). As the temperature approaches the transition point, the concentration of these nuclei becomes larger and they cannot be considered as independent entities; the problem must then be considered as a co-operative phenomenon.

It is interesting to compare (93) with the result that we would have obtained if we had assumed no geometrical constraints in the surface; it is easy to see that under these conditions s would have been given by

$$s = 2\eta/(1 + \eta), \quad (95)$$

which is represented by the dotted curve in figure 18.

In the case of a triangular lattice ($z = 6$, close-packed plane) (91) becomes

$$\exp 2H_c = 3,$$

$$\text{or} \quad \eta_c = 1/\sqrt{3} \sim 0.58, \quad kT_c/\phi = (\ln 3)^{-1} \sim 0.91. \quad (96)$$

This value for the transition temperature was obtained directly by Wannier & Onsager by an elegant method (Wannier 1945) assuming that a single transition temperature exists.

Examples of square surface lattices are the (1, 0, 0) face both in simple cubic and face-centred cubic lattices. An example of a triangular surface lattice is the (1, 1, 1) in the face-centred cubic lattice. In all these cases the nearest neighbour interactions in the surface itself are the same as the nearest neighbour interactions inside the crystal. The transition temperatures (92) or (96) for these surfaces are very high and seem to be of the same order of magnitude or higher than the melting-point T_M of the crystal. In fact, for the solid state of the rare gases for which a nearest neighbour interaction model can be considered as a reasonable approximation, we find from the experimental values $kT_M/\phi \sim 0.7$. We deduce that these surfaces, if the crystal is perfect, must remain essentially flat for all temperatures below the melting-point, apart, of course, from the presence of adsorbed molecules and vacant surface sites.

Another interesting case is that of surfaces for which the nearest neighbour interactions in the surface itself are not only first but also second nearest neighbour bonds, as, for instance, (1, 1, 0) both for simple cubic and face-centred cubic lattices. Then the surface lattice is rectangular and the interactions are ϕ_1 (first nearest neighbour bond) in one direction and ϕ_2 (second nearest neighbour bond) in the other direction. The exact partition function for this lattice has also been given by Onsager (1944). He has shown that the potential energy (or our

surface roughness) follows a curve similar to figure 18, with a vertical tangent at a transition temperature given by

$$\sinh H_{1c} \sinh H_{2c} = 1, \quad H_{1c} = \phi_1/2kT_c, \quad H_{2c} = \phi_2/2kT_c.$$

This formula can be written in the form

$$\frac{2kT_c}{\phi_1} \ln \coth \frac{\phi_1}{4kT_c} = \frac{\phi_2}{\phi_1}. \quad (97)$$

Figure 19 gives kT_c/ϕ_1 as a function of the ratio ϕ_2/ϕ_1 between bond energies. We see that for a given ϕ_1 the transition temperature decreases rather slowly as ϕ_2 decreases; it is only for ratios of the order $\phi_2/\phi_1 \sim 0.1$ that T_c is smaller than (92) by a factor $\frac{1}{2}$. This is probably the case for homopolar crystals. Thus the transition temperature for these surfaces should be of the order of one-half of the melting-point. It could be interpreted as a surface melting of second nearest neighbour bonds.

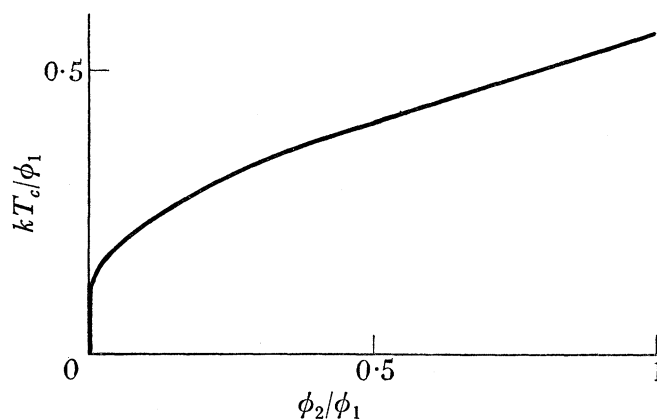


FIGURE 19. Transition temperature for a rectangular unsymmetrical lattice as a function of the ratio between the bond energies in both directions.

Finally, in the case of surfaces containing only second nearest neighbour bonds, as, for instance, (1, 1, 1) for simple cubic crystals, the transition temperature (7) is much lower; it is of the order of ϕ_2/ϕ_1 times the melting-point. At ordinary temperatures these surfaces would therefore be above their transition temperature.

The configurational surface free energy is, in all cases, very small below and at the transition temperature. Above this temperature it decreases roughly linearly with rise of temperature, the slope being $-k \ln 2$ approximately. Therefore the differences in surface free energy between the different faces of a crystal will decrease more and more as the temperature rises and the critical temperatures of the high index surfaces are surpassed, since high index faces have higher surface energies but lower transition temperatures.

The existence of a transition temperature, when it is below the melting-point, should have an observable effect on the adsorption properties of the surface, which clearly depends on the surface roughness. Actually the presence of adsorbable substance will change the equilibrium structure of the surface itself, and its transition temperature. We hope to treat this point in detail elsewhere. Meanwhile, a possible experimental method of testing the existence of a transition temperature would be to prepare, say, a metal crystal with one of

its less dense-packed surfaces exposed, anneal at various temperatures *in vacuo*, quench and test the adsorption properties of the surface. A sharp change in the latter would be expected when the annealing temperature crosses the transition temperature of the surface.

Similar considerations would apply to the influence of the catalytic properties of the surface of some solids on the kinetics of chemical reactions between adsorbed substances, in the case when the catalytic activity is restricted to 'active' points on the surface. Frenkel (1945) suggested that these 'active' points should be identified with the presence of jumps on the surface, assuming that the adsorption of the reacting molecules in the edge of the steps decreases the activation energy for their chemical reaction.

On the other hand, the existence of a transition temperature will not have any influence on the kinetics of growth of the crystal surface. It would if the crystal were perfect. Below the transition temperature the only mechanism of growth would be a two-dimensional nucleation, which we know (part III) is always a very slow process at low supersaturations. Above the transition temperature the growth will be proportional to the supersaturation. Actually the fact that real crystals are imperfect guarantees the presence of the steps required to explain the observed growth at low supersaturations and below the transition temperature; Frank (1949) has shown that, during growth, a dislocation or group of dislocations terminating in the surface sends out closed loops of step in such a way that at any instant the surface is covered by a very high density of steps, practically independently of the number of dislocations present (provided there is at least one). Therefore, even if we observe the growth of a surface for which the critical temperature is below the melting-point, there would hardly be any difference between the rate of growth below and above the critical temperature.

20. *Many-level model: Bethe's approximation*

The two-level model of a crystal surface is clearly an over-simplification. We expect that with a many-level model, which corresponds to the actual crystal surface, the transition temperature should be lowered. In order to study this point we extend in this section Bethe's method to our many-level problem. In this method we assume that in a given region, arbitrarily chosen, the probabilities in which we are interested are independent; we then insert correction factors to take account of the geometrical constraints, and attempt to evaluate them by the requirement of self-consistency.

We shall limit ourselves, for simplicity, to the study of the structure of a (0, 0, 1) surface of a simple cubic crystal. Figure 20 shows a group of five molecules in the crystal surface, whose levels are i, j, k, l, m (at $T = 0$ we would have $i = j = k = l = m = 0$). Let the probability for this configuration be $p(i; j, k, l, m)$, p not being normalized. We assume that

$$p(i; j, k, l, m) = \eta^{|i-j| + |i-k| + |i-l| + |i-m|} \epsilon(j) \epsilon(k) \epsilon(l) \epsilon(m), \quad \eta = \exp\left(-\frac{\phi}{2kT}\right), \quad (98)$$

where ϕ is as usual the nearest neighbour interaction. The factors containing η represent the Boltzmann factors, and the functions ϵ are the correction factors which take into account the influence of geometrical constraints of the outside region on the molecules considered. The factors $\epsilon(x)$ will be less than unity unless $x = 0$; in this case we take $\epsilon(0) = 1$. The level zero corresponds to Bethe's 'right atom', the other levels to different kinds of 'wrong atoms'. By symmetry, $\epsilon(x) = \epsilon(-x)$.

The total probability $p(x)$, for the central molecule to be at the level x , whatever the values of j, k, l, m , is

$$p(x) = \sum_{jklm} p(x; j, k, l, m) = \{f(x)\}^4, \quad (99)$$

where

$$f(x) = \sum_j \eta^{|x-j|} \epsilon(j), \quad (100)$$

and the summations are carried out over all possible levels. Clearly $f(x) = f(-x)$. Following Bethe, the self-consistency condition is that the probability $p(x)$ for the central molecule to be at the level x must be equal to that for one of the molecules in the outer shell to be also at this level. Therefore $p(x)$ can also be written as

$$p(x) = \sum_{i,klm} p(i; x, k, l, m) = \epsilon(x) \sum_i \eta^{|x-i|} \{f(i)\}^3, \quad (101)$$

where we have used (98) and (100). Hence from (99) and (101) we obtain

$$f^4(x) = \epsilon(x) \sum_i \eta^{|x-i|} f^3(i), \quad f^r(x) \equiv \{f(x)\}^r. \quad (102)$$

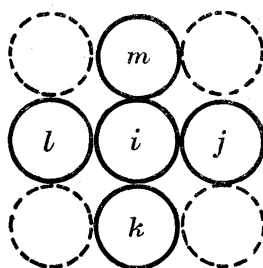


FIGURE 20

The correction factors $\epsilon(x)$ have to be determined from the equations (100) and (102). Now if we divide (102) by $f^3(0)$, use (100), and introduce the functions $g(x) = [f(x)/f(0)]^3$, the equations (102) transform into the system of linear equations

$$g(x) \sum_i \eta^{|x-i|} \epsilon(i) = \epsilon(x) \sum_i \eta^{|x-i|} g(i),$$

which have the only solution

$$\epsilon(x) = g(x) = [f(x)/f(0)]^3. \quad (103)$$

This form of the conditions that $\epsilon(x)$ must satisfy is very convenient for numerical calculations.

The potential energy U , and therefore the surface roughness $s = 2U/\phi$, can also be written in a general form. In fact, the energy corresponding to the configuration of figure 20 is

$$\frac{1}{2}\phi \{ |i-j| + |i-k| + |i-l| + |i-m| \},$$

and therefore the potential energy per molecule U of the surface will be

$$U = \frac{1}{2} \frac{\phi \sum \{ |i-j| + |i-k| + |i-l| + |i-m| \} p(i; j, k, l, m)}{\sum p(i; j, k, l, m)}, \quad (104)$$

where the summations are carried out over all values of i, j, k, l, m . Using (98) and (100) the potential energy or the surface roughness can be written in the form

$$s = \frac{1}{2} \eta \frac{\partial}{\partial \eta} \ln \sum_i f^4(i), \quad (105)$$

where the use of the sign of partial differentiation is to indicate that ϵ is to be treated as constant during the differentiation. Once the $\epsilon(x)$ are known from equations (103) the surface roughness factor is determined from (105).

20.1. Two-level problem

Let us first consider, as an introduction, the two-level case, which is the problem initially considered by Bethe (1935). In this case, from (100) ($i = 0, 1$),

$$f(0) = 1 + \epsilon_1 \eta, \quad f(1) = \epsilon_1 + \eta; \quad \epsilon(0) = 1, \quad \epsilon(1) = \epsilon_1,$$

and formula (103) becomes Bethe's equation

$$\epsilon_1 = \left(\frac{\epsilon_1 + \eta}{1 + \epsilon_1 \eta} \right)^3, \quad (106)$$

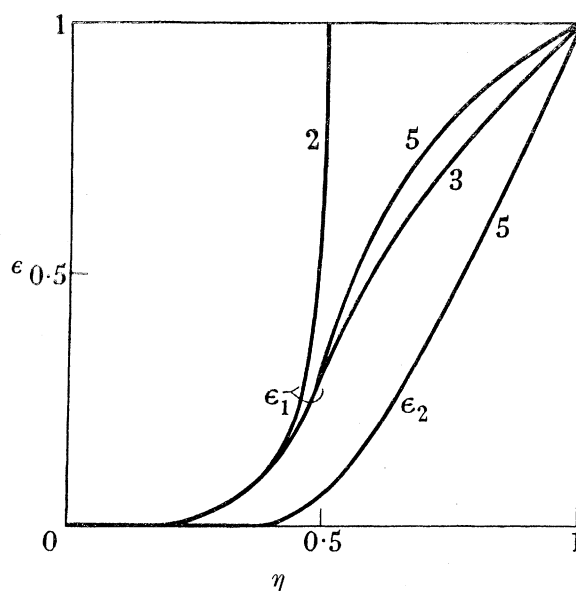


FIGURE 21. Bethe's factors ϵ for the two, three, and five levels.

giving ϵ_1 as a function of η . Figure 21 gives ϵ_1 (curve 2) as a function of η . ϵ_1 is smaller than 1 only for values of η smaller than 0.5. Above $\eta = 0.5$ the only solution of (106) is $\epsilon_1 = 1$. The temperature corresponding to $\eta = 0.5$ has been interpreted as the transition temperature of the corresponding co-operative phenomenon:

$$\eta_c = 0.5, \quad kT_c/\phi = (2 \ln 2)^{-1} \sim 0.72. \quad (107)$$

This value is higher than the value $kT_c/\phi \sim 0.57$ (92) given by the correct treatment of Onsager. On the other hand, the fact that $\epsilon_1 = 1$ above $\eta = 0.5$ cannot be interpreted from a physical point of view, and shows only that the method is not correct. Actually $\epsilon_1 = 1$ means, from the point of view of our problem, that the geometrical constraints have disappeared above the transition temperature, and this is obviously impossible. According to the definition of the factors ϵ , they must be smaller than 1 at all temperatures.

The surface roughness is now given by

$$s = \frac{4\epsilon_1 \eta}{1 + \epsilon_1^3} \frac{1}{1 + \epsilon_1 \eta}. \quad (108)$$

For low temperatures, $s = 4\eta^4$, the same expression as is given by Onsager's treatment. Above $\eta = 0.5$, s is given by formula (95) corresponding to the hypothesis of independency of the probabilities or $\epsilon_1 = 1$. The expression (108) has been represented in figure 18, for comparison with Onsager's result.

20.2. Three-level problem

The simplest many-level problem which corresponds to the structure of a crystal surface is the three-level problem. In this case, using (100) ($i = 1, 0, -1$),

$$f(0) = 1 + 2\epsilon_1\eta, \quad f(1) = f(-1) = \eta + \epsilon_1(1 + \eta^2); \quad \epsilon(0) = 1, \quad \epsilon(1) = \epsilon(-1) = \epsilon_1.$$

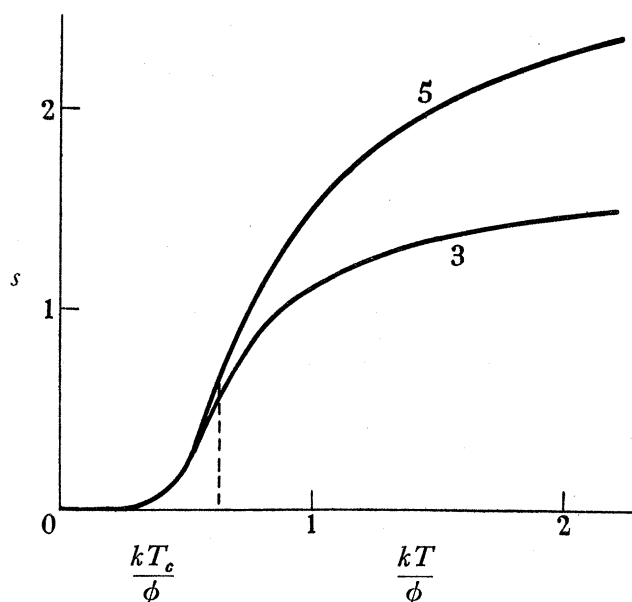


FIGURE 22. The surface roughness s for a three-level and five-level problem, as a function of kT/ϕ .

The general formula (103) now gives the equation

$$\epsilon_1 = \left[\frac{\eta + (1 + \eta^2)\epsilon_1}{1 + 2\eta\epsilon_1} \right]^3 \quad (109)$$

for the calculation of ϵ_1 as a function of η . The result is represented in figure 21 (curve 3). In this case $\epsilon_1 = 1$ is not a solution of (109) for any finite temperature, as we should expect on physical grounds. On the other hand, ϵ_1 has no singularity allowing the definition of a transition temperature. To decide where this transition temperature is we must wait till s is known.

The value of s is easily calculated from (105):

$$s = \frac{8\eta\epsilon_1}{1 + 2\epsilon_1} \frac{1 + \epsilon_1\eta}{1 + 2\epsilon_1\eta}. \quad (110)$$

The result is represented in figure 22 as a function of kT/ϕ ; the curve has a point of inflexion at a temperature given by

$$\eta_c = 0.45, \quad kT_c/\phi \sim 0.63. \quad (111)$$

This temperature can be interpreted as the transition temperature of the three-level problem. It is substantially lower than the transition temperature corresponding to the two-level Bethe problem, but still higher than Onsager's value. The derivative of s with respect to T (which would correspond to the specific heat in our problem) would have a maximum at this transition temperature, but not a singularity.

At low temperatures (110) becomes

$$s = 8\eta^4,$$

which represents the jumps due to the presence in the surface of adsorbed molecules *and* vacant surface sites, which were not allowed in a two-level model. At high temperatures s becomes now larger than 1 (in fact, its maximum value for $\eta = 1$ is 1.8). The reason for that is again that we have now the possibility of jumps of height 2 intermolecular distances, and therefore the number of bonds parallel to the surface per molecule (equal to s) can now be greater than 1.

20.3. Many-level problem

It is interesting to see how the surface roughness behaves with increasing number of levels. In the case of five levels, one obtains the equations

$$\epsilon_1 = \left(\frac{\eta + (1 + \eta^2) \epsilon_1 + \eta(1 + \eta^2) \epsilon_2}{1 + 2\eta\epsilon_1 + 2\eta^2\epsilon_2} \right)^3, \quad \epsilon_2 = \left(\frac{\eta^2 + \eta(1 + \eta^2) \epsilon_1 + (1 + \eta^4) \epsilon_2}{1 + 2\eta\epsilon_1 + 2\eta^2\epsilon_2} \right)^3 \quad (112)$$

for the calculation of $\epsilon_1 = \epsilon(1) = \epsilon(-1)$ and $\epsilon_2 = \epsilon(2) = \epsilon(-2)$. The surface roughness s is given by

$$s = \frac{8\eta}{1 + 2\epsilon_1^{\frac{4}{3}} + 2\epsilon_2^{\frac{4}{3}}} \frac{\epsilon_1 + \eta(\epsilon_1^2 + 2\epsilon_2) + (1 + 3\eta^2) \epsilon_1 \epsilon_2 + 2\eta^3 \epsilon_2^2}{1 + 2\eta\epsilon_1 + 2\eta^2\epsilon_2}. \quad (113)$$

The values of ϵ_1 and ϵ_2 are represented in figure 21 as functions of η and those of s in figure 22 as functions of kT/ϕ . The curve s has again a point of inflexion, defining the transition temperature at a value of kT_c/ϕ which cannot be distinguished from (111). The inclination of the tangent increases and hence the height of the maximum for the derivative of s . We notice that the difference in behaviour between three and five levels is rather small from the point of view of the location of the transition temperature. The reason for that is that the new parameters ϵ which we introduce to represent the new levels are very small in the neighbourhood of the critical point.

The calculations can be carried on to any number of levels. In the vicinity of the transition temperature there is practically no further change. Also the parameters ϵ do not become 1, at any rate for temperatures for which $\eta < 0.8$, in spite of the fact that for an infinite number of levels $\epsilon(x) \equiv 1$ is a solution of equations (100) and (102).

The change in the value of the transition temperature, according to Bethe's method, occurs therefore at the passage from two to three levels. Although we also expect to have a decrease in the correct transition temperature, when the number of levels is increased, we do not know whether this decrease will be as substantial as it is in Bethe's approximation, owing to the anomalous behaviour of the two-level problem in this approximation.

APPENDICES

APPENDIX A. INFLUENCE OF THE MEAN DISTANCE x_0 BETWEEN KINKS ON THE RATE OF ADVANCE OF STEPSA1. *Single step*

We suppose the kinks to be regularly distributed on the step at distances x_0 from each other (figure 23). Let us suppose D_s is independent of direction in the surface; we have to solve equation (14) or

$$x_s^2 \nabla^2 \psi = \psi, \quad \psi = \sigma - \sigma_s, \quad (\text{A1})$$

with the boundary condition $\psi = 0$ for $y = \pm \infty$. We suppose also that there is a current in the edge of the step, governed by the diffusion constant D_e , which is large enough for the current passing directly from the surface to the kinks to be neglected. Since ψ must be periodic in x , with period x_0 , the required solution of (A1) is

$$\psi(x, y) = \sigma\beta \sum_{n=0}^{\infty} c_n e^{\mp l_n y} \cos k_n x; \quad k_n = 2\pi n/x_0, \quad l_n^2 = x_s^{-2} + k_n^2. \quad (\text{A2})$$

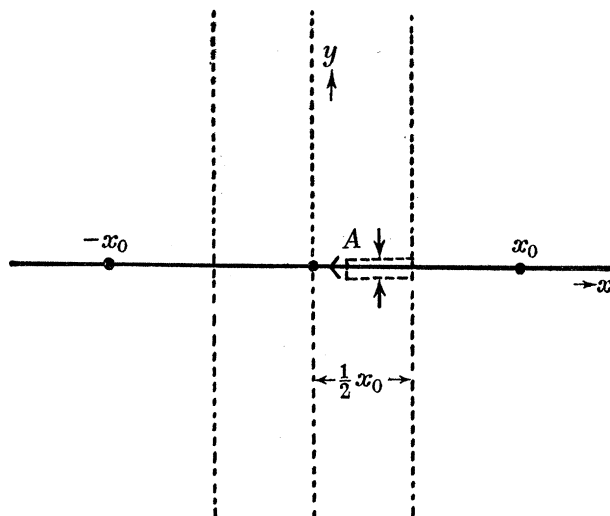


FIGURE 23. Step ($y=0$) with kinks at a distance x_0 from each other.

The minus sign corresponds to $y > 0$, and the plus sign to $y < 0$; the coefficients c_n have to be determined. The current going into one kink ($x = 0$ for instance) will be equal to the current

$$j = D_s n_{s0} (\partial \psi / \partial y)_{y=0}$$

going from the surface to the edge integrated between $-\frac{1}{2}x_0$ and $\frac{1}{2}x_0$. The velocity of the step will then be the result of the current going into all the kinks, and turns out to be

$$v_{\infty} = 2\sigma x_s v \exp(-W/kT) \beta c_0, \quad (\text{A3})$$

which is the general expression (19) given in § 4. We have now to calculate the factor c_0 .

In the edge of the step we shall have a supersaturation σ_e and an expression $\psi_e = \sigma - \sigma_e$, which will be a function of x . In general, $\psi(x, 0) = \beta_1 \psi_e(x)$, where $\beta_1 < 1$ is a retarding factor similar to (17). If the interchange of molecules between the edge and its immediate neighbourhood is rapid, $\beta_1 = 1$. Hence

$$\beta_1 \psi_e(x) = \sigma\beta \sum_{n=0}^{\infty} c_n \cos k_n x. \quad (\text{A4})$$

Near the kinks ($x = 0$ for instance) we shall have $\psi_e(0) = \beta_2\sigma$, where β_2 is another retarding factor corresponding to the interchange between edge and kink. Putting $\beta = \beta_1\beta_2$, we have the condition

$$\sum_{n=0}^{\infty} c_n = 1. \quad (\text{A5})$$

The current in the edge passing through the point A (figure 23), whose co-ordinate is x , is given by

$$j_e = -D_e(dn_e/dx) = -D_e n_{e0} \sigma \beta_2 \sum_{n=0}^{\infty} c_n k_n \sin k_n x, \quad (\text{A6})$$

where (A4) has been used. On the other hand, this current must be equal to that going from the surface to the edge between x and $\frac{1}{2}x_0$, that is to say

$$2D_s n_{s0} \int_x^{\frac{1}{2}x_0} (\partial\psi/\partial y)_{y=0} dx = -2D_s n_{s0} \sigma \beta \left[c_0 (\frac{1}{2}x_0 \operatorname{sgn} x - x)/x_s - \sum_{n=1}^{\infty} (c_n l_n/k_n) \sin k_n x \right], \quad (\text{A7})$$

where $\operatorname{sgn} x$ is 1 for $x > 0$, -1 for $x < 0$ and 0 for $x = 0$. Equating (A6) and (A7) we obtain the coefficients c_n ($n > 0$) as functions of c_0 :

$$c_n/c_0 = (4bc/n^2) [1 + (2c/n) (1 + b^2/n^2)^{\frac{1}{2}}]^{-1}, \quad (\text{A8})$$

with the abbreviations

$$b = x_0/2\pi x_s, \quad c = x_0 a/2\pi x_e^2, \quad x_e^2 = D_e n_{e0} a/D_s n_{s0} \beta_1. \quad (\text{A9})$$

From (A5) and (A8) we obtain

$$1/c_0 = 1 + 4bc \sum_{n=1}^{\infty} \{n^2 [1 + (2c/n) (1 + b^2/n^2)^{\frac{1}{2}}]\}^{-1}. \quad (\text{A10})$$

The series in (A10) can be approximated to by an integral

$$\sum_{n=1}^{\infty} \{n^2 [1 + (2c/n) (1 + b^2/n^2)^{\frac{1}{2}}]\}^{-1} \simeq \int_0^1 \frac{dx}{1 + 2cx(1 + b^2x^2)^{\frac{1}{2}}},$$

which can be evaluated using the transformation $\tan \theta = bx$. The final result for c_0 is

$$\frac{1}{c_0} = 1 + 2bc(b^2 + c^2)^{-\frac{1}{2}} \{f_1(x_1, u_m) + f_2(x_2, u_m)\}, \quad (\text{A11})$$

where $f_1(x_1, u_m) = 2(x_1^2 - 1)^{-\frac{1}{2}} \tan^{-1} \{u_m(x_1^2 - 1)^{\frac{1}{2}}/(x_1 - u_m)\}$,
 $f_2(x_2, u_m) = (1 - x_2^2)^{-\frac{1}{2}} \ln \{(u_m(1 + (1 - x_2^2)^{\frac{1}{2}}) + x_2)/(u_m(1 - (1 - x_2^2)^{\frac{1}{2}}) + x_2)\}$,
 $u_m = b/\{1 + (1 + b^2)^{\frac{1}{2}}\}$, $x_1 = c/b + (c^2/b^2 + 1)^{\frac{1}{2}} > 1$, $x_2 = -c/b + (c^2/b^2 + 1)^{\frac{1}{2}} < 1$.

For $x_0 \rightarrow \infty$, we obtain the result for widely separated kinks; it is easy to see that c_0 is then proportional to $1/x_0$, or to the number of kinks per cm.

The method used to calculate the current going into the kinks is correct, provided the current via the edge is important or $x_e > a$. In the limiting case when $x_e \sim a$ the result of this calculation should be the same as if the current via the edge were neglected altogether. In §4 we have seen that x_e is of the order of a ; under these conditions, and assuming $x_0 \gg a$ and $x_s \gg a$, one obtains from (A9) that $c \gg 1$ and $c/b \gg 1$; then, the rather complicated expression (A11) reduces to

$$1/c_0 = 1 + 2b \ln \{4c/(1 + (1 + b^2)^{\frac{1}{2}})\}, \quad (\text{A12})$$

which is the formula (21) of §4.

A2. *Parallel sequence of steps*

We suppose the steps and kinks are disposed as in figure 24, the kinks forming a rectangular lattice. Let the distance between kinks be x_0 and that between steps y_0 . Between steps the same continuity equation (A1) holds. Again we have periodicity in the x -direction, hence in the interval

$$-\frac{1}{2}y_0 < y < \frac{1}{2}y_0, \quad -\frac{1}{2}x_0 < x < \frac{1}{2}x_0,$$

we have the solution
$$\psi(x, y) = \sigma\beta \sum_{n=0}^{\infty} c_n \frac{\cosh l_n y}{\cosh \frac{1}{2}l_n y_0} \cos k_n x, \quad (\text{A13})$$

where k_n and l_n have the same significance as in (A2). The velocity of every step will be the result of the current going into every kink, equal to the current going from the surface to the step in the range x_0 . The velocity turns out to be

$$v_{\infty} = 2\sigma x_s v e^{-W/kT} \tanh(y_0/2x_s) \beta c_0, \quad (\text{A14})$$

which is the general formula (24) given in § 5. To calculate c_0 we have again the condition

$$\sum_{n=0}^{\infty} c_n = 1 \quad (\text{A15})$$

as before. To evaluate all the $c_n (n > 0)$ as functions of c_0 , we use the same method as in § A1, and from (A15) we deduce for c_0 the rather complicated expression

$$1/c_0 = 1 + 4bc \tanh(y_0/2x_s) \sum_{n=1}^{\infty} \{n^2 [1 + (2c/n) (1 + b^2/n^2)^{\frac{1}{2}} \tanh((n/2e) (1 + b^2/n^2)^{\frac{1}{2}})]\}^{-1}, \quad (\text{A16})$$

where b and c are given by (A9) and

$$e = x_0/2\pi y_0. \quad (\text{A17})$$

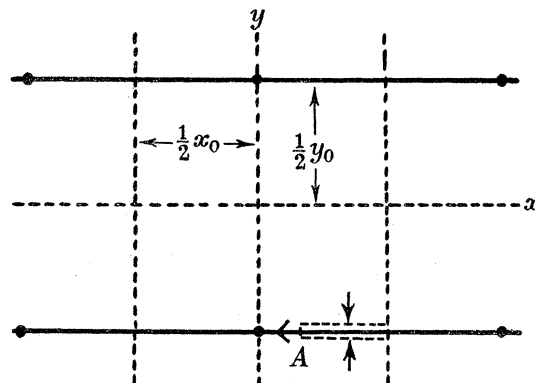


FIGURE 24. Sequence of steps distant y_0 from each other with kinks distant x_0 .

In the limiting case when $x_e \sim a$, and therefore $c \gg 1$, the series in (A16) can be approximately evaluated, replacing the $\tanh x$ by $x/(1+x)$. The approximated result is

$$1/c_0 = 1 + 2b \tanh(y_0/2x_0) [\ln(4c/(1+(1+b^2)^{\frac{1}{2}})) + (2e/b) \tan^{-1} b], \quad (\text{A18})$$

which is the formula (25) given in § 5.

APPENDIX B. THE MUTUAL INFLUENCE OF A PAIR OF GROWTH SPIRALS

We now reconsider, in more detail, the interaction of the growth spirals of a pair of dislocations (like or unlike) whose separation is at least a moderate multiple of ρ_c . We have seen (§ 9.1) that their resultant activity will equal that of one dislocation except in so far as

influences transmitted along the step from the point of meeting modify the rate of rotation of the separate spirals. To examine this effect we first consider a simpler case.

A circular expanding step, whose position is defined by $r = r_1(t)$, is helped on over a small portion of its length, e.g. by meeting another small closed loop of step (a small island nucleus). Re-entrant portions of the curve fill in rapidly, so that we then have $r = r_1(t) + f(\theta, t)$, where θ is the angular polar co-ordinate and t the time. We suppose f small compared with r_1 , and $\partial r/\partial \theta = r'$ small enough for its square to be neglected in expressions for curvature (35) and normal velocity (36):

$$1/\rho = (r^2 + 2r'^2 - rr'') (r^2 + r'^2)^{-3/2} \sim 1/r - r''/r^2 \sim 1/r_1 - \partial^2 f/\partial s^2,$$

$$v = (\partial r/\partial t) r (r^2 + r'^2)^{-3/2} \sim \partial r/\partial t = \partial r_1/\partial t + \partial f/\partial t.$$

Here s is the arc distance $r\theta$. By equation (34) we have then

$$\partial r_1/\partial t + \partial f/\partial t = v_\infty - v_\infty \rho_c/r_1 + v_\infty \rho_c \partial^2 f/\partial s^2.$$

Subtracting the corresponding equation obtained when f is zero, we have

$$\frac{\partial f}{\partial t} = v_\infty \rho_c \frac{\partial^2 f}{\partial s^2}.$$

This is simply the diffusion equation, with an effective diffusivity $v_\infty \rho_c$. Whatever the initial form of f , provided it is confined to a small portion of the circumference and disregarding the closed nature of the curve (as is right, since we are going to apply the result to a spiral instead of a circle), its solution tends rapidly to the form

$$f = A(4\pi\rho_c v_\infty t)^{-1/2} \exp(-s^2/4\rho_c v_\infty t),$$

for which $\int_{-\infty}^{\infty} f ds$ has the constant value A . Thus the growth increment remains constant in area but gradually spreads out along the step.

This result should be approximately valid for deformations of the spiral also, except close to the centre, where r' is no longer negligible. We apply it, then, to a growth spiral which, once in every turn, meets another based on a dislocation a distance l away. Each time this happens the resulting concave region of the growth front fills up rapidly, making an area of increment which we estimate roughly as $(4 - \pi) l^2/8$ from the difference in area between two circular quadrants and a rectangle. This occurs $\omega/2\pi$ times a second at a distance, measured along the step, approximately $l^2/16\rho_c$ from the dislocation. These growth increments now diffuse along the step, but at the same time the spiral continues to rotate, so that while the increment spreads, its centre recedes from the dislocation, the arc distance being expressible approximately as

$$s = \rho_c(l/4\rho_c + \omega t)^2.$$

Near the centre of the spiral the concept of an area diffusing along a line fails; the growth increment which diffuses into the centre is used up in extending the step line faster than would occur spontaneously.

Supposing the diffusion law continued to hold as far as the centre of the spiral and on some fictitious line beyond it, the value of f at this point resulting from one meeting of the growth fronts at a time $t = 0$ would be approximately

$$f_a = \{(4 - \pi) l^2/16(\pi\rho_c v_\infty t)^{1/2}\} \exp[-\rho_c(l/4\rho_c + \omega t)^4/4v_\infty t].$$

This is zero for small or large t , and has a maximum very nearly at the maximum of the exponential factor which occurs at $t = l/12\omega\rho_c$. Inserting this value of t , and at the same time writing $\omega = \epsilon v_\infty/2\rho_c$, where ϵ is a factor representing the increase of rate of rotation over that of an unperturbed single spiral, we have

$$f_{d, \max.} = [(4-\pi)/16] (6\epsilon l^3/\pi\rho_c)^{\frac{1}{2}} \exp[-(\frac{1}{2}\epsilon) (l/3\rho_c)^3].$$

We may alternatively focus attention on the area of incremental growth which would have diffused past the centre, on the same assumptions. This is

$$F_d = [(4-\pi) l^2/16] \operatorname{erfc} [(l/4\rho_c + \omega t)^2 (4v_\infty t/\rho_c)^{-\frac{1}{2}}],$$

where $\operatorname{erfc}(x)$ is the complementary error function $1 - \operatorname{erf}(x)$. As a function of time this has its maximum value at $t = l/12\omega\rho_c$, and is then

$$F_{d, \max.} = [(4-\pi) l^2/16] \operatorname{erfc} [(\frac{1}{2}\epsilon)^{\frac{1}{2}} (l/3\rho_c)^{\frac{3}{2}}].$$

Consideration of either of these expressions, $f_{d, \max.}$ or $F_{d, \max.}$, suffices to show that the influence transmitted into the centre is quite negligible if l much exceeds $3\rho_c$.

For variations of l/ρ_c the first of these functions is a maximum precisely, the second very nearly, when $(l\epsilon^{\frac{1}{2}}/3\rho_c) = 1$. The corresponding maximum values are $0.234\rho_c$ and $0.155\epsilon^{-\frac{1}{2}}\rho_c^2$. We may crudely estimate the order of magnitude of the amount of extra rotation produced by such an increment by dividing by $2\pi\rho_c$ in the first case or $\pi\rho_c^2$ in the second, obtaining 0.037 or $0.049\epsilon^{-\frac{1}{2}}$ of a turn. This occurs once in every turn, i.e. $\epsilon \sim 1.04$ or 1.05 . This result is not directly valuable, for the maxima occur at a separation too small for the validity of approximations used in the treatment; but it does show that at greater separations where the approximations are reasonably valid (say $l > 4\pi\rho_c$) the interaction is quite negligible.

The calculation affirms the surmise that when ρ_c is steadily reduced below the critical value $\frac{1}{2}l$ above which the activity of an unlike pair of dislocations is zero, the activity first rises above that of a single dislocation before settling down to equality with it; but it leaves much doubt as to the actual magnitude of the maximum excess. It is probably a few units per cent, and if it later turns out that importance attaches to the actual value, a step-by-step trajectory calculation must be carried out.

APPENDIX C. PROOF OF CERTAIN FORMULAE IN THE STATISTICS OF KINKS

To prove formulae (65), (66) and (67) in the text, we consider particular processes (figures 25, 26, 27, 28) and we apply the principle of detailed balancing.

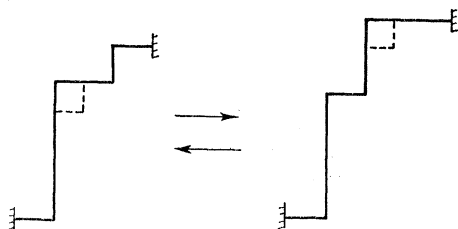


FIGURE 25

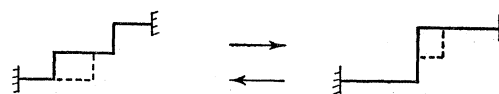


FIGURE 26



FIGURE 27



FIGURE 28

Let us first consider the process shown in figure 25. The molecule denoted by a square is the one which moves. The positions in the shaded regions are supposed to remain the same during the process. In this case the energies of the two configurations are the same, so the probabilities for their occurrence are equal. Hence

$$n_{+r}(x) q(x+1) n_+(x+2) = n_{+(r-1)}(x) n_{+2}(x+1) q(x+2). \quad (\text{C1})$$

Here we have written n_+ for n_{+1} . Later we write g_+ for g_{+1} . It is convenient to introduce a function defined by

$$g_{\pm r}(x) = n_{\pm r}(x)/g(x). \quad (\text{C2})$$

Then (A1) can be written

$$g_{+r}(x) g_+(x+2) = g_{+(r-1)}(x) g_{+2}(x+1). \quad (\text{C3})$$

For the process of figure 26, we need to supply an energy ϕ_2 in going from the left-hand to the right-hand diagram. Hence

$$g_{+2}(x+1) = g_+(x) g_+(x+2) \eta_2^2, \quad (\text{C4})$$

where we have again used (C2) and also the abbreviation

$$\eta_{1,2} = \exp(-\phi_{1,2}/2kT). \quad (\text{C5})$$

Substituting the value (C4) of $g_{+2}(x+1)$ in (C3) we obtain

$$g_{+r}(x) = \{g_+(x)\}^r \eta_2^{2(r-1)}, \quad (\text{C6})$$

as is easily shown by induction on r . Formula (C6) is formula (65) of the text.

We now need an equation relating neighbouring positions. Comparing (C4) and (C6) ($r = 2$) we obtain, immediately,

$$\{g_+(x)\}^2 = g_+(x-1) g_+(x+1). \quad (\text{C7})$$

From the process illustrated by figure 27 we obtain

$$g_+(x+1) \eta_1^2 = g_+(x) g_-(x+1) g_+(x+2),$$

and using the property (C7) we obtain

$$g_+(x) g_-(x) = \eta_1^2, \quad (\text{C8})$$

which is formula (66) in the text.

The general solution of the functional equation (C7) is easily proved to be

$$g_+(x) = g_+(0) e^{cx}, \quad (\text{C9})$$

where $g_+(0)$ and c are arbitrary constants. We now investigate the dependence of the constant c in (C9) on the supersaturation, or more specifically the saturation ratio α defined by the equation

$$N = \alpha N_0 = \alpha(\eta_1 \eta_2)^4. \quad (\text{C10})$$

Here N is the occupation probability for an adsorbed molecule on the surface, and

$$N_0 = \exp\{-2(\phi_1 + \phi_2)/kT\}$$

is clearly the value of N when $\alpha = 1$. Since we are speaking of equilibrium, N is independent of position in the surface. From the process represented by figure 28 we obtain

$$N = g_+(x) g_-(x+1) \eta_1^2 \eta_2^4, \quad (\text{C11})$$

and combining this result with (C8), (C9) and (C10) we obtain

$$\alpha = e^{-c},$$

and therefore (A9) becomes $g_+(x) = g_+(0) \alpha^{-x}$, (C12)

which is equation (67) given in the text.

APPENDIX D. WULFF'S THEOREM

'In a crystal at equilibrium, the distances of the faces from the centre of the crystal are proportional to their surface free energies per unit area.'

A great deal has been written on the general form of this theorem, and von Laue (1943) has given a critical review of the subject. There is no really satisfactory proof of the three-dimensional Wulff theorem even now. The proof for the two-dimensional case given here is believed to have merits not to be found in any earlier proof.

The problem is to find the relation between the shape of the two-dimensional equilibrium nucleus, and the polar diagram of the free energy of a boundary element as a function of its orientation. The shape is fixed by the condition of minimum total free energy for a given area of nucleus. Let (r, ϕ) be the polar co-ordinates (figure 29) of a point T of the crystal boundary S , and let (x, y) be the corresponding Cartesian co-ordinates. Construct a tangent to S at T , and let OM be a perpendicular from the origin to the tangent (length p). Let $f(\theta)$ be the edge free energy per unit length of the element of boundary at T . The line element for the boundary in parametric form is

$$ds = (\dot{x}^2 + \dot{y}^2)^{\frac{1}{2}} dt, \quad (\text{D1})$$

where the dot denotes differentiation with respect to the parameter t . We now choose θ as the parameter. Then the total edge free energy F and area n_0 (number of molecules) of our nucleus are given by

$$F = \int (\dot{x}^2 + \dot{y}^2)^{\frac{1}{2}} f(\theta) d\theta, \quad n_0 = \frac{1}{2} \int (xy - y\dot{x}) d\theta, \quad (\text{D2})$$

respectively. From figure 29, $p = x \cos \theta + y \sin \theta$. (D3)

Let us find the locus of M as T goes over the whole of the curve S . This will give the 'pedal' of S , which is determined by (D3) and the equation obtained from it by partial differentiation with respect to θ . Conversely, if the pedal is known, i.e. p is given as a function of θ , then the (x, y) equation of S can be obtained from the equations

$$\left. \begin{aligned} x &= p \cos \theta - \dot{p} \sin \theta, \\ y &= p \sin \theta + \dot{p} \cos \theta. \end{aligned} \right\} \quad (\text{D4})$$

Using these expressions we can write (D2) in the form

$$F = \int (p + \dot{p}) f d\theta, \quad n_0 = \frac{1}{2} \int (p + \dot{p}) p d\theta. \quad (\text{D5})$$

The problem now is to minimize F subject to the condition of n_0 being constant. Introducing the Lagrange multiplier λ , the appropriate Euler equation giving the minimum condition is

$$\frac{\partial Q}{\partial p} - \frac{d}{d\theta} \left(\frac{\partial Q}{\partial \dot{p}} \right) + \frac{d^2}{d\theta^2} \left(\frac{\partial Q}{\partial \ddot{p}} \right) = 0,$$

where

$$Q = \frac{1}{2} (p + \dot{p}) p - \lambda (p + \dot{p}) f.$$

These two equations reduce to $p + \dot{p} = \lambda (f + \dot{f})$, (D6)

and the solution of this differential equation is

$$p(\theta) = C \sin(\theta - \beta) + \lambda f(\theta),$$

where C and β are arbitrary constants. Now the first term on the right possesses the period 2π ; so that if we choose the origin in such a way that the crystal possesses some rotational symmetry with respect to it (centre of the crystal), we see that $C = 0$. Hence

$$p(\theta) = \lambda f(\theta), \quad (\text{D7})$$

which shows that up to a constant factor the polar diagram of the edge free energy is the pedal of the equilibrium shape of the crystal.

The foregoing theorem, which is a generalization of Wulff's theorem, enables us to study the properties of the critical nucleus in a very general way. First we deduce from (D5), (D6) and (D7) the total edge free energy F_0 of our nucleus:

$$F_0 = 2n/\lambda. \quad (\text{D8})$$

The constant λ can be determined in the following way. Assuming that the shape of the nucleus does not change in the neighbourhood of the equilibrium dimensions, it was shown in § 15.2 (formula 88) that the total edge free energy of the critical nucleus is given by

$$F_0 = 2n_0 kT \ln \alpha. \quad (\text{D9})$$

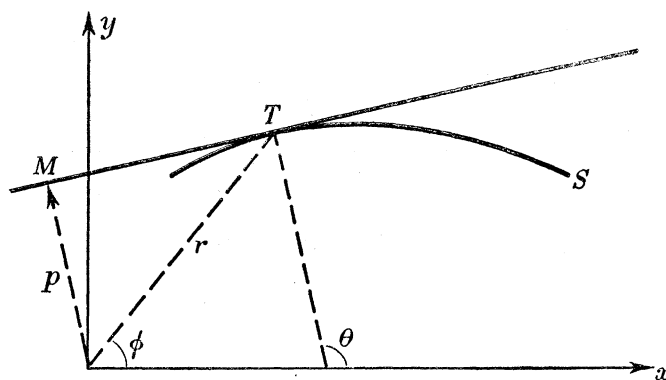


FIGURE 29

Therefore, from (D8) and (D9), $1/\lambda = kT \ln \alpha$,

and (D7) becomes $kT \ln \alpha = f(\theta)/p(\theta)$. (D10)

This equation represents not only a generalization of Wulff's theorem, but also a generalization of the Gibbs-Thomson formula—in two dimensions of course. Knowing $f(\theta)$, equation (D10) gives $p(\theta)$, and hence the shape of the critical nucleus is derived by the following geometrical construction. Draw a radius vector from the origin to the curve of $p(\theta)$ and construct a perpendicular to the radius vector at the point of intersection with the curve. Then the envelope of these perpendiculars, when the radius vector describes a complete revolution, defines the shape of the critical nucleus. Naturally, the curve of $p(\theta)$ will be closed if the free energy per unit length is single-valued. We emphasize here that θ is generally not the same as ϕ , the polar angle in the shape diagram (figure 29).

For the particular points of the step for which the tangent to the shape is normal to the radius vector, $\theta = \phi$ and $p(\theta) = r(\phi)$, and equation (D10) becomes

$$kT \ln \alpha = f(\phi)/r(\phi), \quad (\text{D11})$$

showing that the distance from the centre to one of these particular points is proportional to the edge free energy per unit length at this point, which is the ordinary form of Wulff's theorem. If f or r is independent of ϕ then (D11) becomes the Gibbs–Thomson equation in two dimensions.

It is possible to give a simple expression for the radius of curvature of the nucleus at a point whose polar angle is ϕ in terms of the values of $f(\theta)$ and $f'(\theta)$ at the corresponding point in the edge free-energy diagram. The result is

$$\rho(\phi) = \{f(\theta) + f'(\theta)\} / kT \ln \alpha, \quad (\text{D12})$$

the unit of length again being the intermolecular spacing.

The solution (D7) has been obtained on the assumption that S and its pedal possess continuously turning tangents. When there are sharp corners in S , the solution also applies for all pieces of S possessing continuously turning tangents. However, it may turn out that more than one free-energy diagram corresponds to a given S . To illustrate this, let us consider the polygonal equilibrium shape shown in figure 30, where S is the boundary of the crystal and O is its centre.

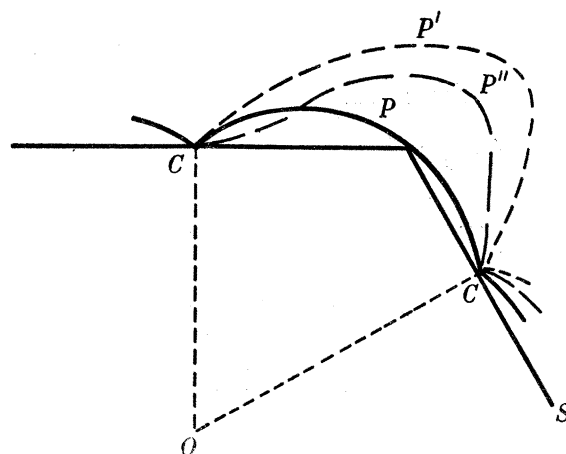


FIGURE 30

It is easily seen geometrically that if the free-energy diagram is that figure P obtained by finding the pedal of S (a number of circular arcs, if S is polygonal), then any curve P' lying entirely outside P , but coinciding with P at the cusps C , will give the same S , namely that given by P . If, however, the free-energy diagram lies entirely inside P , but coincides with P at the cusps C , then we obtain a shape for the crystal S' (different from S) which possesses neither sharp corners nor straight edges, and there is a one-to-one correspondence between S' and the free-energy diagram, so that given S' the free-energy diagram is determined uniquely and vice versa. This is the case in the particular model which we have been considering in part III. In the intermediate cases when the free-energy diagram P'' lies partly within and partly without P , then the corresponding crystal shape S'' will have sharp corners with or without straight segments in the boundary, depending on the actual form P'' .

At $T = 0$ we expect most crystals to be polygonal (or polyhedral, in three dimensions). The question arises: Are the corners rounded when $T > 0$, or can it happen that the equilibrium form remains polyhedral? If the potential energy were like P' in figure 30, and if the entropy correction were insufficient to bring the free-energy diagram within P , then sharp

corners would remain. This seems to be the case for ionic crystals. Shuttleworth (1949) has calculated the potential energies per unit area of the (1, 1, 0) and (1, 0, 0) faces of a number of ionic crystals and finds that their ratio is always greater than 2. Thus it would require temperatures probably above the melting-point to give rounded edges. In the case of metals near their melting-point, it is probable that the free-energy diagram will be within P , therefore the edges will become rounded.

APPENDIX E. AN OUTLINE OF THE MATRIX METHOD OF TREATING CO-OPERATIVE PROBLEMS

Here we give a brief account of the mathematics leading to (93). The general methods are due to Montroll (1941), Kramers & Wannier (1941), Onsager (1944), Onsager & Kaufmann (1946) and Wannier (1945). We consider a chain of identical units, each capable of a range of states μ . Let the chain be $m+1$ units long, so that there are m bonds connecting them (figure 31). Let the state of the r th unit be μ_r . If the units are in given fixed states, each bond contributes $u(\mu_{r+1}, \mu_r)$ to the total energy of the chain, so that the total energy of the chain is

$$\epsilon_i = u(\mu_{m+1}, \mu_m) + u(\mu_m, \mu_{m-1}) + \dots + u(\mu_2, \mu_1). \quad (\text{E } 1)$$

Hence the partition function for the chain is

$$\begin{aligned} f_{m+1} &= \sum_i \exp(-\epsilon_i/kT) \\ &= \sum_{\mu_{m+1}} \sum_{\mu_m} \dots \sum_{\mu_2} \sum_{\mu_1} V(\mu_{m+1}, \mu_m) V(\mu_m, \mu_{m-1}) \dots V(\mu_2, \mu_1), \end{aligned} \quad (\text{E } 2)$$

where

$$V(\mu, \mu') = \exp\{-u(\mu, \mu')/kT\}, \quad (\text{E } 3)$$

and the summations in (E2) are carried out over all possible values of all the μ 's. Since (E2) is in the form of a matrix product, (E3) can be regarded as a matrix, μ being a row index, and μ' a column index.

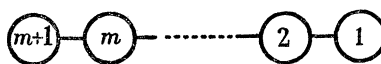


FIGURE 31

If we define

$$\Phi_{m+1}(\mu_{m+1}) = \sum_{\mu_m} \sum_{\mu_{m-1}} \dots \sum_{\mu_1} V(\mu_{m+1}, \mu_m) V(\mu_m, \mu_{m-1}) \dots V(\mu_2, \mu_1), \quad (\text{E } 4)$$

we see from (E2) that

$$\Phi_{m+1}(\mu_{m+1}) = \sum_{\mu_m} V(\mu_{m+1}, \mu_m) \Phi_m(\mu_m). \quad (\text{E } 5)$$

Φ_{m+1} may be called the partial partition function relative to the state μ_{m+1} , and we see that (E5) gives the effect on the partial partition function of a chain by the addition of another unit. The complete partition function f_{m+1} is of course given by

$$f_{m+1} = \sum_{\mu_{m+1}} \Phi_{m+1}(\mu_{m+1}). \quad (\text{E } 6)$$

If the chain is very long, the ratios between the various components of Φ_{m+1} will be the same as those between the corresponding components of Φ_m , so that in the limit as m becomes very large we obtain

$$\Phi_{m+1}(\mu) = \lambda \Phi_m(\mu). \quad (\text{E } 7)$$

Hence from (E6)
$$f_{m+1} = \lambda f_m, \tag{E8}$$

so that λ must be the partition function per unit. Combining (E5), (E6) and (E7) we are confronted by the following eigenvalue problem for λ :

$$\sum_{\mu'} V(\mu, \mu') \psi(\mu') = \lambda \psi(\mu), \tag{E9}$$

which can be written in the contracted notation

$$(V, \psi)(\mu) = \lambda \psi(\mu). \tag{E10}$$

By (E3) the elements of V are all positive, and by (E4) the components of ψ (i.e. the components of Φ) are all positive. This enables us to conclude by theorems due to Frobenius (1908, 1909) that λ is the largest eigenvalue of V . The results used here are that a matrix with positive elements has a largest eigenvalue which is simple and greater in absolute magnitude than any other eigenvalue, and that, moreover, the eigenvector belonging to it has components of only one sign. We may choose this sign to be positive. This eigenvector is the only one with this property.

E1. *The one-dimensional, two-level case*

As a preliminary to the solution of our two-dimensional, two-level problem, we first find the V for the corresponding one-dimensional problem. In this problem the interaction energy between two neighbouring molecules is zero if they have the same level and $\frac{1}{2}\phi_1$ if not. We designate one of the possible levels by $\mu = +1$ and the other by $\mu = -1$. The 'interaction' energy between two neighbours can then be put in the form

$$u(\mu, \mu') = \frac{\phi_1}{2} \frac{1 - \mu\mu'}{2}, \tag{E11}$$

which gives 0 if $\mu = \mu'$ and $\frac{1}{2}\phi_1$ otherwise. Hence from (E3)

$$V(\mu, \mu') = \exp\left\{\frac{1}{2}H(\mu\mu' - 1)\right\}, \tag{E12}$$

where

$$H = \phi_1/2kT. \tag{E13}$$

The operator V in (E12) has the following effect on a general function (which we may interpret, if we please, as the partial partition function):

$$(V, \psi)(\mu) = \psi(\mu) + e^{-H}\psi(-\mu), \tag{E14}$$

using the contracted notation. If we define an operator C by the equation

$$(C, \psi)(\mu) = \psi(-\mu), \tag{E15}$$

we can write V as

$$V = 1 + e^{-H}C, \tag{E16}$$

using (E14). From (E15)

$$C^2 = 1, \tag{E17}$$

so C has the eigenvalues ± 1 , showing that V has the eigenvalues $1 \pm e^{-H}$. The upper sign gives the largest eigenvalue, and hence the partition function per molecule.

In order to use these results in the treatment of the two-dimensional problem, we write V in the form

$$V = Ae^{\frac{1}{2}Hc}, \tag{E18}$$

which is possible in view of (E17), since we have, using (E17) and (E18),

$$V = A(\cosh \frac{1}{2}H + C \sinh \frac{1}{2}H).$$

$$\text{Thus, from (E16),} \quad A^2 = 1 - e^{-2H} = 2e^{-H} \sinh H, \quad (\text{E19})$$

$$\coth \frac{1}{2}\bar{H} = e^H. \quad (\text{E20})$$

$$\text{Hence} \quad V = (2e^{-H} \sinh H)^{\frac{1}{2}} \exp\left(\frac{1}{2}\bar{H}C\right), \quad (\text{E21})$$

where H is given by (E20).

E2. *The two-dimensional, two-level case: rectangular lattice*

In order to treat the two-dimensional case we consider n parallel chains of the same type as before. We shall build up the two-dimensional lattice in two steps by the addition of complete columns of molecules. Thus our 'unit' is the column. In the first stage we include only the 'horizontal' bonds (left-hand, figure 32), and in the second stage we insert the 'vertical' bonds (right-hand, figure 32). We associate with the last element in each chain (the j th chain) the variable μ , which can take the values ± 1 . A complete set of values assigned

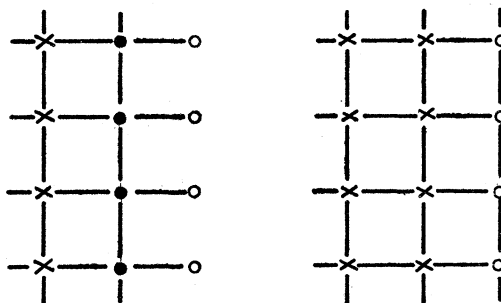


FIGURE 32

to the n variables describes a configuration $(\mu) = (\mu_1, \dots, \mu_n)$ of the last column, which constitutes our unit in the sense of figure 31. Thus the operator which describes the addition of a new column with the horizontal bonds only is

$$V_1 = (2e^{-H} \sinh H)^n \exp\left(\frac{1}{2}\bar{H}B\right) \quad (\text{E22})$$

$$\text{from (E21), where} \quad B = \sum_{j=1}^n C_j, \quad (\text{E23})$$

and the individual operators C_j have the effect

$$(C_j, \psi)(\mu_1, \dots, \mu_j, \dots, \mu_n) = \psi(\mu_1, \dots, -\mu_j, \dots, \mu_n). \quad (\text{E24})$$

We now wish to find the operator which represents the insertion of the vertical interactions, as in the right-hand figure (figure 32). The total energy corresponding to the inclusion of the vertical bonds will be

$$u(\mu_1, \dots, \mu_n) = \sum_{j=1}^{n-1} \frac{\phi_2}{2} \left(\frac{1 - \mu_j \mu_{j+1}}{2} \right), \quad (\text{E25})$$

where $\frac{1}{2}\phi_2$ is the strength of the vertical bond when it is not zero. We assume for generality that ϕ_1 and ϕ_2 are not necessarily equal. The effect of the interaction is to multiply the general term in the partial partition function, represented by one of the 2^n vector components $\psi(\mu_1, \dots, \mu_n)$ by the appropriate factor

$$\exp\{-u(\mu_1, \dots, \mu_n)/kT\}.$$

The corresponding operator is represented by a diagonal matrix. It can be constructed from the simple operators S_1, \dots, S_n which multiply ψ by the sign of its first, ..., n th argument as follows:

$$(S_j, \psi) (\mu_1, \dots, \mu_j, \dots, \mu_n) = \mu_j \psi (\mu_1, \dots, \mu_j, \dots, \mu_n), \quad (\text{E } 26)$$

$$A = \sum_{j=1}^{n-1} S_j S_{j+1}, \quad (\text{E } 27)$$

$$V_2 = \exp \left\{ -\frac{1}{2}(n-1) H' \right\} \exp \left(\frac{1}{2} H' A \right), \quad (\text{E } 28)$$

where

$$H' = \phi_2 / 2kT.$$

Hence the operator associated with our problem is

$$V = V_2 V_1 = \exp \left(-\frac{1}{2} n H \right) \exp \left\{ -\frac{1}{2} (n-1) H' \right\} (2 \sinh H)^{1n} \exp \left(\frac{1}{2} H' A \right) \exp \left(\frac{1}{2} \bar{H} B \right). \quad (\text{E } 29)$$

The largest eigenvalue of V is then the partition function per column of the lattice, and its n th root is the partition function per molecule.

Onsager (1944) has shown that the largest eigenvalue λ_M of $\exp(H'A) \exp(\bar{H}B)$ is given by

$$2 \ln \lambda_M = \gamma(2\pi/n) + \gamma(4\pi/n) + \dots + \gamma(2\pi) + c, \quad (\text{E } 30)$$

where $|c| \leq H'$ and

$$\cosh \gamma(\omega) = \cosh 2H' \cosh 2\bar{H} - \sinh 2H' \sinh 2\bar{H} \cos \omega. \quad (\text{E } 31)$$

This leads to the conclusion that, in our case, the partition function per molecule λ is given by

$$\ln \lambda = -F/kT = \frac{1}{2} \ln (2 \sinh H) - \frac{1}{2} (H + H') + \frac{1}{2\pi} \int_0^\pi \gamma(\omega) d\omega, \quad (\text{E } 32)$$

where

$$\cosh \gamma(\omega) = \cosh H' \cosh \bar{H} - \sinh H' \sinh \bar{H} \cos \omega \quad (\text{E } 33)$$

when $n \rightarrow \infty$. This result is exact, the effect of c disappearing by division with n and the summation converging to a definite integral.

In the special case of quadratic symmetry, $H = H'$, and these results reduce to

$$\cosh \gamma(\omega) = \cosh H \coth H - \cos \omega, \quad (\text{E } 34)$$

since it follows from (E 20) that

$$\sinh H \sinh \bar{H} = \cosh H \tanh \bar{H} = \cosh \bar{H} \tanh H = 1 \quad (\text{E } 35)$$

and

$$\ln \frac{\lambda e^H}{2 \cosh H} = \frac{1}{2\pi} \int_0^\pi \ln \frac{1}{2} \{1 + \sqrt{1 - k_1^2 \sin^2 \omega}\} d\omega, \quad (\text{E } 36)$$

where

$$k_1 = (2 \sinh H) / \cosh^2 H. \quad (\text{E } 37)$$

We cannot reduce (E 36) any further, but the potential energy per molecule U can be given in terms of the tabulated functions. We have

$$U = -\frac{\phi}{2} \frac{d}{dH} (\ln \lambda), \quad (\text{E } 38)$$

which yields

$$S = 2U/\phi = -\frac{d}{dH} (\ln \lambda).$$

From (E 36), (E 37) and (E 38) we finally obtain

$$S = 1 - \frac{1}{2} \left(1 + \frac{2}{\pi} k_2 K_1 \right) \coth H, \quad (\text{E } 39)$$

where $k_1^2 + k_2^2 = 1$, $K_1 = K(k_1) = \int_0^{\frac{1}{2}\pi} (1 - k_1^2 \sin^2 \omega)^{-\frac{1}{2}} d\omega$, (E 40)

the latter integral being the complete elliptic integral of the first kind; formula (E 39) is the formula (93) in the text.

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