CRYSTALLOGRAPHY

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Abstract

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KINETIC EQUATION FOR STEPS ON THE SURFACE OF A CRYSTAL

(Presented by Academician A. V. Shubnikov, 11 VII 1957)

At the present time it has been established that the growth of a crystal from vapor, solution, or melt proceeds by the successive deposition of new layers of substance on its faces. The sources of such layers, or, what is the same, of steps on the crystal surface, are the exits of screw dislocations, and at large supersaturations also two-dimensional nuclei. The thickness of the layers can vary within wide limits—from units to tens of thousands of parameters of the crystal lattice ([1–4]). High steps during growth and equilibrium are stable, i.e., they do not spontaneously break up into echelons of lower steps. In the process of growth the fronts of the layers move, and the velocity of this motion is the greater the smaller the height of the step ([2,3]). Therefore thin layers can overtake thick ones and, merging with them, form still higher steps.

The spreading of layers of different thickness along the crystal face, their interaction with dislocation outlets, coagulation of steps, and also a number of other phenomena connected with the behavior of layers—all this as a whole determines the kinetics of crystal growth. The existing theory of layer-spiral crystal growth ([1]) describes chiefly the behavior of individual layers, without dealing in detail with questions of their interaction. It is therefore natural to attempt to develop a statistics of steps on a crystalline surface.

Let us first consider a one-dimensional problem. Suppose there is an echelon, infinite in both directions, of parallel steps whose heights have random values. Since during growth the steps will coagulate, their number will decrease and the mean height will increase. Let us try to describe quantitatively the course of this process in time.

Denote the density of steps at the point x by $\rho(n, x, t)$, the velocity of steps of height n by $v(n)$, and the relative velocity of two steps $v(n) - v(n')$ by $f(n, n')$. Then

$$\frac{\partial \rho}{\partial t} + v\frac{\partial \rho}{\partial x} = J, \tag{1}$$

where J is the coagulation integral, reflecting the possibility of merging of steps. To find its form, let us compute the change $\frac{\partial \rho}{\partial t}\, dt$ in the density of steps of height

n.

Two effects must be taken into account:

1. The increase in the number of steps of height n upon merging of steps with heights ν and ν', such that $\nu + \nu' = n$:

$$\sum_{\nu+\nu'=n} \rho(\nu, x, t) f(\nu, \nu') \rho(\nu', x, t)\, dt. \tag{2}$$

2. Decrease in the number of steps of height n when they merge with other steps:

$$-\left[\sum_{\nu<n} \rho(\nu, x, t) f(\nu, n) + \sum_{\nu>n} \rho(\nu, x, t) f(n, \nu)\right] \rho(n, x, t)\, dt. \tag{3}$$

Adding (2) and (3) gives the quantity J. Steps with small n coagulate rapidly and do not play an essential role. Therefore the summation in (2) and (3) may, without great error, be replaced by integration. Then we finally obtain:

$$\frac{\partial \rho}{\partial t} + v\frac{\partial \rho}{\partial x} = \int_0^{n/2} \rho(\nu, x, t) f(\nu, n-\nu) \rho(n-\nu, x, t)\, d\nu -$$

$$-\rho(n, x, t)\left[\int_0^n \rho(\nu, x, t) f(\nu, n)\, d\nu + \int_n^\infty \rho(\nu, x, t) f(n, \nu)\, d\nu\right] \tag{4}$$

This nonlinear integro-differential equation is similar in its basic features to the equation of coagulation of colloids ([5–9]).

A complete solution of (4) is apparently very difficult, and we shall restrict ourselves to finding the law of growth with time of the mean size of the steps $\bar{n}$, assuming $\partial\rho/\partial x = 0$. Direct calculation with the aid of (4) shows that, as it should be, the sum of the heights of all steps intersecting a unit segment is conserved:

$$\int_0^\infty n\rho(n, t)\, dn = \int_0^\infty n\rho(n, 0)\, dn = A = \text{const}, \tag{5}$$

where A is the tangent of the angle between the vicinal under consideration and the corresponding close-packed face.

To determine $\bar{n}$ it is also necessary to find $\int_0^\infty \rho\, dn$. We shall assume the function $f(n, n')$ to be homogeneous:

$$f(\lambda n, \lambda n') = \lambda^{-k} f(n, n').$$

The grounds for this assumption will be given below. We shall seek a particular solution of (4) in the form

$$\rho(n,t) = (t+t_0)^{-p}\varphi[n(t+t_0)^{-q}], \tag{6}$$

analogously to how this was done by O. M. Todes in the study of the coagulation equation ([7]). Here t_0 is a constant determined from (7) at $t = 0$. From (4) and (5) it follows that $p = 2q$, $q = 1/(k+1)$. Therefore

$$\int_0^\infty \rho(n,t)\,dn = A(t+t_0)^{-1/(k+1)}; \qquad \bar{n} = \frac{A}{B}(t+t_0)^{1/(k+1)}, \tag{7}$$

where $B = \int_0^\infty \varphi(x)\,dx$; φ is the proper function of the homogeneous integro-differential equation obtained from (4) after substituting expression (6) for ρ. A rigorous justification of the possibility of the representation (6) requires investigating the solvability conditions of the equation for $\varphi(x)$.

The dependence of the speed of motion of steps on their height can be approximated by the expression

$$v(n) = a + \frac{b}{n}, \tag{8}$$

where a and b are constants ([2,3]) depending on the conditions of crystal growth, in particular on the supersaturation. Relation (8) is valid for heights n not exceeding, in order of magnitude, hundreds of elementary lattice parameters.

There are grounds to suppose that the velocities of higher steps depend more weakly on their height. In the case under consideration this can be taken into account qualitatively by assuming

$$f(n,n') \equiv v(n) - v(n') = b\left(\frac{1}{n^k} - \frac{1}{n'^k}\right),$$

where $k \gg 1$ (formula (8) corresponds to $k = 1$). Then in all expressions up to and including (7) one may replace t by bt. This relation shows how, in the process under study, the time scale is connected with the growth conditions of the crystal.

In the initial stage of the process, when the step heights do not exceed hundreds of lattice parameters and $k = 1$, the mean step height increases with time as $\sim \sqrt{t}$, while their total density decreases proportionally to $1/\sqrt{t}$. Subsequently, when the steps become larger, coagulation should proceed more and more slowly:

$$\frac{d\bar{n}}{dt} \sim t^{-k/(k+1)}.$$

The results obtained can be used to describe the process by which roughness arises on the surface of a polished single-crystal sphere immersed in a supersaturated solution of the corresponding substance ([10,11]). Indeed, large steps (of height up to ~ 0.2 mm) can arise in the course of coagulation of those steps of molecular dimensions of which the surface of the polished sphere consisted. Here the step fronts are, of course, not rectilinear, but this should not substantially affect the course of coagulation. Consequently, formulas (7) characterize the transition from microscopic to macroscopic roughness.

Thus, in a number of the simplest cases the behavior of steps on a crystalline surface is described statistically by means of a kinetic equation of type (4).

Up to now we have assumed that the steps are stable. However, under certain conditions lower steps can separate from higher steps. These processes apparently occur especially often during dissolution and evaporation of crystals. To take them into account, the following three terms must be added to the right-hand side of (4):

$$\int_n^{2n} \rho(\nu, x, t) w(\nu, \nu - n)\, d\nu + \int_{2n}^{\infty} \rho(\nu, x, t) w(\nu, n)\, d\nu - \rho(n, x, t) \int_0^{n/2} w(n, \nu)\, d\nu,$$

where $w(\mu, \nu)$ is the probability of decay of a step of height μ into two steps with heights ν and $\mu - \nu$.

It is not difficult to see that the possibility of decay leads to coagulation even in such a system as initially consisted of steps of identical height n_0 ($\rho(n, 0) = \delta(n - n_0)$, δ being the Dirac function). Consequently, in the system under consideration, with time there will appear steps with different heights, including heights exceeding n_0.*

The coagulation equation obtained is easily generalized to the two-dimensional case if one sets

$$\rho(n, \mathbf{r}, t) = \frac{\partial}{\partial s} F(n, \mathbf{r}, t),$$

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* Coagulation in the present case is, of course, not described by equation (4), for which $\delta(n - n_0)$ is a solution.

where $\mathbf{r}$ is a two-dimensional radius vector, $\partial/\partial s$ is the operator of differentiation along the normal to the step front, and $F(n, \mathbf{r}, t)$ is a function whose geometrical meaning is that $z = F(n, \mathbf{r}, t)$ is the equation of a crystal surface composed of identical steps of height n. In the general case the equation of the surface is also expressed in terms of the function F:

$$z = \int_0^\infty nF(n, \mathbf{r}, t)\, dn.$$

(Both of these equations do not take into account the microrelief associated with the presence of steps.)

In conclusion we note that the kinetic equation considered is also suitable for describing coagulation processes in a system of arbitrary particles moving in one direction with different velocities.

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CITED LITERATURE

1. W. K. Burton, N. Cabrera, F. C. Frank, *Phil. Trans.*, Ser. A., **243**, No. 866, 299 (1951).

2. G. G. Lemmlein, E. D. Dukova, *Crystallography*, **1**, issue 1, 112 (1956).

3. A. A. Chernov, *Crystallography*, **1**, issue 1, 112 (1956).

4. G. G. Lemmlein, E. D. Dukova, A. A. Chernov, *Crystallography*, **2**, issue 3, 428 (1957).

5. S. S. Molukovskii, Collection: *Coagulation of Colloids*, 1936, p. 7.

6. N. N. Tunitskii, *ZhETF*, **8**, issue 4, 418 (1938).

7. O. M. Todes, Collection: *Problems of Kinetics and Catalysis*, **7**, 1949, p. 137.

8. S. V. Pshenai-Severin, *DAN*, **91**, No. 5, 865 (1954).

9. N. S. Shishkin, *Clouds, Precipitation, Thunderstorm Electricity*, Moscow, 1952.

10. D. N. Artem' ev, *Method of Crystallization of Spheres and Its Application in the Study of the Form and Structure of Crystalline Matter*, Petrograd,

1914.

11. G. E. Buckley, *Crystal Growth*, ch. IV, IL, 1954.

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