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KINETIC PHASE TRANSITIONS

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The degree of ordering of a binary crystal produced during a phase transition, say during crystallization of a vapor, depends on the kinetics of the process if the particle mobility in the crystal is small. As the deviation from equilibrium increases, the long range order parameter decreases and vanishes at a certain point; thus a phase transition occurs in which supersaturation plays the role of temperature. Such a transition has been termed a kinetic phase transition. Its theory is developed on the basis of an analysis of the kinetics of cooperative phenomena by a method which circumvents the use of an infinite set of linked kinetic equations. Satisfactory agreement with experiments performed on a digital computer is obtained.

1. FORMULATION OF PROBLEM

OSTWALD'S step rule indicates, as is well known, that in principle it is possible for metastable modifications to appear in systems undergoing a phase transition, but says nothing concerning the conditions and mechanism for realizing this possibility. A clarification of the latter circumstance calls for an analysis of concrete systems, and has not been carried out so far. In this paper we consider a microscopic model of crystallization, which actually leads to an appearance of a metastable phase. It turns out here that the transition from a stable atomic structure to an unstable one, occurring with increasing degree of deviation from equilibrium, has the character of a phase transition, which we call critical. The role played by the temperature in ordinary thermodynamic phase transitions is played in kinetic transitions by the degree of deviation from equilibrium.

The model investigated is as follows. We have a semi-infinite crystal with a single corner on a single step (Fig. 1). The crystal and its surrounding medium are made up of particles of type A and B. They can be attached to the crystal at the corner or be detached from it. The attachment and detachment acts are assumed to be perfectly random. The properties of the corner are determined by the type of its component particles, that is by the set $\overset{\kappa\chi}{\underset{\gamma\mu}{\alpha\beta}}$ (Fig. 1), where α, β, κ, χ, λ, μ = A, B. The frequency of attachment of a particle of type γ (γ = A, B) to a kink made up of the group $\underset{\mu}{\beta\kappa}$ is denoted by $w_+(\beta\overset{\chi}{\underset{\mu}{\gamma}})$, and the frequency of detachment of the particle γ from the corner $\beta\overset{\chi}{\underset{\mu}{\gamma}}$ is denoted by $w_-(\beta\overset{\chi}{\underset{\mu}{\gamma}})$. Confinement to these indices corresponds approximately to the nearest-neighbor approximation in the energy interaction of the particles. The quantities $w_\pm(\beta\overset{\chi}{\underset{\mu}{\gamma}})$ represent the specified parameters of the problem. Knowing these, we must find the average velocity of the corner during the stationary growth and the distribution of the particles A and B in the produced crystal, if all its preceding layers are produced as a result of motion of the same corner and if the particles inside the crystal cannot interchange places - the structure is "frozen." The lattice is assumed primitive cubic.

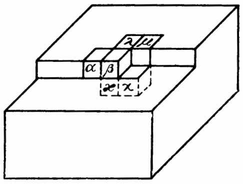

FIG. 1. Entering trihedral corner on the surface of a crystal.

From now on we confine ourselves in the concrete analysis of the solution, to the case

$$w_+\left(\beta\overset{\chi}{\underset{\mu}{\gamma}}\right) = w_+, \tag{1.1}$$

and the frequency of detachment will be represented in the form

$$w_-\left(\beta\overset{\chi}{\underset{\mu}{\gamma}}\right) = \nu \exp\left\{-\frac{\varepsilon_{\beta\gamma} + \varepsilon_{\chi\gamma} + \varepsilon_{\mu\gamma}}{T}\right\}, \tag{1.2}$$

where ν and $\epsilon_{\alpha\beta}$ have the meaning of the oscillation frequency and the binding energy of the particles α and β, and T is the temperature of the crystal. If $\epsilon_{AA} = \epsilon_{BB}$ and $\epsilon_{AB} = \epsilon_{BA}$ (but $\epsilon_{AB} = m\epsilon_{AA}$, $m \neq 1$), then the particles A and B are equivalent and their concentrations in the crystal will be the same under all crystallization conditions. In the case of an ordering alloy, the crystallization leads under conditions close to equilibrium to an ordered crystal when the equilibrium temperature is lower than the Curie temperature ($T_e < T_c$), and to a disordered crystal in

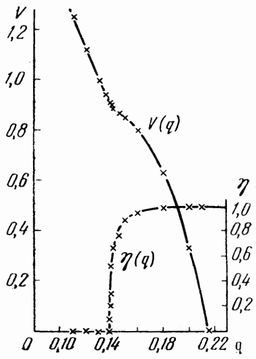

FIG. 2. Dependence of the long-range order parameter η and of the velocity of the corner V on the quantity $q = \exp(-\epsilon_{AA}/T)$. Model experiment with a computer at $\nu/w_+ = 10^4$ and $\epsilon_{AB} = 2\epsilon_{AA}$.

the opposite case. On the other hand, for sufficiently large deviations from equilibrium, practically any particle, once attached to the crystal, remains in it forever, since the forward moving, corner hardly fluctuates. Inasmuch as the acts of attachment of A and B are random, the produced crystals will be disordered. Consequently, with increasing deviation from equilibrium, the degree of long-range order η should change from a value close to unity near equilibrium to zero far from equilibrium. How does η behave in intermediate degrees of supersaturation?

The retention in the lattice of any particle attached to the corner depends on the nearest neighbors of the particle, and also on the entry and retention of the next particle in the corner, that is, on the distribution of A and B along the entire future path of the corner. This dependence determines the collective interaction upon crystallization. The existence of a kinetic collective interaction suggests that the kinetic order-disorder transition should take place at a strictly defined critical supersaturation. The foregoing hypothesis was confirmed by model experiments on a computer[1]. Figure 2 shows plots of the long-range order η and of the velocity V of the corner on the quantity $Q = \exp(-\epsilon_{AA}/T)$, i.e., on the crystal temperature T, obtained in these "experiments" for $\nu/w_+ = 10^4$ and m = 2. At the point of the kinetic phase transition, (q = 0.14) η vanishes and V has a corner singularity. We now proceed to an approximate analytic theory of kinetic phase transitions for the description of the foregoing model.

2. METHOD OF CONSERVATION PROBABILITIES AND FUNDAMENTAL EQUATIONS

Owing to the attachment and detachment of the particles, the corner performs a random walk, during the course of which there takes place the selection of particles which remain forever in the lattice, that is, the formation of the composition and structure of the crystal.

These characteristics can be obtained from an infinite system of coupled kinetic equations for the distribution functions with respect to different atomic configurations making up the corner. It is more effective, however, to use the method of conservation functions, developed earlier for the crystallization of a binary chain[2]

In this case the conservation function $U_{\alpha\beta}$ is the probability that a given particle of type β attached to the corner at the end of an incomplete array terminated by particle α (Fig. 1) will never leave the lattice. The conservation probability defined in this manner is actually the result of averaging over the types of particles κ and λ, which form the corner together with β (Fig. 1), and also over all the distributions of the particles forming a dihedral angle along the step on the entire infinite path of subsequent motion of the corner (particles χ, μ, etc.). The sought quantities, namely the ordering parameter η and the velocity of the comer V, are expressed in terms of $U_{\alpha\beta}$ (see below).

We now set up equations for the conservation probabilities. We break up the lattice, as is customarily done in order-disorder transition problems, into two sublattices with alternating sites. Let $x_\alpha^{(i)}$ be the probability of encountering the particle of type α in a site of the i-th sublattice (i = 1, 2). Then

$$x_A^{(1)} = {}^1/_2(1+\eta), \qquad x_A^{(2)} = {}^1/_2(1-\eta), \qquad x_B^{(1)} = {}^1/_2(1-\eta), \qquad x_B^{(2)} = {}^1/_2(1+\eta). \tag{2.1}$$

We put

$$p\left(\begin{smallmatrix}\varkappa\chi\\ \alpha\beta\gamma\\ \lambda\mu\end{smallmatrix}\right) = w_+\left(\begin{smallmatrix}\chi\\ \beta\gamma\\ \mu\end{smallmatrix}\right) \Big/ \left[w_-\left(\begin{smallmatrix}\varkappa\\ \alpha\beta\\ \lambda\end{smallmatrix}\right) + \sum_\gamma w_+\left(\begin{smallmatrix}\chi\\ \beta\gamma\\ \mu\end{smallmatrix}\right)\right],$$

$$q\left(\begin{smallmatrix}\varkappa\chi\\ \alpha\beta\\ \lambda\mu\end{smallmatrix}\right) = w_-\left(\begin{smallmatrix}\varkappa\\ \alpha\beta\\ \lambda\end{smallmatrix}\right) \Big/ \left[w_-\left(\begin{smallmatrix}\varkappa\\ \alpha\beta\\ \lambda\end{smallmatrix}\right) + \sum_\gamma w_+\left(\begin{smallmatrix}\chi\\ \beta\gamma\\ \mu\end{smallmatrix}\right)\right]. \tag{2.2}$$

The first of these quantities is the probability of attachment of the particle γ to the corner with configuration $\begin{smallmatrix}\kappa\chi\\ \alpha\beta\\ \lambda\mu\end{smallmatrix}$ and the second is the probability of loss of particle from this corner. We introduce further the average probabilities $\bar{p}_{\alpha\beta\gamma}^{(i)}$ and $\bar{g}_{\alpha\beta\gamma}^{(i)}$, neglecting in the averaging the correlations in the types of neighboring particles:

$$\bar{p}_{\alpha\beta\gamma}^{(1)} = \sum_{\varkappa,\chi,\lambda,\mu} p\left(\begin{smallmatrix}\varkappa\chi\\ \alpha\beta\gamma\\ \lambda\mu\end{smallmatrix}\right) x_\varkappa^{(1)} x_\lambda^{(1)} x_\chi^{(2)} x_\mu^{(2)}, \tag{2.3}$$

and analogously for i = 2, interchanging the indices of the sublattices in (2.3). Here and throughout the upper index - of the sublattice - pertains to the first of the lower indices - those of the particle types.

We denote by $U_{\alpha\beta}^{(i)}$ the probability of conserving in the corner the outermost particle the growing array $(\ldots\alpha\beta)$, if α belongs to i-th sublattice. Using a reasoning similar to that used in the solution of the chain problem[2] we get

$$U_{\alpha\beta}^{(1)} = \sum_\gamma \bar{p}_{\alpha\beta\gamma}^{(1)} [U_{\beta\gamma}^{(2)} + (1 - U_{\beta\gamma}^{(2)}) U_{\alpha\beta}^{(1)}],$$

$$U_{\alpha\beta}^{(2)} = \sum_\gamma \bar{p}_{\alpha\beta\gamma}^{(2)} [U_{\beta\gamma}^{(1)} + (1 - U_{\beta\gamma}^{(1)}) U_{\alpha\beta}^{(2)}]. \tag{2.4}$$

Let

$$P_{\alpha\beta\gamma}^{(1)} = \bar{p}_{\alpha\beta\gamma}^{(1)} U_{\beta\gamma}^{(2)} \Big/ \sum_\gamma \bar{p}_{\alpha\beta\gamma}^{(1)} U_{\beta\gamma}^{(2)},$$

$$P_{\alpha\beta\gamma}^{(2)} = \bar{p}_{\alpha\beta\gamma}^{(2)} U_{\beta\gamma}^{(1)} \Big/ \sum_\gamma \bar{p}_{\alpha\beta\gamma}^{(2)} U_{\beta\gamma}^{(1)}. \tag{2.5}$$

The probability $P_{\alpha\beta\gamma}^{(i)}$ is the fraction of the cases in which the array terminated by the pair $\alpha\beta$ will be "bricked in" forever by the particle of type γ, relative to the total number of cases in which this array will be "bricked in" by some particle. Neglecting the correlations again, as in (2.3), we have

$$\sum_{\alpha\beta} x_\alpha^{(1)} x_\beta^{(2)} P_{\alpha\beta\gamma}^{(1)} = x_\gamma^{(2)}, \qquad \sum_{\alpha\beta} x_\alpha^{(2)} x_\beta^{(1)} P_{\alpha\beta\gamma}^{(2)} = x_\gamma^{(1)}. \tag{2.6}$$

The system (2.1)–(2.6) determines η as a function of the frequencies $w_\pm\left(\begin{smallmatrix}\kappa\\ \alpha\beta\\ \lambda\end{smallmatrix}\right)$, i.e., as a function of the temperature of the crystallization and of the partial pressures (or concentrations) of the components in the initial phase.

If the attachment and detachment frequencies are represented in the form (1.1) and (1.2), then $p_{\alpha\beta\gamma}^{(i)} = \bar{p}_{\alpha\beta}^{(i)}$, that is, it does not depend on γ, and

$$P_{\alpha\beta\gamma}^{(1)} = U_{\beta\gamma}^{(2)} / \psi_\beta^{(2)} = P_{\beta\gamma}^{(2)},$$

$$P_{\alpha\beta\gamma}^{(2)} = U_{\beta\gamma}^{(1)} / \psi_\beta^{(1)} = P_{\beta\gamma}^{(1)}, \tag{2.7}$$

where

$$\psi_\beta^{(i)} = \sum_\gamma U_{\beta\gamma}^{(i)}. \qquad (2.8)$$

Equations (2.4) reduce in this case to the form

$$\psi_\alpha^{(1)} = \sum_\beta \frac{\psi_\beta^{(2)}}{s_{\alpha\beta}^{(1)} + \psi_\beta^{(2)}}, \qquad \psi_\alpha^{(2)} = \sum_\beta \frac{\psi_\beta^{(1)}}{s_{\alpha\beta}^{(2)} + \psi_\beta^{(1)}}, \qquad (2.9)$$

where

$$s_{\alpha\beta}^{(i)} = \bar{q}_{\alpha\beta}^{(i)} / \bar{p}_{\alpha\beta}^{(i)}. \qquad (2.10)$$

Since the two sublattices and the two types of particles are equivalent, the system (2.9) and (2.10) should indeed be invariant against the substitutions (1) → (2), (2) → (1), A → B, and B → A, i.e.,

$$\psi_A^{(1)} = \psi_B^{(2)} = \psi_A, \qquad \psi_B^{(1)} = \psi_A^{(2)} = \psi_B, \qquad (2.11)$$

so that (2.9) reduces to two equations

$$\psi_A\left(1 - \frac{1}{s_{AB} + \psi_A}\right) = \frac{\psi_B}{s_{AA} + \psi_B},$$
$$\psi_B\left(1 - \frac{1}{s_{BA} + \psi_B}\right) = \frac{\psi_A}{s_{BB} + \psi_A}. \qquad (2.12)$$

Here and throughout the absence of a sublattice index denotes $i = 1$.

Only two of the equations in (2.6) are independent, since summation over γ transforms each of the lines of (2.6) into an identity. In the investigated case of frequencies of the type (1.1)–(1.2), only one equation is independent, which we can choose to be, for example,

$$\sum_\gamma x_\beta^{(1)} P_{\beta\gamma}^{(1)} = x_\gamma^{(2)}. \qquad (2.13)$$

From this, with account of (2.7) and (2.1), we arrive at the condition

$$(1 + \eta)\left(1 - \frac{1}{s_{AB} + \psi_A}\right) = (1 - \eta)\left(1 - \frac{1}{s_{BA} + \psi_B}\right). \qquad (2.14)$$

Together with (2.21), this condition determines the functions $\eta(q)$, $\psi_A(q)$, and $\psi_B(q)$.

The concentration of particles of any particular type is different in the deep parts of the developing array and in the corner at the end of the same array. The latter concentration $x_{1\alpha}^{1}$ is the fraction of the time during which the end of the array is made up of particles of type α belonging to the i-th sublattice. At the end of the array, w_+ particles are attached per unit time, and out of the particles attached at a given instant of time, the fraction finally retained is ψ. Therefore the actual growth rate is

$$V = w_+ \sum_\alpha x_{1\alpha}^{(1)} \psi_\alpha^{(1)} = w_+ \sum_\alpha x_{1\alpha}^{(2)} \psi_\alpha^{(2)}. \qquad (2.15)$$

The concentration $x_{1\alpha}^{(i)}$, just is in case of polymerization of a chain[2], is determined by the obvious relations

$$x_{1\beta}^{(i)} \psi_\beta^{(i)} \Big/ \sum_\beta x_{1\beta}^{(i)} \psi_\beta^{(i)} = x_\beta^{(i)} \qquad (2.16)$$

whence

$$x_{1A} = \frac{x_A \psi_B}{x_A \psi_B + x_B \psi_A}, \qquad x_{1B} = \frac{x_B \psi_A}{x_A \psi_B + x_B \psi_A} \qquad (2.17)$$

and

$$V = w_+ \frac{\psi_A \psi_B}{x_A \psi_B + x_B \psi_A}. \qquad (2.18)$$

3. ANALYSIS OF THE SOLUTION

From the definition of $s_{\alpha\beta}$ (see 2.10) it follows directly that

$$s_{AB}(q, \eta) = s_{BA}(q, -\eta), \qquad s_{AA}(q, \eta) = s_{BB}(q, -\eta)$$

and consequently

$$\psi_A(q, \eta) = \psi_B(q, -\eta), \qquad (3.1)$$

which is a direct consequence of the equivalence of the particles and of the sublattices, and represents a different form of writing down (2.11). By virtue of (3.1) we have $\psi_A(q, 0) = \psi_B(q, 0)$, that is, the equations

$$\eta = 0, \quad \psi_A = \psi_B = \psi = {}^1\!/_2[(2 - s_{AB} - s_{AA}) + \{(2 - s_{AB} - s_{AA})^2 + 4(2 - s_{AB} - s_{AA})(s_{AB} + s_{AA} - s_{AB}s_{AA})\}^{1/2}] \qquad (3.2)$$

are the solution of the system (2.12) and (2.14). This solution is not unique. We shall seek the other branch separately in the vicinity of the equilibrium ($q \lesssim q_e$) and separately in the region of the kinetic phase transition.

1. Small deviations from equilibrium. In this region the conservation probabilities are small, so that $\psi_\alpha \ll 1$ and the solution (2.12) takes the form

$$\psi_A = \frac{1}{s_{AA}}\left(\frac{1}{s_{AA}s_{BB}} - \frac{(s_{AB} - 1)(s_{BA} - 1)}{s_{AB}s_{BA}}\right)$$
$$\times \left[\frac{1}{s_{AA}}\left(\frac{1}{s_{AA}s_{BB}^2} + \frac{s_{BA} - 1}{s_{BA}s_{AB}^2}\right) + \frac{s_{AB} - 1}{s_{AB}}\left(\frac{s_{AB} - 1}{s_{AB}s_{BA}^2} + \frac{1}{s_{BB}s_{AA}^2}\right)\right]^{-1}$$
$$\psi_B = \frac{(s_{AB} - 1)s_{AA}}{s_{AB}}\psi_A. \qquad (3.3)$$

The growth stops when both quantities (ψ_A and ψ_B) vanish simultaneously, that is, the equilibrium condition is

$$\frac{1}{s_{AA}s_{BB}} - \frac{(s_{AB} - 1)(s_{BA} - 1)}{s_{AB}s_{BA}} = 0. \qquad (3.4)$$

The right side of (3.4) is positive for the growth region and negative for the evaporation region of the crystal.[1)]

If the equilibrium temperature is noticeably lower than the Curie temperature ($q_e < q_c$), then a crystal with $\eta \sim 1$, i.e., an ordered phase, should grow near equilibrium. Therefore we should expect at equilibrium $w_+ \sim \nu q^{3m}$, that is, $Rq^{3m} \sim 1$ where $R = \nu/w_+$. According to (1.1) and (1.2), the detachment and attachment probability (2.2), meaning also $s_{\alpha\beta}$, depends only on the ratio R (and also on q and η). Assuming for estimating purposes $w_+ \sim 10^6$ sec^{-1}, corresponding to a direct entry of the particle into the corner from the gas at a pressure ~10 Torr, and assuming $\nu \sim 10^{12}$ sec^{-1}, we get $R \sim 10^6$. The model experiments were performed for $R = 10^4$ and $R = 10^6$ at $m = 2$ ($\epsilon_{AB} = 2\epsilon_{AA}$). Taking into account the large value of R we obtain tentatively $q_e \ll 1$. The foregoing considerations indicate that it is advisable to seek the solution by expanding $s_{\alpha\beta}$ in a series in $(1 - \eta)$, with account taken of the smallness of q:

$$s_{AB} = Rq^{3m}[1 + 3(1 - \eta)], \qquad s_{BA} = Rq^{m+2}[1 - q^{1-m}(1 - \eta)],$$
$$s_{AA} = Rq^3[1 - q^{1-m}(1 - \eta)]; \qquad s_{BB} = Rq^{2m+1}[1 + (1 - \eta)]. \qquad (3.5)$$

[1)] In the case of decomposition of a crystal, its structure, of course, should be specified beforehand, and only the rate of decrystallization is unknown.

Expressions (3.5) are valid when $q^{1-m}(1-\eta) \ll 1$. Substituting (3.5) in (3.3) and discarding terms of higher order of smallness than q^{m+2} and $(1-\eta)$, we have

$$\psi_A = \frac{1}{R^2 q^{2m+4}} - [Rq^{3m} - 1 + 3(1-\eta)]. \tag{3.6}$$

With the same degree of accuracy we get from (2.14) and (3.6)

$$\eta = 1 - 2 / R^2 q^{2(m+2)} \tag{3.7}$$

and in accordance with (3.6) and (3.3)

$$\begin{aligned} \psi_A &= 1 - Rq^{3m} - 5 / R^2 q^{2(m+2)}, \\ \psi_B &= \psi_A / Rq^{2m+1}. \end{aligned} \tag{3.8}$$

The equilibrium condition in the form $\psi_A = 0$ leads to an equation for q_e

$$1 - Rq_e^{3m} = 5q_e^{4(m-1)} \tag{3.9}$$

and to an equilibrium long-range order parameter

$$\eta_e = 1 - 2q_e^{4(m-1)}. \tag{3.10}$$

It is easy to find that $q_e = 0.215$ and $\eta_e = 0.998$ for $m = 2$ and $R = 10^4$, and $q_e = 0.100$ and $\eta_e = 0.9998$ for $R = 10^6$, is in good agreement with the results of the model experiments[1]. The growth rate in the investigated approximation is

$$V = w_+\psi_A = w_+(1 - Rq^{3m} - 5 / R^2 q^{2(m+2)}). \tag{3.11}$$

For $m = 2$ and $R = 10^4$, formula (3.11) yields $w_+^{-1} \partial v / \partial q |_{q=q_e} = -27.9$, whereas the "experimental" value of this quantity is approximately -28.

2. Vicinity of the kinetic phase transition. In this region $\eta \ll 1$. The differences $\psi_A - \psi$ and $\psi_B - \psi$ are also small, where ψ is the solution for the disordered phase, given in (3.2). Linearizing (2.12) and (2.4) with the aid of these small parameters, we get a homogeneous linear system of equations with respect to $\psi_A - \psi$, $\psi_B - \psi_1$ and η. The condition for the existence of its solution in the form of the vanishing of the corresponding determinant gives an equation for the critical value of q_k, that is, the temperature of the kinetic phase transition:

$$\begin{aligned} D = {} & \frac{2\psi}{(s_{AA}+s_{AB})^2}\left[\frac{1}{(s_{AB}+\psi)^2} + \frac{1}{(s_{AA}+\psi)^2}\right] \\ & \times \left\{\left[\frac{(s_{AB}+\psi)^2}{s_{AA}+\psi} + \frac{\partial s_{AB}}{\partial \eta}\right]\left[1 - \frac{s_{AB}}{(s_{AB}+\psi)^2} + \frac{s_{AA}}{(s_{AA}+\psi)^2}\right]\right. \\ & \left. - \psi\left[\frac{1}{(s_{AB}+\psi)^2}\frac{\partial s_{AB}}{\partial \eta} + \frac{1}{(s_{AA}+\psi)^2}\frac{\partial s_{AA}}{\partial \eta}\right]\right\} = 0. \end{aligned} \tag{3.12}$$

Here all the $s_{\alpha\beta}$ are taken at $\eta = 0$. Numerical solution of (3.12) leads to $q_k = 0.12$ for $R = 10^4$ and $q_k = 0.035$ for $R = 10^6$ $(m = 2)$. In the model experiments, the kinetic phase transitions occur when $q_k = 0.14$ and $q_k = 0.046$.

The character of the vanishing of the ordering parameter as $q \rightarrow q_k$ follows from (2.12) and (2.14) after expansion up to the third powers of η, $\psi_A - \psi$, and $\psi_B - \psi$ inclusive. The symmetry properties discussed above (see (3.1)) lead to the vanishing of the terms quadratic in η from this expansion, so that

$$\eta D + \eta^3 C = 0, \tag{3.13}$$

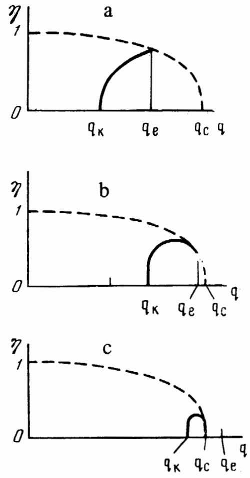

FIG. 3. Schematic $\eta(q)$ dependence for different relations between the Curie temperature and the temperature of equilibrium between crystal and the medium or the quantities q_c and q_e. Dashed lines—thermodynamic curves, solid lines—kinetic curves.

where C is a function of q and the determinant D is written out in (3.12). Consequently, besides the solution $\eta = 0$, there is also the solution

$$\eta = \sqrt{D/C}, \tag{3.14}$$

which vanishes at the point of the kinetic phase transition. Since, in general, D has a root of first order at $q = q_k$, we get

$$\eta \sim \sqrt{q - q_k} \sim \sqrt{T - T_k}. \tag{3.15}$$

Thus, the vanishing of the degree of long-range order at the kinetic phase transition follows the same law as at the point of the thermodynamic order-disorder phase transition in the Bragg-Williams approximation. It is appropriate to note here that the averaging used in (2.3), (2.4), and (2.6) also does not take the correlations into account and is analogous to the Bragg-Williams approximation in the thermodynamic theory. The formulas (3.14) and (3.15) must be judged with allowance for this fact.

The symmetry relation (3.1) leads to an expansion of ψ_A and ψ_B in the form

$$\begin{aligned} \psi_A &= \psi + a\eta + b\eta^2, \\ \psi_B &= \psi - a\eta + b\eta^2, \end{aligned} \tag{3.16}$$

where a and b are functions of q and R. Substituting the expressions (3.16) and (3.2) in (2.18) we obtain for the growth rate

$$V = \begin{cases} w_+\psi, & q \leqslant q_k \\ w_+\psi\left[1 + \eta^2\left(\dfrac{a+b}{\psi} - \dfrac{a^2}{\psi^2}\right)\right], & q \geqslant q_k \end{cases} \tag{3.17}$$

It follows from (3.17) and (3.15), that there exists a corner point on the plot of $G(q)$ that $q = q_k$, again in agreement with Fig. 2.

We considered above a situation in which $q_e \ll q_c$, as shown in Fig. 2 and schematically in Fig. 3a. The dashed lines on Fig. 3 show the thermodynamic equilibrium relations for $\eta(q)$, and the solid lines show the kinetic relations. If $q_e \lesssim q_c$, we can expect of $\eta(q)$ plots of the type shown in Fig. 3b, and if $q_c \lesssim q_e$, plots of the type of Fig. 3c. When $q_c \ll q_e$, the ordered phase may not appear at all, although the crystal is produced in the region of its stability.

The model of the isolated corner on a step, which we have discussed here, is of course too simple to expect quantitative agreement between the characteristics obtained for it and the real situation, when there is a large number of corners and steps. Apparently a less important circumstance is that actually the crystal exchanges particles not directly with the parent medium, but with a layer of adsorbed surface particles. The latter means simply a change in the effective frequencies and of the energies of the particle detachment and attachment. However, the collective interaction is retained during the course of real crystalization. This is manifest in our case in a more complicated fashion, owing to the interaction of the corners and of the steps. But since it is precisely the collective interaction that leads to a kinetic phase transition, it should actually exist. In this connection, attention should be paid to the behavior of the ordered alloys which form a disordered crystal film if sputtered on a sufficiently cold substrate. When the temperature of the substrate is increased, a kinetic phase transition can be expected for such substances.

The kinetic transition discussed above is the analog of a thermodynamic second-order phase transition. It also corresponds apparently to kinetic analogs of first-order transitions, which can be transitions from stable to unstable crystal modifications with increasing degree of deviation from equilibrium (supersaturation, supercooling). Mention should be made here of the formation of amorphous films of germanium, silicon, antimony, or selenium, when sputtered on sufficiently cold substrates. Unfortunately, the author knows of no data on the character of the transition from the crystalline to the amorphous modification under changing kinetic conditions.

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