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GROWTH OF COPOLYMER CHAINS AND MIXED CRYSTALS—TRIAL-AND-ERROR STATISTICS

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I. INTRODUCTION. COOPERATIVITY IN ONE-COMPONENT SYSTEMS

As we know, the atomic structure of the surface and the internal structure of a growing crystal differ from the equilibrium structures. For example, different faces incorporate an impurity in different ways (the sectorial structure of a crystal^[1-3]), and the amount of it in the crystal is not determined by the ordinary phase diagram. The metastable actual structure arising during growth is highly persistent. All of this is also true of copolymer chains that maintain a sequential order and concentration of monomers. Hence, crystallization and polymerization must be treated not only within the framework of statistical thermodynamics, but also that of statistical kinetics. The latter is the topic of this review.

The atoms on the surface of a crystal are bound by collective interaction, both in the thermodynamic and the kinetic sense: the distribution of states (atomic surface configurations) and their rates of variation depend on the structure of the entire surface. The difficulties involved in this cooperative kinetics in single-component systems, and a fortiori in mixed systems, have led the theory of crystal growth to develop along the thermodynamic line. Above all, this development has given rise to the Kossel-Stranskiĭ-Kaĭshev molecular-kinetic theory (see^[4-7]). The latter is based mainly on analyzing the energies of different surface particles. Frenkel's thermodynamic analysis^[8] of step and surface structure started the practice of accounting for entropy terms and complex configurations, leading to the concepts of atomically-smooth and rough surfaces. Barton and Cabrera^[9,10] have taken into account collective interactions in an elementary surface layer, using the analogy with the properties of a two-dimensional ferromagnetic material. They showed that there is a critical relation between the binding energy and the temperature necessary for transition from an ordered, smooth structure to a disordered, rough structure. Further development of the studies^[8-10] has made it possible to treat surface fluctuations spanning tens of interatomic distances,^[11] to propose criteria for the existence of any particular surface structure in terms of entropy of crystallization,^[12-14] to find simple approximate methods for determining the conditions for transition from a smooth to a rough surface^[15,16] and to generalize the concept of such a transition to binary systems,^[17,125,126] to propose and study the possibility of barrier-free motion of a phase boundary,^[18-21] and to begin to analyze the surface structure of ionic crystals.^[22] All these studies, which have constituted the bulk of the work on the theory of crystallization,

have provided a great deal toward understanding the mechanism of crystallization, but they do not contain a truly kinetic approach to the problem.

The theory of nucleation has followed such an approach, starting with the studies of Volmer,^[87,88] Becker and Döring,^[23] and Zel'dovich.^[24] It is developing now,^[25] in particular, along the line of analyzing non-steady-state processes and different types of boundary conditions for the distribution function of the nuclei with respect to numbers of particles.^[26,27,29,30] Collective interaction plays no part in these studies, and this greatly simplifies matters.

Frenkel^[31] has used the kinetic approach in the theory of deposition of vapors on a foreign substrate in connection with the discovery by Semenow and Chariton^[32] of a critical temperature of condensation of molecular beams. Jackson and Chalmers^[110] have studied in general outline growth from a melt as resulting from exchange of molecules between the crystal and the medium. They assumed the forward and backward fluxes of particles to be proportional to the usual exponential factor, while they took the structure of the surface into account by introducing geometric coefficients and coefficients of accommodation. Unfortunately, there is as yet no information on the latter two qualities exact for qualitative estimates.^[110]

The development of a consistent statistical-kinetic theory of crystal growth has been revived in the last few years. It starts with assigning rates of attachment of atoms to different configurations on the surface and rates of detachment of atoms from these configurations. In contrast with previous studies, they have taken collective interactions into account in one way or another in the kinetics. In treating one-component systems, they analyze different spatial configurations, while in treating many-component systems (the main topic of this article), they analyze configurations that differ in arrangement of different types of particles at a kink. No one has yet made any simultaneous accounting for both factors.

One of the central problems in the theory of growth of one-component crystals is still that of elucidating the relation of the growth rate to the supersaturation (or supercooling). The analytical theory of motion of monomolecular steps having kinks of one particular sign^[38] has confirmed the well-known hypothesis that the growth rate depends linearly on the supersaturation and that there is no critical supercooling required for growth of a step. The problem of surface growth is much more complex. Here people have studied most fully the initial stage, the completion of the first monomolecular layer. Kikuchi^[33-34] has made the most thorough analysis. He started with a hexagonally packed

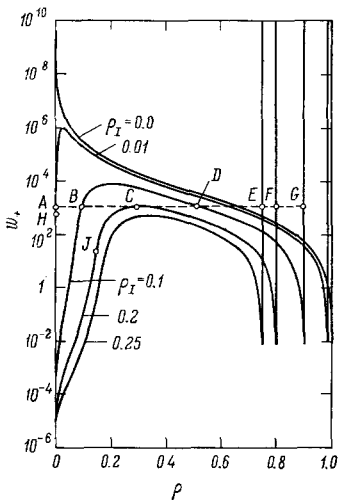


FIG. 1. Relation of the particle flux w_+ onto the surface to the degree of filling ρ of a monomolecular layer by these particles — for various densities of a non-volatile impurity ρ_i in a steady state. [33,34]

surface that was initially atomically smooth, and contained individual immobile, non-volatile impurity particles (active centers). The rest of the net sites that could be filled were vacant, and were gradually filled by particles impinging from the gas. These adsorbed particles can go back into the vapor, or diffuse along the surface at a certain rate. Then one must find the time-variation of the filling of the net.

A generating function was used in [33,34] to obtain the corresponding kinetic equations. It amounted to the probability of transition of the system to a new point in configuration space within the time dt , just as the equations of state are defined in thermodynamics by the partition function (see also [35-36]).

Figure 1 shows the numerical solution for the equations for the static situation in which the particle fluxes to and from the surface are the same. The degree of filling of the net ρ is plotted as the abscissa, and the incident (exchange) flux w_+ as the ordinate. Each curve corresponds to a particular value of the density ρ_i of the impurity. A flux $w_+^{(A)}$ corresponding to the point A permits two densities ρ of the adsorbed layer, corresponding to the points B and G (for $\rho_i = 0.1$). If we start filling with an empty net, we arrive at B, while we get to C by starting with an almost full net. The state D is unstable. One can get onto the right-hand branches of the curves by using fluxes exceeding the critical value for the given density of impurity centers (e.g., when $\rho_i = 0.2$, we must have $w_+ > w_+^{(A)}$). The curves of $w_+(\rho)$ are raised upward with increasing substrate temperature. Figure 2 gives the kinetics of filling of a planar net, in which the dimensionless time $w_+ t$ has been used.

Another approach has been carried out in [37], with numerical solution of the kinetic equations for planar groupings of atoms of dimensions from 2 to 100 particles in the surface layer.

Temkin [39] has treated the steady-state process of growth of a one-component crystal (rather than just the filling of a single layer). In [39], the degree of filling of the planar nets parallel to the growth front is a function of the net number n , as counted along the normal to the front. It varies from 0 to 1, and here the diffuseness of the front automatically results from the kinetic equations. The rates of attachment of particles to the crystal were assumed to be identical for all configurations

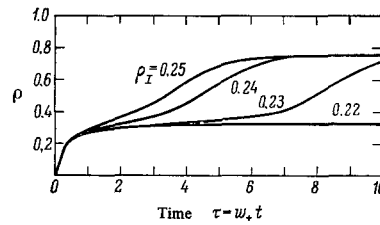


FIG. 2. Kinetics of filling of the surface for various densities ρ_i of a non-volatile impurity.

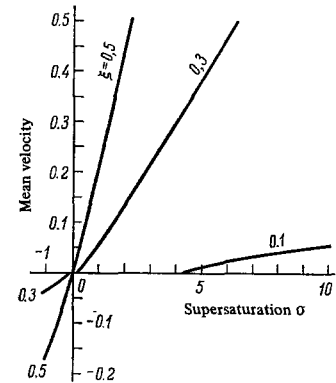


FIG. 3. Relation of the normal velocity V of steady-state growth of a face to the supersaturation σ for a lattice model. [39]

at the phase boundary, while the rate of detachment $\sim \exp(-\epsilon g_n/T)$, where ϵ is the work required per bond to remove an atom from the crystal into the medium, g_n is the average number of neighbors of an atom in the n -th net, and T is the energetic temperature. The surface was assumed to be atomically smooth at the outset. Numerical solution of the kinetic equations showed that there is a critical supersaturation ~ 1 necessary for growth when $\epsilon/T \gtrsim 1.2$, but practically no barrier when $\epsilon/T \lesssim 1.2$ (Fig. 3). This is precisely the value that corresponds in this model to transition from a smooth surface to a rough one under equilibrium conditions. The time-dependence of the growth rate proved to oscillate with a period corresponding to the filling of a single layer. The amplitude of the oscillations declines with increasing roughness (with decreasing ϵ/T).

One-dimensional chains are a very simple object for the statistical-kinetic approach to the kinetics of crystallization of many-component systems. The theory of their growth is also of great independent importance in studying copolymerization, on which much literature has accumulated in the years since the war. [48-52] Most often, polymerization involves strong deviations from equilibrium (Chapter II, Sec. 1). Hence, apparently, in spite of intensive study, the problem has been solved only relatively recently [40-44] of growth of a copolymer chain, taking into account not only random events of attachment of a monomer to the end of the chain, but also detachment of these particles at arbitrary rates. The obtained result (Secs. 2-3) is used in the theory of copolymerization (Sec. 1), in that of non-equilibrium incorporation of impurities in crystals (Sec. 5), in that of formation of a thermodynamically non-equilibrium atomic structure, in crystal growth (Sec. 6), and also in the theory of formation of the folded structure of polymer single crystals. [45-47] The last sections (Secs. 6-8) of this article will discuss the results of building models

for the growth of binary chains and crystals on a computer.

II. CHAIN GROWTH

1. The Matrix Method of Describing Polymerization

Let us pose the problem as follows. We have a medium consisting of m types of monomers. Polymer chains grow in it by attachment of monomers to the ends of these chains. Growth starts on particles of an initiator (or on activated monomers). Let I_α be the probability that the first monomer of the chain should belong to type α . In polycondensation, growth begins with ordinary monomer particles, and the quantities I_α are expressed in terms of the monomer concentration.^[69] Let us denote by $w_{+\alpha\beta}$ the number of monomers of type β that are attached per unit time to the ends of chains ending in monomers of type α , and by $w_{-\alpha\beta}$ the number of β monomers that detach per unit time from the ends of chains having α as the next-to-last particle. We shall assume attachment and detachment to be random events. Chain growth is stopped by reactions of termination, disproportionation, recombination, or chain transfer to a monomer. We shall denote the probability of chain termination at an α particle by T_α . The problem consists in determining the composition of the copolymer chains (concentrations of components, and correlations and distributions of different types of monomers along the chains), the molecular-weight distribution of the chains, the relation of the chain length to composition, etc.

Analysis of this problem began with the studies of Mayo and Lewis,^[53] Simha, Branson, and Wall,^[54,55] Alfrey and Goldfinger,^[56] and Stockmayer.^[57] It has subsequently been continued by a number of authors (including cases of stereoregular polymerization^[58-65]). The cited studies assumed the probabilities of chain continuation by attaching particles of a given type to be fixed. That is, the probability of detachment of particles was practically not taken into account.* In this approximation, growth of a copolymer chain is a Markov process, which can be expressed most economically in matrix language. This is what we shall use below, mainly following Frensdorff and Pariser.^[68]

Thus, let us assume $w_{-\alpha\beta} = 0$, and denote the quantities

$$P_{\alpha\beta} = w_{+\alpha\beta} / (\sum_{\beta} w_{+\alpha\beta} + w_{+\alpha T}) \quad (1.1)$$

as the probabilities of irreversible chain continuation. Here $w_{+\alpha T}$ is the rate of chain termination when terminated by the monomer α . The probabilities of termination are

$$T_\alpha = w_{+\alpha T} / (\sum_{\beta} w_{+\alpha\beta} + w_{+\alpha T}). \quad (1.2)$$

Here and below, the summations are made over all types of monomers. The more usual expressions are obtained by representing the rates of attachment in terms of the rate constants $k_{\alpha\beta}$ of the reactions and monomer concentrations $[M_\alpha]$:

*The theory of equilibrium polymerization developed in this approximation for a system of m components uses m^2 equilibrium constants. [59,69] It must be replaced by a consistent theory leading at equilibrium to m equations involving the chemical potentials (Sec. 3).

$$P_{\alpha\beta} = k_{\alpha\beta} [M_\beta] / (\sum_{\beta} k_{\alpha\beta} [M_\beta] + k_{\alpha T}), \quad T_\alpha = k_{\alpha T} / (\sum_{\beta} k_{\alpha\beta} [M_\beta] + k_{\alpha T}). \quad (1.3)$$

The probabilities $P_{\alpha\beta}$ form a square matrix \hat{P} consisting of m^2 elements, while the sets I_α and T_α are the row vector $\langle I |$ and the column vector $| T \rangle$, respectively. Then the probability of finding a chain of length n is

$$F(n) = \sum_{\alpha_1 \dots \alpha_n} I_{\alpha_1} P_{\alpha_1 \alpha_2} P_{\alpha_2 \alpha_3} \dots P_{\alpha_{n-1} \alpha_n} T_{\alpha_n} \equiv \langle I | \hat{P}^{n-1} | T \rangle. \quad (1.4)$$

Since

$$\sum_{\beta} P_{\alpha\beta} + T_\alpha = 1, \quad \text{i.e., } | T \rangle = | 1 \rangle - | \hat{P} | 1 \rangle = | \hat{1} - \hat{P} | 1 \rangle, \quad (1.5)$$

we have

$$F(n) = \langle I | \hat{P}^{n-1} | 1 \rangle - \langle I | \hat{P}^n | 1 \rangle = \langle I | \hat{P}^{n-1} - \hat{P}^n | 1 \rangle, \quad (1.6)$$

where $| 1 \rangle$ is a unit column vector, and $\hat{1}$ is the unit matrix. If $| p_i \rangle$ and $\langle p_i |$ are eigenvectors of the matrix \hat{P} corresponding to the eigenvalues λ_i , i.e.,

$$| \hat{P} | p_i \rangle = \lambda_i | p_i \rangle, \quad \langle p_i | \hat{P} = \lambda_i \langle p_i | \quad (1.7)$$

and

$$\langle p_i | p_i \rangle = 1,$$

then, upon writing the matrix \hat{P}^n in the form $\hat{P}^n = \sum \lambda_i^n | p_i \rangle \langle p_i |$, we get

$$F(n) = \sum_i \lambda_i^{n-1} (1 - \lambda_i) \langle I | p_i \rangle \langle p_i | 1 \rangle. \quad (1.8)$$

One can easily verify that $\sum_{n=1}^{\infty} F(n) = 1$. Hence, the mean chain length (the degree of polymerization) is

$$\bar{n} = \sum_{n=1}^{\infty} n F(n) = \sum_i \langle I | p_i \rangle \langle p_i | 1 \rangle (1 - \lambda_i)^{-1}, \quad (1.9)$$

while the mean-square length is

$$\bar{n}^2 = \sum_{n=1}^{\infty} n^2 F(n) = \sum_i (1 + \lambda_i) (-\lambda_i)^{-2} \langle I | p_i \rangle \langle p_i | 1 \rangle, \quad (1.10)$$

or, in other words,^[66,69]

$$\left. \begin{aligned} \bar{n} &= \sum_{n=1}^{\infty} n \langle I | \hat{P}^{n-1} | T \rangle = \langle I | (\hat{1} - \hat{P})^{-1} | T \rangle, \\ \bar{n}^2 &= \sum_{n=1}^{\infty} n^2 \langle I | \hat{P}^{n-1} | T \rangle = \langle I | (\hat{1} - \hat{P})^{-2} | T \rangle. \end{aligned} \right\} \quad (1.11)$$

If $T_\alpha = 0$, then, as we see from (1.3), the matrix \hat{P} is stochastic, and its maximum eigenvalue is unity. Then \bar{n} and \bar{n}^2 are infinite, as must be the case in a system in which the chains do not terminate. When $T_\alpha \sim T$ is small but finite, $\bar{n} \sim T^{-1}$ in order of magnitude.

One can find the concentrations x_α ($\alpha = 1, 2, \dots, m$) of the different components in the polymer most easily when $T_\alpha = 0$, i.e., for a long enough chain. Since such a chain is homogeneous,

$$x_\beta = \sum_{\alpha} x_\alpha P_{\alpha\beta}. \quad (1.12)$$

Besides obeying this system of equations, the concentrations x_α obey the normalization condition

$$\sum_{\alpha} x_\alpha = 1. \quad (1.13)$$

The linear system of (1.12) and (1.13) has the solution

$$x_\alpha = Q^{\alpha m} / \text{Det } \hat{Q}, \quad (1.14)$$

where the matrix

$$\hat{Q} = \begin{vmatrix} P_{11} - 1 & P_{21} & \dots & P_{m1} \\ \dots & \dots & \dots & \dots \\ P_{1m-1} & P_{2m-1} & \dots & P_{mm-1} \\ 1 & 1 & \dots & 1 \end{vmatrix},$$

while $Q_{\alpha m}$ is the minor of the α -th element of the last row. For an infinite chain, $\sum_{\beta} P_{\alpha\beta} = 1$. Hence, when we construct the matrix Q , a unit row can be substituted for any of the rows of the matrix (then we have to insert the number of the unit row in place of m in the numerator of (1.14)).

Upon determining the concentrations x_{α} , we can easily find the binary, ternary, etc., distribution functions:

$$x_{\alpha\beta} = x_{\alpha}P_{\alpha\beta}, \quad x_{\alpha\beta\gamma} = x_{\alpha}P_{\alpha\beta}P_{\beta\gamma}, \quad x_{\alpha_1\alpha_2} \dots x_{\alpha_n} = x_{\alpha_1}P_{\alpha_1\alpha_2}P_{\alpha_2\alpha_3} \dots P_{\alpha_{n-1}\alpha_n}. \quad (1.15)$$

The subscripts $\alpha_1\alpha_2 \dots$ here and below are equivalent to $\alpha\beta \dots$. The binary function $x_{\alpha\beta}$ is the fraction of pairs of consecutive particles $\alpha\beta$, as compared with the total number of all possible pairs in the chain. The ternary function $x_{\alpha\beta\gamma}$ is the fraction of $\alpha\beta\gamma$ triplets among all the triplets, etc. The equations (1.15) imply that only pair correlations exist in the chain, while all the others can be expressed in terms of them, in view of (1.1).

The mean concentrations of monomers in the conglomerate of finite chains are the concentrations of the monomers in an infinite chain artificially made up from all the finite ones by the "head-to-tail" principle. Then the probability of finding a monomer β after α in the composite chain will be $P_{\alpha\beta} + T_{\alpha}I_{\beta}$. In fact, β can "attach" to the composite chain either by the same mechanism as in finite chains (the probability $P_{\alpha\beta}$), or else, by ending on α , followed by a statistically independent start with the monomer β (the probability is $T_{\alpha}I_{\beta}$). Hence, the formulas (1.12)–(1.15) hold for a system of finite chains if we substitute $P_{\alpha\beta} \rightarrow P_{\alpha\beta} + T_{\alpha}I_{\beta}$.

Chains of finite length are characterized not only by the mean concentrations x_{α} , but also by the distribution function $f(n, n_{\alpha})$. It is the fraction of chains of length n containing n_{α} particles of type α , with respect to all the chains of arbitrary length and composition. We can derive the distribution $f(n, n_{\alpha})$ by using the generating function

$$G(s, n) = F^{-1}(n) \sum_{n_{\alpha}} s^{n_{\alpha}} \langle n_{\alpha} | \hat{P}^{n-1} | T \rangle = F^{-1}(n) \sum_{\mathbf{s}} \lambda_{\mathbf{s}}^{-1} \langle I | \hat{P}_{\mathbf{s}} | \rho_{\mathbf{s}} | 1 \rangle, \quad (1.16)$$

where $F^{-1}(n)$ is a normalizing factor: $f(n, n_{\alpha}) F^{-1}(n)$ is the fraction of chains containing n_{α} monomers α with respect to chains of length n ; $|\rho_{\mathbf{s}}\rangle$, $\langle \rho_{\mathbf{s}}|$, and $\lambda_{\mathbf{s}}$ are the eigenvectors and eigenvalues of the matrix $\hat{P}_{\mathbf{s}}$, which can be obtained by multiplying the α -th column of \hat{P} by \mathbf{s} . The generating function makes it possible to calculate the different moments of the distribution $f(n, n_{\alpha})$. For example, the mean number of α particles in chains of length n is $[\partial G(s, n)/\partial s]_{\mathbf{s}=1}$, while the mean square of this number is $\partial/\partial \mathbf{s} \left(\mathbf{s} \frac{\partial G}{\partial \mathbf{s}} \right)_{\mathbf{s}=1}$.

Now, let us illustrate the presented general theory with concrete results for a binary system ($\alpha, \beta, \dots = A, B$). For an infinite chain, according to (1.12)–(1.15),

$$\left. \begin{aligned} x_A &= P_{BA}/(P_{AB} + P_{BA}), & x_B &= P_{AB}/(P_{AB} + P_{BA}), \\ x_{AA} &= P_{BA}P_{AA}/(P_{AB} + P_{BA}), & x_{BB} &= P_{AB}P_{BB}/(P_{AB} + P_{BA}), \\ x_{AB} &= x_{BA} = P_{AB}P_{BA}/(P_{AB} + P_{BA}). \end{aligned} \right\} \quad (1.17)$$

The length distribution is

$$F(n) = a_1(1 - \lambda_1)\lambda_1^n + a_2(1 - \lambda_2)\lambda_2^{n-1}, \quad (1.18)$$

where

$$\lambda_{1,2} = \{2 - (P_{AB} + P_{BA}) - (T_A + T_B) \pm [(P_{AB} + P_{BA})^2 + 2(P_{AB} - P_{BA})(T_A - T_B) + (T_A - T_B)^2]^{1/2}\} / 2, \\ a_{1,2} = \frac{1}{2} \left\{ 1 \pm \frac{(P_{AB} + P_{BA}) - (T_A - T_B)(T_A - T_B)}{[(P_{AB} + P_{BA})^2 + 2(P_{AB} - P_{BA})(T_A - T_B) + (T_A - T_B)^2]^{1/2}} \right\}.$$

If the termination probabilities are small in comparison with the probabilities of continuation ($T_{\alpha} \ll 1$), then

$$\lambda_1 \approx 1 - (P_{AB}T_B + P_{BA}T_A)P_{AB}^{-1} + P_{BA}, \quad \lambda_2 \ll 1, \quad a_1 \approx 1, \quad a_2 \ll 1.$$

Hence, long chains are distributed according to the power law:

$$F(n) \approx (1 - \lambda_1)\lambda_1^{n-1}, \quad (1.19)$$

which is equivalent to the distribution of Flory (see^[51,57]). When $T_A = T_B = T$, the power law holds for any n , and is characterized by the value of T alone:

$$F(n) = T(1 - T)^n. \quad (1.20)$$

When neither of the polymers can polymerize separately ($P_{AA} = P_{BB} = 0$) and $T_{\alpha} \ll 1$,

$$F(n) \approx [(T_A + T_B)(P_{AB}P_{BA})^{(n-1)/2} / 2] + [(T_A + T_B)(I_A - I_B)(-P_{AB}P_{BA})^{(n-1)/2} / 2]. \quad (1.21)$$

The opposite limiting case in which blocks of identical monomers are formed ($P_{AA} \gg P_{AB}$, $P_{BB} \gg P_{BA}$) is characterized by the distribution

$$F(n) = I_A T_A P_{AA}^{n-1} + I_B T_B P_{BB}^{n-1}. \quad (1.22)$$

The system for which $P_{AA}P_{BB} = P_{AB}P_{BA}$ occupies a special place between the two cited limiting cases. Then, in an infinite chain $x_{AA} = x_A^2$, $x_{BB} = x_B^2$, and $x_{AB} = x_{BA} = x_A x_B$. That is, the distribution is chaotic with respect to types of particles. The entire theory in this case looks as though $w_{+\alpha\beta} = w_{+\beta}$.^[57] The length distribution is

$$F(n) = \left[1 + \frac{(P_{AB} + P_{BA}) - (I_A - I_B)(T_A - T_B)}{P_{AA} + P_{BB}} \right] (1 - P_{AA} - P_{BB})(P_{AA} + P_{BB})^{n-1}. \quad (1.23)$$

The general expression for the mean chain length is:

$$\bar{n} = \frac{a_1}{1 - \lambda_1} + \frac{a_2}{1 - \lambda_2} = \frac{P_{AB} + P_{BA} + I_A T_B + I_B T_A}{P_{AB}T_B + P_{BA}T_A + T_A T_B}, \quad (1.24)$$

while the mean relative variance of the length distribution is

$$\frac{\bar{n}^2 - \bar{n}^2}{\bar{n}^2} = \frac{2(P_{AB} + P_{BA} + T_A + T_B) - (P_{AB}T_B + P_{BA}T_A + T_A T_B)}{P_{AB} + P_{BA} + I_A T_B + I_B T_A} - 2 \frac{P_{AB}T_B + P_{BA}T_A + T_A T_B}{(P_{AB} + P_{BA} + I_A T_B + I_B T_A)^2} - 1. \quad (1.25)$$

The relative variance of concentration of the component A throughout the system can be obtained from the generating function.^[68] For large n and small T_{α} , the variance is

$$(\bar{n}_A^2 - \bar{n}_A^2) / \bar{n}_A^2 = P_{AB}(\bar{n}P_{BA})^{-1} [2(P_{AB} + P_{BA})^{-1} - 1]. \quad (1.26)$$

Polymers having an almost regular alternation of monomers ($P_{AB} \sim P_{BA} \sim 1$) are characterized by a small variance, while polymers having block structures ($P_{AB}, P_{BA} \sim 1$) have a large variance.

While studying the problem of the mean distribution of concentration in a polymer by using a generating function of many variables, Hijmans^[67] proved in general form that this distribution is Gaussian.

A generalization of the presented theory to the case in which the continuation probabilities are functions of a large number of subscripts, rather than two, is given in^[65,67] for infinite chains, and for finite chains in^[69]. It amounts to renumbering the transition probabilities (e.g., in a binary system) and correspondingly increasing the order of the matrix \hat{P} .

The ideas that I have presented require some refinement for polycondensation, in which no special initiator is needed. The process simply involves reaction of the monomers among themselves and with the polymer chains, and, hence, the probabilities I_α are determined by the monomer concentrations. Peller^[68,69] has studied a model in which the total amount of monomer units in the system is preassigned. The continuation probabilities $P_{\alpha\beta}$ are also preassigned, and are considered to be constant throughout the process. If N is the total number of molecules in the final product (including monomer and polymer) and X_α are the total numbers of monomer units of type α in the chains in the free state, then

$$\langle X | 1 \rangle = N \bar{n} = N \langle I | (\hat{1} - \hat{P})^{-1} | 1 \rangle. \quad (1.27)$$

This equation holds if^[69]

$$\langle I | = N^{-1} \langle X | \hat{1} - \hat{P} |. \quad (1.28)$$

One can derive the same result by strict balancing with respect to each type of monomer particle. The mean chain length in the discussed model of polycondensation is

$$\bar{n} = \langle X | 1 \rangle / \langle X | T \rangle, \quad (1.29)$$

since $N = \langle X | T \rangle$, in view of (1.28) and (1.1). Formulas characterizing the features of polycondensation, as well as the features arising upon chain termination by disproportionation and recombination, are contained in^[69].

2. Reversible Chain Growth

Everywhere above, we assumed the chain-continuation probabilities $P_{\alpha\beta}$ to be known (Eqs. (1.2) and (1.3)). If the rates of termination $w_{-\alpha\beta}$ are comparable with the attachment rates $w_{+\alpha\beta}$ (near equilibrium), then the concentrations of monomers at the ends and in the interior of each chain differ. Hence, the probability of attachment of a monomer is no longer the probability of chain continuation. Consequently, it becomes necessary to solve the problem in the general formulation given at the beginning of Sec. 1. We shall begin with analyzing the growth of an infinitely long chain, assuming the rate of termination to be zero.

Let us denote a half-infinite chain ending with the monomer α by $(\dots \alpha)$, that ending with the pair $\alpha\beta$ by $(\dots \alpha\beta)$, etc. Then the probabilities

$$\left. \begin{aligned} \frac{p_{\alpha\beta\gamma}}{(\dots \alpha\beta) \rightarrow (\dots \alpha\beta\gamma)} &= w_{+\beta\gamma} / (w_{-\alpha\beta} + \sum_{\gamma} w_{+\beta\gamma}), \\ \frac{q_{\alpha\beta}}{(\dots \alpha\beta) \rightarrow (\dots \alpha)} &= w_{-\alpha\beta} / (w_{-\alpha\beta} + \sum_{\gamma} w_{+\beta\gamma}) \end{aligned} \right\} \quad (2.1)$$

define the fraction of cases in which a chain $(\dots \alpha\beta)$ adds on one of the monomers (γ), or loses its last particle (β) (Fig. 4a). Attachment of this particle does not yet mean that the final chain will contain it, and chain growth is no longer a Markov process. However, it can be reduced to the Markov method of conservation functions,^[40,42,44] which consists in the following.

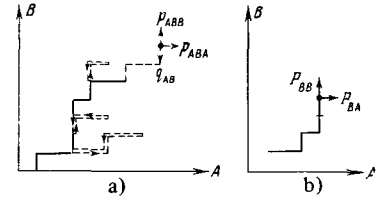


FIG. 4. Graphical depiction of a binary chain in the process of formation. A horizontal unit segment denotes an A particle, and a vertical segment denotes a B particle. The solid line denotes the portion of the growing chain that will never break down in the future. The dotted line shows the "impermanent" particles that the chain will lose sooner or later. a) The end of the chain consists of "impermanent" particles, and has the three possibilities indicated by arrows for future movement; b) the end of the chain made of "permanent" particles can permanently advance either upward or to the right.

Let us choose arbitrarily $N(\dots \alpha\beta)$ chains. In the process of growth by exchanging particles with the medium, some of them will lose only the particle β , others will lose the particles β and α , etc. However, there will also be those that elongate to infinity in the growth process, without having lost any of the particles $(\dots \alpha\beta)$ that they had at the outset. Let us denote the fraction of the chains of this last type with respect to all those chosen by $U_{\alpha\beta}$, while the absolute number of conserved chains is $N U_{\alpha\beta}$. What does it consist of? In order to have conservation of $(\dots \alpha\beta)$, the next monomer $\gamma = A, B, \dots$ must attach to it and remain forever. In the first round, $N \sum_{\gamma} p_{\alpha\beta\gamma} U_{\beta\gamma}$ monomers will undergo this operation of being immured. The remaining $N \sum_{\gamma} p_{\alpha\beta\gamma} (1 - U_{\beta\gamma})$ chains (from among those that didn't immediately break down in the first round) will return to the original configuration $(\dots \alpha\beta)$. Among these, $N \sum_{\gamma} p_{\alpha\beta\gamma} (1 - U_{\beta\gamma}) U_{\alpha\beta}$ chains will be conserved from the second, third, etc., rounds. Hence,

$$U_{\alpha\beta} = \sum_{\gamma} p_{\alpha\beta\gamma} [U_{\beta\gamma} + (1 - U_{\beta\gamma}) U_{\alpha\beta}]. \quad (2.2)$$

Another method of deriving the system (2.2) has been developed in^[40]. This system of m^2 non-linear equations amounts to m equations for the quantities $\psi_\alpha = \sum_{\beta} \Phi_{\alpha\beta}$, where $\Phi_\alpha = w_{+\alpha\beta} U_{\alpha\beta}$:

$$\Phi_{\alpha\beta} = w_{+\alpha\beta} \sum_{\gamma} p_{\alpha\beta\gamma} U_{\beta\gamma} / (q_{\alpha\beta} + \sum_{\gamma} p_{\alpha\beta\gamma} U_{\beta\gamma}) = w_{+\alpha\beta} \psi_\beta / (w_{-\alpha\beta} + \psi_\beta), \quad (2.3)$$

Hence,

$$\psi_\alpha = \sum_{\beta} w_{+\alpha\beta} \psi_\beta / (w_{-\alpha\beta} + \psi_\beta)^{-1}. \quad (2.4)$$

The quantity ψ_α means the total flux of particles that attach forever to $(\dots \alpha)$. This flux consists of the fluxes $\Phi_{\alpha\beta}$ of monomers β . Hence, the fraction of cases in which the chain $(\dots \alpha)$ is permanently continued by the monomer β is

$$P_{\alpha\beta} = w_{+\alpha\beta} U_{\alpha\beta} / \psi_\alpha. \quad (2.5)$$

In a binary system, according to (2.17)

$$\left. \begin{aligned} x_A &= \Phi_{BA} \psi_A / (\Phi_{AB} \psi_B + \Phi_{BA} \psi_A), & x_B &= \Phi_{AB} \psi_B / (\Phi_{AB} \psi_B + \Phi_{BA} \psi_A), \\ x_{AA} &= \Phi_{AA} \Phi_{BA} / (\Phi_{AB} \psi_B + \Phi_{BA} \psi_A), & x_{BB} &= \Phi_{BB} \Phi_{AB} / (\Phi_{AB} \psi_B + \Phi_{BA} \psi_A), \\ x_{AB} &= x_{BA} = \Phi_{AB} \Phi_{BA} / (\Phi_{AB} \psi_B + \Phi_{BA} \psi_A). \end{aligned} \right\} \quad (2.6)$$

Now let us find the rate of elongation of the chain. Let

$x_{1\alpha}$ be the fraction of the time during which the chain ends with particles of type α . Then $n \sum_{\alpha\beta} x_{1\alpha} w_{+\alpha\beta} U_{\alpha\beta}$ particles will be attached to the $N(\dots\alpha)$ chains per unit time and conserved forever. That is, the mean rate of directed movement of the end of each chain is

$$V = \sum_{\alpha} x_{1\alpha} \psi_{\alpha}. \quad (2.7)$$

In order to determine $x_{1\alpha}$, we note that permanent attachment of a particle β to a chain ending with the particle α gives a pair $\alpha\beta$ in the interior. Hence,

$$x_{1\alpha} w_{+\alpha\beta} U_{\alpha\beta} / \sum_{\alpha\beta} x_{1\alpha} w_{+\alpha\beta} U_{\alpha\beta} = x_{1\alpha} \Phi_{\alpha\beta} / \sum_{\alpha} x_{1\alpha} \psi_{\alpha} = x_{\alpha\beta}. \quad (2.8)$$

If we sum (2.8) over β , we get a system of equations with respect to $x_{1\alpha}$. In the two-component case we get

$$\left. \begin{aligned} x_{1A} &= \Phi_{BA} / (\Phi_{AB} + \Phi_{BA}), & x_{1B} &= \Phi_{AB} / (\Phi_{AB} + \Phi_{BA}), \\ V &= (\Phi_{AB} \psi_B + \Phi_{BA} \psi_A) / (\Phi_{AB} + \Phi_{BA}). \end{aligned} \right\} \quad (2.9)$$

The equations (2.8), together with the conditions $\sum_{\beta} x_{\alpha\beta} = \sum_{\beta} x_{\beta\alpha} = x_{\alpha}$, $\sum_{\alpha} x_{1\alpha} = 1$, and $\sum_{\alpha} x_{\alpha} = 1$, is a complete system for determining both $x_{1\alpha}$ and $x_{\alpha\beta}$. As we should expect, the calculations performed in this way for a two-component system give the same expressions for $x_{\alpha\beta}$ as (2.6) does. Evidently, this approach is another way of solving the problem without explicit introduction of the probabilities $\hat{P}_{\alpha\beta}$.

The distribution functions for binary, ternary, etc. configurations of chain ends can be obtained from relations analogous to (2.8). Thus,

$$x_{1\alpha\beta} \Phi_{\beta\gamma} / \sum_{\beta} x_{1\beta} \psi_{\beta} = x_{\alpha\beta\gamma} = x_{\alpha\beta} P_{\beta\gamma} = x_{1\alpha} \Phi_{\alpha\beta} P_{\beta\gamma} / \sum_{\alpha} x_{1\alpha} \psi_{\alpha}, \quad (2.10)$$

Hence,

$$x_{1\alpha\beta} = x_{1\alpha} \Phi_{\alpha\beta} / \psi_{\beta} = x_{1\alpha} w_{+\alpha\beta} / (w_{-\alpha\beta} + \psi_{\beta}), \quad (2.11)$$

That is, the distribution functions for chain ends are decomposable into pair products, just as the internal functions $x_{\alpha\beta}$ are. However, the correlation is effected here by the quantities $\Phi_{\alpha\beta} / \psi_{\beta}$, rather than $\Phi_{\alpha\beta} / \psi_{\alpha}$. If we solve the equations (2.11) simultaneously with the conditions $\sum_{\alpha} x_{1\alpha\beta} = x_{1\beta}$ and $\sum_{\alpha} x_{1\alpha} = 1$ in the two-component case, we get (2.9) again. At equilibrium between the chain and the medium, when $\psi_{\alpha} = 0$ (see Sec. 3), (2.11) transforms into the obvious balance equation $x_{1\alpha\beta} w_{-\alpha\beta} = x_{1\alpha} w_{+\alpha\beta}$. This distinction from (2.11) indicates that the end distribution function shifts upon deviation from equilibrium. The relation of the distribution functions $\bar{x}_{\alpha\beta}$, which express the relative fraction of cases in which the pair $\alpha\beta$ sits at the end of the chain and the functions $x_{1\alpha\beta}$, which express the fraction of the time during which the end of the chain is formed by the pair $\alpha\beta$ is given by the formula

$$x_{1\alpha\beta} = \bar{x}_{\alpha\beta} \tau_{\alpha\beta} / \sum_{\alpha\beta} \bar{x}_{\alpha\beta} \tau_{\alpha\beta}, \quad (2.12)$$

where $\tau_{\alpha\beta}$ is the mean lifetime of the pair $\alpha\beta$ at the end of the chain:

$$\tau_{\alpha\beta} = (w_{-\alpha\beta} + \sum_{\gamma} w_{+\beta\gamma})^{-1}. \quad (2.13)$$

We shall now find the diffusion coefficient of the end of the chain in the process of growth. In order to do this,

let us write down the equation of motion of the end, i.e., the equation for the probability density $n(k, t)$ of finding the end at a point situated k interatomic distances from the origin at the moment t of time:

$$\frac{\partial n}{\partial t} = - \sum_{\alpha\beta} (x_{1\alpha} w_{+\alpha\beta} - x_{1\alpha\beta} w_{-\alpha\beta}) \frac{\partial n}{\partial k} + \frac{1}{2} \sum_{\alpha\beta} (x_{1\alpha} w_{+\alpha\beta} + x_{1\alpha\beta} w_{-\alpha\beta}) \frac{\partial^2 n}{\partial k^2}; \quad (2.14)$$

Here the first and second differences in k have been replaced by the corresponding derivatives. As we should have expected, (2.14) is a diffusion equation with drift. The expression involving $-\partial n / \partial k$ is the mean translational velocity of the end, which is equivalent to (2.7). The diffusion coefficient is

$$D_t = \sum_{\alpha\beta} (x_{1\alpha} w_{+\alpha\beta} + x_{1\alpha\beta} w_{-\alpha\beta}) / 2 = (V/2) + \sum_{\alpha\beta} x_{1\alpha} w_{+\alpha\beta} w_{-\alpha\beta} (w_{-\alpha\beta} + \psi_{\beta})^{-1}. \quad (2.15)$$

At equilibrium,

$$\overset{\circ}{D}_t = \sum_{\alpha\beta} \overset{\circ}{x}_{1\alpha} \overset{\circ}{w}_{+\alpha\beta}. \quad (2.16)$$

Here and everywhere below, the symbol "O" over a letter indicates the equilibrium value of the corresponding parameter.

The exact solution derived above of the problem of polymerization of a many-component system is easily generalized to the case of interaction between particles that are more remote from one another than nearest neighbors.

Lauritsen, Di Marzio, and Passaglia^[41,43] have also derived an exact solution of the general problem of growth of a copolymer chain, independently and almost simultaneously with the author.^[40,42,44] They started with a system of stationary kinetic equations

$$\begin{aligned} dx_{1\beta}^{(n+1)} / dt &= \sum_{\alpha} x_{1\alpha}^{(n)} w_{+\alpha\beta} + \sum_{\gamma} x_{1\beta\gamma}^{(n+2)} w_{-\beta\gamma} - \\ &\quad - x_{\beta}^{(n+1)} \sum_{\gamma} w_{+\beta\gamma} - \sum_{\alpha} x_{\alpha\beta}^{(n+1)} w_{-\alpha\beta} = 0, \end{aligned} \quad (2.17)$$

$$dx_{1\alpha\beta}^{(n+1)} / dt = x_{1\alpha}^{(n)} w_{+\alpha\beta} + \sum_{\gamma} x_{1\alpha\beta\gamma}^{(n+2)} w_{-\beta\gamma} - x_{1\alpha\beta}^{(n+1)} \sum_{\gamma} w_{+\beta\gamma} - x_{1\alpha\beta}^{(n+1)} w_{-\alpha\beta} = 0, \quad (2.18)$$

etc. Here, $x_{1\alpha}^{(n)}$, $x_{1\alpha\beta}^{(n)}$, etc., are the fractions of the chains of length n that end at the instant of time t in the particle α , the pair $\alpha\beta$, etc., as compared with the total number of chains having any lengths and terminations. Let us assume that: 1) only pair correlations exist in the distribution of the chains over different end configurations:

$$x_{1\alpha\beta\gamma}^{(n+2)} = x_{1\alpha\beta}^{(n+1)} x_{1\beta\gamma}^{(n+2)} / x_{\beta}^{(n+2)}, \quad (2.19)$$

and 2) the distribution function does not depend on n for long enough chains. A considerable part of^[41] is devoted to proving these statements. In terms of probabilities of conservation for $n = \infty$, the first of the assumptions is simply a consequence of the fact that $U_{\alpha\beta}$ and $P_{\alpha\beta}$ are functions of two subscripts alone. If we use (2.19) with $n = \infty$, we can represent Eq. (2.18) in the form

$$J_{\alpha\beta} = x_{1\alpha} w_{+\alpha\beta} - x_{1\alpha\beta} w_{-\alpha\beta} = x_{\alpha\beta} \sum_{\gamma} (w_{+\beta\gamma} - x_{1\beta\gamma} x_{1\beta}^{-1} w_{-\beta\gamma}) \equiv x_{1\alpha\beta} \psi_{\beta}. \quad (2.20)$$

This gives rise to an equation for ψ_{β} that exactly agrees with (2.4). Thus both approaches^[40,41] lead to identical results. If the number of components $m > 2$, then it is very hard to solve (2.4). Hence, in^[41] they propose an iteration method suitable for numerical calculations for determining ψ_{α} as $\lim_{n \rightarrow \infty} \psi_{\alpha}^{(n)}$, where

$$\psi_{\alpha}^{(n)} = \sum_{\beta} w_{+\alpha\beta} \psi_{\beta}^{(n-1)} (w_{-\alpha\beta} + \psi_{\beta}^{(n-1)})^{-1}. \quad (2.21)$$

The flux $J_{\alpha\beta}$ is the fraction of chains (... α) that increase their lengths by unity by adding β , or the fraction of chains (... $\alpha\beta$) immured per unit time ($\sum_{\alpha\beta} J_{\alpha\beta} = V$).

Lauritzen and his coauthors have shown that, for any finite n ,

$$J_{\beta}^{(n)}/x_{1\beta}^{(n)} = J_{\alpha\beta}^{(n)}/x_{1\alpha\beta}^{(n)} = \dots = \psi_{\beta} \quad (2.22)$$

and it does not depend on n . Together with (2.20), this makes it possible to find the steady-state length distribution of the chains:

$$x_{1\alpha}^{(n-1)} = \sum_{\alpha} x_{1\alpha}^{(n-1)} w_{+\alpha\beta} (w_{-\alpha\beta} + \psi_{\beta})^{-1}, \quad (2.23)$$

where

$$x_{1\alpha}^{(1)} = x_{\alpha}^{(0)} w_{+\alpha} (w_{-\alpha} + \psi_{\alpha})^{-1}. \quad (2.24)$$

In a system that permits chains of any length, a steady-state distribution is never attained if the process begins with a state that contains polymers of finite length. However, when a time considerably exceeding n/V has elapsed, we can speak of a steady-state distribution of the chains of length $\sim n$ and less. As equilibrium is approached, $V \rightarrow 0$, and the stated criterion becomes more and more rigid.

If we denote

$$\hat{\Psi} \equiv \|\Psi_{\alpha\beta}\|, \quad \Psi_{\alpha\beta} = w_{+\alpha\beta}/(w_{-\alpha\beta} + \psi_{\beta}), \quad (2.25)$$

we have

$$|x_1^{(n+1)}\rangle = |\hat{\Psi}^n |x_1^{(1)}\rangle. \quad (2.26)$$

Since $\psi_{\alpha} = \sum_{\beta} \Psi_{\alpha\beta} \psi_{\beta}$, the non-linear operator $\hat{\Psi}$ has a single eigenvalue. Here the ψ_{α} are the components of the corresponding eigen column vector $|\psi\rangle$. Hence, the fraction of the chains of length n is

$$\langle 1 | x_1^{(n+1)} \rangle = \langle 1 | \hat{\Psi}^n | x_1^{(1)} \rangle, \quad (2.27)$$

where $\langle 1 |$ is the unit row vector. Hence, the length distribution function has the form

$$F(n) = \langle 1 | \hat{\Psi}^{n-1} | x_1^{(1)} \rangle / \langle 1 | (1 - \hat{\Psi})^{-1} | x_1^{(1)} \rangle, \quad (2.28)$$

while the mean length is

$$\bar{n} = \langle 1 | (1 - \hat{\Psi})^{-2} | x_1^{(1)} \rangle / \langle 1 | (1 - \hat{\Psi})^{-1} | x_1^{(1)} \rangle. \quad (2.29)$$

Let us return now to the general case, taking into account initiation and termination of chains. Let j_{+I} be the number of initiator particles arising per unit volume and unit time, and w_{-I} be the rate of deactivation of each center. Further, let $w_{+I\alpha}$ be the rates of attachment (+) and detachment (-) of the monomer α at the center I . The rates $w_{+\alpha T}$ characterize chain termination at the particle α . Then the initial stages of the process are described by the following conservation probabilities: 1) U_I is the probability that a generated center will never in the future decompose, so that chain growth will succeed in starting; 2) $U_{I\alpha}$ is the probability that the particle α will never leave after attaching to the initiator, and finally, 3) $U_{\alpha T} = 1$, for reactivation of terminated chains is forbidden. The conservation probabilities obey equations quite analogous to (2.2) and (2.3):

*We assume that $w_{-\alpha T} = 0$, i.e., the chain doesn't regain activity. In the converse case, the subscript T must denote a state having a certain lifetime (long in comparison with $w_{\pm\alpha\beta}$).

$$\begin{aligned} U_I &= \sum_{\alpha} P_{I\alpha} \{U_{I\alpha} + (1 - U_{I\alpha}) U_I\} = \\ &= \sum_{\alpha} w_{+I\alpha} U_{I\alpha} / (w_{-I} + \sum_{\alpha} w_{+I\alpha} U_{I\alpha}) = (\psi_I + w_{+IT}) / [w_{-I} + (\psi_I + w_{+IT})], \end{aligned} \quad (2.30)$$

where

$$\begin{aligned} P_{I\alpha} &= w_{+I\alpha} / (w_{-I} + \sum_{\alpha} w_{+I\alpha} + w_{+IT}), \quad \psi_I = \sum_{\alpha} w_{+I\alpha} U_{I\alpha}, \\ U_{I\alpha} &= \sum_{\beta} P_{I\alpha\beta} [U_{\alpha\beta} + (1 - U_{\alpha\beta}) U_{I\alpha}] + P_{I\alpha T} = \frac{\psi_{\alpha} + w_{+\alpha T}}{w_{-I\alpha} + (\psi_{\alpha} + w_{+\alpha T})}, \end{aligned} \quad (2.31)$$

where

$$P_{I\alpha\beta} = w_{+\alpha\beta} / (w_{-I\alpha} + \sum_{\beta} w_{+\alpha\beta} + w_{+\alpha T}),$$

while ψ_{α} has its previous meaning (see (2.2) and (2.3)). Thus,

$$\psi_I = \sum_{\alpha} w_{-I\alpha} (\psi_{\alpha} + w_{+\alpha T}) (w_{-I\alpha} + \psi_{\alpha} + w_{+\alpha T})^{-1}, \quad (2.32)$$

$$\psi_{\alpha} = \sum_{\beta} w_{+\alpha\beta} (\psi_{\beta} + w_{+\beta T}) (w_{-\alpha\beta} + \psi_{\beta} + w_{+\beta T})^{-1}. \quad (2.33)$$

The summation is made everywhere over A, B, \dots (with summation over the state T excluded). By beginning the solution "from the end", from (2.33), we can find ψ_{α} , and then ψ_I by (2.32). In terms of these quantities, the probabilities of irreversible continuation are

$$\left. \begin{aligned} P_{I\alpha} &\equiv I_{\alpha} = w_{+I\alpha} U_{I\alpha} / (\psi_I + w_{+IT}), \\ P_{\alpha\beta} &\equiv w_{+\alpha\beta} U_{\alpha\beta} / (\psi_{\alpha} + w_{+\alpha T}), \\ P_{\alpha T} &\equiv T_{\alpha} = w_{+\alpha T} / (\psi_{\alpha} + w_{+\alpha T}). \end{aligned} \right\} \quad (2.34)$$

Along with the results of Sec. 1, these quantities give a complete solution of the problem of the composition of the chains, the length distribution, etc.

The rate of polymerization, in the sense of the total number of chains irreversibly created per unit time is

$$R = j_{+I} \sum_{\alpha=T, A, B} w_{+I\alpha} U_{I\alpha} = j_{+I} (\psi_I + w_{+IT}). \quad (2.35)$$

At large deviations from equilibrium, $U_{\alpha\beta} \approx 1$, and $P_{\alpha\beta}$ does not depend on the supercooling. In the converse case, it is considerably dependent. Eq. (2.33) does not have a solution $\psi_{\alpha} = 0$, which would correspond to thermodynamic equilibrium in the system without chain termination. Now always $\psi_{\alpha} > 0$. That is, the chains grow even under thermodynamically unfavorable conditions (at equilibrium $P_{\alpha\beta} \sim T_{\alpha}$). Evidently, the physical reason for this phenomenon consists in the following. In the presence of an initiator, there is always a certain fraction of polymer chains, owing to fluctuations in the solution (or the melt). A fraction of these chains becomes fixed (with probabilities T_{α}), and drops out of the fluctuational exchange, thus shifting the distribution. The dead chains are replaced by new ones by diffusion in size space, etc.: a flux is established in the system between the monomer reservoir and the output, with a rate determined by the rate of termination. Under the conditions of a superheated system, this flux decreases its entropy, and consumes the energy stored in the active molecules. Since $P_{\alpha\beta}$ and T_{α} are comparable, the product of the described reaction of "tunneling through a potential barrier" will be of low molecular weight. If the dead chains are reactivated, then the effect will not take place.

3. Analysis of the Growth of a Binary Chain and Its Relation to Thermodynamics

For a two-component system of infinite chains, the fundamental system of equations (2.4) acquires the form

$$\left. \begin{aligned} \psi_A (w_{-AA} - w_{+AA} - \psi_A) / (w_{-AA} + \psi_A) &= w_{+AB} \psi_B / (w_{-AB} + \psi_B), \\ \psi_B (w_{-BB} - w_{+BB} - \psi_B) / (w_{-BB} + \psi_B) &= w_{+BA} \psi_A / (w_{-BA} + \psi_A). \end{aligned} \right\} (3.1)$$

In a single-component system consisting of particles of type A, the rates $w_{+\alpha\beta} = 0$. Then (3.1) leads to the obvious equalities $\psi_A = V = w_{+AA} - w_{-AA}$, and $D_t = (w_{+AA} + w_{-AA})/2$. The relations appropriate to small concentrations of the components are analyzed in Sec. 5. Here we shall treat the general case in which the concentrations of the two components are comparable.

First of all, let us consider equilibrium and compare the kinetic with the thermodynamic formulas. As we know,^[71] the partition function for a chain has the form

$$Z = \left(\prod_{\alpha=A, B} N_{\alpha!} / \prod_{\alpha=A, B} N_{\alpha\beta!} \right) (h\nu T^{-1})^N \exp [-(N_A \epsilon_{AA} + N_B \epsilon_{BB} + 2N_{AB} W) T^{-1}], \quad (3.2)$$

where N is the total number of particles in the chain ($N \gg 1$), N_A and N_B are the numbers of A and B particles ($N_A + N_B = N$), $N_{\alpha\beta}$ is the number of $\alpha\beta$ pairs, and $W = \epsilon_{AB} - [(\epsilon_{AA} + \epsilon_{BB})/2]$ is the energy of mixing. The term $(h\nu/T)^N$ is the high-temperature ($h\nu \ll T$) approximation for the vibrational part of the partition function. Here ν is the "geometric mean"^[72] frequency of the thermal vibrations of the particles in the chain. If we minimize the free energy of the chain, $-T \ln Z$, over the concentration of pairs $x_{AB} = N_{AB}/N$, keeping the numbers N_{α} of particles of each type constant, we get the equilibrium relations for $x_{\alpha\beta}$ and x_{α} :

$$\frac{x_{AB}^{\circ}}{x_{AA}^{\circ} x_{BB}^{\circ}} = e^{-2W/T}. \quad (3.3)$$

The chemical potential μ_{α} of component α in the chain is obtained by minimizing $-T \ln Z$ over N_{α} under the condition that the structure of the chain (i.e., the concentration x_{AB}) has its equilibrium value:

$$\mu_{\alpha} = -T \ln \frac{x_{\alpha}^{\circ}}{x_{\alpha\alpha}^{\circ}} + \epsilon_{\alpha\alpha} + T \ln h\nu/T. \quad (3.4)$$

If $\mu_{\alpha c}$ is the chemical potential of particles of type α in the medium, then phase equilibrium between the chain and the medium will take place when

$$\frac{x_{\alpha}^{\circ}}{x_{\alpha\alpha}^{\circ}} = h\nu T^{-1} e^{-(\mu_{\alpha c} - \epsilon_{\alpha\alpha})/T}. \quad (3.5)$$

When the $\mu_{\alpha c}$ are fixed, the conditions (3.3) and (3.5), along with the equalities $\sum_{\alpha\beta} x_{\alpha\beta}^{\circ} = 1$ and

$x_{AB}^{\circ} = x_{BA}^{\circ}$, determine the equilibrium concentrations (x_{α}°), the chain structure ($x_{\alpha\beta}$), and the equilibrium

temperature. In particular, after $x_{\alpha\beta}^{\circ}$ and x_{α}° have been eliminated, (3.5) and (3.3) give a condition for the equilibrium temperature. This is:

$$[h\nu T^{-1} e^{-(\mu_{Ac} - \epsilon_{AA})/T} - 1] [h\nu T^{-1} e^{-(\mu_{Bc} - \epsilon_{BB})/T} - 1] = e^{-2W/T}. \quad (3.6)$$

Now, let us find the relations for the same quantities

x_{α}° , $x_{\alpha\beta}^{\circ}$, and T from the kinetic equations, bearing in mind the fact that $\psi_{\alpha} = 0$ at equilibrium. In fact, any particle that has attached to the end of the chain must at equilibrium leave it sooner or later. That is, $U_{\alpha\beta} = 0$. When the ψ_{α} are small in comparison with the corresponding rates, the system (3.1) is transformed into a linear, homogeneous system. The condition that its determinant should be zero is the condition of equilibrium:

$$\frac{w_{+AB} w_{+BA} w_{-AA} w_{-BB}}{w_{-AB} w_{-BA} w_{+AA} w_{+BB}} - \left(\frac{w_{-AA}}{w_{+AA}} - 1 \right) \left(\frac{w_{-BB}}{w_{+BB}} - 1 \right) = 0. \quad (3.7)$$

If the left-hand side of (3.7) is positive, then, $\psi_{\alpha} > 0$, as we can show by studying (3.1) and the chain grows. If the left-hand side is negative, the chain decomposes.

The concentrations x_{α}° and $x_{\alpha\beta}^{\circ}$ arise from (2.6) upon setting $\psi_{\alpha} = 0$:

$$\begin{aligned} \frac{x_{\alpha}^{\circ}}{x_{\alpha\alpha}^{\circ}} &= \psi_{\alpha} / \Phi_{\alpha\alpha} = w_{-\alpha\alpha} / w_{+\alpha\alpha}, \\ \frac{x_{AB}^{\circ}}{x_{AA}^{\circ} x_{BB}^{\circ}} &= \Phi_{AB} \Phi_{BA} / \Phi_{AA} \Phi_{BB} = \\ &= w_{+AB} w_{+BA} w_{-AA} w_{-BB} / w_{-AB} w_{-BA} w_{+AA} w_{+BB}. \end{aligned} \quad (3.8)$$

If we denote

$$w_{-\alpha\beta} / w_{+\alpha\beta} = \nu \mathcal{K}_{\beta} e^{\epsilon_{\alpha\beta}/T}, \quad (3.9)$$

(3.8) gives us expressions of exactly the same form as the thermodynamic relations (3.5) and (3.3), while (3.7) gives us (3.6), if we assume

$$\mathcal{K}_{\beta} = hT^{-1} e^{-\mu_{\beta c}/T}. \quad (3.10)$$

Consequently,* the quantity $\epsilon_{\alpha\beta}$ introduced in (3.9) actually has the meaning of the bonding energy of the particles α and β . As we see from (3.9), the frequency ν is the mean frequency of vibrations of the particles in the lattice in the sense of (3.2). As we should expect, the

equilibrium quantities x_{α}° and $x_{\alpha\beta}^{\circ}$ in (3.8) depend neither on the potentials of the particles in the medium nor on the potential barriers for crystal-medium transition. They are only functions of the temperature and the energies $\epsilon_{\alpha\beta}$.

It is convenient to carry out the study by using the quantity $q = \exp(\epsilon_{AA}/T)$ (where $0 < q < 1$) instead of the temperature, and by expressing $\epsilon_{\alpha\beta}$ in terms of ϵ_{AA} :

$$\left. \begin{aligned} \epsilon_{BB} &= n\epsilon_{AA}, \quad \epsilon_{AB} = \epsilon_{BA} = m\epsilon_{AA}, \\ 2W &= (2m - n - 1)\epsilon_{AA} = s\epsilon_{AA}. \end{aligned} \right\} \quad (3.11)$$

Let us take $w_{+\alpha\beta} = w_{+} c_{\beta}$, where the constant w_{+} characterizes the rate of incidence of particles of any type on the end of the chain, and c_{β} is the concentration of β particles in the medium ($c_A + c_B = 1$). Then we get from (3.7) the equation of the liquidus line $c_A(q)$, and,

based on (2.6), the solidus line $x_A^{\circ}(q)$:

$$\begin{aligned} c_A &= \frac{1}{2} [1 - Rq^{s+1} (1 - q^{n-1}) (1 - q^s)^{-1}] + \\ &+ \frac{1}{2} \{ [1 - Rq^{s+1} (1 - q^{n-1}) (1 - q^s)^{-1}]^2 - [4Rq^{s+1} (Rq^n - 1) (1 - q^s)] \}^{1/2}, \\ x_A &= c_A / [c_A + q^{n-1} (Rq - c_A)], \end{aligned} \quad (3.12)$$

where $R = \nu/w_{+}$. When $w_{+\alpha\beta} = w_{+} c_{\beta}$, the diffusion coefficient of the end of the chain $D_t = w_{+}$.

For an ideal solution in which $W = 0$ (i.e., $s = 0$),

$$c_A = (1 - Rq^n) (1 - q^{n-1})^{-1}, \quad x_A = c_A / Rq = 1 - Rq^n [Rq (1 - q^{n-1})]^{-1}. \quad (3.13)$$

The phase diagram corresponding to (3.13) has the form of a "cigar", whose shape and orientation depend on R and n . When $n = 1$, it degenerates into a straight line parallel to the horizontal axis.

Figure 5 shows the phase diagram constructed from (3.12) for particles A and B that are equivalent but not

*We recall the $\epsilon_{\alpha\beta}$ becomes more negative as the corresponding bond becomes stronger.

identical in properties. That is, $\epsilon_{AA} = \epsilon_{BB}$ ($n = 1$), and $\epsilon_{Ac} = \epsilon_{Bc} = 0$. Here we have assumed that $m = 2$, $\bar{R} = 2, 3, 5$. The analogous curves for $m = 3/2$, $n = 1$, $\bar{R} = 2$, and $\bar{R} = 5$ (Fig. 6) give a picture of how the phase diagrams deform as we vary the binding energies, vibration frequencies, and density of the substance crystallizing out of the mother medium. The latter relation is determined by the ratio of R to the rate w_+ : the greater the total pressure of the two components in the gas phase is, the greater w_+ is, and the smaller is R .

The concept of phase diagrams can also be extended into the kinetic field.^[73] Here Eq. (2.6) makes it possible actually to find these diagrams. The deviation from equilibrium is carried out by varying any of the parameters q , c , and \bar{R} . For example, each value of \bar{R} corresponds to a liquidus line $c_A(q, \bar{R})$ and a solidus line $x_A(q, \bar{R})$. Now, if we keep the temperature (q) and the relative concentrations of the components (c_A) constant, and decrease R , then crystallization will set in, and produce a chain of composition $x_A(q, R)$ that differs from $\bar{x}_A(q, \bar{R})$ and can be determined from (2.6). The function $x_A(q, R)$ defines a new, kinetic solidus line. Figure 5 shows such a curve for $R = 4$ for the values of c and q corresponding to the liquidus line $\bar{R} = 5$. The value $R = 4$ corresponds to an overall increase in the density of the A and B particles in the medium by $\sim 20\%$, the partial composition remaining invariant. A still greater increase in the density of the substance crystallizing in the medium, with consequent increase in the deviation from equilibrium, will shift the solidus line more strongly toward the liquidus. When $R \rightarrow 0$, (3.1) implies that $\psi_\alpha \rightarrow w_+$, and $x_A(q, 0)$ coincides with the liquidus line $c_A(q, 0)$. This latter circumstance is physically quite clear: all the particles attaching to the end of the chain never leave it thereafter, composition selection does not occur, and the chain copies the composition of the mother medium, as well as its chaotic structure: $x_{\alpha\beta} = x_\alpha x_\beta$. An analog of this process is diffusionless crystallization (see the end of Sec. 6).

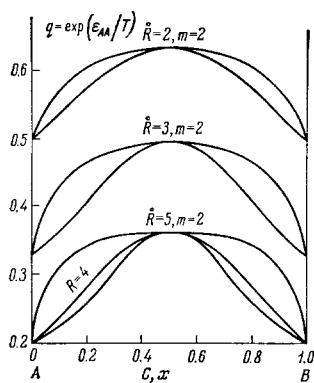


FIG. 5

FIG. 5. Phase diagrams of a system of equivalent particles having $m = 2$. The solidus line $R = 4$ is the kinetic curve corresponding to the equilibrium diagram $\bar{R} = 5$.

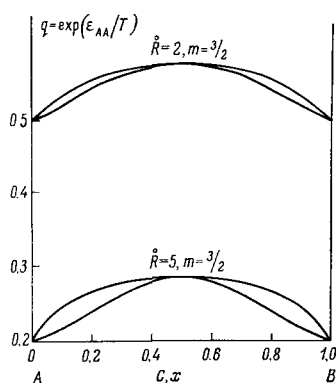


FIG. 6

FIG. 6. Phase diagrams of equivalent particles for $m = 3/2$.

Non-equilibrium composition and structure of the chain is a substantial effect, which increases with increasing supersaturation. According to the data of Fig. 5, with a $\sim 20\%$ deviation from equilibrium ($R = 4$) and with $q = 0.3$, the composition of the chain deviates from the equilibrium value ($\bar{x}_A = 0.710$) by about 7% ($x_A = 0.760$), while the concentration difference between the mother medium ($c_A = 0.920$) and the chain varies by about 25% , i.e., $(x_A - \bar{x}_A)/(c_A - \bar{c}_A) \sim 0.25$.

One can easily derive an exact analytical solution of (3.1), and hence, of the whole problem, with arbitrary deviations from equilibrium for equivalent particles satisfying the relations (3.11) with $n = 1$ ($\epsilon_{AA} = \epsilon_{BB}$), together with the conditions $\epsilon_{Ac} = \epsilon_{Bc}$ and $c_A = c_B = 0.5$. Namely,

$$\begin{aligned} \psi_A = \psi_B = \psi &= \\ &= \frac{w}{2} \{ [(1 - Rq - Rq^m)^2 + 2Rq(1 + q^{m-1} - 2Rq^m)]^{1/2} + (1 - Rq - Rq^m) \}, \\ V = \psi, \quad D_k = w_+, \quad x_A = x_B = x_{1A} = x_{1B} &= 0.5, \quad (3.14) \\ x_{AA} = x_{BB} = x_{1AA} = x_{1BB} = 1/4(Rq + \psi w_+^{-1}), \quad x_{AB} = x_{BA} = x_{1AB} &= \\ &= x_{1BA} = 1/4(Rq + \psi w_+^{-1}). \end{aligned}$$

The condition of equilibrium has the form $1 + q^{m-1} - 2Rq^m = 0$. In particular, these formulas imply that the chain being produced becomes less ordered as its rate of growth increases. In the limit as $R \rightarrow 0$ or $q \rightarrow 0$, $\psi \rightarrow w_+$, and $x_{\alpha\beta} \rightarrow 1/4$. The diffusion coefficient $D_k \sim w_+$ does not depend on the supersaturation. Figure 7 shows graphs of V/w_+ , x_{AA} , and x_{AB} as functions of R/R for various temperatures: $q = 10^{-2}$, 10^{-4} , and 10^{-6} , and for $m = 1$ or 2 . The physical parameters corresponding to $q \sim 10^{-4}$, $m = 1, 2$ are: $\epsilon_{AA}/T = 9$, or when $T = 0.6$ kcal/mole ($T \sim 300^\circ\text{K}$), $\epsilon_{AA} \sim 5.4$ kcal/mole, $R = 10^5$.

One can get a general analytical solution of (3.1) in terms of $w_{\pm\alpha\beta}$ only in the limiting cases $\psi_\gamma \ll w_{-\alpha\beta}$, $w_{-\alpha\alpha} \sim w_{+\alpha\alpha}$, and $\psi_\gamma \gg w_{-\alpha\beta}$, $w_{-\alpha\alpha} \sim w_{+\alpha\alpha}$.

The exact theory of copolymerization thus developed has been tested by simulating the process on a computer (Sec. 7).

4. Growth of Chains on Templates. Biopolymers

The structure of a solitary copolymer chain is generated at its growing end. Another process is also of interest: the growth of one chain on another, where the sequence of monomers in the new chain depends also on the structure of the substrate. Such a situation (in the three-dimensional case) is realized in the crystallization of alloys (Sec. 6). If the influence of the substrate is decisive, the problem of the structure of the new chain vanishes, for it is a copy of the template-substrate. The latter process is the basis of the replication and renaturation of nucleic acids. In this case, the rate of the process and the probability of errors of reproduction of the template structure remains as the object of the theory. As we know,^[74,75] a nucleic-acid molecule is a helix wound together from two polymer chains. Each chain is built of four types of nucleotides: adenine (A), thymine (T), guanine (G), and cytosine (C). Adenine in one chain sits opposite thymine in the other, and guanine opposite cytosine. As a rule, the probability of configurations differing from these complementary pairs

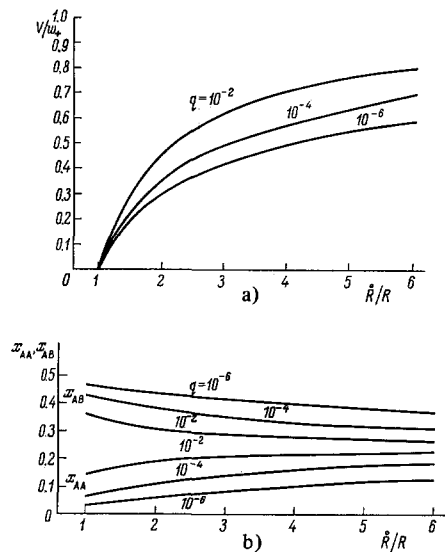


FIG. 7. Dependence on the supersaturation of the growth rate (a) and the structure (b) of a chain made of equivalent particles ($x_A = x_B = 0.5$).

AT and GC does not exceed 10^{-7} . Denaturation consists in breakdown of the double helix into single chains (strands). This process is cooperative, occurs, in a narrow range near the melting point, and is reversible. Apparently, melting can begin either at one end of the helix or at random sections of the double chain by breaking of bonds. The reverse process, renaturation, also goes through a stage of nucleation, or attachment of the two strands together, originally by only a few bonds.^[86] Further combination proceeds from the site of first contact, and in particular, from the ends of the chains, by a zipper mechanism. The tab of the zipper advances, making random errors, and hanging up in various ways on different pairs. In replication, the deposition of individual nucleotides on the template chain and their polycondensation can occur either from one end, or randomly.^[75,79] The rates of deposition (in replication) or of attachment (in renaturation) are determined by diffusion of nucleotides onto the template chain and by molecular processes of desolvation of the individual nucleotides or those linked in a chain. Here people have discussed exclusively statistical-kinetic processes in which the rates of the individual events are assumed to be known. In this sense, the problems listed above are similar, and totally equivalent for the zipper model.

The approximate calculations of random deposition for one-component polycondensation^[77-79] start with the idea that each cell of the new chain may be either: 1) empty, 2) occupied by a nucleotide adsorbed on the template, 3) occupied by a nucleotide already incorporated in the new chain. A fourth state assumes the presence in the solution near the cell of a nucleotide that hasn't yet been joined to it. In^[75,79], an excited "growth center" is involved instead of the latter state. Calculation for the zipper model is based on kinetic equations for the concentrations of the cited states of the cells and higher-order distribution functions (binary and ternary) for random deposition. The estimates of Vol'kenshtein and his associates^[76] have shown, in particular, that the time of replication simply involving

deposition of nucleotides amounts to ~ 1 sec, instead of the experimental $\sim 10^3$ sec. Consequently, one has to take into account the finite rate of the polymerization process. The corresponding rate constant is of the order of $\sim 10^4$ sec $^{-1}$ in the model used in^[76].

The stage limiting the experimentally observable rate of renaturation may be the formation of attachment nuclei.^[86] The formation of the new chain on the template is actually the formation of a new layer on a one-dimensional crystal. Within the framework of this unified view, growth from a few centers corresponds to tangential (layered) growth of crystals, while growth starting at random points corresponds to normal growth (i.e., growth along the normal to the substrate).^[10-21] The former mechanism of crystallization is characteristic of substances having a large surface energy (in comparison with kT), when the deviation from equilibrium is small.^[38] The latter is characteristic of small surface energies of the crystal-medium boundary and of large supercooling (or supersaturation), when nucleation is no longer a problem, and the surface becomes atomically rough. We can assume that an analogous situation must also occur in the template synthesis of chains.

The problem of chaotic polycondensation^[76-79] (normal growth) in a one-component model is analogous to the well-known problem of bulk crystallization in a volume, which Kolmogorov^[80] solved exactly for an infinite volume as early as 1937, and which Todes^[81] subsequently developed. The formulation and solution of the problem in terms of a one-dimensional model consists in the following. Let $I(t)$ (cm $^{-1}$ sec $^{-1}$) be the probability density of initiation of polymerization (nucleation) of the second chain at the time t , and $V(t)$ be the rate of growth of the chain along the template, which is long in comparison with $(V/I)^{1/2}$. We have to find the probability $p(t)$ that a randomly chosen cell will be occupied at the instant t by a nucleotide incorporated by polymerization. The probability $dq(t)$ that polymerization will happen in a random cell within the time from t to $t + dt$ is, first, proportional to the probability $q = 1 - p(t)$ that this cell has remained unpolymerized up to the instant t . Second, in order that polymerization occur in the interval from t to $t + dt$, a nucleus must have been formed at an earlier time interval from t' to $t' + dt'$ at a distance

$$l = \pm \int_{t'}^t V(t') dt' \text{ from the chosen point, in the interval}$$

$d l = V(t) dt$. The latter event has a probability $I(t') dt' V(t) dt$. Hence, the probability of polymerization of the chosen cell within the time from t to $t + dt$ owing to the fact that a chain has arrived there from some nucleus is

$$dq = -2q \int_0^t V(t) dt I(t') dt' = -2q d \int_0^t I(t') \int_{t'}^t V(t'') dt'' dt', \quad (4.1)$$

Hence,*

$$p = 1 - \exp \left(-2 \int_0^t I(t') dt' \int_{t'}^t V(t'') dt'' \right). \quad (4.2)$$

If adsorption of nucleotides onto the template occurs

*The given simple method of derivation can also be extended to the three-dimensional case, with the well-known result^[80]

$$p(t) = 1 - \exp \left\{ -\frac{4\pi}{3} \int_0^t I(t') \left[\int_{t'}^t V(t'') dt'' \right]^3 dt' \right\}.$$

considerably faster than polymerization, then their concentrations (and hence also the quantities I and V) can be considered constant. In this case,

$$p = 1 - e^{-IVt^2}, \quad (4.3)$$

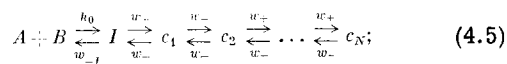
and the characteristic replication time is

$$\tau = (IV)^{-1/2}. \quad (4.4)$$

Formation of bonds between the deposited nucleotides when they combine into the nucleus of a new chain apparently requires not only surmounting of the barriers involving desolvation and other molecular processes, but also local twisting of the chains at the site of formation of the nucleus. The barrier involved in this process is not yet known.

Approach of the system to thermodynamic equilibrium (e.g., by raising the temperature to the melting point) must lead to $I \rightarrow 0$, $V \rightarrow 0$, in line with the general principles of crystallization, independently of the mechanisms of nucleation and rate of growth. On the other hand, decrease of temperature and consequent decrease in mobility of the particles reduces the growth rate, as has been observed in numerous experiments on crystallization in melts, viscous solutions, and in the solid phase. Biopolymerization processes can be no exception, and indeed, the temperature-dependence of the rate of formation of adenine-uridine helices, as studied by Ross and Sturtevant,^[82,83] is bell-shaped.^[89,90] Such behavior is also characteristic of other renaturation and replication processes.

Consequently, analysis of the kinetics of formation of biopolymers near equilibrium requires one to take into account the reversibility of the individual elementary events. As applied to one-component chains, such an accounting has been made in connection with the experiments of^[82,83] by Saunders and Ross,^[84] by Flory,^[85] and by other authors.^[86,86] The kinetic pattern of the process has the form^[85]



Here A and B are the nucleotides forming a two-particle nucleus of the new chain and their concentrations, c_1 and I are the concentrations of chains of length i and AB nuclei, N is the overall length of the chain, while the transition rates w_{\pm} are the same for all stages except the first, which is characterized by the constants k_0 , w_{-1} . We are required to find the number of chains irreversibly formed in the system per unit time. For large N, the solution is evidently given by Eq. (2.35), where $j_+ = k_0AB$, $w_{\pm}I\alpha = w_{\pm}\alpha\beta = w_{\pm}$. With these parameters, according to (2.31), (2.30), and (2.35), we have

$$U_{I\alpha} = (w_+ - w_-)/w_+, \quad U_I = (w_+ - w_-)/(w_+ - w_- + w_-), \quad (4.6)$$

$$R = k_0AB(1 - w_-w_+^{-1})/[1 - (w_- - w_+)w_+^{-1}]. \quad (4.7)$$

The expression (4.7) differs somewhat from the erroneous expression given in^[85]. The factor $1 - w_-w_+^{-1}$ defines the supercooling (or supersaturation) in the system. It vanishes at the equilibrium temperature, and increases (to unity) with falling temperature. Together with the exponential decline of k_0 with the temperature, this factor gives rise to a maximum on the temperature-dependence of the experimentally observable rate.

The situation becomes more complicated in many-component chains, such as nucleic acids. However, one can find analytical expressions for the rates of growth of such chains, both by the method of conservation functions,^[91] and by using the general formulas of physico-chemical kinetics.^[92,123] Wetmur and Davidson^[86] have performed machine calculations for chains made of two types of complementary pairs. Let us take up the analytical theory in greater detail.

Let there be an infinite template chain consisting of m types of particles. A second chain made of particles of the same types is growing on it from infinity on the left. The second chain is generated by random attachments and detachments of particles at its end. The juxtaposed particles of the first and second chains form the complementary pairs AT, TA, GC, and CG. Consequently, growth of the second chain on the first is equivalent to growth of a unitary chain made of "pair" particles with a previously assigned structure. We shall consider the rates $w_{\pm}\alpha\beta$ of formation and decomposition of pairs (attachment and detachment of pair particles) to be known.

If complementarity breaks down during the growth of the second chain on the first (e.g., a loop is formed), then a mutation has occurred. In the language of crystallization, it is equivalent to capture of an impurity particle. The problem consists in determining the rate of growth and probability of mutation.

Let us consider a chain ending in the already-formed pair particles $\alpha_1\alpha_2$. The particle α_3 is supposed to follow after them, but hasn't been formed yet ($\alpha_1, \alpha_2, \alpha_3 \dots = AT, TA, GC, CG$). In this state, the chain has only two possibilities: either α_3 is produced, or α_2 breaks down. The probabilities of these events are, respectively

$$p_{\alpha_1\alpha_2\alpha_3} = w_{+\alpha_2\alpha_3}/(w_{-\alpha_1\alpha_2} + w_{+\alpha_2\alpha_3}), \quad q_{\alpha_1\alpha_2\alpha_3} = w_{-\alpha_1\alpha_2}/(w_{-\alpha_1\alpha_2} + w_{+\alpha_2\alpha_3}). \quad (4.8)$$

Let us find the probability $U_{\alpha_1\alpha_2\alpha_3 \dots}$ that the pair $\alpha_1\alpha_2$ that has already been formed on the end of the double chain will remain there forever, under the condition that the next particles must be $\alpha_3\alpha_4 \dots$. By a treatment analogous to that used in deriving the equations (2.2) for the conservation probability, we arrive at the relation

$$U_{\alpha_1\alpha_2 \dots} = p_{\alpha_1\alpha_2\alpha_3} [U_{\alpha_2\alpha_3 \dots} + (1 - U_{\alpha_2\alpha_3 \dots}) U_{\alpha_1\alpha_2 \dots}]. \quad (4.9)$$

Upon expressing $U_{\alpha_2\alpha_3 \dots}$ analogously in terms of $U_{\alpha_3\alpha_4 \dots}$, etc., we get

$$U_{\alpha_1\alpha_2 \dots} = U_{\alpha_{M-1}\alpha_M \dots} \left[1 + \sum_{k=1}^{M-3} \prod_{i=1}^k w_{-\alpha_i\alpha_{i+1}} w_{+\alpha_{i+1}\alpha_{i+2}}^{-1} U_{\alpha_{M-1}\alpha_M \dots} + \prod_{i=1}^{M-2} w_{-\alpha_i\alpha_{i+1}} w_{+\alpha_{i+1}\alpha_{i+2}}^{-1} \right]^{-1}. \quad (4.10)$$

However, if the zipper locks on the M-th cell, then $w_{-\alpha_{M-1}\alpha_M} = 0$, $U_{\alpha_{M-1}\alpha_M} = 1$, and (4.10) gives the conservation function for a finite chain (with a lock at the end):

$$U_{\alpha_1\alpha_2 \dots \alpha_M} = \left[1 + \sum_{k=1}^{M-2} \prod_{i=1}^k w_{-\alpha_i\alpha_{i+1}} w_{+\alpha_{i+1}\alpha_{i+2}}^{-1} \right]^{-1}. \quad (4.11)$$

For an infinite chain without a lock, the M - 2 in (4.11) is replaced by ∞ .

The mean rate of elongation of the infinite chain is

$$V = \tau^{-1}, \quad (4.12)$$

where τ is the average time (over all possible chain configurations) necessary for irreversible advance of the boundary of the polymerized portion by one pair of nucleotides (a cell). The time required for irreversible advance of the boundary from α_1 to α_2 in an arbitrarily chosen configuration $\alpha_0\alpha_1\alpha_2 \dots \alpha_N \dots$, amounts to

$$\tau_{\alpha_0\alpha_1\alpha_2} = (w_{-\alpha_0\alpha_1} + w_{+\alpha_1\alpha_2})^{-1} k_{\alpha_0\alpha_1\alpha_2} \dots, \quad (4.13)$$

where $k_{\alpha_0\alpha_1\alpha_2} \dots$ is the average (over the assembly of identical chains $\alpha_0\alpha_1\alpha_2 \dots$) number of trials for the irreversible transition $\alpha_0\alpha_1\alpha_2 \rightarrow \alpha_0\alpha_1\alpha_2 + \dots$. The arrow symbolizes the boundary of the polymerized portion of the chain.

The probability that a boundary occurring at the particle α_1 will never henceforth return to this site is $p_{\alpha_0\alpha_1\alpha_2} U_{\alpha_1\alpha_2} \dots$. The probability of a reversible event, i.e., return to α_1 , is $1 - p_{\alpha_0\alpha_1\alpha_2} U_{\alpha_1\alpha_2} \dots$. Since the subsequent behavior of the end doesn't depend on its prior history, the probability of $(k-1)$ fold return is $(1 - p_{\alpha_0\alpha_1\alpha_2} U_{\alpha_1\alpha_2} \dots)^{k-1}$, while the probability that the end will lie at α_1 k times amounts to

$$p_{\alpha_0\alpha_1\alpha_2} U_{\alpha_1\alpha_2} \dots (1 - p_{\alpha_0\alpha_1\alpha_2} U_{\alpha_1\alpha_2} \dots)^{k-1}. \quad (4.14)$$

The derived distribution function (4.14) over the number of visits implies that

$$k_{\alpha_0\alpha_1\alpha_2} = \sum_{k=1}^{\infty} k p_{\alpha_0\alpha_1\alpha_2} U_{\alpha_1\alpha_2} \dots (1 - p_{\alpha_0\alpha_1\alpha_2} U_{\alpha_1\alpha_2} \dots)^{k-1} = (p_{\alpha_0\alpha_1\alpha_2} U_{\alpha_1\alpha_2} \dots)^{-1}. \quad (4.15)$$

In order to obtain V , we must still average $\tau_{\alpha_1\alpha_2} \dots$ over the chain configurations. Let us start with chains in which the probability $x_{\alpha_1\alpha_2} \dots \alpha_M$ of the region $\alpha_1\alpha_2 \dots \alpha_M$ can be represented in the form

$$x_{\alpha_1\alpha_2} \dots \alpha_M = x_{\alpha_1\alpha_2} x_{\alpha_2\alpha_3} \dots x_{\alpha_{M-1}\alpha_M} / x_{\alpha_2\alpha_3} \dots x_{\alpha_{M-1}\alpha_M}.$$

In this case, on the basis of (4.13) and (4.15) we have

$$\begin{aligned} \tau &= \lim_{M \rightarrow \infty} \sum_{\alpha_1 \dots \alpha_M} \tau_{\alpha_1\alpha_2} \dots \alpha_M \dots x_{\alpha_1\alpha_2} \dots \alpha_M \\ &= \lim_{M \rightarrow \infty} \sum_{\alpha_1 \dots \alpha_M} \frac{x_{\alpha_1 \dots \alpha_M}}{w_{+\alpha_1\alpha_2}} \left(1 + \sum_{k=1}^{\infty} \prod_{i=1}^k \frac{w_{-\alpha_i\alpha_{i+1}}}{w_{+\alpha_{i+1}\alpha_{i+2}}} \right) \\ &= \sum_{\alpha_1\alpha_2} \frac{x_{\alpha_1\alpha_2}}{w_{+\alpha_1\alpha_2}} + \lim_{M \rightarrow \infty} \left[\sum_{k=1}^{M-2} \sum_{\alpha_1 \dots \alpha_{k+2}} \left(\frac{x_{\alpha_1}}{x_{\alpha_{k+1}}} \right)^{1/2} Q_{\alpha_1\alpha_2} \dots Q_{\alpha_k\alpha_{k+1}} \frac{x_{\alpha_{k+1}\alpha_{k+2}}}{w_{+\alpha_{k+1}\alpha_{k+2}}} \right. \\ &\quad \left. + \sum_{\alpha_1, \alpha_M} \left(\frac{x_{\alpha_1} x_{\alpha_M}}{w_{+\alpha_M\alpha_{M+1}}} \right)^{1/2} \hat{Q}_{\alpha_1\alpha_M}^{M-1} \left(1 + \sum_{k=M}^{\infty} \prod_{i=M}^k \frac{w_{-\alpha_i\alpha_{i+1}}}{w_{+\alpha_{i+1}\alpha_{i+2}}} \right) \right] \\ &= \lim_{M \rightarrow \infty} \left[\sum_{\alpha\beta\gamma} \left(\frac{x_{\alpha}}{x_{\beta}} \right)^{1/2} \left(\frac{1 - \hat{Q}^{M-1}}{1 - \hat{Q}} \right)_{\alpha\beta} \frac{x_{\beta\gamma}}{w_{+\beta\gamma}} \right. \\ &\quad \left. + \sum_{\alpha\alpha_M} (x_{\alpha} x_{\alpha_M})^{1/2} Q_{\alpha\alpha_M}^{M-1} \left(1 + \sum_{k=M}^{\infty} \prod_{i=M}^k \frac{w_{-\alpha_i\alpha_{i+1}}}{w_{+\alpha_{i+1}\alpha_{i+2}}} \right) \right] \\ &= \sum_{\alpha\beta\gamma} (x_{\alpha}/x_{\beta})^{1/2} x_{\beta\gamma}/w_{+\beta\gamma} (1 - \hat{Q})_{\alpha\beta}^{-1}. \quad (4.16) \end{aligned}$$

The matrix \hat{Q} introduced here has the elements $Q_{\alpha\beta} = x_{\alpha\beta} w_{-\alpha\beta} / (x_{\alpha} x_{\beta})^{1/2} w_{-\alpha\beta}$. The last process of taking a limit in (4.16) is valid when the second term in the next-to-last expression in (4.16) vanishes when $M \rightarrow \infty$. The time τ is infinite, and $V = 0$, when $\text{Det} \parallel 1 - \hat{Q} \parallel = 0$.

In the case of two components A and B, the last equa-

tion reduces to

$$\left(1 - \frac{x_{AA} w_{-AA}}{x_A w_{+AA}} \right) \left(1 - \frac{x_{BB} w_{-BB}}{x_B w_{+BB}} \right) = \left(\frac{x_{AB}}{x_A x_B} \right)^2 \frac{w_{-AB} w_{-BA}}{w_{+AB} w_{+BA}}. \quad (4.17)$$

If the sequence of bases in the chain is random, then $x_{\alpha\beta} = x_{\alpha} x_{\beta}$, and the formulas (4.16)–(4.17) go over into the corresponding expressions of [91], which were derived in a somewhat different way. Chains for which $\text{Det} \parallel \hat{1} - \hat{Q} \parallel > 0$ (i.e., the left-hand side of (4.17) is greater than the right) will grow (for the given values of $w_{\pm\alpha\beta}$), while the others will dissolve (or exist in equilibrium). Thus, a selection of the structure of the chains that are reproduced under the given conditions can occur.

Wetmur and Davidson [86] have averaged the rate numerically for a random distribution of AT and GC pairs along the chain. Here the ratio of rates of formation and decomposition of a given pair did not depend on the types of neighbors it had ($w_{-\alpha\beta}/w_{+\alpha\beta}$ depended only on β). As many as 2^6 and 2^8 possibilities were tried for the first six or eight pairs. For the remaining cells of the chain, they used the ratios of rates averaged under the assumption that the pairs were distributed randomly at their given concentrations. They used the quantities $w_{+AT}/w_{-AT} = 1.04 \times 10^5 \exp(8000/RT)$, and $w_{+GC}/w_{-GC} = 1.04 \times 10^5 \exp(8935/RT)$, while for the first pair these ratios were considered to be smaller by a factor of 34 $\exp(-7000/RT)$. If the chain is composed of repeating sets $\alpha_1\alpha_2 \dots \alpha_r$, then we have from (4.11) with $M \rightarrow \infty$,

$$U_{\alpha_1\alpha_2 \dots \alpha_r} = \frac{1 - \prod_{i=1}^r \frac{w_{-\alpha_i\alpha_{i+1}} w_{-\alpha_{i+1}\alpha_{i+2}}}{w_{+\alpha_{i+1}\alpha_{i+2}}}}{1 + \sum_{k=1}^r \prod_{i=1}^k \frac{w_{-\alpha_i\alpha_{i+1}} w_{-\alpha_{i+1}\alpha_{i+2}}}{w_{+\alpha_{i+1}\alpha_{i+2}}}}, \quad (4.18)$$

$$\alpha_{r+1} = \alpha_1, \quad \alpha_{r+2} = \alpha_2.$$

In this case, there is a total of r conservation probabilities, which can be obtained from (4.18) by cyclic permutations of the indices. The rate of growth is

$$V = \left[\sum_{\alpha_1 \dots \alpha_r} w_{+\alpha_1\alpha_2}^{-1} U_{\alpha_1 \dots \alpha_r}^{-1} \right]^{-1}, \quad (4.19)$$

where the summation is performed over all the cyclic permutations of the indices $\alpha_1\alpha_2 \dots \alpha_r$. If the discussed period of r particles contains $r x_{\alpha\beta}$ $\alpha\beta$ pairs, then the numerator of (4.18) for all cyclic permutations of indices is equal to $1 - \prod_{\alpha\beta} (w_{-\alpha\beta}/w_{+\alpha\beta})^{r x_{\alpha\beta}}$, so that the condi-

tion of equilibrium has the form $\sum_{\alpha\beta} x_{\alpha\beta} \ln w_{+\alpha\beta}$

$= \sum_{\alpha\beta} x_{\alpha\beta} \ln w_{+\alpha\beta}$. That is, it will be the same for configurations having the same relative numbers of $\alpha\beta$ pairs. The probability of mutation was also estimated in [91].

The growth rate of a chain having a preassigned structure can be found also by using a generalization [92, 123] of a well-known method in the theory of nucleation. [87, 88] Let us denote by x_{ik} the concentration of chains that have been polymerized as far as the cell k , inclusive, at a given instant of time. Then the steady-state flux R of chains satisfies the equations of conservation of chains:

$$R = x_{ik} w_{+\alpha_k\alpha_{k+1}} - x_{i+1k} w_{-\alpha_k\alpha_{k+1}}. \quad (4.20)$$

This chain of equalities extends to infinity for chains that are unbounded on the right ($M \rightarrow \infty$), while it requires a supplementary condition on the cell M if it is the last one. If we multiply the first of the equalities of (4.20) by unity, the second by $w_{-\alpha_1\alpha_2} w_{\alpha_2\alpha_3}^{-1}$, and the

k th by $\prod_{i=1}^{k-1} w_{-\alpha_i\alpha_{i+1}} (w_{+\alpha_{i+1}\alpha_{i+2}})^{-1}$, and add the

results, we can eliminate all the x_{1k} except x_{11} and x_{1M} :

$$R = \frac{x_{11} w_{+\alpha_1\alpha_2}^{-1} x_{1M} \prod_{i=1}^{M-2} w_{-\alpha_i\alpha_{i+1}} w_{+\alpha_{i+1}\alpha_{i+2}}^{-1} w_{-\alpha_{M-1}\alpha_M}}{1 + \sum_{k=1}^{M-2} \prod_{i=1}^k w_{-\alpha_i\alpha_{i+1}} w_{+\alpha_{i+1}\alpha_{i+2}}^{-1}} \quad (4.21)$$

For chains that terminate at the cell M , $w_{-\alpha_{M-1}\alpha_M}$ will be zero. The second term in the numerator will vanish, while the reciprocal of the denominator will be the conservation probability (4.11). Then (4.21) will be an analog of the formula (2.35) for chains with an assigned structure. It is clear from what I have said that the conservation probabilities lend a graphic character here to the Volmer^[87,88] procedure of summation of (4.20) and vice versa. If the chain is infinite on both sides, and the cell $k = 1$ is not the origin of the chain, then the concentration x_{11} can be calculated as the fraction of the time that the end of the polymerized portion spends in the cell α_1 in the sequence $\dots \alpha_1\alpha_2\dots$. The rates of elongation thus obtained coincide with (4.16) and (4.19).

III. GROWTH OF CRYSTALS

5. Capture of Impurities

Capture of impurities by a growing crystal includes at least three groups of phenomena: 1) atomic surface processes: attachment and detachment of impurity particles at kinks, steps, and other surface configurations; 2) diffusion of impurities in the crystal in its inhomogeneous initial distribution; 3) diffusion of impurities in the mother medium.^[94-101]

The least studied feature remains the distribution coefficient involving the atomic processes at the surface, the kinetic "seeding" coefficient that figures in all diffusion problems, and with which this section is concerned.

As experiment has shown, the kinetic coefficient is crystallographically anisotropic,^[103,104,107] and can either decline or increase with increasing growth rate.^[104-107] This dependence is the principal topic of the theory.

The capture coefficient is

$$K = x_B/c = J_B/c_B (J_A + J_B); \quad (5.1)$$

Here x_B and c are the concentrations of the impurity in the crystal and in the medium near the crystallization front (at distances small in comparison with the characteristic macroscopic diffusion distances), J_A and J_B are the fluxes of the main substance (A) and the impurity (B) into the crystalline phase (the quantity $J_A + J_B = V$ is the normal growth rate, if J_α and V are expressed in numbers of particles arriving per atomic site per second). The fluxes J_α are defined as the mean rates of attachment and detachment of the two types of particles for the given surface structure. In turn, the structure of

the surface (chap. I) depends on the degree of deviation from equilibrium. With small deviations, we can express the fluxes phenomenologically within the framework of the thermodynamics of irreversible processes:

$$J_\alpha = \sum_\beta \kappa_{\alpha\beta} \Delta\mu_\beta, \quad (5.2)$$

Here $\Delta\mu_\beta$ is the difference of chemical potentials of the component β in the mother medium and the crystal, while the $\kappa_{\alpha\beta}$ are the kinetic coefficients. An analysis of relations like (5.1)–(5.2) for binary systems having no cross terms in (5.2) has been made in^[73,108].

On this basis, phase diagrams have been obtained for low growth rates and arbitrary concentrations of the components.

The dependence of the kinetic (non-equilibrium) distribution coefficient on the growth rate can be easily derived by assuming that: 1) the rates of attachment and detachment $w_{\pm B}$ of impurity particles (units per atomic site per second) do not depend on the amount or identities of their neighbors (i.e., on the surface structure); and 2) the concentration of the impurity on the surface is the same as the volume concentration (x_B). Then

$$J_B = w_{+B}c - w_{-B}x_B, \quad (5.3)$$

and (5.1) and (5.3) imply that

$$K = \frac{w_{+B}c - w_{-B}x_B}{w_{+B}c - w_{-B}x_B} V. \quad (5.4)$$

At equilibrium, $V = 0$, and $K = K = w_{+B}/w_{-B}$, while near it

$$K = \frac{K}{1 + Vw_{-B}^{-1}}, \quad (5.5)$$

The discussed simple model ignores collective processes on the growing surface and the "immuring effect": it is harder for an impurity particle to return to the medium if it has failed to leave the surface before being covered by the intrinsic particles. This effect is greater with greater growth rates. It manifests a mechanism of crystal growth by numerous trials and errors. The more trials that are made in finally establishing a given structural site, the closer the crystal structure is to the equilibrium structure.

In growth from the melt, the number of trials occurring for each final attachment can be as high as 10^6 (for $V \sim 10^{-2}$ cm/sec $\sim 3 \times 10^{-5}$ sec $^{-1}$ and an exchange flux of $\sim 10^{10}$ – 10^{11} sec $^{-1}$). In growth from a solution, this number is considerably smaller, since the activation energy for attachment of particles is larger, and this means that the exchange flux is smaller. For an activation energy $E \sim 20$ kcal/mole,^[111] a concentration $c_A \sim 10^{-1}$, and atomic vibration frequencies $\nu \sim 10^{12}$ sec $^{-1}$ and $T \sim 650^\circ\text{K}$, the mean flux to the surface is $\nu c_A \exp(-E/kT) \sim 10^5$ sec $^{-1}$. Then, if the growth rate amounts to $\sim 3 \times 10^{-6}$ cm/sec $\sim 10^2$ sec $^{-1}$, then the average number of trials onto the faces will be $\sim 10^3$. The rates at steps (and kinks) will be at least one or two orders of magnitude higher. Thus, actually the number of trials will be ~ 10 . The numbers of trials will be larger in growth involving surface diffusion. The number of trials is approximately equal to the relative supersaturation at the growth site. If we assume that the supersaturation at the surface is an order of magnitude smaller than in the bulk of the solution, then the

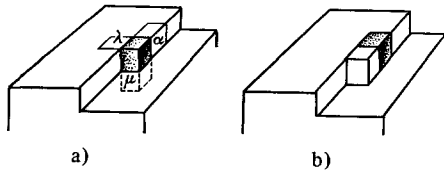


FIG. 8. a) An impurity atom (stripped) at a kink; b) an impurity atom covered by an intrinsic atom.

number of trials 10^3 corresponds to a reasonable supersaturation of $\sim 1\%$.

Let us proceed now to calculate for concrete models: an isolated kink,^[112,42,70] and an assembly of kinks of the same sign at a step^[113] in an approximation involving small impurity concentration ($c \ll 1$). We shall assume that an impurity particle can leave the crystal only from a position at a kink (Fig. 8a). Occurrence in the surface layer, the edge of a step (Fig. 8b), or the bulk of the crystal are equivalent to permanent capture. In growth at an isolated kink (Fig. 8),

$$J_A = w_+ \left(\begin{matrix} A \\ A \end{matrix} \right) U \left(\begin{matrix} A \\ A \end{matrix} \right), \quad J_B = w_+ \left(\begin{matrix} A \\ B \end{matrix} \right) U \left(\begin{matrix} A \\ B \end{matrix} \right); \quad (5.6)$$

Here and below, $w_{\pm} \left(\begin{matrix} \lambda \\ \mu \end{matrix} \right)$ are the rates of attachment and detachment of particles at a kink composed of the particles α , λ , and μ (Fig. 8), while $U \left(\begin{matrix} \lambda \\ \mu \end{matrix} \right)$ is the probability

of its permanent conservation at this kink. Since the impurity concentration is small, $\lambda = \mu = A$, and we can conveniently denote $w_{\pm} \left(\begin{matrix} A \\ A \end{matrix} \right) = w_{\pm} \alpha \beta$. If we calculate the probabilities of conservation by the formulas of Secs. 2-3, we have for small impurity concentration:

$$K = c^{-1} w_{+AB} w_{+AA} / \{ (w_{+AA} + w_{-AB}) (w_{+AA} - w_{-AA}) + w_{-AB} w_{-BA} \}. \quad (5.7)$$

Let us now express $w_{\pm} \alpha \beta$ in terms of the concentrations and the temperature. Let us consider an assembly of non-interacting kinks. Let c_k denote the fraction of the kinks occupied by impurity particles. At equilibrium, the flux of impurity particles reaching the kinks is equal to the reverse flux of particles from the kinks into the medium. Hence, $c_k = w_{+AB} / w_{-AB}$.

Further, let us denote by c_s and c_e the fraction of the sites in the surface layer and in the edge of a step occupied by impurity atoms. For these,

$$w_{-BA} c_e = w_{+AA} c_k, \quad c_e / c_s = c_k / c_e = w_{-BA} / w_{+BA}.$$

We can express the same ratios of the equilibrium concentrations in terms of the binding energies of the impurity particles to the particles of the crystal and the medium, or more exactly, in terms of the heat of formation of the corresponding solid solutions: zero-dimensional for the kinks, one-dimensional for the edges of steps, and two-dimensional for the surface layer of the crystal. It is very simple to write down the expressions for the heats of formation for a lattice model for the mother medium. As we know, this model assumes that the particles of the liquid are located on the same space

lattice as the crystal bordering on it, while the binding energy (per bond) between the "solid" (s) particles ϵ_{ss} and the "liquid" (l) particles ϵ_{ll} are assumed to differ. The energy of a single bond between liquid and solid atoms is denoted as ϵ_{ls} , while the energy of a single bond of an impurity particle with a "crystalline" or "liquid" particle is denoted as ϵ_{is} or ϵ_{il} .

Transfer of impurity particles from the bulk of the lattice liquid to a state of adsorption on the surface of a simple cubic lattice requires a work $\xi = (\epsilon_{il} - \epsilon_{is}) + (\epsilon_{ls} - \epsilon_{ll})$, since this requires interchange of places of the impurity particle in question and one of the "liquid" particles bound to the surface by one bond. The surface energy per unit bond is $\mathcal{A} = \epsilon_{ls} - [(\epsilon_{ss} + \epsilon_{ll})/2]$. Using these two quantities, we can express the work required to transfer an impurity particle from an end row of atoms of a step to a kink or from the surface layer to the edge of a step. In both cases, one is bond is replaced by il, and one sl bond by ss. Hence, the sought energy is

$$(\epsilon_{il} - \epsilon_{is}) + (\epsilon_{ss} - \epsilon_{sl}) = \xi - 2\mathcal{A}. \quad (5.8)$$

Hence,

$$w_{-BA} / w_{+BA} = c_e / c_s = c_k / c_e = e^{-(\xi - 2\mathcal{A})/T} \equiv \xi. \quad (5.9)$$

Finally, we can introduce the distribution coefficients for a kink, an edge, and a surface: $K_k = c_k / c$, $K_e = c_e / c$, and $K_s = c_s / c$, and transform (5.7) into the form

$$K_s = K_k (1 + \sigma) / \{ [1 + w_{-AA} w_{-AB}^{-1} (1 + \sigma)] \sigma + \xi \}, \quad \sigma \equiv (w_{+AA} - w_{-AA}) / w_{+AA}. \quad (5.10)$$

If the rate of detachment is proportional to $\exp(-\Delta E/T)$, where ΔE is the change in energy of the system upon detachment, then $w_{-AA} / w_{-AB} \sim \xi^{-2}$ for transfer of particles from a kink to the adsorbed layer, and $w_{-AA} / w_{-AB} \sim \xi^{-3}$ for kink-to-medium transfers.

With increasing supersaturation at constant temperature, the capture coefficient of the impurity by a step increases at small supersaturations for substances for which the adsorption energy of the impurity is small in comparison with twice the surface energy of the pure surface ($\xi < 2\mathcal{A}$, $\xi > 1$). Conversely, the capture coefficient of a strongly adsorbed impurity decreases with increasing supersaturation ($\xi > 2\mathcal{A}$, $\xi < 1$). The obtained result is quite understandable: the probability that a particle of a strongly-adsorbed impurity will be conserved at a kink is close to unity even at low supersaturations. Hence, increasing the supersaturation simply increases the number of intrinsic particles that can attach to the crystal in the period of time between successive attachments of impurity particles. Thus the capture coefficient declines with increasing supersaturation (cf. (5.4)). However, if the adsorption energy of the impurity at a kink is small, then the impurity atom will be captured only when the intrinsic particles succeed in "immuring" it immediately after it has deposited at the kink, i.e., at high enough supersaturations. Thus the capture coefficient increases with the supersaturation.

At low supersaturations ($\sigma \rightarrow 0$), (5.10) implies that $K_s \rightarrow K_k / \xi = K_e$. That is, a kink captures the impurity in an amount corresponding to the equilibrium value for a step, as must happen in the adopted one-dimensional model. Nevertheless, under conditions close to equili-

brium, a step must actually capture the equilibrium amount of the impurity appropriate to the surface layer and the interior. The reason for the discrepancy involves the model of an isolated kink. It neglects the fact that the succeeding rows of particles are deposited along the edge of the step, thereby transforming edge atoms into surface-layer atoms. A model taking into account the movement of the aggregate of kinks on a step avoids this defect.^[113] Equation (5.10) should give a correct answer at rather large deviations from equilibrium, since under these conditions each kink acts independently of the rest.

According to^[113], a step inclined from the (01) direction on the surface of a simple cubic lattice by a small angle whose tangent is p will give rise to a capture coefficient

$$K_s = \frac{\overset{\circ}{K}_s (1 + \sigma) / [1 + w_{-AA} (1 + \sigma) w_{-AB}^{-1} \sigma + \xi + \xi (\xi - 1) (1 - 2\sigma (\sigma + \sqrt{\sigma^2 + 4p(1 + \sigma)})^{-1})]}{(5.11)}$$

Here we don't find that $K_s \rightarrow \overset{\circ}{K}_e$ as $\sigma \rightarrow 0$, such as happens in (5.10) in treating a single kink. Rather,

$K_s \rightarrow \overset{\circ}{K}_s$, which is physically quite justified.

We can get some picture of the order of magnitude of the ratio w_{-BA}/w_{-AA} by assuming each of these rates to be proportional to $\exp(-\Delta E/T)$, where ΔE is the energy required to remove the particle. If a kink exchanges particles preferentially with the adsorbed layer, and the potential barriers are small, then $\Delta E_{-AB} = 2[(\epsilon_{iL} - \epsilon_{iS}) + (\epsilon_{sL} - \epsilon_{iL})] = 2\xi$. If it exchanges with the interior of the crystal, then $\Delta E_{-AB} = 3\xi$. If, as before, we consider an intrinsic particle that has been transferred from a kink to the adsorbed layer to be "solid", we have $\Delta E_{-AA} = 4[(\epsilon_{iS} - \epsilon_{sS}) + (\epsilon_{iS} - \epsilon_{iL})] = 4A$. If we consider it "liquid," then $\Delta E_{-AA} = 2(\epsilon_{iL} - \epsilon_{sS})$. When an intrinsic particle is transferred into the interior of the mother medium, $\Delta E_{-AA} = \Delta H$, where ΔH is the heat of fusion (or sublimation if the medium is gaseous).

K_s deviates from the equilibrium value $\overset{\circ}{K}_s$ more rapidly with increasing supersaturation as the density p of kinks decreases. When $\xi > 1$, the coefficient K_s increases with increasing σ , while it declines when $\xi < 1$. At large supersaturations, the third term in the denominator of (5.11) is small, and the expression (5.11) goes over into the formula (5.10) for capture by an isolated kink, as it should. Figure 10 shows the nature of the

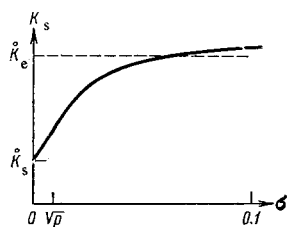


FIG. 9

FIG. 9. Dependence on the supersaturation of the capture coefficient of an impurity by a step.

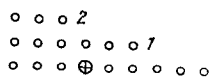


FIG. 10

FIG. 10. Surface layer of atoms containing a step and a kink. O - atoms of the fundamental substance; ⊕ - impurity atom.

$K_s(\sigma)$ relation when $\xi > 1$ and p is very small (i.e., at low temperatures).

The derivation of Eq. (5.11) amounts to taking into account the correlation between an impurity atom on the edge and the nearest kink to it on the right (kink 1 in Fig. 10). If, conversely, we take into account the correlation between the edge and impurity atoms and the nearest kink to the left (kink 2 in Fig. 10), while all other kinks are considered to be distributed at random, then we can easily calculate c_s , just as was done above. It turns out that here the $K_s(\sigma)$ relation is the same as before, but with the quantity $p\xi$ playing the role of p . Thus, for a strongly adsorbed impurity ($\xi < 1$), correlation with the left-hand (approaching) kink is more substantial than with the right-hand (departing) kink, but vice versa when $\xi > 1$.

The treatment given above dealt with inclined steps having $p \gg 2\xi = 2 \exp(A/T)$. The smaller the slope of the step is, the more K_s deviates from the equilibrium

value $\overset{\circ}{K}_s$ with increasing supersaturation σ . This deviation must be greatest of all for a close-packed (01) step. In order to estimate the capture of impurity by this step, we shall assume that $p \sim 2\xi$ in (5.11). In practice, the kink density on a (01) step is not too small (a typical value is $\xi \sim 0.1$), while the supersaturation σ near the step is usually much less than unity. Under these conditions, the $K_s(\sigma)$ relation is considerably simplified.

When $\xi > 1$, we get simply $K_s = \overset{\circ}{K}_s$. That is, the capture coefficient is practically independent of the supersaturation. When $\xi < 1$, we get

$$K_s = \overset{\circ}{K}_s / (1 + \sigma \sigma_0^{-1}), \quad (5.12)$$

where $\sigma_0 = \xi^2 w_{-AB}/w_{-AA}$. When $\sigma \gg \sigma_0$, one can write this formula in the form $c_s = w_{+AB}/(w_{+AA} - w_{-AA})$. This means that all the impurity particles reaching the kinks are captured by the step. The transition to total capture of the impurity reaching the kinks takes place at lower and lower supersaturations as adsorption becomes stronger (i.e., as ξ becomes smaller). The quantity σ_0 is extremely sensitive to the value of the adsorption parameter ξ . Thus, in the case of exchange between the step and the adsorbed layer, $\sigma_0 \sim \xi^4$. In order that the dependence of K_s on σ should be considerable at supersaturations of $\sim 1\%$, it suffices to have $\xi = 1/3$.

In growth from a melt, the quantity $(w_{+AA} - w_{-AA})/w_{-AA}$, which plays the role of the supersaturation, is very small. This is because the supercooling near the surface is usually small in comparison with the equilibrium temperature. On the other hand, the adsorption energy ξ here cannot be large.

Hence we should expect that $K_s \sim \overset{\circ}{K}_s$ in growth from a melt.

Let us find the coefficient $\overset{\circ}{K}_s$ within the framework of the applied model for the case of a condensed medium. We shall consider the general case of an arbitrary lattice, since the conclusions given above must hold for any lattice, rather than a simple cubic one alone. Let us assume in advance that an impurity atom in the interior of the medium and one located in the crystal will have the same energy of interaction with an adjacent particle of the medium and the same vibrational free energy. In

this case, $\overset{\circ}{K}_S = \exp(n\mathcal{E}/2T)$, where n is the number of nearest neighbors in the lattice. We can easily generalize the formula giving the ratio $\overset{\circ}{K}_S/\overset{\circ}{K}_K$ to the case of an arbitrary lattice. Namely, if m is the number of inter-phase bonds per surface atom of the crystal, then

$$\overset{\circ}{K}_S/\overset{\circ}{K}_K = \xi^{-[(n/2)-m]}. \quad \text{Thus we get}$$

$$\overset{\circ}{K}_S = e^{[(n-m)\mathcal{E} - (n-2m)\mathcal{A}]/T}. \quad (5.13)$$

If we assume in (5.13) that $m = 0$, then we get the equilibrium distribution coefficient between the bulk of the phases:

$$\overset{\circ}{K} = e^{n(\mathcal{E}-\mathcal{A})/T}. \quad (5.14)$$

The calculations made above of the non-equilibrium, kinetic distribution coefficient of impurities stem from the assumption that the impurity particles incorporated into the edge of a step or into the surface layer cannot leave the crystal. Nevertheless, this is not always so,^[108] especially for particles having low energy of adsorption.

This fact can most simply be taken into account by the factor $\exp(-a/v\tau_e)\exp(-a/V\tau_s)$, where v is the rate of growth of the step, V is the normal growth rate, and τ_e and τ_s are the impurity relaxation times at the edge of a step and in the surface layer. The activation energies for relaxation, as determined by the loss of impurity, are: from an edge to the surface $\sim 2\mathcal{E}$, from the edge to the interior $3\mathcal{E}$, from the surface layer to the surface $4\mathcal{E}$, and from the surface layer into the interior $5\mathcal{E}$.

If D_i is the diffusion coefficient of the impurity in the crystal and h is the height of the step being deposited (it can also be an echelon of elementary steps), then at normal growth rates $V \gg D_i/h$, all the impurity captured by the surface will remain in the crystal forever, but when $V \ll D_i/h$, diffusional equilibrium must set in.^[102]

Figure 11 shows the experimental variations of the capture coefficients for aluminum and phosphorus by the (111) face of silicon growing from the melt.^[114] A substantial change in capture actually occurs at $Va/D_i \sim 1$ ($a \sim 3 \times 10^{-8}$ cm). The plateau corresponding to high growth rates must be equal to $\overset{\circ}{K}_S$. According to (5.13) and (5.14),

$$\overset{\circ}{K}_S = \xi^m \overset{\circ}{K}^{(n-m)/n} \quad (5.15)$$

In the diamond structure, an elementary step on the (111) face is formed by two atomic layers, of which the surface layer is only one. Hence the capture coefficient of an impurity by a step is

$$K_{st} = (\overset{\circ}{K} + \xi^{-1} \overset{\circ}{K}^{3/4})/2. \quad (5.16)$$

Experiment gives $\overset{\circ}{K} = 0.002$ for aluminum in silicon, and 0.35 for phosphorus.^[114] Hence, according to (5.16), the capture coefficients K_{st} for a step are respectively equal to 0.011 and 0.7. The experimental values of the same quantities corresponding to the maximum values in Fig. 11 are 0.012 and 0.75. The agreement for the adopted model is even too good.

Capture of colloidal inclusions and the concept of the adsorbed layer. We shall take up now capture of colloidal

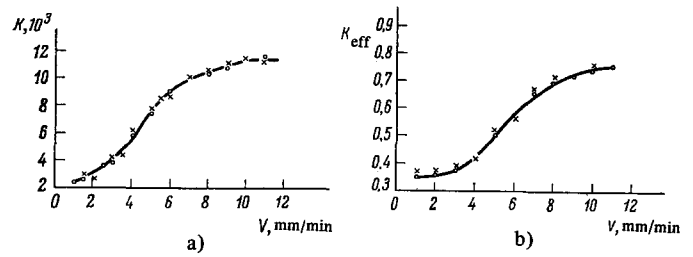


FIG. 11. Variation of the capture coefficient of aluminum (a) and of phosphorus (b) by silicon.^[114]

idal inclusions from the mother medium by a crystal growing from solution. This process differs considerably from capture of an atomic impurity, but can also be treated in the spirit of probabilistic notions.

Inclusions of colloidal dimensions ($\sim 10^{-5}-10^{-7}$ cm) can be residues of the mother medium occurring near the growth front at a distance $\sim 10^{-6}-10^{-7}$ cm. A number of experiments have indicated that the properties of boundary layers differ from those of the massive liquid.^[115-116] In particular, the liquid in a layer of up to $10^{-5}-10^{-6}$ cm is apparently partially ordered at the boundary with the crystal. Here, according to Abdrakhmanova and Deryagin,^[117] the time needed to establish an equilibrium structure in the layer amounts to minutes. The crystallochemical aspects of the structure of molecular adsorption have been studied by Hartman^[118] and by Kern and by Monier and their associates.^[119-120,127] The more strongly the layer of mother solution is adsorbed on the growing face, the more slowly this face must grow, and the more strongly it must capture inclusions. Indeed, as Petrov has established,^[121] capture of inclusions occurs most intensively at the faces of KNO_3 crystals whose atomic arrangement is most favorable for epitaxy of ice and adsorption of water. Kuznetsov^[120,122] has shown that the most slowly growing pinacoid face of corundum under hydrothermal conditions shows the thickest adsorbed layer of water upon contact with water vapor.

The presented facts permit us to imagine a pattern of capture of colloidal inclusions as follows. We shall consider growth in layers for the sake of explicitness. Atomically smooth regions of the surface are covered by an adsorbed layer of solution. This partly ordered layer is inhomogeneous: it must contain regions that are statistically enriched in some of the components of the solution, regions adsorbed on defects of the surface, regions differing from the others in their internal structure, etc. The lifetimes in the adsorbed state for all these fragments of the adsorbed film must differ. Their amounts must be proportional to an exponential factor containing the corresponding energies u . Apparently, the sizes of the regions can fluctuate from atomic to colloidal dimensions.

Each new crystalline layer deposited on the surface clears away and/or partially orders the adsorbed layer. The steps play the role of "blades" that clear away the film. If a step finds a more strongly adsorbed region on its path, then its motion is retarded, and a cavity remains in the freshly produced layer. This can give rise to an inclusion. Whether this alternative happens or not depends on whether the island of adsorbed layer

can persist until a new growth layer arrives and the cavity is made deeper, whereupon its disappearance becomes even more difficult, etc. If the relaxation time of the island is τ , its dimension in the direction perpendicular to the growing face is l , and the normal growth rate of the face is V , then the time required for "immuring" the inclusion is l/V , while the probability of this event is $\exp(-l/V\tau)$. To generalize this relation, one can say that the probability of capture is $\sim \exp(-V_c/V)$, where V_c is the characteristic rate of relaxation. The time, and correspondingly the rate, of relaxation are determined by concrete mechanisms about which nothing is yet known. In particular, an island can disappear by being overgrown. The closed step surrounding the island will overgrow it under the influence of the supersaturation at the growth front and the tendency of the linear energy of the step to a minimum. The linear energy will play the major role at relatively low supersaturations in the system and at low V , so that the overgrowth time will prove to be independent of the growth rate. In this case, the value of τ will depend on the kinetic coefficient of crystallization at the island-step boundary. In general, the latter differs from the kinetic coefficient for other regions of the surface. If the remaining island is desorbed as a whole (which is probable only for very small specimens $\sim 10^{-7}$ cm), then τ is simply its lifetime to the instant of detachment. The case will also be analogous when the island is structurally rearranged, and perhaps loses a part of its components. The list of mechanisms can be easily extended, but this is hardly necessary yet. In one way or another, we should expect that

$$V_c \sim e^{-U/T}, \quad (5.17)$$

where U is the activation energy of the relaxation process. Consequently, the concentration of colloidal inclusions

$$C = C_0 \exp[-V_c V^{-1} + uT^{-1}], \quad (5.18)$$

where C_0 is constant. That is, we should expect a linear dependence in the coordinate system $\ln C$, $1/V$, and $\ln V_c$, $1/T$. The latter relation is obeyed more exactly as the ratio u/T becomes smaller in comparison with $\ln C_0/C$.

The presented ideas couldn't be tested until recently for lack of experimental data. However, recently Hadjee (see^[122]) has made a thorough study of capture of colloidal impurities by crystals of artificial quartz growing from hydrothermal solutions containing several weight percent of Na_2CO_3 . A series of arguments is given in^[132] indicating proportionality between the amount of the Na_2O impurity in quartz and the amount of colloidal inclusions in it.

Figure 12 shows a treatment of the data for the basal plane of quartz in coordinates of $\ln C$ and $1/V$. The slope of the obtained straight line determines V_c for a particular value of the temperature.

The temperature-dependence should have been determined from a set of slopes on the graph of $\ln C$ plotted as a function of $1/V$. Owing to lack of such data, the quantity used was the temperature-dependence of the rate beyond which the amount of inclusions in the crystal begins to grow markedly. Of course, this is actually not a strictly defined rate, but is a narrow range in the

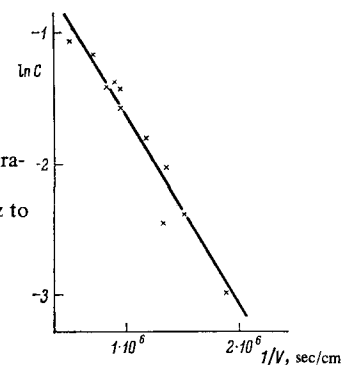


FIG. 12. Relation of the concentration C of colloidal impurities (Na_2O) captured by the basal plane of quartz to its growth rate V .

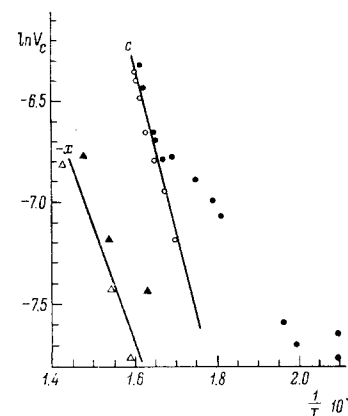


FIG. 13. Relation of the critical growth rate V_c to the temperature T . \circ — states in which the pyramid of the growth base is free of inclusions; \bullet — states in which this pyramid contains inclusions; Δ , \blacktriangle — the same for the growth pyramid of the x face.

vicinity of V_c , as is implied by (5.18). The $V_c(T)$ relation thus obtained is plotted in Fig. 13. The corresponding activation energy is ~ 38.6 kcal/mole. The absolute value of V_c in the studied temperature range amounts to $(0.4-1.4) \times 10^{-7}$ cm/sec.

For comparison, let us recall that the activation energy for the kinetic coefficient for the basal plane of quartz in an alkaline solution amounts to 20 kcal/mole, while it is 14 kcal/mole for the minor rhombohedral face, and 40 kcal/mole for the major rhombohedral face.^[111]

It is essential to note the strong anisotropy of capture of inclusions: their amount in the different growth pyramids differs severalfold. Hence, we must associate capture specifically with surface phenomena. Formation of colloidal particles in the bulk of the melt, if it happens, should affect only the total number of inclusions, i.e., the pre-exponential factor C_0 .

The film of solvent, together with the impurities, may be responsible for the existence of a critical supersaturation required for onset of growth. Namely, the islands in it may form a palisade of blocks against step movement.^[128] Growth also stops when the time for establishment of equilibrium in the film, which completely shields the surface, becomes less than the time that it takes for renewal of the surface, i.e., the time for deposition of a new layer.^[130]

6. Collective Interaction in Crystallization Kinetics

Let us continue to treat the growth of a three-dimensional crystal by movement of an isolated kink, while dropping the assumption that the concentration of one of the components of the binary system is small. Now we

shall concentrate attention on the dependence of the atomic structure (i.e., the packing of the different types of particles into the crystal structure) on the conditions of crystallization. Of course, such a dependence can be manifested only as long as the structure of the newly formed crystal does not change after it is formed. In particular, a necessary condition for satisfying this requirement is that the diffusion coefficient in the solid phase should be small.

The most convenient case for analysis is when the concentrations of the components in the crystal remain constant, independently of the conditions of growth. The simplest example satisfying this requirement is a binary system of equivalent (but not identical) particles A and B with rates of detachment that can be represented in the form

$$w_-(\alpha\beta) = \nu e^{-(\varepsilon_{\alpha\beta} + \varepsilon_{\lambda\beta} + \varepsilon_{\lambda\alpha})/T}, \quad (6.1)$$

Here, for the equivalent particles,

$$\varepsilon_{AA} = \varepsilon_{BB}, \quad \varepsilon_{AB} = \varepsilon_{BA} = m\varepsilon_{AA}, \quad (6.1')$$

$$w_+(\alpha\beta) = w_+, \quad (6.1'')$$

If we consider the lattice to be preassigned (e.g., a simple cubic lattice), then the structure of the crystal will be characterized by long- and short-range order in the distribution of the A and B particles over the sites. An ideally ordered crystal has alternate A and B atoms at the sites, and consists of interpenetrating sublattices 1 and 2. As we know, the degree of long-range order η is the ratio of the difference of the numbers of A and B atoms at the sites of sublattice 1 to the total number of sites of type 1. Each temperature of a growing crystal has its own thermodynamic-equilibrium value $\overset{\circ}{\eta}$ of the parameter. However, the actual order in the crystal grown at this temperature differs: it depends on the conditions of crystallization. We can naturally call this quantity the kinetic value of the long-range order parameter.

If the mother medium is disordered with respect to distribution of A and B particles (gas, liquid, or amorphous), while the events of attachment of particles are random, then the kinetic value of η must be smaller than the thermodynamic value. Correspondingly, the kinetic value of the entropy is larger than the equilibrium value for a given temperature of crystallization. When the flux of particles into the crystalline phase is large in comparison with the counterflux, the crystal will no longer grow in an ordered form. On the other hand, if A and B form an ordered alloy with a Curie

temperature T_C , and if $T < T_C$, then the long-range order parameter will be close to the equilibrium value when crystallization is slow enough. That is, it will not differ greatly from unity. Hence, at one particular temperature of the crystal, the latter will have an order ranging from zero to unity, depending on the degree of deviation from equilibrium. Will this variation be smooth or abrupt? To answer this, we turn to Fig. 8. Each new β particle attaching to a kink will be conserved there forever or not, depending on the composition of the kink (the identities of α , λ , and μ) and also on what

type of particle (γ) will deposit at the kink after it (see Fig. 8b). In turn, the probability of conservation of this new particle depends on the probability of conservation of the next particle that covers it, etc., in addition to its immediate surroundings. Hence, the probability of filling a given lattice site is determined by its entire structure formed up to the given instant, i.e., by a collective correlational interaction. On this basis, we can naturally expect that there will be a fully determined deviation from equilibrium, with an order-disorder transition occurring in the growing crystal. That is, a distinctive kinetic phase transition must occur. The supersaturation or another parameter characterizing the deviation from equilibrium will play the role of the temperature.

An approximate theory of the described processes has been developed in^[13], and it consists in the following. Let $x_\alpha^{(i)}$ be the probability of finding a particle of type α at a site of the i th sublattice ($i = 1, 2$). Then

$$\left. \begin{aligned} x_A^{(1)} &= (1 + \eta)/2, & x_A^{(2)} &= (1 - \eta)/2, \\ x_B^{(1)} &= (1 - \eta)/2, & x_B^{(2)} &= (1 + \eta)/2. \end{aligned} \right\} \quad (6.2)$$

Let us denote

$$\left. \begin{aligned} p(\alpha\beta\gamma) &= w_+(\beta\gamma) / [w_-(\alpha\beta) + \sum_\gamma w_+(\beta\gamma)], \\ q(\alpha\beta) &= w_-(\alpha\beta) / [w_-(\alpha\beta) + \sum_\gamma w_+(\beta\gamma)]. \end{aligned} \right\} \quad (6.3)$$

The first of these quantities is the probability of

attachment of a γ particle to the kink $\alpha\beta$, while the latter is the probability that this kink will lose the particle β . Further, let us introduce the mean probabilities $\bar{p}_{\alpha\beta\gamma}^{(1)}$ and $\bar{q}_{\alpha\beta}^{(1)}$, neglecting correlations in the types of adjacent particles during the averaging:

$$\left. \begin{aligned} \bar{p}_{\alpha\beta\gamma}^{(1)} &= \sum_{\lambda\chi\mu} p(\alpha\beta\gamma) x_\lambda^{(1)} x_\chi^{(1)} x_\mu^{(2)}, \\ \bar{q}_{\alpha\beta}^{(1)} &= \sum_{\lambda\chi\mu} q(\alpha\beta) x_\lambda^{(1)} x_\chi^{(1)} x_\mu^{(2)}, \end{aligned} \right\} \quad (6.4)$$

and analogously for $i = 2$, replacing the indices of the sublattices by their opposites in (6.4). Here and everywhere below, the superscript (of the sublattice) refers to the first of the subscripts (types of particles).

Let us denote by $\Psi_{\alpha\beta}^{(i)}$ the probability of conservation at a kink of the last particle of the growing series (... $\alpha\beta$), with α belonging to the i th sublattice. Further, let $\Sigma \Psi_{\beta\gamma}^{(i)} = \Psi_{\beta}^{(i)}$. Both sublattices and both types of particles are equivalent, and hence

$$\Psi_A^{(1)} = \Psi_B^{(2)} = \Psi_A, \quad \Psi_B^{(1)} = \Psi_A^{(2)} = \Psi_B. \quad (6.5)$$

Let us assume the elementary rates to be expressed in the form of (6.1), and note that in this case $\bar{p}_{\alpha\beta\gamma} \equiv \bar{p}_{\alpha\beta}$. Then we have, after considerations analogous to those of Sec. 2, a system of equations for Ψ_A and Ψ_B :

$$\left. \begin{aligned} \Psi_A [1 - (S_{AB} + \Psi_A)^{-1}] &= \Psi_B / (S_{AA} + \Psi_B), \\ \Psi_B [1 - (S_{BA} + \Psi_B)^{-1}] &= \Psi_A / (S_{BB} + \Psi_A), \\ S_{\alpha\beta}^{(i)} &= \bar{q}_{\alpha\beta}^{(i)} / \bar{p}_{\alpha\beta}^{(i)}. \end{aligned} \right\} \quad (6.6)$$

In an approximation neglecting correlations,

$$\sum x_\beta^{(1)} \bar{p}_{\beta\gamma}^{(1)} = x_\gamma^{(2)}, \quad \bar{p}_{\beta\gamma}^{(1)} \equiv U_{\beta\gamma}^{(2)} / \Psi_\beta^{(2)}. \quad (6.7)$$

Hence, upon taking (6.2) into account, we arrive at a condition which, together with (6.6), determines $\eta(q, R)$, $\Psi_A(q, R)$, and $\Psi_B(q, R)$:

$$(1 + \eta) [1 - (S_{AB} + \Psi_A)^{-1}] = (1 - \eta) [1 - (S_{BA} + \Psi_B)^{-1}]. \quad (6.8)$$

In proceeding to analyze the solution, we note that $\Psi_A(q, \eta) = \Psi_B(q, \eta)$. That is, the equation

$$\Psi_A(q, 0) = \Psi_B(q, 0) \equiv \Psi = \{(2 - S_{AB} - S_{AA}) - [(2 - S_{AB} - S_{AA})^2 + 4(S_{AB} - S_{AA})(1 - S_{AB})]^{1/2}\} / 2, \quad \eta = 0, \quad (6.9)$$

is a solution of the system (6.7)–(6.8) in the disordered phase. It is not the only one. It is easier to seek the other branch separately in the region of small and large supersaturations.

The equilibrium value of the parameter $q = \bar{q}$ is determined by the equation

$$S_{AA}^{-1} S_{BB}^{-1} - S_{AB} S_{BA}^{-1} (S_{AB} - 1) (S_{BA} - 1) = 0, \quad (6.10)$$

Here a positive value of the left-hand side corresponds to growth, and a negative value to evaporation.

If the equilibrium temperature is appreciably lower

than the Curie temperature ($\bar{q} < q_C$), then a crystal having $\eta \sim 1$ must grow near equilibrium, i.e., an ordered phase. Hence, at equilibrium we should expect

that $R\bar{q}^{3m} \sim 1$, where $R = \nu/w_+$. The probabilities of detachment and attachment in (6.3) (and this means $S_{\alpha\beta}$ as well) depend only on the ratio R (and also on q and η). If we assume for an estimate that $w_+ \sim 10^6 \text{ sec}^{-1}$, which corresponds to direct incidence of particles on the kink at a pressure of ~ 10 Torr, and that $\nu \sim 10^{12} \text{ sec}^{-1}$, we get $R \sim 10^6$. Model experiments have been performed for $R = 10^4$ and $R = 10^6$ with $m = 2$ ($\epsilon_{AB} = 2\epsilon_{AA}$). Taking into account the large value of

R , we find as a preliminary that $\bar{q} \ll 1$. These considerations indicate that it is expedient to seek a solution by expanding $S_{\alpha\beta}$ in a series in $(1 - \eta)$, taking into account the smallness of q , as well as of Ψ_A and Ψ_B . The corresponding calculations give

$$\left. \begin{aligned} \Psi_A &= 1 - Rq^{3m} - 5[R^2q^{2(m+2)}]^{-1}, \\ \Psi_B &= \Psi_A/Rq^{2m+1}. \end{aligned} \right\} \quad (6.11)$$

The condition of equilibrium in the form $\Psi_A = 0$, which is equivalent to (6.9), leads to an equation for \bar{q} :

$$1 - R\bar{q}^{3m} = 5\bar{q}^{4(m-1)} \quad (6.12)$$

and an equilibrium long-range order parameter:

$$\bar{\eta} = 1 - 2\bar{q}^{4(m-1)}. \quad (6.13)$$

When $m = 2$ and $R = 10^4$, we easily find that $\bar{q} = 0.215$, $\bar{\eta} = 0.998$; and when $R = 10^6$, then $\bar{q} = 0.100$, $\bar{\eta} = 0.9998$ (in good agreement with the results of model experiments (Sec. 5)).

The growth rate in the approximation under study is:

$$V = w_+ \Psi_A = w_+ \{1 - Rq^{3m} - 5[R^2q^{2(m+2)}]^{-1}\}. \quad (6.14)$$

For $m = 2$ and $R = 10^4$, Eq. (6.14) gives

$$\frac{1}{w_+} \frac{\partial V}{\partial q} = -27.9,$$

whereas the "experimental" value of this quantity is ~ -28 .

In the vicinity of the kinetic phase transition, $\eta \ll 1$. The differences $\Psi_A - \Psi$ and $\Psi_B - \Psi$ are also small, where Ψ is the solution for a disordered phase in (6.9). If we linearize (6.6) and (6.8) by using these small parameters, we get a homogeneous linear system of equations in $\Psi_A - \Psi$, $\Psi_B - \Psi$, and η . The condition for it to have a solution, namely, that the corresponding determinant \mathcal{L} should vanish, gives an equation for the critical value q_{cr} , i.e., the temperature of the kinetic phase transition.

Numerical solution for the condition $\mathcal{L} = 0$ gives $q_{cr} = 0.12$ for $R = 10^4$, and $q_{cr} = 0.035$ for $R = 10^6$ ($m = 2$). In model experiments, the kinetic phase transitions occur when $q_{cr} = 0.14$ and $q_{cr} = 0.046$.

Equations (6.6) and (6.8), after they have been expanded up to the third power in η , $\Psi_A - \Psi$, and $\Psi_B - \Psi$, inclusive, indicate the way in which the order parameter vanishes as $q \rightarrow q_{cr}$ ($q \geq q_{cr}$). The symmetry properties discussed above make the quadratic terms in η vanish in the expansion, so that

$$\eta \mathcal{L} - \eta^3 \mathcal{C} = 0, \quad (6.15)$$

where \mathcal{C} is a function of q . Hence, in addition to the solution $\eta = 0$, we have also another one:

$$\eta = (\mathcal{L}/\mathcal{C})^{1/2}, \quad (6.16)$$

The latter vanishes at the kinetic phase-transition point, since \mathcal{L} generally has a first-order root at $q = q_{cr}$:

$$\eta \sim (T - T_{cr})^{1/2}. \quad (6.17)$$

Thus, the degree of long-range order in a kinetic phase transition vanishes according to the same law as at a point of thermodynamic order-disorder phase transition in the Bragg-Williams approximation. It is à propos to note here that the averaging procedures used in (6.4) and (6.7) also neglect correlations. In this sense, they are analogous to the Bragg-Williams approximation in the thermodynamic theory.

Using the symmetry properties in η and the equality $V = w_+ \Psi_A \Psi_B / (x_A \Psi_B + x_B \Psi_A)$, we have for $|\eta| \ll 1$:

$$V = \begin{cases} w_+ \Psi, & q < q_{cr}, \\ w_+ \Psi \{1 - \eta^2 [(a + b) \Psi^{-1} - a^2 \Psi^{-2}]\}, & q > q_{cr}; \end{cases} \quad (6.18)$$

Here a and b are functions of q and R .

Equations (6.18) and (6.17) imply the existence of a cusp on the graph of $V(q)$ at $q = q_{cr}$ (see below, Fig. 23).

We considered above the situation when $\bar{q} \ll q_C$, as is shown schematically in Fig. 14a. The dotted lines in Fig. 14a show the thermodynamic $\eta(q)$ relations, while the solid lines show the kinetic relations. If $\bar{q} \lesssim q_C$, then we can expect $\eta(q)$ relations like Fig. 14b, but these like Fig. 14c when $q_C \lesssim \bar{q}$. When $q_C < \bar{q}$, an ordered phase may not appear at all, although the crystal is growing in a region where it is stable. The latter is not very probable under actual conditions, since the crystal will rearrange even in the solid phase.

The model discussed here of an isolated kink on a step is too simple, of course, to expect quantitative agreement between the characteristics derived for it and a real situation in which there are many kinks and steps. Furthermore, a crystal actually exchanges particles not only directly with the mother medium, but also

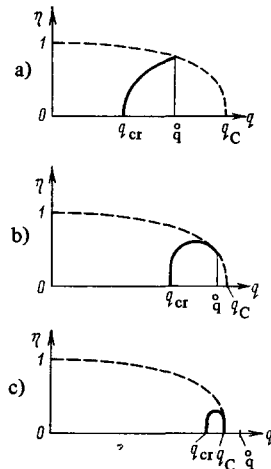


FIG. 14. Equilibrium (dotted lines) and kinetic (solid lines) temperature-dependences of the long-range order: a) $q_{cr} < \bar{q} < q_C$; b) $q_{cr} < q_C \leq \bar{q}$; c) $q_C < q_{cr} < \bar{q}$.

with the layer of adsorbed surface particles. The latter implies an increase in the effective values of the rates and energies of detachment and attachment of particles, and an improvement in selection of particles, i.e., approach to the equilibrium structure.

However, collective interaction still holds in an actual crystallization, but is manifested only in a more complex way, owing to the interaction of kinks and steps. However, since it is precisely the collective interaction that gives rise to the kinetic phase transition, it must actually exist. In this regard, we should consider the behavior of alloys that become ordered after having formed a disordered crystalline film when sputtered on a cold enough substrate. We should expect a kinetic phase transition upon lowering the substrate temperature for such substances.

The kinetic transition discussed above is an analog of a second-order thermodynamic transition. Apparently, kinetic analogs of first-order transitions also exist. These might prove to be transitions from stable modifications to unstable ones upon increasing the deviations from equilibrium (supersaturation, supercooling) under which the crystal is growing. Here we should recall the formation of amorphous films of germanium, silicon, antimony, or selenium, when sputtered on a cold enough substrate. Unfortunately, I know of no data on the nature of the transition from crystalline to amorphous modifications as the kinetic conditions are varied.

a) **Diffusionless crystallization.** In the general case, collective interaction determines not only the structure, but also the composition of the crystal. Hence, the existence is not ruled out of kinetic phase transitions in the concentration of one of the components: at growth rates above a critical value, the distribution coefficient must become unity, and possess a singularity. Such a situation would imply a transition to diffusionless crystallization, if growth is occurring from the melt.^[124] Of course, diffusionless, or more exactly, "selectionless" crystallization can occur from a gas phase as well. A calculation has been made on the basis of this hypothesis^[124] only for a one-dimensional model, which excludes singularities. As one should have expected, the positions of the impurity atoms in the one-dimensional "crystalline" chain proved to be correlated at low growth rates, and they gradually became random as the

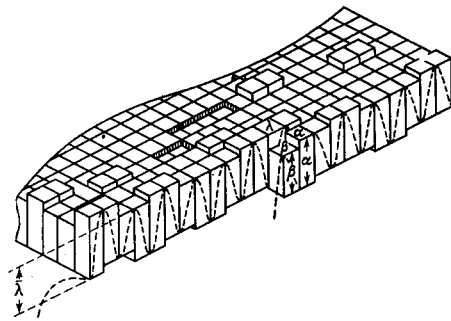


FIG. 15. Elementary plate of a polymer crystal having a single kink on the edge. The polymer chain is indicated by the dotted lines.

rate was increased. The transition occurred in the region where the mean time for irreversible transfer of a particle from the one-dimensional liquid phase into the crystalline phase became less than the time for diffusional exchange of places in the liquid phase.

b) **Growth of crystalline polymers.** Figure 15 makes evident a typical mechanism of growth of a polymeric crystalline layer. A new strip is being produced at its edge by packing of the chain-like molecules, which are indicated in Fig. 15 by dotted lines. Each new fold is represented in Fig. 15 by an elongated parallelepiped. One of the central problems of the theory is the relation of the mean thickness $\bar{\lambda}$ of the layer to the conditions of crystallization. The thermodynamic theory^[47] determines $\bar{\lambda}$ from the free-energy minimum at the temperature of crystallization. The kinetic approach,^[45,46] which is briefly discussed below, takes into account substantially the degree of deviation from equilibrium.

The length of each new segment being packed in a kink on the edge of the crystal (see Fig. 15) may be arbitrary, in general, from 0 to ∞ . Hence, growth by the mechanism reflected in Fig. 15 is identical to the growth of an ordinary crystal from particles of an infinite number of types. The work required (and this implies, the rates as well) for formation and decomposition of a segment of length β depends on the lengths of its nearest neighbors α and λ , i.e., $w_{\pm} = w_{\pm}(\alpha\beta\lambda)$. When $\lambda = \text{const.}$, the effect of the substrate is the same for all positions of the kink, and the problem is reduced to growth of a chain (Sec. 2) with a continuous spectrum of types of particles: $\alpha, \beta, \gamma \dots$ taking on (with varying probabilities) any values from 0 to ∞ . The results of Sec. 2 are easily generalized to this case by replacing the probabilities x_{α}, x_{β} , etc., by $x_{\alpha}d\alpha, x_{\alpha\beta}d\alpha d\beta$, etc., and replacing summation by integration. The fundamental algebraic equations (2.4) and (1.15) are transformed into integral equations:

$$\left. \begin{aligned} \psi(\alpha) &= \int_0^{\infty} w_{+}(\alpha, \beta) \psi(\beta) [w_{-}(\alpha, \beta) + \psi(\beta)]^{-1} d\beta, \\ x(\alpha) &= \int_0^{\infty} x(\alpha) w_{+}(\alpha, \beta) [w_{-}(\alpha, \beta) + \psi(\beta)]^{-1} \psi^{-1}(\alpha) d\beta. \end{aligned} \right\} (6.19)$$

The problem posed by these relations hasn't been solved yet. Furthermore, we don't know the behavior of a system with rates w_{\pm} depending on three or four subscripts. However, general considerations and the results of this section allow us to expect collective effects. In particular, it is precisely the collective interaction that must give rise to the experimentally-observed sta-

bility of the thicknesses of polymer crystals, which differ under different conditions of growth. Considerably simpler models have been studied up to now. Namely, the pioneering theory of Lauritzen and Hoffman^[45] assumes the lengths of all segments to be constant and to be identical with the critical size of the nucleus in the direction parallel to the fundamental regions of the chains. Frank and Tosi^[46] have treated the kinetics of motion of a kink (Fig. 15) by the method of Volmer^[87,88] (Eqs. (4.20) and (4.21)). They allowed the height β to vary once, under the condition that $\lambda = \alpha = \text{const.}$ (after the variation, they also assumed that $\beta = \text{const.} \neq \alpha, \lambda$). The rate of motion of the kink naturally depends on β and λ . Using it as a weighting function, we can find the mean value of the difference $\beta - \lambda$ (over the assembly of identical plates having different values of β). The value of λ for which this mean vanishes is adopted in^[46] as the mean thickness of the layer.

IV. COMPUTER SIMULATION OF GROWTH

7. Chain Growth

The simulation program was written to correspond with a sequence of events occurring upon crystallization. It began with selecting a particle α ($\alpha = A, B$) as the initial particle. At the first instant of discrete time, an A particle should have a probability $w_{+\alpha A} / \sum_{\beta} w_{+\alpha\beta}$ of attaching to it, and a B particle should have a probability $w_{+\alpha B} / \sum_{\beta} w_{+\alpha\beta}$. If a B particle has attached, then three possibilities can be realized in the next step: attachment of γ ($\gamma = A, B$) with a probability $p_{\alpha\beta\gamma}$ or detachment of β with a probability $q_{\alpha\beta}$. The values of

the eight quantities $p_{\alpha\beta\gamma}$ and the four quantities $q_{\alpha\beta}$ were found from assigned rates $w_{\pm\alpha\beta}$, using Eqs. (2.1). Any particular step (attachment of A or B, or detachment of the last particle) was chosen by a random-number generator. The latter produced at each instant of discrete time (i.e., at each step) a random number between zero and unity. This interval was divided into two parts proportional to the probabilities $w_{+\alpha A} / \sum_{\beta} w_{+\alpha\beta}$ and $w_{+\alpha B} / \sum_{\beta} w_{+\alpha\beta}$ to decide the problem of attachment to the single initial particle α . If the random number was in the left-hand part of the interval, an A particle was added (written in memory), and a B particle if in the right-hand part. For chains having two or more particles, the interval (0, 1) was divided into three parts proportional to $p_{\alpha\beta A}$, $p_{\alpha\beta B}$, and $q_{\alpha\beta}$. Simultaneously, a tally was taken of the number of cases in which the end was formed of any particular pair. Thus the quantities $x_{\alpha\beta}$ were determined. Analysis of the chain in the intervals between steps gave the quantities x_{α} and $x_{\alpha\beta}$ as averages over the entire chain including its end. The latter introduced no appreciable error into the result when the chain length (usually $\sim 10^3$ particles) appreciably exceeded the dimensions D_c/V of the region subject to fluctuations. The chain grew to a length of 10^3 in 2–3 minutes of machine time on the IBM 7094 (the time increases with decreasing supersaturation).

The first group of initial parameters provided for a test of (3.14) for

$$\left. \begin{aligned} w_{+\alpha\beta} &= w_{\pm} c_{\beta}, & w_{\pm} &= 2, & c_A = c_B &= 0.5, \\ w_{-\alpha\beta} &= v e^{\varepsilon_{\alpha\beta} T}, & \varepsilon_{AA} &= \varepsilon_{BB}; & \varepsilon_{AB} &= 2\varepsilon_{AA}, \\ v &= 3, & R &= 3/2, & q &= 0.5. \end{aligned} \right\} \quad (7.1)$$

The results of the experiments, together with the

Value of parameters (formula number)	x_A		x_B		x_{AB}		x_{BA}	
	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.
(7.1)	0.500 0.499 0.500	0.500	0.500 0.501 0.500	0.500	0.297 0.294 0.297	0.296	0.297 0.295 0.297	0.296
(7.2)	0.606 0.603 0.621 0.621	0.608	0.394 0.397 0.379 0.379	0.392	0.296 0.270 0.278 0.278	0.270	0.269 0.270 0.278 0.278	0.270
(7.3)	0.868 0.877	0.877	0.132 0.123	0.123	0.115 0.111	0.110	0.115 0.112	0.110
Value of parameters (formula number)	x_{AA}		x_{BB}		v		Mean number of steps for attachment of one particle (experimental)	
	exp.	theor.	exp.	theor.	exp.	theor.		
(7.1)	0.202 0.204 0.202	0.204	0.203 0.206 0.203	0.204	0.913 0.940 0.913	0.943	3.5	
(7.2)	0.336 0.333 0.342 0.345	0.338	0.125 0.126 0.101 0.100	0.122	0.424 0.423 0.340 0.339	0.406	10.5	
(7.3)	0.753 0.766	0.766	0.017 0.011	0.013	0.304 0.278	0.303	9.5	

values calculated from (7.1), are given in the first row of the table, which contains values of x_{α} , $x_{\alpha\beta}$, and V . The rate expresses the mean number of particles attaching per unit time. The time scale is determined by the rate w_+ . The last column of the table contains the experimental numbers obtained by dividing the number of particles in the chain by the total number of attachments and detachments required to build it. The second row of the table corresponds to the values (in the notation of (3.11)):

$$\left. \begin{aligned} w_{+\alpha\beta} &= 1, & w_{-\alpha\beta} &= \nu_{\beta} e^{\epsilon_{\alpha\beta}/T}, \\ m &= 2, & n &= 1, & q &= 0,7, & \nu_A &= 2, & \nu_B &= 4. \end{aligned} \right\} \quad (7.2)$$

The lack of symmetry in the properties of the particles is expressed here in differing "vibrational frequencies" ν_{β} . The third row also provides for dissymmetry in the rates of incidence:

$$\left. \begin{aligned} w_{+AA} &= 1, & w_{+AB} &= 0,7, & w_{+BA} &= 0,2, & w_{+BB} &= 0,3, \\ w_{-\alpha\beta} &= \nu_{\beta} e^{\epsilon_{\alpha\beta}/T}, & m &= 2, & n &= 1, \\ a &= 0,5, & \nu_A &= 1,5, & \nu_B &= 6. \end{aligned} \right\} \quad (7.3)$$

The theoretical values for cases (7.2) and (7.3) were found by numerical solution. Several trials were made for each set of parameters, with different values of the starting point in the random-number generator program. Hence there are several numbers in all the columns containing experimental data. The table indicates good agreement between the calculated and experimental values, and again confirms the exactness of the developed theory.

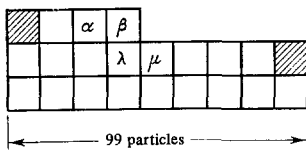


FIG. 16

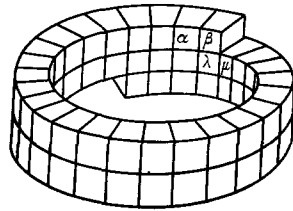


FIG. 17

FIG. 16. A kink at the edge of a two-dimensional crystal.

FIG. 17. Cyclic edge conditions in the construction of a two-dimensional net on a computer lead to building a helical structure.

8. Growth of a Binary Net

In these experiments, a binary two-dimensional crystal grew by motion of a single kink along its edge (Fig. 16). When the kink had advanced to the right to the end of a horizontal row of atoms, the program provided for possibility of attachment of new particles to the beginning of the next row, so that growth of the crystal took place by winding a row of atoms upon itself (Fig. 17). The rates of attachment and detachment obeyed the equations

$$w_{+}(\alpha\beta) = 1, \quad w_{-\alpha\beta} = \nu e^{(\epsilon_{\alpha\beta} + \epsilon_{\lambda\beta})/T}, \quad n = 1, \quad m = 2, \quad (8.1)$$

This predetermined the equivalence of the A and B particles and the actually-observed equality of their concentrations ($x_A = x_B = 0.5$). The object of study was the order of distribution of the particles over the lattice sites.

The program for motion of a kink was written in the same way as that for motion of the end of a chain (Sec. 7). However, the rates now depended on three indices (see (8.1)). The growing crystal consisted of rows of 99 particles each (see Fig. 16). Crystallization began with ordered and disordered seeds having different concentrations of A and B, and consisting of ~300 particles (~3 rows). The parameter varying from trial to trial was the ratio $R = \nu/w_+$. For a constant vibration rate ν , this meant a change in the vapor pressure in the system. The temperature T of the crystal was assumed constant: $q = 0.1$.

The experiments showed that equilibrium of a disordered seed with the medium occurs at $\bar{R}_d = 6.15 \times 10^3$ ($\bar{R}_d^{-1} = 1.54 \times 10^{-4}$), while an ordered seed does not change in dimensions for a rather long period when $\bar{R}_o = 9.774 \times 10^3$ ($\bar{R}_o^{-1} = 1.03 \times 10^{-4}$). This phenomenon is quite natural, and is explained by the difference in chemical potentials between an ordered and a disordered crystal. Correspondingly, the equilibrium vapor pressure over an ordered crystal is less than over a disordered crystal. Here the relative difference between these pressures (the relative supersaturation that the

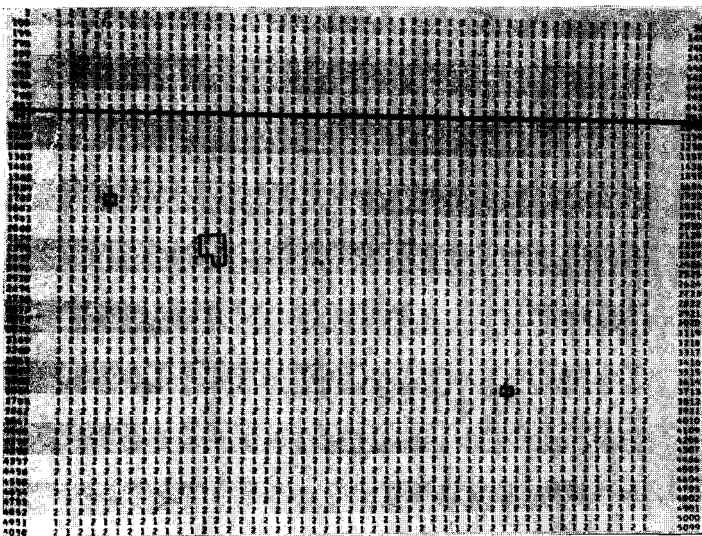


FIG. 18. A two-dimensional crystal grown at a supersaturation of ~14%.

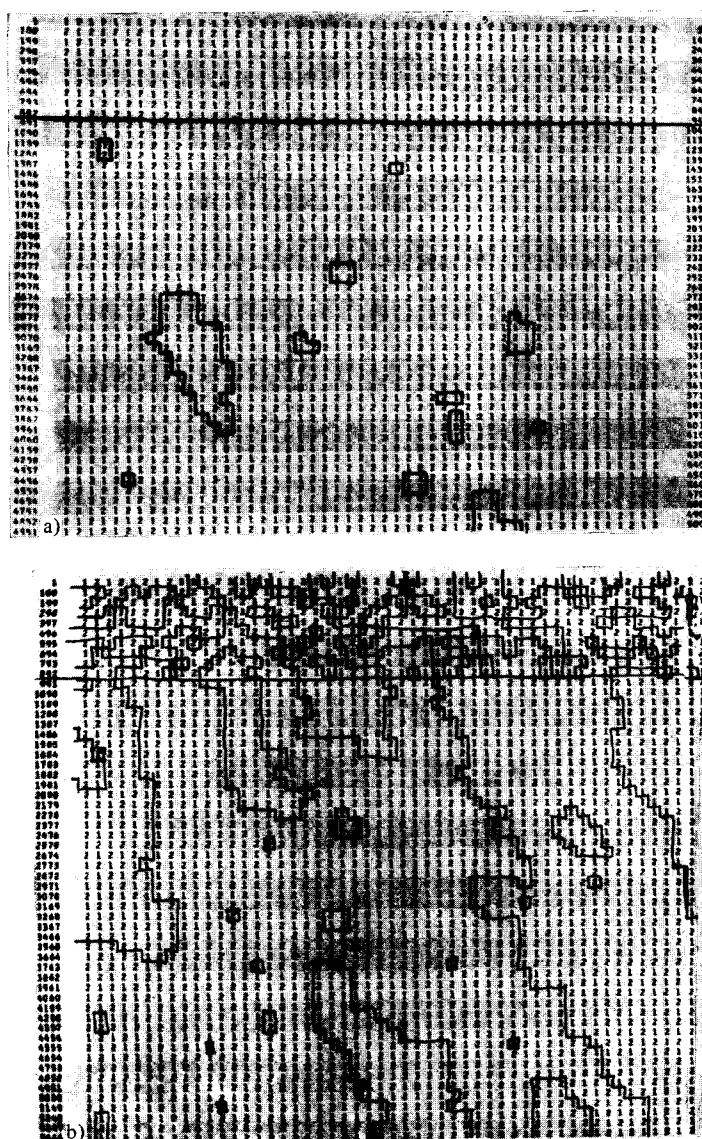


FIG. 19. A two-dimensional crystal grown at a supersaturation of $\sim 230\%$; a) on an ordered seed; b) on a disordered seed.

one crystal could create over the other) $(\bar{R}_d^{-1} - \bar{R}_0^{-1})/\bar{R}_0^{-1}$ was quite appreciable, being $\sim 50\%$.

The relation of the crystal structure to the rate of crystallization (or the supersaturation) was determined in experiments with ideally ordered seeds. The structures of the two-dimensional crystals are shown in Fig. 18–20, which are photocopies of the printout of the machine. The numerals 1 indicate particles of type A, and the numerals 2 indicate particles of type B. The crystal, a region of which is shown in Fig. 18, was grown at $R^{-1} = 1.17 \times 10^{-4}$, i.e., at a supersaturation of $\sim 14\%$. This region is practically completely ordered. Its only defects are two misplaced atoms and a small (5-particle) antiphase domain. At $R^{-1} = 3.3 \times 10^{-4}$, which corresponds to a supersaturation of $\sim 230\%$, the crystal now contains a considerably higher density of boundaries of antiphase domains (Fig. 19a). When $R^{-1} = 10 \times 10^{-4}$, i.e., at a vapor pressure ten times as high as the equilibrium pressure, the density of domain boundaries

is so great that it is almost impossible to discern ideally-ordered regions of dimensions greater than ten interatomic distances (Fig. 20). It is evident from what I have said that it is practically impossible to grow a perfect crystal (in the sense of lacking domain boundaries) on a disordered seed, since growth on this seed begins only at supersaturations that ensure an appreciable density of defects.

In growth on a disordered seed, the domain boundaries run directly from the seed into the body of the crystal. However, the mean density of boundaries at a sufficient distance from the seed does not depend on how many defects it has (Fig. 19b).

Single domains (arising at supersaturations of 20–30%) have the form of bands stretched out at a small angle to the direction of motion of the crystallization front, as we see in Fig. 21 (in this case, we mean by the front the row of atoms along which the kink moves). Sometimes a domain tapers off before the end

of the crystallization, but considerably more often, it continues to the edge of the crystal (Fig. 21). The elongated shape of the domains is quite natural: approach of two boundaries implies approach of their exit points on the growth front, and an increase in the local density of surface energy. Hence, it has a low probability. The interaction between the exit points of the boundaries at the growth front, which determines the mechanism of this repulsion, is purely correlational, and is effected by the kink.

With decreasing supersaturation, the radius D_c/V of correlational interaction increases. This means also that the width of each domain strip must increase in proportion to D_c/V (D_c is the diffusion coefficient of the kink). While each domain will be practically completely ordered, the order of the crystal as a whole will approach zero as its dimensions increase.

Figure 22 shows the relation of the rate of motion of the kink to the "vapor pressure" in the system, i.e., the parameter $R^{-1} = w_s/\nu$. The velocity of the kink was calculated as the number of particles deposited per total

time calculated by the machine, $\sum_{\alpha\beta} N \binom{\alpha\beta}{\lambda} \tau \binom{\alpha\beta}{\lambda}$,

where $N \binom{\alpha\beta}{\lambda}$ is the number of cases in which the kink is formed by the triplet $\alpha\beta$. The effect of a single anti-phase domain on the growth rate could be traced in a trial with $R^{-1} = 1.25 \times 10^{-4}$ (a supersaturation of $\sim 20\%$): the velocity of the kink was 0.318 before the domain had appeared, but 0.297 afterward.

9. Growth of a Three-Dimensional Crystal

The main content of the experiments described below on three-dimensional crystallization was to test the hypothesis of kinetic phase transitions (Sec. 6).

Crystallization in the three-dimensional case was also simulated by motion of a single kink along a step (see Fig. 8). The probabilities of attachments and detachments were determined by the expressions (6.3), while the time of crystallization was calculated, as in Sec. 8, by the formula

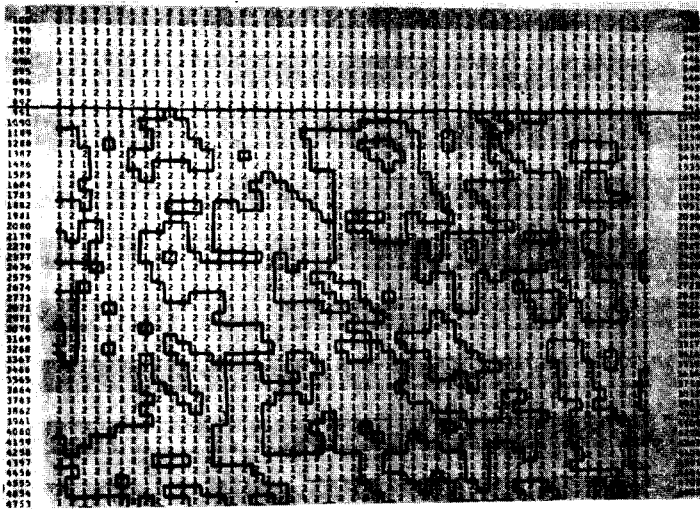


FIG. 20. A two-dimensional crystal grown at a supersaturation of 100%.

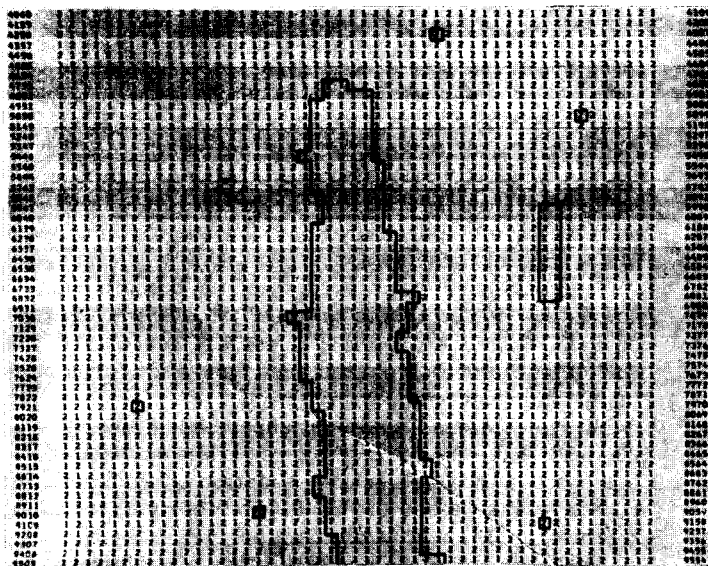


FIG. 21. A solitary domain in the form of a strip at a supersaturation of 25%.

where
$$\tau(\alpha\beta_{\lambda\mu}^{xy}) = (w_-(\alpha\beta_{\lambda}^x) + \sum_{\gamma} w_+(\beta\gamma_{\lambda}^y))^{-1}$$

The program for motion of the kink applied not only cyclic conditions in going from row to row within a given layer, but also from layer to layer: the last row of the preceding layer was considered to adjoin the first row of the next layer. Each row consisted of 99 particles, and each layer of 49 rows, i.e., of 4851 particles, while the entire crystal had 32 layers, i.e., 1.5×10^5 particles. Under the described cyclic conditions, the

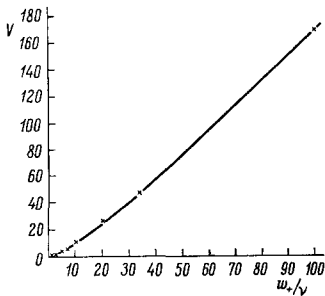


FIG. 22. Rate of motion of the kink as a function of the vapor pressure in the system.

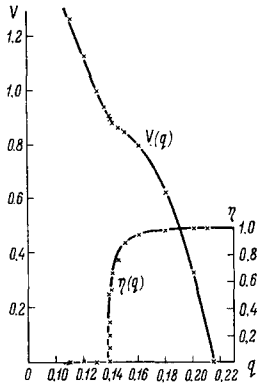


FIG. 23. Degree of long-range order η and velocity V of the kink as functions of the temperature of the crystal for a fixed composition of the medium with $R = 10^4$.

geometric shape of the crystal is a torus having one kink on the surface.

The three-dimensional crystallization was performed with equivalent particles A and B, since it was assumed

that $w_+(\frac{\kappa}{\alpha\beta}) = w_+$ for any α, β, κ , and λ :

$$w_-(\frac{x}{\alpha\beta}) = \nu e^{(\epsilon_{\alpha\beta} + \epsilon_{x\beta} + \epsilon_{\lambda\beta})/T},$$

$$\epsilon_{AB} = \epsilon_{BA} = 2\epsilon_{AA} = 2\epsilon_{BB}.$$

Two series of trials were run for two fixed values of the ratio $R = \nu/w_+$: 10^4 and 10^6 . The sought quantities were the velocity of motion of the kink and the degree of long-range order η .

Figure 23 shows the results for $R = 10^4$. The $\eta(q)$ curve clearly shows the existence of a critical value $q_{CR} = 0.1385$ at which η vanishes. That is, transition occurs from an ordered to a disordered phase. The trial for $R = 10^6$ gives $q_{CR} = 0.046$. Equilibrium between the crystal and the medium occurs at $\bar{q} = 0.215$ for $R = 10^4$, and $\bar{q} = 0.10$ for $R = 10^6$. Since both of the corresponding equilibrium temperatures are below the Curie temperature, the crystals at equilibrium and near it are almost completely ordered.

The binary correlation function $(x_{AB}/x_A x_B) - 1$, which determines the degree of short-range order, has a cusp at $q = q_{CR}$ (Fig. 24).

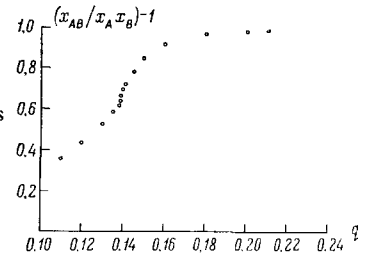
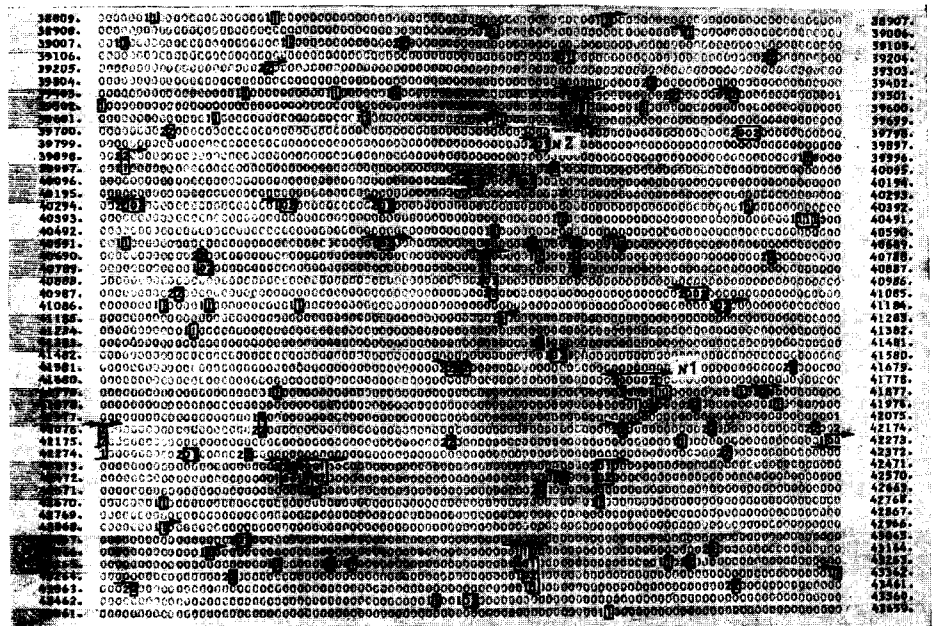


FIG. 24. Short-range order as a function of the temperature of crystallization.

FIG. 25. The ninth layer of a 32-layer three-dimensional crystal grown by shuttle motion of a single kink.



The structure of a crystal grown at low supersaturations is highly perfect. As in the two-dimensional case, it is disturbed only by isolated atoms occurring in foreign sites, as well as by small antiphase domains. The number of these defects increases with increasing supersaturation. Figure 25 shows the ninth layer of a crystal grown at $q = 0.16$ for $R = 10^4$, and having $\eta = 0.947$. The regions filled with zeroes have a perfect structure. The domain boundaries are sketched in. The domains that extend into the previous layer are indicated by arrows to the left, while arrows to the right are drawn from those that extend into the next layer. New volume domains begin most often with the formation of nuclei, or planar domains of two or three, or much more rarely of five or six particles. The shape of the domains is rather isometric. For example, the number of particles in the cross-section of domain No. 2 by the growth front varies thus: 6, 11, 11, 4. Domain No. 1 ends in the layer shown in Fig. 25, and has 2, 9, 8, and 6 particles in the previous layers. The reason for such substantial difference in shape of domains in two- and three-dimensional crystals consists in the fact that, in the latter case, a single domain emerges at the growth front with a closed contour that tends to contrast its length (i.e., the surface energy of the domain wall) upon growth of the next layer. This leads to rapid tapering-off of volume domains.

The number of domains declines rapidly with increasing dimensions. If domain formation obeyed the thermodynamic theory of fluctuations (the theory of nucleation), then we should expect the logarithm of the density of domains of a given size to decline linearly as their surface energy increases. However, the decline is actually slower. This is still another confirmation of the inapplicability of a purely thermodynamic treatment to the problem of the defect content of a growing crystal.

The velocity of motion $V(q)$ of the kink is shown in Fig. 23. In the region of values $q \sim q_c$, where $\eta \sim 1$ and varies slowly, the growth rate increases almost linearly with decreasing q . However, as we approach q_{cr} , the growth rate increases more slowly, while the function $V(q)$ has a cusp at $q = q_{cr}$. Apparently, the reason for this consists in the fact that the decrease in the long-range order η in the region $q \gtrsim q_{cr}$ increases the chemical potential of the crystal. In turn, this reduces the effective supersaturation in comparison with the value corresponding to $\eta \sim 1$ and the given value of q . After η has vanished, the crystal structure varies slightly, and only with regard to short-range order. Hence, the $V(q)$ relation for $q < q_{cr}$ resumes its previous almost-linear trend.

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