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Abstract

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CRYSTALLIZATION OF A MULTICOMPONENT CHAIN

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The elementary acts in the formation of a crystal or polymer chain are the acts of attachment and detachment of individual particles (atoms, molecules, etc.). It may apparently be assumed (especially in growth from the gas phase) that each of these acts occurs randomly and independently of the preceding one, and a probabilistic approach to the crystallization process may be carried out.

Let us consider a semi-infinite chain composed of arbitrary particles of n kinds. We shall denote the kinds of particles by $a, b, c, \ldots$. A chain ending with a group of particles α, β, γ will be written in the form $(\ldots\alpha\beta\gamma)$, where each of the letters α, β, and γ takes the values $a, b, c, \ldots$, and where the dots symbolize the particles preceding α. Let the medium surrounding the chain also consist of particles $a, b, c, \ldots$, which may attach themselves to the end of the chain. Suppose that the frequency of attachment of a particle of kind β to a chain ending with a particle of kind α is $w_{+\alpha\beta}$ and does not depend on particles situated in the chain more deeply than α. Any particle β situated at the end of the chain $(\ldots\alpha\beta)$ may leave the chain with frequency $w_{-\alpha\beta}$, likewise not depending on elements more deeply situated than α. We shall first use discrete time, i.e., assume that attachment or detachment of particles occurs only at separate instants. Then at each of these instants, for the chain $(\ldots\alpha\beta)$ there are $m+1$ possibilities: either to attach a particle γ $(\gamma = a, b, c, \ldots)$ and pass into one of the configurations $(\ldots\alpha\beta\gamma) = (\ldots\alpha\beta a), (\ldots\alpha\beta b) \ldots$, or to lose the particle β and become $(\ldots\alpha)$. The probabilities of the corresponding transitions are equal to

$$p_{(\ldots\alpha\beta)\to(\ldots\alpha\beta\gamma)}^{\alpha\beta\gamma} = \frac{w_{+\beta\gamma}}{w_{-\alpha\beta} + \sum_\gamma w_{+\beta\gamma}}, \qquad q_{(\ldots\alpha\beta)\to(\ldots\alpha)}^{\alpha\beta} = \frac{w_{-\alpha\beta}}{w_{-\alpha\beta} + \sum_\gamma w_{+\beta\gamma}}. \quad (1)$$

Here and below the summation is carried out over all kinds $a, b, c, \ldots$. Successive random attachments and detachments of particles lead to the end of the chain performing random walks. At equilibrium of the chain with the medium, the directed motion of the end in either direction is absent. In the case of growth of the chain, its end, while continuing to perform fluctuations, moves on average in the direction of elongation of the chain, and in the case of decay—in the direction of its shortening. The problem is to find the structure of the growing chain and the rate of its elongation, if the quantities $w_{\pm\alpha\beta}$ are known.

We shall characterize the required structure by the probability $x_{\alpha\beta}$ of encountering, in the depth of the chain, a pair of adjacent particles α and β. In other words, $x_{\alpha\beta}$ is the fraction of pairs $\alpha\beta$ among all the pairs present in the chain.

The probability $x_\alpha = \sum_\beta x_{\alpha\beta}$ is the relative concentration in the chain of particles of kind α, i.e.,

$$\sum_{\alpha\beta} x_{\alpha\beta} = \sum_\alpha x_\alpha = 1. \tag{2}$$

It is further obvious that

$$\sum_\beta x_{\alpha\beta} = \sum_\beta x_{\beta\alpha} = x_\alpha. \tag{3}$$

It should be emphasized that the probabilities $x_{\alpha\beta}$ and x_α refer to the finally formed, "frozen" part of the chain, which is situated so far from its end that it is never destroyed during its wanderings in the course of growth.

To formulate and solve the equations obeyed by $x_{\alpha\beta}$, it is necessary to introduce the probabilities $U_{\alpha\beta}$ and $P_{\alpha\beta}$, to which we now turn.

Choose arbitrarily N chains $(\dots\alpha\beta)$. In the course of growth, through exchange of particles with the medium, some of them will lose only particle β, others β and α, and so on. There will, however, also be some which in the course of growth will lengthen to infinity without losing any of the particles $(\dots\alpha\beta)$ that were present at the initial moment. We denote the fraction of chains of this latter type relative to all those selected by $U_{\alpha\beta}$. Equations for the probabilities $U_{\alpha\beta}$ were obtained by the author in ([1]). Here we shall use another method, proposed by A. N. Kolmogorov in a discussion with him of the results of this work. Namely, of the N chains $(\dots\alpha\beta)$, as a result of all subsequent steps $NU_{\alpha\beta}$ of them are preserved. On the other hand, after the first step $Np_{\alpha\beta\gamma}$ chains will pass into the state $(\dots\alpha\beta\gamma)$. Of these, as a result of all subsequent steps, those which are preserved entirely, and hence preserve also the configuration $(\dots\alpha\beta)$, number

$$N\sum_\gamma p_{\alpha\beta\gamma}U_{\beta\gamma}$$

while

$$N\sum_\gamma p_{\alpha\beta\gamma}(1-U_{\beta\gamma})$$

are destroyed. But each of the disintegrating chains $(\ldots\alpha\beta\gamma)$ must sooner or later turn into a chain $(\ldots\alpha\beta)$, and therefore from the

$$N \sum_{\gamma} p_{\alpha\beta\gamma}(1 - U_{\beta\gamma})$$

disintegrating chains $(\ldots\alpha\beta\gamma)$, the configuration $(\ldots\alpha\beta)$ will be preserved by

$$NU_{\alpha\beta} \sum_{\gamma} p_{\alpha\beta\gamma}(1 - U_{\beta\gamma})$$

of them. Thus, in all, from N chains $(\ldots\alpha\beta)$ there will be preserved

$$N \sum_{\gamma} p_{\alpha\beta\gamma} \left[U_{\beta\gamma} + (1 - U_{\beta\gamma})U_{\alpha\beta}\right]$$

specimens. Consequently,

$$U_{\alpha\beta} = \sum_{\gamma} p_{\alpha\beta\gamma} \left[U_{\beta\gamma} + (1 - U_{\beta\gamma})U_{\alpha\beta}\right]. \tag{4}$$

The permanent preservation of the chain $(\ldots\alpha\beta)$ occurs by the permanent addition to it of a particle of some kind γ, i.e., by the formation of the chain $(\ldots\alpha\beta\gamma)$. Let us find the probability of this transformation $P_{\ldots\alpha\beta\gamma}$ $\left(\sum_{\gamma} P_{\ldots\alpha\beta\gamma} = 1\right)$. Consider again N arbitrary chains $(\ldots\alpha\beta)$. Of these, as a result of the first step, $Nq_{\alpha\beta}$ will disintegrate, while $Np_{\alpha\beta\gamma}$ will turn into chains $(\ldots\alpha\beta\gamma)$. Among the latter, $Np_{\alpha\beta\gamma}U_{\beta\gamma}$ will be preserved forever, while

$$N \sum_{\gamma} p_{\alpha\beta\gamma}(1 - U_{\beta\gamma})$$

will return to the state $(\ldots\alpha\beta)$.

As a result of the second attempt there will arise

$$N \left[\sum_{\gamma} p_{\alpha\beta\gamma}(1 - U_{\beta\gamma})\right] p_{\alpha\beta\gamma}U_{\beta\gamma}$$

preserved chains $(\ldots\alpha\beta\gamma)$, and

$$N \left[\sum_{\gamma} p_{\alpha\beta\gamma}(1 - U_{\beta\gamma})\right] q_{\alpha\beta}$$

chains will disintegrate. Continuing the reasoning, we obtain that of the N selected chains $(\dots\alpha\beta)$, the following number will pass, without disintegrating, into the state $(\dots\alpha\beta\gamma)$:

$$Np_{\alpha\beta\gamma}U_{\beta\gamma}\left\{1+\left[\sum_{\gamma}p_{\alpha\beta\gamma}(1-U_{\beta\gamma})\right]+\left[\sum_{\gamma}p_{\alpha\beta\gamma}(1-U_{\beta\gamma})\right]^2+\dots\right\}=\frac{Np_{\alpha\beta\gamma}U_{\beta\gamma}}{1-\sum_{\gamma}p_{\alpha\beta\gamma}(1-U_{\beta\gamma})}=\frac{NU_{\alpha\beta}p_{\alpha\beta\gamma}U}{\sum_{\gamma}p_{\alpha\beta\gamma}U_{\beta}} \tag{5}$$

pieces, and $NU_{\alpha\beta}q_{\alpha\beta}/\sum_{\gamma}p_{\alpha\beta\gamma}U_{\beta\gamma}=N(1-U_{\alpha\beta})$ pieces will decay. In deriving these formulas, equations (4) were used. From (5) it follows that the fraction of chains $(\dots\alpha\beta)$ that are preserved by the attachment of γ, relative to all preserved chains, is

$$P_{\dots\alpha\beta\gamma}=\frac{p_{\alpha\beta\gamma}U_{\beta\gamma}}{\sum_{\gamma}p_{\alpha\beta\gamma}U_{\beta\gamma}}=\frac{w_{+\beta\gamma}U_{\beta\gamma}}{\sum_{\gamma}w_{+\beta\gamma}U_{\beta\gamma}}=P_{\beta\gamma}. \tag{6}$$

Consequently,

$$x_{\beta\gamma}=x_{\beta}P_{\beta\gamma}, \tag{7}$$

and the probability of the configuration $\dots\alpha\beta\gamma\delta$ is $x_{\dots\alpha}P_{\alpha\beta}P_{\beta\gamma}P_{\gamma\delta}$.

Among the m^2 equations (7), only m^2-m are linearly independent, since summation of (7) over γ turns them into m identities. The system becomes complete if the relations (2) and (3) are taken into account. Its solution in the case of two components a and b has the form

$$x_{aa}=\frac{\Phi_{aa}\Phi_{ba}}{\Phi_{ab}\psi_b+\Phi_{ba}\psi_a},\qquad x_{bb}=\frac{\Phi_{bb}\Phi_{ab}}{\Phi_{ab}\psi_b+\Phi_{ba}\psi_a},$$

$$x_{ab}=x_{ba}=\frac{\Phi_{ab}\Phi_{ba}}{\Phi_{ab}\psi_b+\Phi_{ba}\psi_a}, \tag{8}$$

where $\Phi_{\alpha\beta}=w_{+\alpha\beta}U_{\alpha\beta}$ and $\psi_{\alpha}=\sum_{\beta}\Phi_{\alpha\beta}$. Formulas (8) determine the desired structure of the chain.

Let us now denote by $x_{1\alpha}$ the fraction of continuous time during which a particle α is present at the end of the crystallizing chain $\left(\sum_{\alpha}x_{1\alpha}=1\right)$. Then the rate of chain elongation is

$$V=\sum_{\alpha\beta}x_{1\alpha}w_{+\alpha\beta}U_{\alpha\beta}=\sum_{\alpha}x_{1\alpha}\psi_{\alpha}. \tag{9}$$

The quantity V is the total number of particles permanently attaching to the chain per unit time. The fraction of pairs $\alpha\beta$ formed in this process is

$$\frac{x_{1\alpha} w_{+\alpha\beta} U_{\alpha\beta}}{\sum_{\alpha\beta} x_{1\alpha} w_{+\alpha\beta} U_{\alpha\beta}} = \frac{x_{1\alpha}\Phi_{\alpha\beta}}{\sum_{\alpha} x_{1\alpha}\psi_{\alpha}} = x_{\alpha\beta}. \tag{10}$$

Summing equations (10) over β, then solving them with respect to $x_{1\alpha}$ and substituting the result into (9), we obtain the rate of chain elongation. In the case of two components

$$x_{1a} = \frac{\Phi_{ba}}{\Phi_{ab} + \Phi_{ba}}; \qquad x_{1b} = \frac{\Phi_{ab}}{\Phi_{ab} + \Phi_{ba}}; \qquad V = \frac{\Phi_{ab}\psi_b + \Phi_{ba}\psi_a}{\Phi_{ab} + \Phi_{ba}}. \tag{11}$$

In the case of two components it is easy to verify that equations (10), together with the normalization conditions for $x_{1\alpha}$, x_{α}, and the condition $x_{ab} = x_{ba}$ following from (3), make it possible to find both $x_{1\alpha}$ and $x_{\alpha\beta}$. (The result of calculating $x_{\alpha\beta}$, of course, coincides with (8).) Therefore, using equations (10) together with the indicated conditions in fact represents another method of solving the problem, without using the probabilities $P_{\alpha\beta}$.

Analogously to the one-dimensional-chain case considered here, one may pose the problem of the formation of two- and three-dimensional Kossel crystals, where attachment and detachment of particles occur, respectively, at two- and three-dimensional reentrant corners (kinks). This is already a problem of collective interaction, which makes it very complex. However, it is precisely collective interaction that can lead to the interesting effect of "phase

transition." Indeed, a crystal formed at small deviations from equilibrium must have a thermodynamically equilibrium structure from the point of view of the arrangement of particles of different kinds. At temperatures lower than the Curie temperature, this structure is ordered. Conversely, at large supersaturations, when practically any particle that reaches the kink remains in it, the distribution of different particles in the crystal obtained from a disordered medium will also be disordered. Therefore, if the thermodynamically equilibrium structure is ordered and if exchange of positions between particles in the lattice is impossible, then the cooperativity of the crystallization phenomenon may lead to the existence of some narrow region of supersaturations—or, perhaps, even of a single supersaturation—at which a transition from order to disorder occurs. In this case there should take place a peculiar "phase transition," in which the role of temperature is played by the supersaturation.

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[1] A. A. Chernov, Coll. Intern. CNRS, No. 152, 1965, p. 283.

Note: Figure translations are in progress. See original paper for figures.