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WITH ASYMMETRIC SINGLE ELEMENTS**

**I. EQUILIBRIUM ORIENTATION
DISTRIBUTION**

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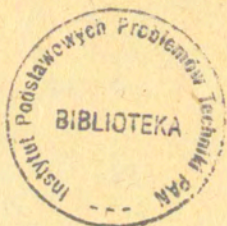


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THE THEORY OF ORIENTED NUCLEATION WITH ASYMMETRIC SINGLE
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INTRODUCTION.

Kinetic theory of nucleation prepared in late forties by Turnbull and Fisher¹ was successfully used by many authors for the interpretation of phase transitions like crystallization in melts and solutions, condensation of vapors, or microcracks formation in solids²⁻⁴. The classical theory of Turnbull and Fisher assumes spherical symmetry and isotropy of single elements involved in the nucleation process. Nevertheless, the theory provides reasonable results not only for metals or inert gases, but also for isotropic materials of asymmetric and/or anisotropic particles, i.e. in polymers⁵⁻⁷.

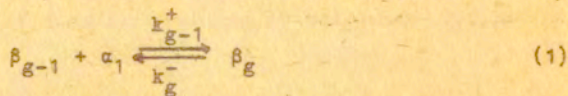
The present paper shows, that the classical theory of nucleation can not be used to discuss phase transitions in preoriented systems of asymmetric particles, and proposes a new revised theory of nucleation. The proposed theory converges qualitatively to the classical one for the case of isotropic systems of asymmetric particles, providing an explanation for the apparent validity of the classical approach for such systems.

The basic assumption of the new approach is that a proper

orientation of an asymmetric single element is required (with respect to the asymmetric growing cluster) to have the single element attached. In fact the idea was already introduced by Ziabicki^{8,9} a few years ago. In those papers the classical theory was modified by reducing the effective molar fraction of single elements involved in the cluster growth due to the requirements of a proper orientation. This modification introduced rather intuitively led to several qualitatively new conclusions, but also predicted much stronger effects on the orientation distribution of resulting crystals⁹ than it should be expected. Difficulties concerned also the question how to calculate the reduced molar fraction of the elements, and physical interpretation of the modification. The questions are answered in the present paper in which the fundamental equations of kinetics of cluster growth are developed starting with basic assumptions concerning the kinetics of bimolecular reactions of addition and dissociation.

RATE OF CLUSTER FORMATION IN ORIENTED SYSTEMS.

The classical assumption in the nucleation theories is that bimolecular reactions of addition and dissociation between a single element of the mother phase, α_1 , and a cluster composed of g elements, β_g , dominate over possible types of other reactions in such a system, and is decisive for the process. Thus, formation of aggregates of a new phase is described by the following hierarchy of coupled bimolecular reactions:



where g denotes size of the cluster defined as: $g = V_g/V_0$, i.e. volume of the cluster, V_g , reduced by the volume of a single element, V_0 . Kinetics of formation of the aggregates and, in particular, nucleation rate are controlled by the set of the rate constants: k_g^+ , k_g^- .

To discuss kinetics of the transformation (nucleation rate) one has to formulate a set of kinetic equations describing the net production rate of clusters at any step in the hierarchy (1). The equations should be completed by a continuity equations for the number of clusters with various sizes. The crucial point for this paper is the form of the kinetic equations, especially for asymmetric single elements involved in the aggregation process.

Let N_1 denote the number of single elements α_1 of the mother phase, and N_g the number of clusters of size $g(\beta_g)$ in the system. The system may also contain N_0 solvent particles playing a role of space filling elements. Probability that a bimolecular collision in the system is the desired collision of a cluster β_g and a single element α_1 is given by the product of the molar fractions of the specified elements: $[\beta_g] \cdot [\alpha_1]$, assuming that $[\beta_g]$ and $[\alpha_1]$ are independent.

$$[\beta_g] = \frac{N_g}{N_0 + \sum_{i=1}^{\infty} N_i} \quad (2a)$$

and

$$[\alpha_1] = \frac{N_1}{N_0 + \sum_{i=1}^{\infty} N_i} \quad (2b)$$

Following the classical theories of nucleation we assume that the concentration of clusters is negligibly small as compared with the concentration of single elements: $\Sigma [\beta_g] \ll [\alpha_1]$. With the assumption concentration of single elements can be expressed by the simple formula:

$$[\alpha_1] \approx \begin{cases} 1 & \text{for } N_0 = 0 \quad (\text{no solvent particles in the system}) \\ \frac{N_1}{N_0 + N_1} = c, & \text{c-molar concentration of the solution.} \end{cases} \quad (3)$$

To have a reference system for the discussion, spherical and isotropic single elements (α_1) will be assumed first. In such a system the net rate of production of clusters, β_g , can be obtained from the general laws of chemical kinetics:

$$J_g = k_{g-1}^+ [\beta_{g-1}][\alpha_1] - k_g^- [\beta_g]. \quad (4)$$

The first term in the formula being a bimolecular term of addition reaction is proportional to the fraction of the bimolecular collisions of clusters β_{g-1} with elements α_1 among the whole number of possible bimolecular collisions in the system. The second term responsible for dissociation is in fact proportional to the fraction of all collisions involving clusters β_g although it looks like a monomolecular term. Any collision of cluster β_g with any other element from the system may lead to the dissociation. The rate constants k_{g-1}^+ , k_g^- for addition and dissociation reactions, respectively, are expressed in reciprocal time, and thus the flux J_g is expressed in the same units.

Additional restrictions concerning effectivity of the

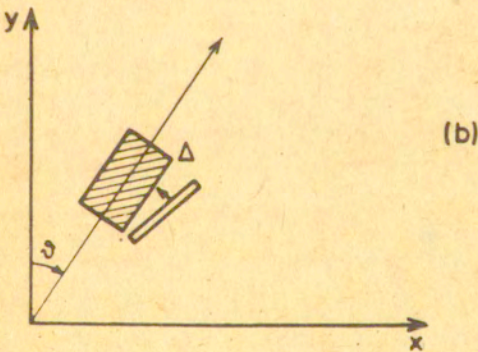
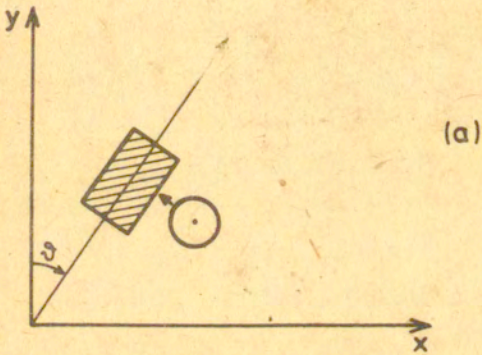


Fig.1. Cluster growth from spherical (a) and orientable (b) single elements. Δ - the tolerance angle.

bimolecular collisions should appear if the single elements, α_1 , are asymmetric in shape and/or anisotropic. It is obvious that a compliant orientations of an asymmetric element, α_1 , and the growing asymmetric cluster, β_g , are required to have an effective addition reaction during the collision time (Figure 1b). Nevertheless, fraction of single elements oriented exactly as the cluster is zero, and a requirement of exact orientations should lead to zero rate of the reaction of addition. In fact the collision time is short but finite, and during that time, Δt , the asymmetric colliding elements may adjust their orientations as a result of short range interactions and rotational Brownian motions. It is natural to assume some finite tolerance angle $\Delta \theta$ to determine the effective fraction of single elements with a favorable orientation. We discuss further the kinetics of aggregation for a system of oriented mother phase with orientation distribution of amorphous elements described by a normalized distribution function $w_1(\theta)$. The effective molar fraction of the elements with favorable orientation in such an oriented system is given by the following formula⁸:

$$[\alpha_1]_{\theta}^* = [\alpha_1] \int_{\theta - \frac{\Delta}{2}}^{\theta + \frac{\Delta}{2}} w_1(\theta) d\theta \quad (5)$$

$[\alpha_1]$ denotes molar fraction of single elements of the mother phase in the system. It allows us to propose a formula for a differential flux dJ_g^{θ} of clusters β_g oriented at θ within a differential angle $d\theta$:

$$dJ_g^\ominus = k_{g-1}^+ d[\beta_{g-1}]_\ominus [\alpha_1]_\ominus^* - k_g^- d[\beta_g]_\ominus \quad (6)$$

where $d[\beta_{g-1}]$ and $d[\beta_g]_\ominus$ denote the differential molar fraction of clusters β_{g-1} and β_g , respectively, oriented at \ominus . The rate constants k_{g-1}^+ , k_g^- are orientation independent. Introducing φ normalized orientation distribution functions of clusters of fixed sizes g , $\chi_g(\ominus)$ ($g = 2, 3, 4, \dots$), the differential molar fractions of clusters in formula (6) can be expressed by the following way:

$$d[\beta_g]_\ominus = [\beta_g] \chi_g(\ominus) d\ominus \quad (7)$$

where $[\beta_g]$ denotes the total molar fraction of clusters β_g in the system.

The differential flux (eq.6) completed with formulas (5) and (7) leads to the following expression describing angular distribution density of the flux:

$$j_g(\ominus) = \frac{dJ_g^\ominus}{d\ominus} = k_{g-1}^+ [\beta_{g-1}] [\alpha_1] \chi_{g-1}(\ominus) \int_{\ominus-\frac{\Delta}{2}}^{\ominus+\frac{\Delta}{2}} w_1(\ominus) d\ominus - k_g^- [\beta_g] \chi_g(\ominus) \quad (8)$$

We discuss two asymptotic cases of equation (8):

(a) very small tolerance angle, i.e. strong angular discrimination of single elements in the cluster formation process, $\frac{\Delta}{\Omega} \ll 1$,

(b) no angular restrictions, $\frac{\Delta}{\Omega} = 1$.

Ω denotes the full angle of the orientation space of the elements, $\Omega = \int_{\Omega} d\ominus$. For rodlike and spherical particles $\Omega = 4\pi$.

Formula (8) for the case of no angular restrictions leads to the classical formula (4).

For very small tolerance angles Δ , the angular distribution density assumes following asymptotic form:

$$j_g(\underline{\vartheta}) = k_{g-1}^+ [\beta_{g-1}] [\alpha_1] \chi_{g-1}(\underline{\vartheta}) w_1(\underline{\vartheta}) \Delta - k_g^- [\beta_g] \chi_g(\underline{\vartheta}) \quad (9)$$

The tolerance angle Δ appears only in the bimolecular term in formula (9) being responsible for the reaction of addition, but does not appear symmetrically in the dissociation term. It should considerably change the equilibrium constant of the transition and reduce the rate of cluster growth. The effect of angular discrimination for the addition reaction should be expected in oriented as well as in unoriented systems of asymmetric and/or anisotropic elements. For an unoriented, macroscopically isotropic system the total flux of clusters obtained integrating formula (9) with a uniform orientation distribution function of single elements, $w_1 = 1/\Omega$ evidently shows strong cut by the factor of Δ/Ω in frequency of the reaction of addition:

$$j_g^{izo} = \int_{\Omega} j_g(\underline{\vartheta}) d\underline{\vartheta} = k_{g-1}^+ \frac{\Delta}{\Omega} [\beta_{g-1}] [\alpha_1] - k_g^- [\beta_g] \quad (10)$$

($g = 2, 3, 4, \dots$)

The flux j_g^{izo} is similar in the form to the flux in a system of spherical single elements (eq.4). The difference concerns only the rate constant for the reaction of addition, k_{g-1}^+ . In conclusion, the model of cluster growth taking into account spherical single elements can be satisfactorily used for phase

transition processes in unoriented systems of asymmetric elements by modifying only the rate constant for the reaction of addition:

$$\tilde{k}_{g-1}^+ = k_{g-1}^+ \frac{\Delta}{\Omega} \quad (11)$$

The rate constant for dissociation is unchanged. $\tilde{k}_g^- = k_g^-$.

THERMODYNAMIC AND KINETIC ASPECTS OF THE PARAMETER Δ .

Theoretical analysis of the kinetics of chemical reactions based on the statistical thermodynamics provides some estimation for the steric factor $\frac{\Delta}{\Omega}$. In the absolute reaction theory¹⁰ the rate constants for the reaction of addition are expressed by the partition functions of the substrate particles, f_i , and the active complex, f^* :

$$k^+ = \frac{kT}{h} \frac{f^*}{\prod_i f_i} e^{-E^*/kT} \quad (12)$$

E^* denotes activation energy of diffusion, h is the Plank constant. On the other hand classical collision theory proposes an Arrhenius-type formula for the rate constant:

$$k^+ = P Z e^{-E^*/kT} \quad (13)$$

Z denotes a number of bimolecular collisions in a unit time, P is a steric factor introduced formally to fit the formula to experimental results. Often, the formal steric factor is on the

order of 10^{-8} - 10^{-9} , and considerably reduces the rate constants estimated from the frequency of bimolecular collisions, especially for more complex substrate particles. The steric factor P corresponds to the factor $\frac{\Delta}{\Omega}$ in our theory. Physical interpretation of the factor may result from comparison of the statistical absolute reaction theory (eq.12) and the classical collision theory (eq.13). The number of bimolecular collisions estimated by statistical thermodynamics is:

$$Z = \frac{kT}{h} \frac{f_R^2}{f_T^2} \quad (14)$$

f_R and f_T are the partition functions ^{of} rotational and translational motions of a substrate particle. It allows us to estimate the formally introduced factor Δ/Ω . We list some examples of the steric factor $\frac{\Delta}{\Omega}$ calculated for a few types of colliding particles:

(a) two atoms $\frac{\Delta}{\Omega} = 1$ (no steric restrictions)

(b) a particle composed of two atoms colliding with a multi-atomic particle:

$$\frac{\Delta}{\Omega} = \left(\frac{f_V}{f_R}\right)^4 \quad (15)$$

(c) for two colliding multiatomic particles:

$$\frac{\Delta}{\Omega} = \left(\frac{f_V}{f_R}\right)^5 \quad (16)$$

The ratio $\frac{f_V}{f_R}$ of the partition functions for vibrational and rotational motions ¹⁰ is on the order of 10^{-1} - 10^{-2} . The steric

factor estimated by the theory of active complex varies then from 1 for atoms to 10^{-10} for multiatomic particles. The theory provides a physical explanation for such a strong reduction in the rate constant calculated for multiatomic particles. It is related to loss of 3 translational and 3 rotational degrees of freedom when the active complex is formed and appearance of 6 vibrational degrees of freedom, instead. The low values of the steric factor are related to some steric conditions which should be satisfied for the internal and simultaneous redistribution of the degrees of freedom.

One can conclude that the tolerance angle Δ for asymmetric particles, i.e. rodlike single elements, should be very small, and the asymptotic formula for the angular distribution of the flux (eq.9) could be used. The formula can be rewritten in the following form using the reduced rate constant (eq.11):

$$j_g(\underline{\vartheta}) = \bar{k}_{g-1}^+ [\beta_{g-1}] [\alpha_1] \chi_{g-1}(\underline{\vartheta}) H(\underline{\vartheta}) - \bar{k}_g^- [\beta_g] \chi_g(\underline{\vartheta}) \quad (17)$$

($g = 2, 3, 4, \dots$)

where $H(\underline{\vartheta}) = \Omega w_1(\underline{\vartheta})$ denotes an orientation dependent factor which is higher or lower than unity in an oriented system, depending upon the angle $\underline{\vartheta}$:

$$H(\underline{\vartheta}) > 1 \text{ for the range of } \underline{\vartheta} \text{ where } w_1(\underline{\vartheta}) > 1/\Omega$$

$$\text{and } H(\underline{\vartheta}) < 1 \text{ for } w_1(\underline{\vartheta}) < 1/\Omega.$$

In the range of the orientation angle where $H(\underline{\vartheta}) > 1$ the flux is intensified by the orientation comparing to the unoriented system, while beyond that range the flux is lowered. In an unoriented system $H(\underline{\vartheta}) = \text{const.} = 1$.

In an unoriented system of asymmetric single elements the

reaction rate constants satisfy following thermodynamic condition at the state of equilibrium ($J_g^{iso} = 0$, eq.10):

$$\frac{\tilde{k}_{g-1}^+}{\tilde{k}_g^-} = \frac{[\beta_g]}{[\beta_{g-1}]} = \exp(-\delta\tilde{F}_g^0/kT) \quad (18)$$

We assume here that the system does not contain any solvent particles, $[\alpha_1] \ll 1$. $\delta\tilde{F}_g^0 = \tilde{\Delta F}_g - \tilde{\Delta F}_{g-1}$ denotes the difference in free energy of formation of clusters β_g and β_{g-1} . On the other hand

$$\frac{\tilde{k}_{g-1}^+}{\tilde{k}_g^-} = \frac{k_{g-1}^+}{k_g^-} \frac{\Delta}{\Omega} = \exp\{-[\delta F_g^0 - kT \ln(\Delta/\Omega)]/kT\} \quad (19)$$

where δF_g^0 is the difference in free energy of formation of clusters β_g and β_{g-1} expected for spherical single elements without any steric restrictions ($\Delta = \Omega = 4\pi$). The change in free energy accompanying cluster growth in unoriented systems of asymmetric single elements depends on the tolerance angle (cf. eq.18 and 19):

$$\delta\tilde{F}_g^0 = \delta F_g^0 - kT \ln(\Delta/\Omega) \quad (20)$$

The second term in eq.(20) related to the tolerance angle provides a positive contribution to the free energy of cluster formation ($\Delta/\Omega < 1$), and is purely entropic in nature as resulting from the classification of single elements into

effectively and uneffectively oriented in the system.

Formula (20) shows that the tolerance angle does not appear in fact as an additional model parameter in the theory, and the measured thermodynamic characteristics of the phase transition are already modified by the steric factor. Measured critical temperature, \bar{T}_{cr}^0 , of the phase transition in the un-oriented systems is also a function of the angle Δ :

$$\frac{1}{\bar{T}_{cr}^0} = \frac{1}{T_{cr}^0} - \frac{k}{|\Delta h^0|} \ln(\Delta/\Omega) \quad (21)$$

T_{cr}^0 denotes the critical temperature which should be expected for the system without any angular restrictions. Δh^0 is the heat of transformation per single element. Formula (21) shows that the steric effect related to the tolerance angle reduces the real critical temperature, \bar{T}_{cr}^0 , and the reduction is stronger for smaller Δ . The ratio \bar{T}_{cr}^0/T_{cr}^0 calculated on the basis of eq.(21) is plotted in Figure 2.

The equilibrium thermodynamic conditions can be determined for an oriented system assuming zero net production of clusters oriented at $\underline{\vartheta}$, and the equilibrium cluster size distribution of clusters oriented at a fixed angle $\underline{\vartheta}$ is given by:

$$\frac{[\beta_g] x_g(\underline{\vartheta})}{[\beta_{g-1}] x_{g-1}(\underline{\vartheta})} = \exp [-\bar{\delta F}_g(\underline{\vartheta})/kT] \quad (22)$$

The change in free energy $\bar{\delta F}_g(\underline{\vartheta})$ accompanying addition of a single element α_1 to a cluster β_{g-1} oriented at $\underline{\vartheta}$ can be expressed for the oriented system in the following form:

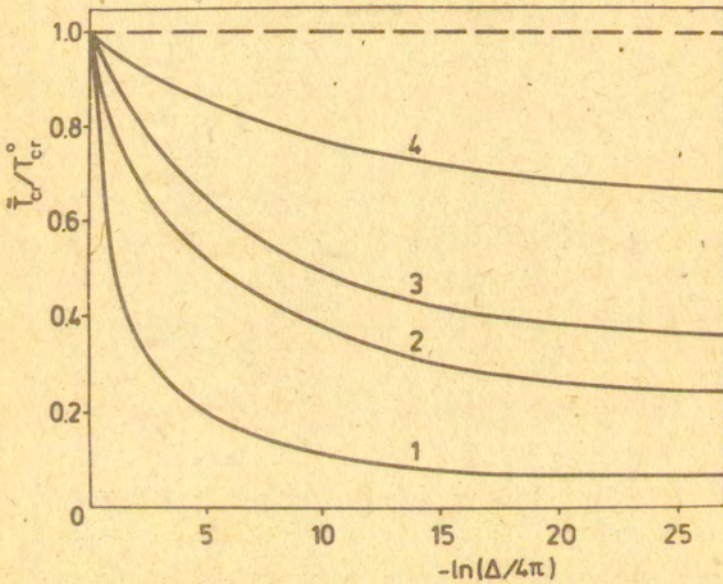


Fig.2. Depression of the critical temperature as a function of the tolerance angle Δ calculated for $kT_{cr}^0/|\Delta h^0|=1$ (1), 5 (2), 10 (3) and 20 (4).

$$\delta \tilde{F}_g(\underline{\vartheta}) = \delta \tilde{F}_g^0 - kT \ln(H(\underline{\vartheta})[\alpha_1]) \quad (23)$$

$\delta \tilde{F}_g^0$ is the change in free energy calculated for the system in ~~an~~ unoriented state (eq.20) without any solvent present. The second energy term in eq.(23) is related to the dilution of the system by a solvent, $[\alpha_1]$, as well as to orientation of single elements, $H(\underline{\vartheta})$. It is interesting to note that the tolerance angle Δ does not influence the thermodynamic effects of orientation. Critical transition temperature \tilde{T}_{cr} calculated for such an oriented system is a function of the dilution as well as the angle $\underline{\vartheta}$:

$$\frac{1}{\tilde{T}_{cr}(\underline{\vartheta})} = \frac{1}{\tilde{T}_{cr}^0} - \frac{k}{|\Delta h^0|} \ln(H(\underline{\vartheta})[\alpha_1]) \quad (24)$$

\tilde{T}_{cr}^0 is the critical temperature in the unoriented and undiluted system. Any dilution changes the energy of the transition (eq. 23) by the term $-kT \ln[\alpha_1]$ which is always positive, and obviously lowers the critical temperature, while the contribution to the energy resulting from the orientation distribution of single elements can be positive or negative, depending upon the angle $\underline{\vartheta}$. For some range of the orientation angle $\underline{\vartheta}$ the angular density of single elements is enhanced by the orientation, and $H(\underline{\vartheta}) > 1$. Beyond that range, where the angular density is lowered by the orientation, $H(\underline{\vartheta}) < 1$. The present theory leads to a general conclusion that critical temperature in oriented systems is a function of the orientation angle. To discuss the orientation effect on the critical temperature zero content of solvent particles is assumed ($[\alpha_1] = 1$). In the

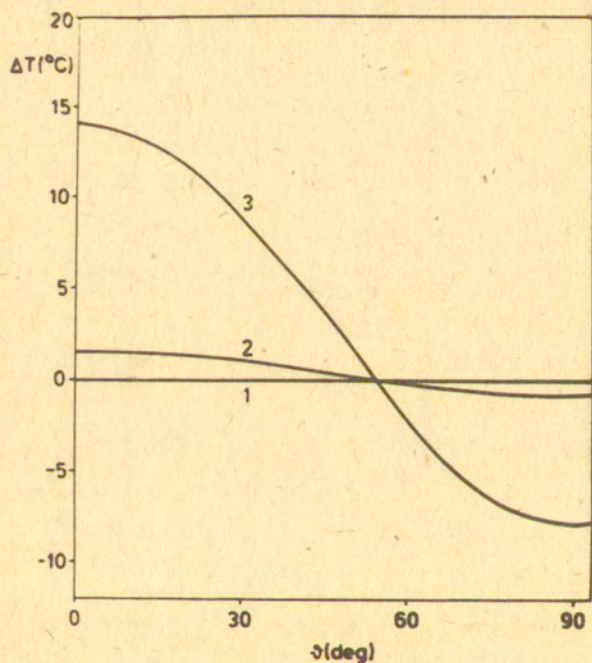


Fig.3. The supercooling effect as a function of the orientation angle ϕ calculated for polyethylene under uniaxial stress Δp . (1) $\Delta p=0$, (2) $\Delta p=10^6$ dynes/cm², (3) $\Delta p=10^7$ dynes/cm².

range of $\underline{\theta}$ where $H(\underline{\theta}) > 1$ the critical temperature predicted for the oriented system by eq.(24) is higher than the critical temperature in unoriented systems, and is lower beyond that range (Fig.3). It is interesting to note that orientation elevates the critical temperature, as it was widely accepted, but also decreases it in the same system depending upon the orientation angle $\underline{\theta}$.

ORIENTATION DISTRIBUTION OF SINGLE ELEMENTS.
EQUILIBRIUM AND STEADY-STATE DISTRIBUTIONS.

Orientation distribution of single elements, $w_1(\underline{\theta})$, appears as a primary function in the set of equations describing kinetics of cluster formation (crystallization), and affects thermodynamics of phase transitions in such systems. Orientation of single elements can be induced, depending on the nature of the orientable elements, by external electric or magnetic fields, or by mechanical forces. The elements subjected to an external steady orienting potential achieve the equilibrium state of orientation described by the normalized Boltzmann distribution

$$w_1(\underline{\theta}) = w_{eq}(\underline{\theta}) = e^{-U(\underline{\theta})/kT} / \int e^{-U(\underline{\theta})/kT} d\theta \quad (25)$$

$U(\underline{\theta})$ is an orientation-dependent potential energy of a single element in the field, i.e. energy of an electric (magnetic) dipole in an external electrostatic (magnetic) field. Mechanical forces may also lead to a Boltzmann-type equilibrium distribution in systems with some structural constraints (polymer networks with permanent crosslinks, where the statistical chain

segments are the orientable elements). For example, uniaxial elongation of a Gaussian polymer network leads to an equilibrium orientation distribution of the statistical segments¹¹, and the potential energy assumes following form for not too high deformations:

$$U(\phi) = U^0 - kT \ln \left[1 + \frac{p_{xx}}{2N\nu kT} (3 \cos^2\phi - 1) \right] \quad (26)$$

U^0 is an isotropic contribution to the energy, p_{xx} is the uniaxial stress, N - number of statistical segments in a chain, ν - number of chains in a unit volume of the network.

In systems subjected to a flow and dissipating energy (viscosity), steady-state orientation distribution of orientable particles can be achieved for steady and potential velocity fields, i.e. steady elongational flow. The steady-state orientation distribution is also a Boltzmann-type distribution¹² although it is not an equilibrium one:

$$w_{st}(\underline{\phi}) = \exp [-U^*(\underline{\phi})/kT] / \int_{\Omega} \exp [-U^*(\underline{\phi})/kT] d\underline{\phi} \quad (27)$$

$U^*(\underline{\phi})$ is an orientation-dependent flow potential of the hydrodynamic field. For rotational ellipsoids suspended in a viscous matrix^{9,13}:

$$U^*(\underline{\phi})/kT = - R\phi(\underline{\phi})/D_{rot} \quad (28)$$

$\phi(\underline{\phi})$ denotes potential of the velocity field, R is a shape factor, and D_{rot} is the rotational diffusion coefficient.

The change in free energy, $\delta\tilde{F}_g(\underline{\phi})$ calculated with the

equilibrium or steady-state orientation distribution of single elements assumes the following form:

$$\tilde{\delta F}_g(\underline{\xi}) = \tilde{\delta F}_g^0 + U(\underline{\xi}) + C \quad (29)$$

where C is an isotropic energy term:

$$C = -kT \left[\frac{\Omega}{\int \exp(-U(\underline{\xi})/kT) d\underline{\xi}} \right]$$

The potential energy $U(\underline{\xi})$ (or flow potential $U^*(\underline{\xi})$) contributes directly to the energy effect of the cluster growth as the only orientation-dependent term. The external field does not contribute to the energy of cluster formation only if the potential energy is isotropic ($U(\underline{\xi}) = \text{const.}$), and eq.(29) reduces to the isotropic form:

$$\tilde{\delta F}_g(\underline{\xi}) = \tilde{\delta F}_g^0 = \text{const.} \quad (30)$$

It was assumed that $[a_1] = 1$.

KINETICS OF ORIENTED NUCLEATION.

The general conservation law for the number of elements in the systems (including clusters) will be formulated in a space defined as a Cartesian product $g \times \Omega$ of a space of the cluster size, g , and the orientation angle Ω . Introducing a time-dependent and continuous distribution function of the elements defined in the product space, $\eta(g, \underline{\xi}; t)$, the conservation law for the number of all particles in the system (including clusters) is expressed by the integral:

$$\int_1^{\infty} \int_{\Omega} \eta(g, \underline{\vartheta}; t) dg d\underline{\vartheta} = \frac{\sum_{g=1}^{\infty} N_g(t)}{N_0 + N_1} = \frac{N_1}{N_0 + N_1} = \text{const.} \quad (31)$$

Differential equation of continuity equivalent to the integral conservation law (eq. 31) assumes following form:

$$\frac{\partial}{\partial t} \eta(g, \underline{\vartheta}; t) + \frac{\partial}{\partial g} j_g(g, \underline{\vartheta}; t) + \text{div}_{\underline{\vartheta}} \underline{j}_{\underline{\vartheta}}(g, \underline{\vartheta}; t) = 0 \quad (32)$$

$j_g, \underline{j}_{\underline{\vartheta}}$ are the components of the flux defined in the product space $g \times \Omega$: $\underline{j} = (j_g, \underline{j}_{\underline{\vartheta}})$. In this paper we assume zero rotational diffusion constants for all clusters in the system:

$$D_{\text{rot}}^g = 0, \quad (g \geq 2)$$

and as a result of the assumption the angular component of the flux is zero, $\underline{j}_{\underline{\vartheta}} = 0$. It allows us to simplify the continuity equation (32) which for clusters ($g \geq 2$) and for discrete space of cluster size, g , reduces to the following form:

$$\frac{\partial \eta_g(\underline{\vartheta}; t)}{\partial t} + j_{g+1}(\underline{\vartheta}; t) - j_g(\underline{\vartheta}; t) = 0, \quad (g = 2, 3, \dots) \quad (33)$$

where $\eta_g(\underline{\vartheta}; t) = [\beta_g] \chi_g(\underline{\vartheta}, t)$. Rotational diffusion constant of single elements is assumed to be high as compared to the constants for clusters ($D_{\text{rot}}^1 \gg D_{\text{rot}}^g$), and the diffusion equation for $g = 1$ should be solved taking into account the effect of rotation diffusion as well as consumption of single elements in the process of cluster growth. It leads to a non-equilibrium

nucleation theory which will be published by the authors¹⁴ soon.

In the present paper the set of kinetic equations (17) is solved assuming equilibrium or steady-state distribution of single elements (eqs.25,27), and steady-state distribution of clusters at any orientation angle, $\frac{\partial \eta_g(\underline{\theta}; t)}{\partial t} = 0$. It leads to a constant flux of clusters:

$$j_2(\underline{\theta}) = j_3(\underline{\theta}) = \dots = j_g(\underline{\theta}) = \dots = j_{st}(\underline{\theta}) \quad (34)$$

For the steady-state conditions the kinetic equations of the cluster growth assume following form:

$$j_{st}(\underline{\theta}) = \tilde{k}_{g-1}^+ \eta_{g-1}(\underline{\theta}) [\alpha_1] H_{g-1}(\underline{\theta}) - \tilde{k}_g^- \eta_g(\underline{\theta}) \quad (35)$$

In general $H_g(\underline{\theta})$ might vary with g for the growing cluster.

Multiplying left and right side of eqs.(35) by the product $\prod_{i=2}^{g-1} \tilde{k}_i^- / (\tilde{k}_i^+ [\alpha_1] H_i(\underline{\theta}))$ and adding successive equations, steady-state nucleation rate is obtained in the form dependent on the orientation angle $\underline{\theta}$:

$$j_{st}(\underline{\theta}) = \frac{\tilde{k}_1^+ [\alpha_1]^2 H_1^2(\underline{\theta}) / \Omega_1}{1 + \sum_{n=2}^{\infty} \prod_{i=2}^n [\tilde{k}_i^- / (\tilde{k}_i^+ [\alpha_1] H_i(\underline{\theta}))]} \quad (36)$$

or in the form (cf.eq.19):

$$j_{st}(\underline{\theta}) = \frac{[\alpha_1] H_1(\underline{\theta})/s_2}{\sum_{g=1}^{\infty} \frac{\exp(\tilde{\Delta F}_g(\underline{\theta})/kT)}{k_g^+ [\alpha_1] H_g(\underline{\theta})}} \quad (37)$$

where the orientation-dependent free energy of cluster formation

$$\tilde{\Delta F}_g(\underline{\theta}) = \sum_{i=2}^g \delta F_i^0 - kT \sum_{i=2}^g \ln([\alpha_1] H_{i-1}(\underline{\theta})) \quad (g = 2, 3, 4, \dots) \quad (38)$$

and $\tilde{\Delta F}_1(\underline{\theta}) = 0$.

In unoriented and non-diluted systems:

$$\tilde{\Delta F}_g(\underline{\theta}) = \tilde{\Delta F}_g^0 = \sum_{i=2}^g \delta F_i^0$$

The overall nucleation rate in oriented systems should be calculated by integrating the angular density of the flux (eq.37) over the full range of the orientation angle $\underline{\theta}$:

$$j_{st}^{tot} = \int_{\Omega} j_{st}(\underline{\theta}) d\underline{\theta} = \frac{[\alpha_1]}{\Omega} \int_{\Omega} \frac{H_1(\underline{\theta}) d\underline{\theta}}{\sum_{g=1}^{\infty} \frac{\exp(\tilde{\Delta F}_g(\underline{\theta})/kT)}{k_g^+ [\alpha_1] H_g(\underline{\theta})}} \quad (39)$$

In unoriented systems eq.(39) reduces to the form typical for the classical nucleation theory¹⁵:

$$j_{st}^0 = [\alpha_1] / \sum_{g=1}^{\infty} \frac{1}{k_g^+} \exp(\tilde{\Delta F}_g^0/kT) \quad (40)$$

Formula (40) was directly used by several authors^{16, 17} to

discuss kinetics of oriented crystallization in polymers by using an average free energy of the phase transition only in the formula as a function of the degree of molecular orientation (applied stress) and independent of the orientation angle:

$$j_{st}^{tot} = f(\Delta F = \langle \Delta F(\underline{h}) \rangle)$$

$\langle \Delta F(\underline{h}) \rangle$ denotes an average free energy calculated over the ansamble of end-to-end vector of polymer chains in the oriented system. It led to qualitatively different results which obviously did not provide the authors with any sort of orientation distribution of the nucleation rate as well as with any conclusion concerning orientation distribution of crystals resulting from the nucleation kinetics. In our theory the total nucleation rate is calculated as the integral of the angular distribution of the nucleation rate over the full range of the angle $\underline{\phi}$ (eq.39).

Neglecting the effect of rotational diffusion of clusters (high production rate and/or small rotational diffusion constants) the orientation distribution of crystals resulting from the steady-state nucleation process is given by the formula⁹:

$$v_{st}(\underline{\phi}) = j_{st}(\underline{\phi}) / \int_{\Omega} j_{st}(\underline{\phi}) d\underline{\phi} \quad (41)$$

The rate constants \tilde{k}_g^+ of the reaction of addition are needed to calculate nucleation rates in this theory. In general, the rate constants for the reaction of addition as well as for dissociation are controlled by the energy barriers which appear during the process. If the reaction of addition is accompanied by an increase in free energy then the energy barrier should be

composed of the activation energy of diffusion, E_D , and the positive change in free energy, δF . Otherwise the energy barrier is E_D . The same philosophy applies to the dissociation process, and the energy barriers should be:
for addition:

$$U^+ = E_D + \frac{1}{2}(\delta F + |\delta F|) \quad (42)$$

and for dissociation:

$$U^- = E_D - \frac{1}{2}(\delta F - |\delta F|) \quad (43)$$

With the rate constants \tilde{k}_g^+ controlled by the energy barriers given by eq.(42) the steady-state angular density of the flux (eq.37) assumes following form:

$$j_{st}(\underline{\phi}) \approx \text{const.} \exp(-E_D/kT) \frac{[\alpha_1] H_1(\underline{\phi})}{\sum_{g=2}^{\infty} \exp[\tilde{\Delta F}_g(\underline{\phi})/kT]} \quad (44)$$

If $\tilde{\Delta F}_g > 0$ for every cluster size g then the formula (44) provides: $j_{st}(\underline{\phi}) = 0$, and no nucleation is predicted. Nucleation and crystal growth occur in those systems where $\frac{\partial}{\partial g} \tilde{\Delta F}_g(\underline{\phi}) < 0$ for $g > g^*(\underline{\phi})$. Then in an approximation:

$$j_{st}(\underline{\phi}) \approx \text{const.} \exp\left(-\frac{E_D}{kT}\right) \left[-\frac{1}{kT} \frac{\partial^2 \tilde{\Delta F}(\underline{\phi})}{\partial g^2}\right]_{g^*}^{\frac{1}{2}} \frac{[\alpha_1] H_1(\underline{\phi})}{\Omega} \quad (45)$$

$$\times \exp[-\tilde{\Delta F}^*(\underline{\phi})/kT]$$

$\tilde{\Delta F}^*(\vartheta)$ denotes critical energy of cluster formation.

The formulas (eq.44 and 45) proposed by our theory resemble to a certain extent the classical expressions for the nucleation rate in unoriented systems. The difference concerns free energy of cluster formation (or its critical energy, ΔF^*) as well as the additional term $[\alpha_1] H_1(\vartheta)$ which appears in the new approach as a dilution term. The dependence of the nucleation rate on the orientation angle ϑ is related to free energy of cluster formation which is orientation-dependent and to the dilution term $[\alpha_1] H_1(\vartheta)$ which appears in addition to the energy effects. The modification of free energy of transition concerns the bulk term only:

$$\tilde{\Delta f}(\vartheta) = \lim_{g \rightarrow \infty} \frac{\partial F_g(\vartheta)}{\partial g} = \Delta f^0 - kT \{ \langle \ln H(\vartheta) \rangle + \ln[\alpha_1] \} \quad (46)$$

Δf^0 is the bulk transition free energy per single element in the unoriented system. $\langle \ln H(\vartheta) \rangle$ is an average value calculated over the set of $H_1(\vartheta)$ values possible in the system and appearing during the cluster growth.

The thermodynamic characteristics of phase transitions in the oriented systems are modified by the orientation as a result of the modification in bulk free energy of the transition (eq.46) only.

EXAMPLE CALCULATIONS

The role of the factor $H(\vartheta)$ in the kinetics of oriented nucleation and in the orientation distribution of resulting

crystals is discussed using free energy of cluster formation in a simple form:

$$\tilde{\Delta F}_g(\underline{\phi}) = \tilde{\Delta f}(\underline{\phi})g + ag^{\frac{3}{2}} \quad (47)$$

composed of the bulk and surface terms. Factor a is proportional to the surface free energy density. It leads to the following expression for the angular distribution of the nucleation rate (eq.45):

$$j_{st}(\underline{\phi}) \approx \text{const.} \exp\left(-\frac{E_D}{kT}\right) \frac{[\alpha_1] H_1(\underline{\phi})}{\Omega} \\ \times \frac{\tilde{\Delta f}^2(\underline{\phi})}{(kT a^3)^{\frac{3}{2}}} \times \exp\left[-\frac{4a^3}{27kT \tilde{\Delta f}^2(\underline{\phi})}\right], \quad (48)$$

and to the orientation distribution density of crystals (eq.41) in the form:

$$\bar{v}_{st}(\underline{\phi}) = C H_1(\underline{\phi}) \tilde{\Delta f}^2(\underline{\phi}) \exp\left[-\frac{4a^3}{27kT \tilde{\Delta f}^2(\underline{\phi})}\right] \quad (49)$$

where the normalization constant:

$$C = \int H_1(\underline{\phi}) \tilde{\Delta f}^2(\underline{\phi}) \exp\left[-\frac{4a^3}{27kT \tilde{\Delta f}^2(\underline{\phi})}\right] d\underline{\phi}.$$

Numerical results are obtained starting with the orientation distribution of single elements produced by a hydrodynamic

field (eq.27). The elements in the form of rotational ellipsoids suspended in a viscous matrix are assumed to be subjected to uniaxial extensional flow. The resulting steady-state orientation distribution of the elements leads to^{8,9}:

$$H(\theta) = \frac{A^{\frac{3}{2}} \exp(-A)}{W(A^{\frac{3}{2}})} \exp(A \cos^2 \theta), \quad (50)$$

where

$$W(A^{\frac{3}{2}}) = \exp(-A) \int_0^{\frac{1}{2}} e^{x^2} dx.$$

The hydrodynamic factor A is proportional to the normal stress difference, Δp , and depends on the asymmetry of the kinetic elements (axial ratio), viscosity and temperature^{9,13}. For extensional flows $A > 0$. Figure 4 shows the orientation distribution density of single elements computed from eq.(50) for the hydrodynamic field with $A = 1$, and corresponding orientation distribution density of crystals. The theory predicts considerable sharpening of crystal orientation distribution as compared with the distribution of kinetic elements in the mother phase. Orientation factors

$$f_{or} = \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2} \quad (51)$$

computed for the preoriented single elements and for the kinetically-controlled distribution of crystals are presented in Figure 5, as functions of the hydrodynamic parameter A . The computed orientation factor of crystals is extremely sensitive to the orientation of single elements in the mother phase, and

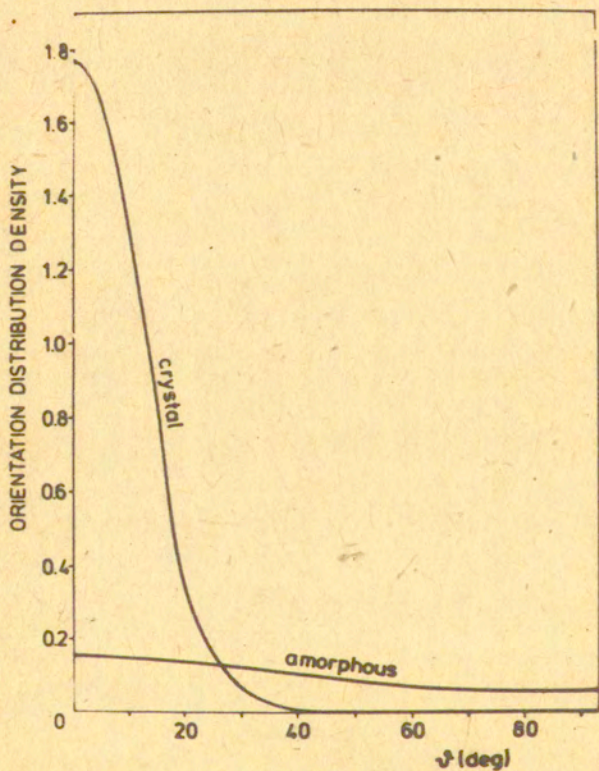


Fig.4. Orientation distribution densities of single elements (amorphous) computed from eq.(50) ($A=1$), and resulting crystals (crystal) computed from eq. (49).

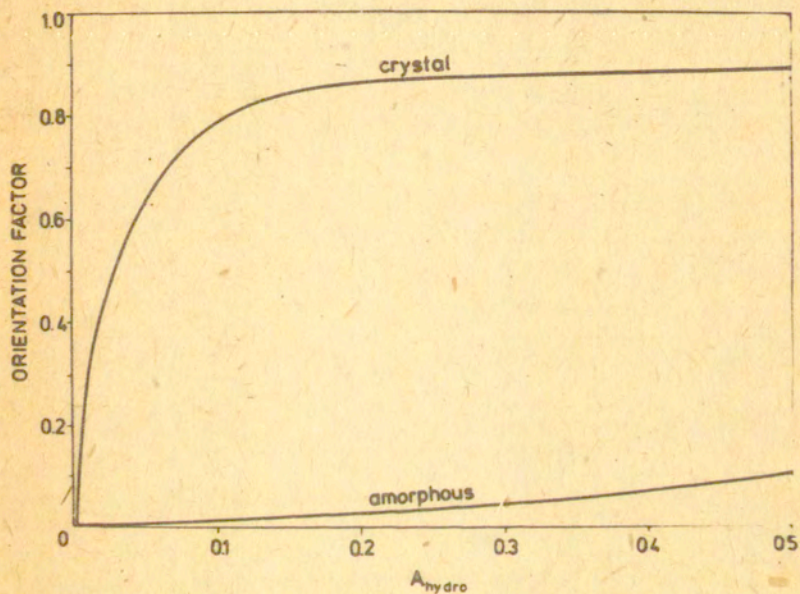


Fig.5. Orientation factor f_{or} (eq.51) computed for single elements preoriented by the hydrodynamic field (eq.50) as a function of the parameter A_{hydro} (amorphous), and for resulting crystals (eq.49).

any relatively small orientation of the elements results in high orientation of crystals.

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Summary.

A new theory of oriented nucleation was formulated in this paper starting with some ideas proposed earlier by Ziabicki⁸, and concerning some steric restrictions for the cluster formation of rod-like single elements. Kinetic equations of the cluster growth in the preoriented systems were formulated starting with the general laws of chemical kinetics. A finite tolerance angle, Δ , was introduced to determine the effective fraction of single elements with favorable orientation. A compliant orientation of a single particle and a growing cluster was required to have the particle effectively attached to the cluster. Physical nature of the steric restrictions for the reaction of addition was also discussed in the paper basing on the statistical mechanics. It is interesting to note that the introduced model parameter Δ characterizing steric restrictions does not influence thermodynamic and kinetic effects of orientation in the crystallization process. The tolerance angle affects only melting temperature in the unoriented state, T_m^0 , and reduces it. The reduction in T_m^0 is stronger the narrower is the angle Δ .

Formulas describing free energy of crystallization, melting temperature and nucleation rate were derived for the oriented systems of asymmetric (rod-like) single elements. The derived thermodynamic and kinetic characteristics of the transition in such systems are dependent on the orientation angle. Orientation elevates melting temperature or decreases it in the same system depending upon the orientation angle. The orientation-dependent degree of supercooling affects

much stronger in the dependence of nucleation rate on the orientation angle. Theory predicts considerable increase in orientation of resulting clusters (crystals) as compared with the orientation of single elements in the mother phase. Example calculations are presented for polyethylene chain segments preoriented by hydrodynamic field during uniaxial extensional flow.

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