

5.53 — POLIMERY

7.77 — TERMODYNAMIKA PRZEMIAN
FAZOWYCH

Leszek Jarecki

**THEORY OF ORIENTED NUCLEATION
WITH ASYMMETRIC SINGLE ELEMENTS**

**II. EFFECTS OF ROTATIONAL
DIFFUSION**

32/1984

P. 269



WARSZAWA 1984

Praca wpłynęła do Redakcji dnia 16 lipca 1984 r.

56980



Na prawach rękopisu

Instytut Podstawowych Problemów Techniki PAN

Nakład 150 egz. Ark.wyd. 2,1. Ark.druk.3,25.

Oddano do drukarni w lipca 1984 r.

Nr zamówienia 511/84.

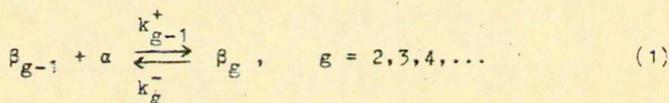
Warszawska Drukarnia Naukowa, Warszawa,
ul.Sniadeckich 8

Leszek Jarecki
Pracownia Fizyki Polimerów
IPPT PAN, Warszawa

THEORY OF ORIENTED NUCLEATION
WITH ASYMMETRIC SINGLE ELEMENTS
II. EFFECTS OF ROTATIONAL DIFFUSION *)

INTRODUCTION

Nucleation of new phase in amorphous matrix proceeds via aggregation of single elements into clusters which can grow in size if some thermodynamic conditions are satisfied. It is widely assumed in the theories of nucleation that bimolecular reactions of addition and dissociation between single elements α of the amorphous matrix and aggregates β are dominating over other types of possible reactions of aggregation. Denoting β_{g-1} as a cluster composed of $g-1$ single elements α , the bimolecular reaction between the cluster and a kinetic element α reads



where the rate constants k_{g-1}^+ for the reaction of addition, and k_g^- for dissociation control kinetics of the aggregation process.

In the classical approach the kinetic theories of nucleation¹⁻³ consider single elements α as spherical particles and are valid for monoatomic materials (metals, inert gases). Net rate of production of clusters β_g per unit volume, j_g , by the addition - dissociation reaction (1) reads in those theories

*) Part I "Equilibrium Orientation Distribution" was published in IPTR Reports 20/1981.

$$j_g = k_{g-1}^+ n_{g-1} [a] - k_g^- n_g, \quad g = 2, 3, 4, \dots \quad (2)$$

and the rate constants k_{g-1}^+ , k_g^- are controlled by activation energy of translational diffusion and by change in chemical potential of the kinetic element α accompanying addition to the cluster β_{g-1} . Recently arbitrariness in evaluating the rate constants has been eliminated, and k_{g-1}^+ , k_g^- have been explicitly defined⁴. $[a]$ denotes molar fraction of single elements

$$[a] = \frac{n_1}{n_0 + \sum_{g=1}^{\infty} n_g} \quad (3)$$

n_1 , n_g are numbers of particles α and clusters β_g per unit volume, respectively, and n_0 denotes number of solvent particles (if present) in the unit volume. Usually, for non-diluted systems $[a]$ is assumed to be unity in the classical approach to the nucleation theory. The system of coupled kinetic eqs. (2) is completed there¹⁻³ by the system of continuity equations for number of clusters which for discrete variable g read^{3,5}

$$\frac{dn_g}{dt} + j_{g+1} - j_g = 0 \quad (g = 2, 3, 4, \dots) \quad (4)$$

No diffusion or other transport terms appear in eq.(4) because the aggregating system is assumed to be uniform and isotropic.

Other types of possible bimolecular reactions, for example between the aggregates, and higher order multimolecular reactions are assumed usually to be much less frequent and are neglected in the continuity eq.(4). One explains it by the fact that molar fractions of aggregates of a particular size g

are much smaller in comparison to the fraction of single kinetic elements α at the initial and intermediate stages of the aggregation process. Also mobilities of the aggregates are much lower, and rate constants for aggregation reaction between two clusters are considerably reduced.

This approach originally applied by Turnbull and Fisher² for metals has been adapted next for polymers in isotropic state by Frank and Tosi³ and by Hoffman and Lauritzen⁵ without any change in the form of kinetic eqs.(2), and spherical symmetry of single kinetic element remained silently assumed. It is obvious that in the case of polymers (chain segments) and the majority of real transforming systems the single elements exhibit shape asymmetry and can not be treated as spherical particles. Despite of the incorrect assumption the theories provide qualitatively good conclusions for isotropic systems, where orientation distribution of the asymmetric kinetic elements α is uniform. The asymmetry which should affect the coupled system of bimolecular reaction (1), and modify kinetic eqs.(2) becomes ineffective on the macroscopic level in the case of isotropic systems⁶.

Macroscopic anisotropy induced by external forces orienting asymmetric single elements requires introduction of the asymmetry into the system of eqs.(2) and (4) to describe kinetics of nucleation in a proper way. The role of molecular asymmetry on kinetic eqs.(2) has been touch first by Ziabicki⁷, who has introduced a criterion for compliant orientation of a single kinetic element and a cluster to have the bimolecular reaction of addition effective. The criterion for compliant orientation was defined there⁷ by introducing so called "tolerance angle" Δ , first as a molel parameter and next it has been derived from first principles using statistical physics methods⁸ and has become a physical parameter. The compliant orientation condition reduces fraction of single kinetic elements effective in the bimolecular reaction of aggregation (1), and kinetic equations assume a differential form dependent on the orientation angle $\underline{\theta} = (\theta, \varphi, \eta)$ ⁸

$$dj_g(\underline{\vartheta}) = \tilde{k}_{g-1}^+ dn_{g-1}(\underline{\vartheta}) [a] \langle w_1(\underline{\vartheta}) \rangle_{\Delta} - k_g^- dn_g(\underline{\vartheta}), \quad (5)$$

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

The differential flux of production of clusters β_g within the differential range of orientation angle, $d\underline{\vartheta}$, (per unit volume) is controlled by a modified rate constant for the reaction of addition

$$\tilde{k}_{g-1}^+ = k_{g-1}^+ \frac{\Delta}{\Omega}, \quad (6)$$

where Δ/Ω is fraction occupied by the tolerance angle Δ in the full range of the orientation angle, Ω . For example, for uniaxial asymmetry of the single kinetic elements

$$\Delta = \iint_{\Delta} \sin\theta \, d\theta \, d\varphi, \quad \Omega = 4\pi$$

The dissociation rate constant, k_g^- , is not affected by the particle asymmetry. $\langle w_1(\underline{\vartheta}) \rangle_{\Delta}$ is an average value of a normalized orientation distribution function of single elements a in the range of the tolerance angle, Δ , calculated around the orientation angle $\underline{\vartheta}$

$$\langle w_1(\underline{\vartheta}) \rangle_{\Delta} = \frac{1}{\Delta} \int_{\Delta} w_1(\underline{\vartheta}) \, d\underline{\vartheta} \quad (7)$$

$w_1(\underline{\vartheta})$ denotes the orientation distribution function of single elements, $dn_g(\underline{\vartheta})$ denotes differential number of clusters of size g at the orientation angle, $\underline{\vartheta}$, within the range $d\underline{\vartheta}$.

For small tolerance angle Δ , and/or not to sharp orientation distribution of single elements, $w_1(\underline{\vartheta})$, the average value

(eq.7) can be approximated by the distribution function alone

$$\langle w_1(\xi) \rangle_{\Delta} = w_1(\xi) \quad (8)$$

The angle-dependent kinetic eqs.(5) reduce for the case of isotropic state of the system to the following form independent of the orientation angle

$$\frac{dj_g}{d\xi} = \frac{j_g^0}{\Omega} = \text{const}_g, \quad (g = 2, 3, 4, \dots) \quad (9)$$

where

$$j_g^0 = \tilde{k}_{g-1}^+ n_{g-1} [\alpha] - k_g^- n_g \quad (10)$$

is total flux of production of clusters β_g (per unit volume) in the full range of orientation angle in the isotropic, un-oriented system.

Eqs.(10) are similar in their form to the kinetic eqs.(2) proposed by the classical theories for spherical single elements, and the difference concerns only the rate constant for the reaction of addition, \tilde{k}_{g-1}^+ , modified by the asymmetry (see eq.6). This fact allows to apply the classical approach proposed originally for metals and inert gases for phase transformations in unoriented systems composed of asymmetric single elements with the only change concerning interpretation of the rate constants for the reaction of addition. But the system of kinetic equations (5) is not reducible to the classical form if the system composed of asymmetric single elements exhibits any degree of orientation. Kinetics of aggregation appears to be strongly affected by the external forces inducing molecular orientation in the system, and the total flux of clusters of size g in full range of the orientation angle calculated for

oriented systems varies from that predicted by the classical approach, and reads

$$j_g^{or} = \tilde{k}_{g-1}^+ n_{g-1} [\alpha] \chi_g - k_g^- n_g \quad , \quad (11)$$

and

$$\chi_g = \Omega \int_{\Omega} w_g(\xi) \langle w_1(\xi) \rangle_{\Delta} d\xi \quad , \quad (12)$$

where $w_g(\xi)$ denotes normalized orientation distribution function of clusters β_g . For the isotropic case, $\chi_g = 1$.

To solve basic questions concerning kinetics of nucleation in anisotropic state it is necessary to complete the system of angle-dependent kinetic eqs.(5) with a system of continuity equations for number of single elements α and for number of clusters of any cluster size g . Continuity equations (4) proposed in earlier papers for spherical elements are no longer valid for nucleation in an anisotropic state. Rotational diffusion terms should appear in the continuity equations as a result of anisotropy produced by external orienting forces. It introduces rotational diffusion constants of single elements and clusters into the theory of nucleation as additional kinetic parameters controlling the process.

Continuity equations will be formulated in this paper for aggregation from anisotropic phase composed of asymmetric single elements and oriented by external potential forces. It will allow to formulate the problem of nucleation in such systems in a correct way. Some asymptotic cases of the corrected nucleation theory will be discussed in this paper in terms of relative role of characteristic times which will appear, namely so called settle time, τ_s , directly related to rotational diffusion constant of single kinetic elements and to the applied potential forces, and crystallization half period, $t_{1/2}$. Translational diffusion effects will be neglected in this

paper, and the system under consideration is assumed to be an uniform, but anisotropic continuum. Example computations are performed for polyethylene.

EQUATIONS OF CONTINUITY

In general, continuity equations for angular distributions of number of clusters β_g ($g = 2, 3, 4, \dots$) as well as for the angular distribution of single elements ($g = 1$) should be defined in a space of translational (\underline{r}) and rotational ($\underline{\hat{g}}$) variables. It is assumed in this paper that clusters of all sizes, g , as well as single kinetic elements α exhibit shape asymmetry, so the orientation distribution functions can be easily defined as distributions of symmetry axes of the elements.

Let $dN_g(\underline{r}, \underline{\hat{g}}, t)$ will be a number of clusters β_g or number of single elements ($g = 1$) within the volume element $d\underline{r}$ around a point \underline{r} of the translational space, and oriented within the differential angle range, $d\underline{\hat{g}}$, around an orientation angle $\underline{\hat{g}}$ at any moment of time, t . Distribution function of clusters β_g or single elements ($g = 1$) normalized in the translational-rotational space, $\mathbb{R}^3 \times \Omega$, at any moment of time, t , reads

$$\psi_g(\underline{r}, \underline{\hat{g}}, t) = \frac{1}{N_g(t)} \frac{dN_g(\underline{r}, \underline{\hat{g}}, t)}{d\underline{r} d\underline{\hat{g}}}, \quad (g = 1, 2, 3, \dots) \quad (13)$$

$N_g(t)$ denotes total number of clusters of size g or single elements ($g = 1$) at the moment of time t in a macroscopic volume of the system, V .

Conservation equations for the number of clusters dN_g and for the number of single elements dN_1 , read

$$\frac{\partial}{\partial t} dN_g(\underline{r}, \underline{\vartheta}, t) = -\text{div}_r(\dot{\underline{r}}_g dN_g) - \text{div}_\vartheta(\dot{\underline{\vartheta}}_g dN_g) - [dj_{g+1}(\underline{r}, \underline{\vartheta}, t) - dj_g(\underline{r}, \underline{\vartheta}, t)]d\underline{r}, \quad (g = 1, 2, 3, \dots) \quad (14)$$

div_r and div_ϑ denote operators of divergence in 3-dimensional translational (physical) space, and in the rotational space of the orientation (Euler) angles, respectively. Cluster size g is treated here, after Frank and Tosi³, as a discrete variable. The change in number of clusters of particular size g in time at the point $(\underline{r}, \underline{\vartheta})$ (see eq.14) is controlled, in general, by translational and rotational diffusions of the clusters as well as by net effect of production of the clusters, dj_g , in the aggregation process and consumption in the process of their further growth, dj_{g+1} . For $g=1$ (single elements) the flux dj_1 will be defined later in this paper. It is assumed in this paper that the system under consideration is subjected to external orienting potential forces, and that the resulting potential energy of any cluster or single element, $U_g(\underline{\vartheta})$, is uniform and constant in time, and it depends only on the orientation angle $\underline{\vartheta}$. With this uniform potential energy taken into consideration the translational velocity, $\dot{\underline{r}}_g$, of any cluster or any single element α is controlled only by translational diffusion resulting from translational Brownian motion

$$\dot{\underline{r}}_g = -D_g^{\text{tr}}(\underline{\vartheta}) \text{grad}_r \ln \Psi_g(\underline{r}, \underline{\vartheta}, t). \quad (15)$$

Tensor of translation diffusion $D_g^{\text{tr}}(\underline{\vartheta})$ of a cluster β_g or single element depends also on the orientation angle $\underline{\vartheta}$. Angular velocity, $\dot{\underline{\vartheta}}$, is controlled both, by the rotational diffusion resulting from rotational Brownian motion and by the angle-dependent potential energy $U_g(\underline{\vartheta})$ of the cluster or single element α . Assuming slow rotational motions, what is

generally satisfied for polymers and other high viscosity materials, the angular rate of rotation reads⁹

$$\dot{\underline{\xi}}_g = - \frac{D_g^{\text{rot}}}{\underline{\xi}_g} \text{grad}_{\underline{\xi}} [\ln \Psi_g(\underline{r}, \underline{\xi}, t) + U_g(\underline{\xi})/kT] , \quad (16)$$

where $\frac{D_g^{\text{rot}}}{\underline{\xi}_g}$ denotes rotational diffusion tensor of the cluster of size g . Substituting translational and rotational velocities (eqs.15 and 16) into the conservation eqs.(14) one obtains following expressions with two diffusion terms on the right hand side

$$\begin{aligned} & \frac{\partial}{\partial t} [N_g(t) \Psi_g(\underline{r}, \underline{\xi}, t)] + \frac{dj_{g+1}}{d\underline{\xi}} - \frac{dj_g}{d\underline{\xi}} = \\ & = N_g(t) \text{div}_{\underline{r}} [D_{\underline{\xi}}^{\text{tr}}(\underline{\xi}) \text{grad}_{\underline{r}} \Psi_g] + N_g(t) \text{div}_{\underline{\xi}} [D_g^{\text{rot}} \text{grad}_{\underline{\xi}} \Psi_g + \\ & + \Psi_g \text{grad}_{\underline{\xi}} \frac{U_g(\underline{\xi})}{kT}] , \quad (g = 1, 2, 3, \dots) \end{aligned} \quad (17)$$

To solve the problem of nucleation the system will be considered in this paper, starting from this point, as uniform but anisotropic continuum. Similar assumption of uniformity has been also put in the classical theories of nucleation which have dealt with isotropic states of the matter, and the translational transport term in the continuity equation has vanished as well as the rotational diffusion term. With the assumption of uniform and anisotropic continuum the rotational diffusion term still remains on the right hand side of eqs. (17), and it is responsible for rotational Brownian motion of clusters and the orienting potential effects. The distribution function $\Psi_g(\underline{r}, \underline{\xi}, t)$ can be expressed then by an orientation distribution function of clusters β_g (or single elements), $w_g(\underline{\xi}, t)$

$$v_g(\underline{r}, \underline{\hat{g}}, t) = \frac{1}{V(t)} w_g(\underline{\hat{g}}, t), \quad (18)$$

where the distribution function, w_g , is normalized

$$\int_{\Omega} w_g(\underline{\hat{g}}, t) d\underline{\hat{g}} = 1,$$

and $V(t)$ denotes volume of the system at the moment of time, t . Thus, the continuity eqs.(17) assume following form with only one diffusional term responsible for rotational diffusion in the presence of orienting potential forces

$$\begin{aligned} & \frac{\partial}{\partial t} [n_g(t) w_g(\underline{\hat{g}}, t)] + \frac{dj_{g+1}}{d\underline{\hat{g}}} - \frac{dj_g}{d\underline{\hat{g}}} = \\ & = D_g^{\text{rot}} n_g(t) \text{div}_{\underline{\hat{g}}} \left[\text{grad}_{\underline{\hat{g}}} w_g + w_g \text{grad}_{\underline{\hat{g}}} \frac{U_g(\underline{\hat{g}})}{kT} \right], \quad (g = 1, 2, 3, \dots) \quad (19) \end{aligned}$$

$n_g(t) = N_g(t)/V(t)$ is time-dependent number of clusters of size g or single elements α in unit volume of the system.

Eqs.(19) integrated by sides over the full range of the orientation angle $\underline{\hat{g}}$ reduce to the continuity eqs.(4) proposed in classical theories formulated for spherical particles. The continuity eqs.(19) proposed here for anisotropic, uniform systems reduce also to the classical form (eqs.4) for the case of isotropic state ($\text{grad}_{\underline{\hat{g}}} w_g = 0$, $\text{grad}_{\underline{\hat{g}}} U_g = 0$, $g = 1, 2, 3, \dots$).

Continuity equation for angular distribution of orientation of total mass, $dm/d\underline{\hat{g}}$, in the system can be obtained from eqs.(19) by multiplying them by sides by the mass $m_{\alpha g}$ of cluster β_g for all sizes g starting with $g = 1$ (single elements α), and adding them next by sides. One obtains then

$$\frac{\partial}{\partial t} \frac{dm(\underline{\vartheta})}{d\underline{\vartheta}} + m_{\alpha} \lim_{G \rightarrow \infty} \left[G \frac{dj_{G+1}}{d\underline{\vartheta}} - \sum_{g=1}^G \frac{dj_g}{d\underline{\vartheta}} \right] =$$

$$= m_{\alpha} \lim_{G \rightarrow \infty} \sum_{g=1}^G g n_g D_g^{\text{rot}} \text{div}_{\underline{\vartheta}} \left[\text{grad}_{\underline{\vartheta}} w_g + w_g \text{grad}_{\underline{\vartheta}} \frac{U_g(\underline{\vartheta})}{kT} \right]. \quad (20)$$

m_{α} denotes mass of single element α , $dm/d\underline{\vartheta}$ is angular distribution of total mass in unit volume of the system. Any change in the angular distribution of mass is possible only via rotational diffusion term on the right hand side of eq.(20), and

$$\lim_{G \rightarrow \infty} \left[G \frac{dj_{G+1}}{d\underline{\vartheta}} - \sum_{g=1}^G \frac{dj_g}{d\underline{\vartheta}} \right] = 0, \quad (21)$$

because there is no creation of mass at any orientation angle, $\underline{\vartheta}$. Condition equation (21) allows to determine angular distribution of rate of consumption of single elements, $dj_1/d\underline{\vartheta}$, oriented at $\underline{\vartheta}$. Assuming that $\lim_{G \rightarrow \infty} dj_{G+1}/d\underline{\vartheta} = 0$ one obtains from eq.(21)

$$\frac{dj_1}{d\underline{\vartheta}} = - \sum_{g=2}^{\infty} dj_g/d\underline{\vartheta} \quad (22)$$

STEADY-STATE NUCLEATION AND MOBILE SINGLE ELEMENTS

Earlier theories of nucleation, valid for spherical particles and for isotropic systems, have discussed kinetics of transformation at so called steady-state approximation^{1-3,5}. That approximation has concerned steady-state distribution of clusters (see eqs.4), and it has made possible to solve the

system of kinetic eqs.(2) analytically. The steady-state approximation for the number of clusters in eqs.(4) implies constant fluxes of cluster production of all sizes g

$$j_g = j_{g+1} = \text{const.}, \quad (g = 2, 3, \dots) \quad (23)$$

In the case of asymmetric single elements and anisotropic systems the set of kinetic eqs.(5) is even more complex and it is necessary to make an approximation analogous to that one done in the classical approach, otherwise analytical solution of the nucleation problem becomes impossible to obtain. Such an approximation has been already done in recent papers^{6,8} on this subject, where by the analogy to the classical approach the angular distributions of cluster production, $dj_g/d\Omega$, have been assumed to be constant for all cluster sizes, $g \geq 2$. It results in equal left hand sides of all kinetic eqs.(5), what makes the system of equations much easier to be solved analytically, and the solution can be found following widely accepted classical procedure of calculations. Physical meaning of the simplifying steady-state approximation in this theory is easy to understand from the continuity eqs.(19) if some additional approximations are made concerning rotational mobilities of clusters and that of single elements. Rotational motions of clusters are much reduced in comparison to rotational motions of single kinetic elements, particularly for bigger ones, because of higher mass and bigger dimensions of clusters. The approximation of vanishing rotational diffusion constants for all clusters

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

and non-zero rotational diffusion for single kinetic elements

$$D_1^{\text{rot}} \neq 0$$

emphasize the role of higher rotational mobility of single elements in the nucleation process, and they also simplify the system of continuity equations in this theory. Thus, for clusters the continuity equations reduce to the following form with zero rotational diffusion term

$$\frac{\partial}{\partial t} [n_g(t) w_g(\xi, t)] + \frac{dj_{g+1}(\xi, t)}{d\xi} - \frac{dj_g(\xi, t)}{d\xi} = 0, \quad (24)$$

($g \geq 2$)

It means that at the steady-state approximation the angular distributions of number of clusters β_g with the particular size $g \geq 2$ is constant in time

$$\frac{\partial}{\partial t} [n_g(t) w_g(\xi, t)] = 0. \quad (25)$$

The steady-state approximation and the assumption of hindered rotational motions of clusters result in equal angular distributions of the cluster production fluxes for all sizes g at any moment of time, t

$$\frac{dj_2(\xi, t)}{d\xi} = \frac{dj_3(\xi, t)}{d\xi} = \dots = \frac{dj_{st}(\xi, t)}{d\xi}, \quad (26)$$

and the steady-state angular distribution of nucleation rate, $dj_{st}(\xi, t)/d\xi$, may vary in time, but the angular distribution of clusters for any cluster size remains still steady.

The steady-state approximation does not concern the distribution of single kinetic elements if the so called steady-state angular distribution of nucleation rate is non-zero, $dj_{st}(\xi, t)/d\xi \neq 0$. Then the single kinetic elements are

consumed in the aggregation processes if the reactions of addition are dominating or they are produced if dominating are reactions of dissociation. Steady-state distribution of single elements is possible only in the case of equilibrium state at temperatures above the melting point, where $dj_{st}/d\hat{\xi} = 0$, and the orientation distribution assumes stationary Boltzmann form, controlled only by the angle-dependent potential energy of single elements⁸, $U_1(\hat{\xi})$

$$w_1(\hat{\xi}) = C \exp[-U_1(\hat{\xi})/kT] \quad (27)$$

Angular distribution of nucleation rate has been already derived from the system of kinetic eqs.(2) recently⁶ with the steady-state approximation for rod-like single elements, and reads

$$\frac{1}{n_1(t)} \frac{dj_{st}}{d\hat{\xi}} = \text{const. } w_1(\hat{\xi}, t) \exp\left\{-\frac{\Delta F_{iso}^*}{kT \left[1 - \frac{kT}{\Delta f_{iso}} \ln(4\pi[\alpha_1]w_1)\right]^2}\right\} \quad (28)$$

where $\hat{\xi} = (\theta, \varphi)$ denotes two spherical angles. ΔF_{iso}^* , Δf_{iso} are critical free energy of cluster formation and bulk free energy of the transformation per unit volume in isotropic, undeformed state, respectively. For crystallization from melt $[\alpha_1] = 1$. Similar expression with slightly modified logarithmic term in the exponent was derived recently for polymer chains with chain statistics and distribution of chain conformations taken into consideration¹⁰. One concludes from eq.(28) that kinetics of phase transformation in oriented systems is very sensitive to actual orientation distribution of single elements, $w_1(\hat{\xi}, t)$, at the moment of time, t . Recently⁸, kinetics of nucleation was discussed with the approximation of equilibrium, Boltzmann distribution, controlled by the orienting potential alone

(eq.27), and it is valid, in reality, only for temperatures above the melting point ($T > T_m$). There was no satisfactory explanation for such an approximation provided in that paper. In general, function $w_1(\underline{\xi}, t)$ depends also on time, and should satisfy conservation equation for single elements.

For the purpose of this paper single elements will be considered as rod-like particles with uniaxial symmetry and two spherical angles ξ, θ describing orientation of the element. Thus, the continuity equation for orientation distribution of single kinetic elements w_1 , obtained from eq.(19) for $g=1$ by substitution of equation (22) for the flux of single elements, dj_1 , assumes following form

$$\frac{\partial w_1(\underline{\xi}, t)}{\partial t} + \frac{1}{n_1(t)} [w_1 \dot{n}_1 + \frac{dj_2}{d\underline{\xi}} + \sum_{g=2}^{\infty} \frac{dj_g}{d\underline{\xi}}] = D_1^{\text{rot}} L_g(w_1, U_1) \quad (29)$$

where $L_g(w_1, U_1) = \text{div}_{\underline{\xi}} [\text{grad}_{\underline{\xi}} w_1 + w_1 \text{grad}_{\underline{\xi}} U_1 / kT]$, and \dot{n}_1 is the rate of consumption of single elements in the aggregation process. This equation when integrated by sides over the full range of the orientation angle $\underline{\xi}$ reduces to the following form which allows to express \dot{n}_1 in terms of the integral of angular distributions of all fluxes, $dj_g/d\underline{\xi}$

$$\dot{n}_1(t) + \int_{\Omega} (dj_2 + \sum_{g=2}^{\infty} dj_g) = 0, \quad (30)$$

because

$$\int_{\Omega} L_g(w_1, U_1) d\underline{\xi} = 0 \quad \text{and} \quad \int_{\Omega} w_1(\underline{\xi}, t) d\underline{\xi} = 1.$$

Total rate of transformation of single elements into aggregates per unit volume of the system, \dot{n}_1 , can be expressed by

the integral (eq.30) of angular distribution of consumption rate of single elements by all growing clusters over full range of the orientation angle.

On the other hand, the total rate of consumption of single elements in the aggregation process, \dot{n}_1 , as well as number of untransformed single elements, n_1 , can be expressed by normalized to unity time-dependent degree of transformation, $X(t)$, by following formulas

$$n_1(t) = n_1^0 [1 - X(t)] , \quad (31)$$

$$\dot{n}_1(t) = -n_1^0 \dot{X}(t) , \quad (32)$$

where n_1^0 denotes initial number of single elements per unit volume at zero degree of transformation, $X = 0$, and $\dot{X}(t)$ is the rate of transformation at any moment of time, t . Substituting eqs.(30)-(32) into eq.(29) the continuity equation for orientation distribution of single elements in the aggregating anisotropic system assumes following form

$$\frac{\partial w_1(\underline{\xi}, t)}{\partial t} + \frac{\dot{X}(t)}{1 - X(t)} \left[\frac{\frac{dj_2}{d\underline{\xi}} + \sum_{g=2}^{\infty} \frac{dj_g}{d\underline{\xi}}}{\int_{\Omega} (dj_2 + \sum_{g=2}^{\infty} dj_g)} - w_1(\underline{\xi}, t) \right] = D_1^{\text{rot}} L_g(w_1, U), \quad (33)$$

$$\text{and } X(t) = 1 - \exp\left[-\int_0^t dt' \left(\sum_{g=2}^{\infty} \frac{dj_g}{n_1(t')} + \frac{dj_2}{n_1(t')} \right)\right] . \quad (33a)$$

Continuity eq.(33) can be used for transformation processes following schemes of primary, secondary or both, primary and secondary nucleations by choosing proper expressions for the fluxes, $\frac{dj_g}{d\underline{\xi}}(\underline{\xi}, t)$. Assuming only primary, steady-state nucleation the kinetic term in eq.(33) reduces to the form dependent on angular distribution of the nucleation rate

$$\frac{\frac{dj_2}{d\varphi} + \sum_2 \frac{dj_g}{d\varphi}}{\int_{\Omega} (dj_2 + \sum_2 dj_g)} = \frac{\frac{dj_{st}}{d\varphi}}{\int_{\Omega} dj_{st}} \quad (34)$$

and eq.(33) reads

$$\frac{\partial w_1}{\partial t} + \frac{\dot{\chi}}{1 - \chi} \left[\frac{dj_{st}/d\varphi}{\int_{\Omega} dj_{st}} - w_1 \right] = D_1^{\text{rot}} L_{\varphi}(w_1, U_1) . \quad (35)$$

The second order differential equation (35) contains non-linear term

$$\frac{dj_{st}(w_1)/d\varphi}{\int_{\Omega} dj_{st}}$$

(compare eq. 28) and has to be solved numerically. Nevertheless, some asymptotic behaviour of the equation and its effect on the nucleation process can be discussed in qualitative terms without the necessity of performing of complex numerical calculations.

Two global kinetic characteristics control orientation distribution of single elements: the total transformation rate, $\dot{\chi}$, and rotational diffusion constant, D_1^{rot} , of single kinetic elements. The kinetic term on the left hand side of eq.(35), proportional to $\dot{\chi}$, accounts for the effects related to angle-dependent nucleation rate, while the right hand side term is responsible for rotational diffusion and the orienting potential effects. The role of those two terms accounting for two independent processes is controlled by the two global (independent of the angle of orientation) kinetic characteristics, $\dot{\chi}$ and D_1^{rot} . The rotational diffusion term will predominate the

effects of angle-dependent kinetics in eq.(35) in those cases where $\dot{X}/D_1^{\text{rot}} \ll 1$, and solution of eq.(35) will be controlled mainly by rotational diffusion of single elements and the orienting potential energy of single elements, $U_1(\vartheta)$. The angle-dependent kinetics of nucleation will affect the resulting orientation distribution of single elements marginally. For the other asymptotic case where $D_1^{\text{rot}}/\dot{X} \ll 1$, the rotational diffusion term will be suppressed by the kinetic one, and the orientation distribution, w_1 , will be controlled mainly by the orientation-dependent nucleation rate.

ORIENTATION DISTRIBUTION CONTROLLED BY ROTATIONAL DIFFUSION

At temperatures above critical melting point, T_m^0 , process of transformation does not occur ($X=0$, $\dot{X}=0$) and eq.(35) reduces to typical rotational diffusion equation with orienting potential present

$$\frac{\partial w_1}{\partial t} = D_1^{\text{rot}} L_{\vartheta}(w_1, U_1) \quad , \quad (36)$$

and a general solution of eq.(36) assumes form

$$w_1(\vartheta, t) = C \exp[-U_1(\vartheta)/kT] + \sum_1 \exp[-\lambda_1 D_1^{\text{rot}} t] z_1^{(i)}(\vartheta) \quad , \quad (37)$$

where λ_1 and $z_1^{(i)}$ are the corresponding eigenvalues and eigenfunctions, respectively. Solution (37) converges in time to the stationary, Boltzmann form given by the first term, where C denotes normalization constant. The case of temperatures above the melting point is no more interesting from the point of view of this paper dealing with nucleation. Boltzmann orientation distribution will be assumed as an initial condition for nucleation which can proceed below the equilibrium melting point, T_m^0 .

For small undercoolings (temperatures close to the equilibrium melting point, T_m^0) crystallization rate is small, and rotational diffusion constant high enough to fulfil the condition $\dot{\chi}/D_1^{\text{rot}} \ll 1$. In this case the non-linear term in eq.(35) is small, and thus orientation distribution of single elements is practically controlled by the diffusion term on the right-hand side of the equation.

Initial condition for the solution is assumed in the form of Boltzmann distribution controlled only by the orienting potential, which corresponds to the stationary distribution, as it is at temperatures above the melting point, T_m^0

$$w_1(\underline{\xi}, t=0) = w_1^0(\underline{\xi}) = C \exp[-U_1(\underline{\xi})/kT], \quad (38)$$

where C is a normalizing constant.

Introducing a small parameter ϵ defined as the ratio of the initial nucleation rate and the diffusion constant

$$\epsilon = -\dot{n}_1(w_1^0)/n_1(t)D_1^{\text{rot}} = G^* \int_{\Omega} dj_{st}^0/D_1^{\text{rot}}, \quad (39)$$

where $dj_{st}^0 = dj_{st}(w_1^0(\underline{\xi}))$ and G^* is a constant, continuity eq.(35) can be expressed for small undercoolings in the following form

$$\frac{1}{D_1^{\text{rot}}} \frac{\partial w_1}{\partial t} + \epsilon K(t) \left[\frac{dj_{st}(w_1)/d\underline{\xi}}{\int_{\Omega} dj_{st}} - w_1 \right] = L_{\xi}(w_1, U_1), \quad (40)$$

where the time-dependent coefficient $K(t) = \int_{\Omega} dj_{st} / \int_{\Omega} dj_{st}^0$ is expected to be not higher than unity. Solution of the equation can be found in terms of a series expansion over the small parameter ϵ .

$$w_1(\underline{\xi}, t) = \sum_{i=0}^{\infty} \epsilon^i w_1^{(i)}(\underline{\xi}, t). \quad (41)$$

The expansion approach allows to transform the non-linear

conservation eq.(40) the following system of linear, non-uniform equations for the expansion terms, $w_1^{(i)}(\vartheta, t)$

$$\frac{1}{D_1^{\text{rot}}} \frac{\partial w_1^{(i)}}{\partial t} - L_{\vartheta}(w_1^{(i)}, U_1) = f_i(w_1^0, w_1^{(1)}, \dots, w_1^{(i-1)}) \quad (42)$$

(i = 1, 2, 3, ...)

where the non-uniformity terms $f_i(\dots)$ on the right-hand side of any i-th equation are determined by the solutions of previous i-1 equations, and by the initial distribution, w_1^0 .

For the purpose of this paper orientation distribution of single elements at small undercoolings will be determined with the first order approximation with respect to the small parameter

$$w_1(\vartheta, t) = w_1^0(\vartheta) + \epsilon w_1^{(1)}(\vartheta, t) + O(\epsilon^2). \quad (43)$$

The first correction term, $w_1^{(1)}$, satisfies following linear equation

$$\frac{1}{D_1^{\text{rot}}} \frac{\partial w_1^{(1)}}{\partial t} - L_{\vartheta}(w_1^{(1)}, U_1) = - \left(\frac{dj_{st}^0/d\vartheta}{\int_{\Omega} dj_{st}^0} - w_1^0 \right), \quad (44)$$

where $(dj_{st}^0/d\vartheta)/\int_{\Omega} dj_{st}^0$ shows angular density of the nucleation rate resulting directly from the initial Boltzmann distribution, w_1^0 .

Exact solution of eq.(44) is obtained in this paper for rod-like single elements subjected to a uniaxial potential

$$U_1(\vartheta) = - A^2 kT \cos^2 \vartheta. \quad (44a)$$

It represent one of the most interesting types of uniaxial orientation, where the potential exhibits its minimum at the

orientation axis ($\theta = n\pi$; $n = 0, 1, 2, \dots$). This form of the potential governs, for example, orientation distribution of statistical segments of polymer chains in uniaxially extended Gaussian network at not to high extensions¹¹, where the coefficient $A^2 = \Delta p v_0 / kT$. Δp denotes difference of the normal stresses, v_0 is volume per one statistical segment of a chain. For example, for polyethylene chains $v_0 = 1.63 \times 10^{-22} \text{ cm}^3$, and for the orienting stress, Δp , in the range of $10^7 - 10^9$ dynes/cm² values of the coefficient A^2 are in the range of 0.03 - 3 at temperatures close to the melting point.

The initial condition (eq.38) requires that the correction terms, $w_1^{(i)}(\theta, t)$, should satisfy following initial conditions

$$w_1^{(i)}(\theta, t) = 0. \quad (46a)$$

Boundary conditions for the functions controlled by the "cosine square" potential (eq.44a) concern only the zenithal angle θ , and require periodicity of the correction functions corresponding to the periodicity of the applied potential U_1

$$w_1^{(i)}(\theta = 0, t) = w_1^{(i)}(\theta = n\pi, t), \quad (46b)$$

and

$$\left. \frac{\partial w_1^{(i)}}{\partial \theta} \right|_{\theta = n\pi} = 0, \quad (n = 0, 1, 2, \dots) \quad (46c)$$

what satisfies the condition of zero flux of the rotational diffusion of single elements at the orientation axis ($\theta = n\pi$).

The first correction function at the case of uniaxial potential given by eq.(44a) is found in the form of a series expansion into even Legendre polynomials

$$w_1^{(1)}(\theta, t) = \sum_{n=0}^{\infty} b_n(t) P_{2n}(\cos\theta), \quad (47)$$

with time dependent expansion coefficients

$$b_n(t) = \frac{4n+1}{2} \int_{-1}^1 P_{2n}(\cos\theta) w_1^{(1)}(\theta, t) d(\cos\theta). \quad (47a)$$

The series expansion over even Legendre polynomials satisfies boundary conditions (eqs.46b,c). The expansion coefficients $b_n(t)$ determined for the initial condition (eq.46a) read

$$b_0(t) = 0,$$

$$b_n(t) = \sum_{i=1}^{\infty} \beta_{ni} (1 - \exp(-\lambda_i t)), \quad n \geq 1 \quad (48)$$

where β_{ni} are coefficients dependent on the applied orienting potential.

Eigenvalues λ_i are determined applying the theory of perturbation¹² in the second order of approximation with respect to the applied potential, and they are increasing with increasing subscript "i".

$$\lambda_1 < \lambda_2 < \dots < \lambda_n < \dots$$

The perturbation theory requires not to high values of the coefficient A^2 of the potential. The smallest eigenvalue λ_1 which approximately reads

$$\lambda_1/D_1^{\text{rot}} = 6 - 4A^2/7 + 64A^4/343 + \dots \quad (49)$$

corresponds to the longest characteristic time, $\tau_s = 1/\lambda_1$, being a "settle time" for the system.

At the case of small undercoolings solution (eq.47) converges to its stationary form during the nucleation, and orientation distribution of single elements approaches its stationary form

$$w_1^{st}(\vartheta) = \lim_{t/\tau_s \rightarrow \infty} w_1(\vartheta, t) = C \exp[-U_1(\vartheta)/kT] + \epsilon \sum_{n=1}^{\infty} \sum_{i=1}^{\infty} \beta_{ni} P_{2n}(\cos\vartheta) + O(\epsilon^2). \quad (50)$$

For the terms related to the settle time ($i = 1$) the coefficients β_{ni} read

$$\beta_{11} = -\frac{5}{24\pi} \left(1 + \frac{2}{21} A^2 - \frac{1772}{21609} A^4\right) [f_c^0 - f_a^0 - \frac{108}{245} A^2 \left(1 - \frac{2}{539} A^2 + \dots\right) (\xi_c^0 - \xi_a^0)]$$

$$\beta_{21} = -\frac{12}{49} A^2 \left(1 - \frac{2}{539} A^2 + \dots\right) \beta_{11}, \quad (51)$$

$$\beta_{n1} = 0 \quad \text{for } n \geq 3.$$

f_c^0 , f_a^0 are crystalline and amorphous orientation factors, respectively, corresponding to the initial Boltzmann distribution, and

$$\xi_c^0 = \int_{-1}^1 \frac{1 \, dj_{st}^0/d\vartheta}{\int_{-1}^1 dj_{st}^0} P_4(\cos\vartheta) \, d(\cos\vartheta), \quad (52)$$

$$\xi_a^0 = \int_{-1}^1 w_0(\vartheta) P_4(\cos\vartheta) \, d(\cos\vartheta).$$

The stationary solution (eq.50) slightly deviates off the Boltzmann form, and the deviation is the smaller the slower is the nucleation process, and the faster is rotational diffusion. The solution shows that at small undercoolings rotational diffusion predominates kinetic effects of nucleation. The settle time, τ_s , is slightly increased by the orienting potential (compare eq.49) in comparison to the isotropic, unstressed state. It means that the orienting forces slightly delay achievement of stationary orientation distribution. At the discussed condition $\epsilon \ll 1$ crystallization half period

$$t_{1/2} \gg \tau_s,$$

and the stationary state is achieved practically at the initial stages of the transformation process with the degree of crystallinity close to zero.

Example numerical computations are performed for polyethylene subjected to the uniaxial "cosine square" potential assuming $A^2=1$. Stationary orientation distributions of statistical segments, assumed in this paper as amorphous single elements, computed from eq.(50) for small undercoolings, and initial Boltzmann distribution are presented in Figure 1 for several values of small parameter ϵ . Deviation from the Boltzmann distribution increases with increasing small parameter, and the stationary distribution flattens.

Figure 2 shows angular distributions of nucleation rate reduced by total initial nucleation rate (integrated over the whole range of the orientation angle)

$$\frac{dj_{st}(w_1)/d\theta}{\int_{\Omega} dj_{st}^0}$$

computed from eq.(28) for polyethylene, and corresponding to the initial as well as to final, stationary orientation

distributions (eqs.27, 50,51) for several values of the small parameter, ϵ .

The results presented in Fig.1 and 2 confirm extremely strong effects of the amorphous orientation on the nucleation rate and its angular distribution. It leads to the conclusion that a decrease of the rotational diffusion constant and/or an increase in the rate of transformation (increase of ϵ) result in depression of the nucleation rate.

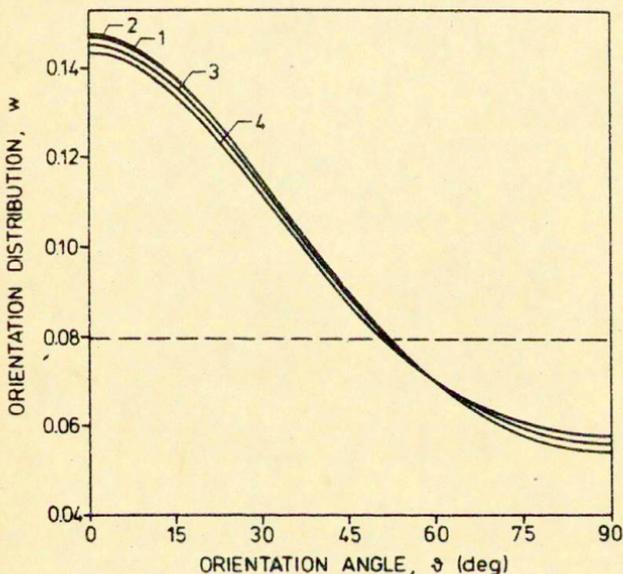


Fig.1. Normalized orientation distribution of statistical chain segments accompanying nucleation, and controlled by rotational diffusion, for polyethylene subjected to the uniaxial orienting potential (eq.45) with $A^2=1$. Curve (1) - Boltzmann distribution (zero nucleation rate). Curves (2,3,4) show stationary distributions computed from eq.(50) for $\epsilon = .01, .1, .2$, respectively. Temperature of the transition, $T_c = T_m^0 - 5K$.

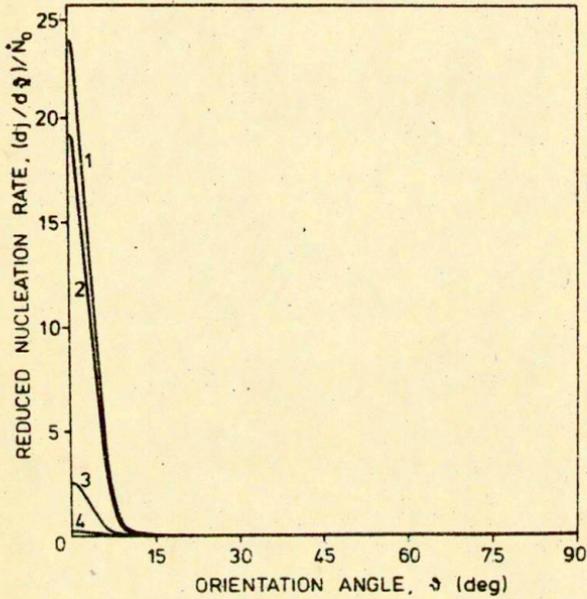


Fig. 2. Reduced angular distribution of nucleation rate in polyethylene, subjected to the uniaxial orienting potential (eq.45) at $A_c=1$, computed for Boltzmann distribution of single elements (curve 1), and stationary distributions (2,3,4) corresponds to $\epsilon=.01, .1, .2$). Temperature of the transition, $T_c = T_c^0 - 5K$.

ORIENTATION DISTRIBUTION CONTROLLED BY KINETICS
OF NUCLEATION AND CRYSTALLIZATION

The other extreme form, reverse to that one already discussed in this paper is assumed by the continuity eq.(35) for $D_1^{\text{rot}}/\dot{X} \ll 1$. In this case diffusional term in the equation is reduced considerably, and the resultant orientation distribution of single elements is expected to be controlled by kinetic term being responsible for kinetic effects of nucleation and crystallization. Introducing another small parameter

$$\delta = D_1^{\text{rot}}/\dot{X}(w_1^0), \quad (53)$$

$X(w_1^0)$ denotes rate of crystallization corresponding to w_1^0 , and the continuity equation assumes in this case following form which contains fully expressed non-linear kinetic term on the left-hand side

$$\frac{1}{X} \frac{\partial w_1}{\partial t} + \frac{1}{1-X} \left[\frac{dj_{st}(w_1)/d\vartheta}{\int_{\Omega} dj_{st}} - w_1 \right] = \delta L_g(w_1, U_1) M(\underline{g}, t), \quad (54)$$

and

$$M(\underline{g}, t) = \int dj_{st}(w_1^0) / \int dj_{st}(w_1).$$

Condition (53) is satisfied for systems exhibiting high crystallization rate (e.g. high-speed spinning of fibers) and/or high supercooling where rotational diffusion constant is much reduced by higher viscous friction forces of rotational motion at lower temperatures. It should be also mentioned that degree of transformation, X , in the systems is assumed to be far from the total one ($X=1$).

The solution of the non-linear, second order differential eq.(54) will be found assuming initial conditions in the form of Boltzmann distribution and zero-degree of transformation at the initial moment of the nucleation process:

$$X(t=0) = 0.$$

Then, applying conversion of time, t into degree of transformation, X , and assuming that $dX/dt > 0$ at any moment of time, the equation (54) can be rewritten in the form dependent on variables X and ξ

$$\frac{\partial w_1}{\partial X} + \frac{1}{1-X} \left[\frac{dj_{st}(w_1)/d\xi}{\int_{\Omega} dj_{st}} - w_1 \right] = \delta L_{\delta}(w_1, U_1) M(\xi, X) \quad (55)$$

An asymptotic case of eq.(55) obtained for small parameter $\delta \rightarrow 0$ will be discussed first. It corresponds to rotational diffusion constants tending to zero and/or to crystallization rates increasing to infinity. The asymptotic form of the equation with diffusional term on the right-hand side reduced to zero, shows first order, non-linear differential equation with orientation angle, ξ , remaining as a parameter

$$\frac{du_0}{dX} + \frac{1}{1-X} \left[\frac{dj_{st}(u_0)/d\xi}{\int_{\Omega} dj_{st}} - u_0 \right] = 0 \quad (56)$$

The asymptotic eq.(56) is no longer controlled by the orienting potential, U_1 , but the potential still affects solution of the equation via boundary (initial) condition which assumes Boltzmann orientation distribution, at zero degree of transformation

$$u_0(\xi, X=0) = w_1^0(\xi) = C \exp[-U_1(\xi)/kT] \quad (57)$$

Solution of the asymptotic eq.(56) should be normalized, and it can be shown in the form of series expansion over the variable, X

$$u_0(\underline{\xi}; X) = \sum_{i=0}^{\infty} X^i \varepsilon_i(\underline{\xi}) \quad (58)$$

where the first few expansion functions, ε_i , read

$$\varepsilon_0(\underline{\xi}) = w_1^0(\underline{\xi}) = C \exp[-U_1(\underline{\xi})/kT], \quad (59a)$$

$$\varepsilon_1(\underline{\xi}) = w_1^0(\underline{\xi}) - \frac{dj_{st}^0(w_1^0)/d\underline{\xi}}{\int_{\Omega} dj_{st}^0(w_1^0)}, \quad (59b)$$

$$\varepsilon_2(\underline{\xi}) = \varepsilon_1(\underline{\xi}) \left[1 - \frac{1}{2} f'_{|w_1^0} \right] + \frac{dj_{st}^0/d\underline{\xi}}{2 \left(\int_{\Omega} dj_{st}^0 \right)} \int_{\Omega} \varepsilon_1(\theta) f'_{|w_1^0} d\theta. \quad (59c)$$

where $f'_{|w_1^0} = \frac{d}{dw_1} \left(\frac{dj_{st}^0/d\underline{\xi}}{\int_{\Omega} dj_{st}^0} \right)_{|w_1^0}$.

The expansion functions $\varepsilon_i(\underline{\xi})$ are dependent on the initial orientation distribution (eq.57) controlled by the orienting potential. Solution (58) of the continuity equation in the asymptotic form (eq.56) proposed for hindered rotational diffusion does not converges to any stationary form with increasing degree of transformation, X.

Solution of ec.(57) can be obtained very easily using numerical methods and it confirms the conclusion, that stationary solution of the conservation equation does not exists at the conditions of hindered rotational diffusion and very fast crystallization. Numerical computations were performed for polyethylene assuming uniaxial "cosine square" orienting potential, and the computed orientation distributions of single elements are shown in Figure 3 for various degrees of

transformation. It is seen in this Figure that orientation distribution of single element flattens with increasing degree of transformation, X , from the highest orientation at the initial moment of transformation ($X=0$), to the uniform one at a certain degree of transformation ($X=.3$). Thus, nucleation proceeds at the condition of non-stationary orientation distribution of single elements, and its rate should lower in time of transformation as a result of the observed flattening of the orientation distribution. The corresponding decrease and flattening of the angular distribution of nucleation rate is shown in Figure 4 where the curves presented are computed for polyethylene from eq.(28) at the undercooling, $\Delta T=50^{\circ}\text{C}$.

Coming back to the continuity eq.(55) with rotational diffusion term on the order of small parameter, solution of the equation can be expressed in the form of a series expansion over the parameter, δ

$$w_r(\underline{\xi}, X) = u_0(\underline{\xi}, X) + \sum_{i=1}^{\infty} \delta^i u_i(\underline{\xi}, X), \quad (60)$$

where u_0 denotes solution of eq.(56) obtained for zero rotational diffusion constant ($\delta=0$). Substitution of the series expansion (eq.60) into the continuity eq.(55) leads to the following system of first order linear differential equations for the expansion functions u_i

$$\frac{du_1}{dX} + \frac{1}{1-X} [f'(u_0) - 1]u_1 = L_{\xi}(u_0, U_1)q_1(u_0), \quad (61)$$

where

$$q_1(u_0) = \int_{\Omega} dj_{st}(w_1^0) / \int_{\Omega} dj_{st}(u_0),$$

$$\frac{du_2}{dX} + \frac{1}{1-X} [f'(u_0) - 1]u_2 = q_2(u_0, u_1) - \frac{1}{1-X} u_1^2 f''(u_0)/2, \quad (62)$$

where $q_2(u_0, u_1) = q_1(u_0)L_{\xi}(u_1, U_1) - L_{\xi}(u_0, U_1) \int \frac{dj_{st}}{dw_1} \Big|_{u_1} / \int_{\Omega} dj_{st}(u_0)$

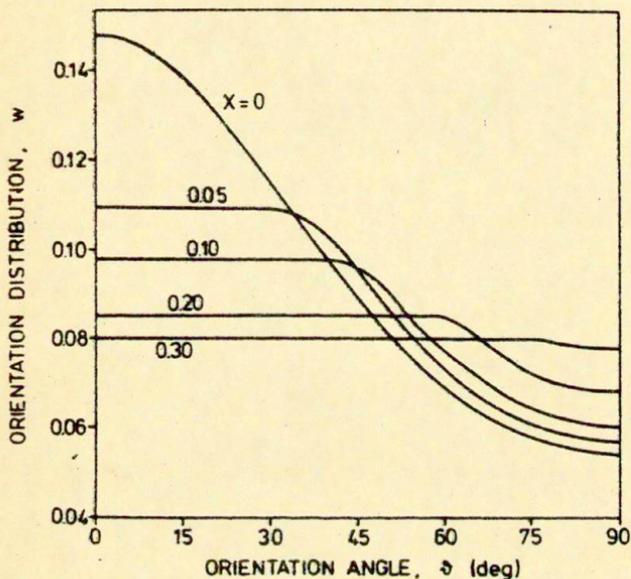


Fig. 3. Normalized orientation distributions of statistical chain segments controlled by kinetics of transformation in polyethylene subjected to uniaxial orienting potential with $A^2=1$. Computations are performed from eq.(56) and shown for various degrees of transformation indicated in the Figure starting with Boltzmann distribution of the segments at $X=0$. Temperature of transformation $T_c = T_m^0 - 50K$.

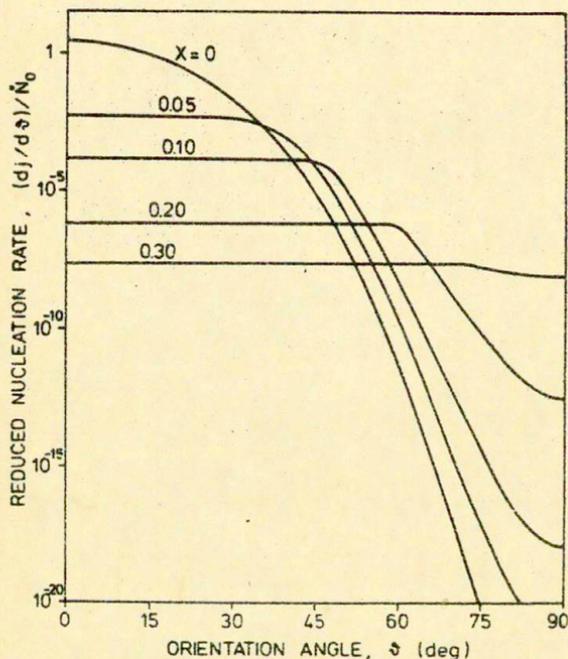


Fig. 4. Angular distribution of reduced nucleation rate computed for polyethylene, subjected to uniaxial orienting potential (eq.44a) with $A^0=1$ at the condition of totally hindered rotational diffusion effects ($D_{rot}^{eff}/k=0$). Computations are performed for various degrees of transformation, X, starting with Boltzmann distribution of statistical amorphous segments at $X=0$. Temperature of the transition $T_c = T_m^0 - 50K$.

where

$$f'(u_0) = \frac{d}{dw_1} \left[\frac{dj_{st}(w_1)/d\xi}{\int_{\Omega} dj_{st}} \right] \Big|_{u_0}$$

and $f''(u_0)$ denotes the second corresponding derivative. Solution of eqs.(61,62) read

$$u_1(\xi, X) = \frac{1}{\mu(\xi, X)} \int_0^X \mu(\xi, X') L_{\xi}[u_0(\xi, X'), u_1] q_1(u_0) dX' \quad (63)$$

$$u_2(\xi, X) = \frac{1}{\mu(\xi, X)} \int_0^X \mu(\xi, X') \left\{ q_2(u_0, u_1) - \frac{u_1^2}{2(1-X')} f''(u_0) \right\} dX', \quad (64)$$

etc.

where

$$\mu(\xi, X) = \exp \left[\int_0^X \frac{f'(u_0) - 1}{1 - Y} dY \right] \quad (65)$$

Obtained formulas (eqs.63,64) are not easy for qualitative discussion unless they are shown in the series expansion over degree of transformation X

$$u_i(\theta, X) = \sum_{j=0}^{\infty} X^j u_{i,j}(\theta) \quad (i = 1, 2, 3, \dots) \quad (66)$$

The expansion functions, $u_{i,j}$, can be derived directly from eqs.(63,64) by substitution the functions u_i in the form of the series expansion, and the solution u_0 of the continuity eq.(58), obtained for $\delta = C$, also as the expansion over X into the equations.

Function u_1 , which is first correction term to the orientation distribution of single elements, proportional to small parameter δ , appears to have the first non-zero term of the order of X^2 in the series expansion form. Thus, for $i = 1$

$$u_{10} = u_{11} = 0, \quad (67a)$$

$$u_{12} = -\frac{1}{2} \operatorname{div}_{\theta} [\operatorname{grad}_{\theta} \frac{dj_{st}^0(w_1^0)/d\xi}{\int_{\Omega} dj_{st}^0} + \frac{dj_{st}^0(w_1^0)/d\xi}{\int_{\Omega} dj_{st}^0} \operatorname{grad}_{\theta} U_1] q_1(u_0) \quad (67b)$$

The second correction of the order of δ^2 to the orientation distribution, u_2 , is even less sensitive to X than u_1 at unitial stages of transformation, and first non-zero term is of the order of X^3 in the series expansion form.

Combining the results for the case of nucleation at the regime of slow rotational diffusion and relatively fast transformation, the resultant orientation distribution can be approximated, for not to high degrees of transformations, by following formula

$$w_1(\underline{\theta}, X) = u_0(\underline{\theta}, X) + [X^2 u_{12} + \sigma(X^3)]\delta + [\sigma(X^3)]\delta^2 + \dots, \quad (68)$$

where the first term on the right-hand side, u_0 , is solution of the asymptotic continuity equation for $\delta = 0$ (completely hindered rotational diffusion) given by eq.(58). The effect of small parameter δ on the orientation distribution appears to be much reduced, particularly at initial stages of the transformation process where $X \ll 1$, by lack of terms of orders lower than X^2 in the correction terms. So, the solution of continuity equation for the regime of $\dot{X}/D_1^{\text{rot}} \ll 1$ can be very

well approximated by the solution (eq.58) obtained for zero rotational diffusion constant. One concludes also that at the regime $\dot{X}/D_1^{\text{rot}} \ll 1$, orientation distribution of single elements does not achieve any stationary and oriented form as the $\delta = 0$ solution does.

CRYSTALLINE VS. AMORPHOUS ORIENTATION

Continuity equation for orientation distribution of the mass of the system transformed into clusters, i.e. the crystalline mass orientation distribution, can be derived from the system of continuity equations for orientation distribution of clusters, formulated earlier in this paper. Following the assumption of totally hindered rotational motion of clusters, the continuity equation for the orientation distribution of transformed mass, derived from the system of eqs.(24) by adding all the equations by sides and assuming steady-state nucleation, reads

$$\frac{d\psi}{dt} + \frac{\dot{X}}{X} \left[\psi - \frac{dj_{st}(w_1)/d\hat{g}}{\int_{\Omega} dj_{st}} \right] = 0, \quad (69)$$

where the normalized orientation distribution of transformed mass is defined

$$\psi(\hat{g}, t) = \frac{\sum_2 dn_g(\hat{g}, t)}{\int_{\Omega} \sum_2 dn_g(\hat{g}, t)}. \quad (70)$$

It is also assumed, that

$$\lim_{g \rightarrow \infty} (dj_g/d\hat{g}) = 0.$$

Solution of the first order, linear eq.(69) with the assumption of zero degree of transformation at the initial moment of time, $X(t=0) = 0$, reads

$$\Psi(\vartheta, t) = \frac{1}{X(t)} \int_0^t \dot{X} \frac{dj_{st}(w_1(\vartheta, t'))/d\vartheta}{\int_{\Omega} dj_{st}} dt' \quad , \quad (71)$$

where $X(t)$ is degree of transformation at the moment of time, t . The function under integral in eq.(71) depends, in general, on the orientation distribution, w_1 , which is time-dependent, and the distribution Ψ is affected at any moment of time by history of amorphous orientation during the transformation process. Thus, rotational diffusion of single elements should influence crystalline orientation according to the ratio D_1^{rot}/\dot{X} the same way as it does for amorphous orientation.

At the initial moment of the transformation process, solution (eq.71) reduces to

$$\Psi^0(\vartheta) = \lim_{t \rightarrow 0} \Psi(\vartheta, t) = \frac{dj_{st}^0(w_1^0)/d\vartheta}{\int_{\Omega} dj_{st}^0} \quad , \quad (72)$$

and the crystalline orientation distribution function at $t=0$ equals to initial angular distribution of nucleation rate resulting from w_1^0 , and it is not affected, obviously, by the rotational diffusion.

Amorphous and crystalline uniaxial orientations are usually characterized by orientation factors

$$f_a = 2\pi \int_{-1}^1 w_1 P_2(\cos\vartheta) d(\cos\vartheta) \quad \text{and} \quad f_c = 2\pi \int_{-1}^1 \Psi P_2(\cos\vartheta) d(\cos\vartheta) \quad (73)$$

Effects of rotational diffusion occurring in amorphous matrix on the orientation factors f_a and f_c will be discussed below for the regimes $\dot{X}/D_1^{\text{rot}} \ll 1$ and $D_1^{\text{rot}}/\dot{X} \ll 1$.

1. Amorphous and Crystalline Orientation
at the Regime $\dot{X}/D_1^{\text{rot}} \ll 1$.

For an uniaxial orientation the orientation distribution of single elements expanded in a series over Legendre polynomials with the accuracy to the correction term of the order of ϵ reads

$$w_1(\theta, t) = w_1^0(\theta) + \epsilon \sum_{n=1}^{\infty} \sum_{i=1}^{\infty} \beta_{ni} (1 - \exp(-t/\tau_i)) P_{2n}(\cos\theta) \quad (74)$$

where $\tau_i = 1/\lambda_i$ are time characteristics of the system, and β_{ni} are constants. The corresponding orientation factor of the amorphous matrix, f_a , converges to its stationary value, and reads

$$f_a(t) = f_a^0 + (4\pi/5) \epsilon \sum_{i=1}^{\infty} \beta_{1i} (1 - \exp(-t/\tau_i)) \quad (75)$$

where f_a^0 denotes initial amorphous orientation factor.

Taking into consideration effects of the settle time only ($\tau_s = \tau_1$) the orientation factor f_a assumes following form with the accuracy to the term linear in ϵ (compare eqs.50,51)

$$f_a(t) = f_a^0 - \frac{1}{6} \epsilon (1 - \exp(-t/\tau_s)) (1 + 2A^2/21 - 1772A^4/21609 + \dots)$$

$$\times [f_c^0 - f_a^0 - 108A^2(1 - 2A^2/539 + \dots)(g_c^0 - g_a^0)/245] + O(\epsilon^2)$$

(76)

where f_c^0 is the initial orientation factor of resulting aggregates, and g_a^0 and g_c^0 are the moments presented by eqs.(52).

Amorphous orientation factor, as predicted by eq.(76), drops down with increasing time starting from its initial value f_a^0 , and achieves stationary value as $t/\tau_s \rightarrow \infty$.

$$f_a^{st} = \lim_{t/\tau_s \rightarrow \infty} f_a(t) \quad (77)$$

The final, stationary orientation factor for amorphous matrix is slightly lower than the initial one by the correction term of the order of ϵ . The decrease in the orientation factor is related to the kinetics of the transformation process and it is the higher, the slower is rotational diffusion of the single elements and the faster is the transition process. Under this regime the main change in the amorphous orientation, according to eq.(76), occurs at very early stages of the transformation process (at $t \ll t_{1/2}$), where the degree of transformation is very low, $X \ll 1$. Thus, the transformation under the regime is accompanied practically by the stationary orientation of amorphous matrix. Kinetic effects of transformation are very much reduced by rotational diffusion of single elements, and do not affect much the equilibrium distribution. Under the regime crystalline orientation distribution also changes in time, mainly at the beginning of the transformation process, and the distribution of transformed material can be derived from eq.(71) substituting

$$\dot{X} = G^* \int_{\Omega} dj_{st}/n_1(t=0),$$

and assuming $X \ll 1$. Then for low degrees of transformation,

$$\Psi(\theta, t) \approx \frac{\int_0^t \int_C w_1(\theta, t) \exp\left[-\frac{\Delta F_{iso}^*/kT}{1 - (kT/\Delta f_{iso}) \ln(4\pi w_1)}\right] dt}{\int_0^t \left\{ \int_{\Omega} w_1 \exp\left[-\frac{\Delta F_{iso}^*/kT}{1 - (kT/\Delta f_{iso}) \ln(4\pi w_1)}\right] d\theta \right\} dt}, \quad (78)$$

where $w_1(\theta, t)$ is given by eq.(74)

At higher degrees of transformation the ratio $t/\tau_s \rightarrow \infty$, and orientation distribution of single elements as well as resultant orientation distribution of transformed mass, Ψ , approach their stationary forms. Thus, for $X < 1$ eq.(71) reduces to

$$\lim_{t/\tau_s \rightarrow \infty} \Psi(\theta, t) = \Psi_{st}(\theta) = \frac{dj_{st}(w_1^{st})/d\theta}{\int_{\Omega} dj_{st}}, \quad (79)$$

and crystalline orientation distribution function equals to angular distribution of nucleation rate at the stationary amorphous distribution, w_1^{st} .

Figure 5 shows the behaviour of amorphous, f_a , and crystalline, f_c , orientation factors predicted by the present theory for polyethylene crystallizing at low undercoolings, and oriented by "cosine square" uniaxial potential (eq.50). The orientation factor f_a slightly drops down within a range of low degrees of transformation from their initial values f_a^0 (computed for w_1^0 , and f_c^0 computed for Ψ^0 (ec.72)) to value remaining constant over the whole range of the transformation. X. Fig.5 shows relatively high values for the crystalline orientation factor, f_c , which remain practically constant at the time of transformation.

2. Amorphous and Crystalline Orientation
at the Regime $D_1^{\text{rot}}/\dot{\chi} \ll 1$.

Amorphous and crystalline orientation factors will be discussed first for the asymptotic case, $D_1^{\text{rot}}/\dot{\chi} = 0$. The asymptotic amorphous orientation factor, $f_{a,\delta=0}$ can be computed numerically using orientation distribution w_1 determined numerically from the continuity equation in the asymptotic form (eq.56) for any degree of transformation.

For lower degrees of transformation, the distribution of single elements, w_1 , has been determined in the form of series expansion over X (eq.58), and the related amorphous orientation factor drops down linearly with increasing X at initial stages of the transformation process

$$f_{a,\delta=0}(X) = f_a^0 - (f_c^0 - f_a^0)X + O(X^2), \quad (80)$$

where f_a^0 , f_c^0 are initial amorphous and crystalline orientation factors corresponding, respectively, to w_1^0 and Ψ^0 initial orientation distributions, and $f_c^0 - f_a^0 > 0$.

For the case of $D_1^{\text{rot}}/\dot{\chi} = 0$ continuity equations for amorphous and crystalline orientation distributions read

$$\frac{dw_1}{dX} + \frac{1}{1-X} \left[\frac{dj_{st}(w_1)/d\xi}{\int_{\Omega} dj_{st}} - w_1 \right] = 0, \quad (81)$$

$$\frac{d\Psi}{dX} - \frac{1}{X} \left[\frac{dj_{st}(w_1)/d\xi}{\int_{\Omega} dj_{st}} - \Psi \right] = 0, \quad (82)$$

and their combination leads to

$$\frac{d}{dX} [(1 - X)w_1 + X\bar{w}] = 0 \quad (83)$$

Eq.(83) with the initial condition $w_1 = w_1^0$ at $X = 0$ provides

$$\bar{w}_{\delta=0}(\underline{\xi}, X) = \frac{1}{X} [w_1^0 - (1 - X)w_1(\underline{\xi}, X)] , \quad \text{for } X > 0 \quad (84)$$

where

$$\lim_{X \rightarrow 0} \bar{w}_{\delta=0}(\underline{\xi}, X) = \bar{w}^0(\underline{\xi}, X) = \frac{dj_{st}(w_1^0)/d\underline{\xi}}{\int_{\Omega} dj_{st}^0} \quad (85)$$

And, consequently, crystalline orientation factor is expressed by the corresponding amorphous orientation factor and degree of transformation

$$f_{c, \delta=0}(X) = \frac{1}{X} [f_a^0 - (1 - X)f_{a, \delta=0}(X)] , \quad (86)$$

and

$$\lim_{X \rightarrow 0} f_{c, \delta=0} = f_c^0 = 2\pi \int_{-1}^1 P_2(\cos\theta) \frac{dj_{st}^0/d\underline{\xi}}{\int_{\Omega} dj_{st}^0} d(\cos\theta) \quad (87)$$

For low degrees of transformation substitution of eq.(80) into eq.(86) provides

$$f_{c, \delta=0}(X) = f_c^0 - [(f_c^0 - f_a^0) + \frac{1}{2} \frac{\partial^2 f_a}{\partial X^2} \Big|_{X=0}] X + \theta(X^2) \quad (88)$$

Eq.(88) predicts similar behaviour of the crystalline orientation factor as it is predicted for amorphous orientation with higher slope related to the second derivative term in the eq.

Assuming $D_1^{\text{rot}}/\dot{X} \ll 1$ the differential eq.(83) assumes following form with correction term of the order of $\delta = D_1^{\text{rot}}/\dot{X}$

$$\frac{\partial}{\partial X} [(1-X)w_1 + X\bar{w}] = \delta(1-X)L_g(w_1, U_1)M(\theta, X)|_{w_1} \quad (89)$$

where $w_1(\theta, X)$ and operator $L_g(\cdot)$ are given by eqs.(60) and (29), respectively, and $M(\theta, X)|_{w_1} = \int dj_{st}(w_1^0) / \int dj_{st}(w_1(X))$.

Crystalline orientation distribution determined from eq.(89) with the first correction proportional to δ taken into account, reads

$$\bar{w}_{0,\delta}(\underline{\theta}, X) = \bar{w}_{0,\delta=0}(\underline{\theta}, X) + \delta \frac{1}{X} \left[\int_0^X (1-X')L_g(w_{1,\delta=0}, U_1) \cdot$$

$$M(\theta, X)|_{w_{1,\delta=0}} dX' - (1-X)u_1(\underline{\theta}, X) \right] + \mathcal{O}(\delta^2) \quad (90)$$

$w_{1,\delta=0}$ denotes orientation distribution of single elements at $D_1^{\text{rot}}/\dot{X} = 0$, u_1 is given by eq.(63).

Substitution of the orientation distribution w_1 in the form of series expansion over degree of transformation (eq.68) into eq.(90) leads, for low degrees of transformation, to

$$\begin{aligned} \bar{w}_{0,\delta}(\underline{\theta}, X) = & \bar{w}_{0,\delta=0}(\underline{\theta}, X) + \delta[Xu_{12} + \\ & + \frac{1}{X} \int_0^X (1-X')L_g(w_{1,\delta=0}, U_1)M(\theta, X)|_{w_{1,\delta=0}} + \mathcal{O}(\delta^2) \end{aligned} \quad (91)$$

u_{12} in the correction term is given by eq.(67b).

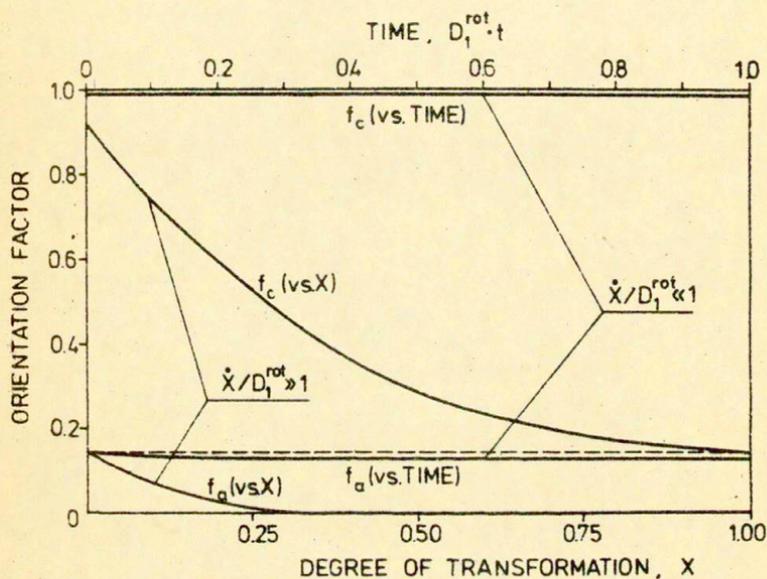


Fig. 5. Amorphous, f_a , and crystalline, f_c , orientation factors vs. degree of transformation, X, or time, $t \cdot D_1^{\text{rot}}$, shown for diffusion controlled ($\dot{X}/D_1^{\text{rot}} \ll 1$) and kinetics controlled ($\dot{X}/D_1^{\text{rot}} \gg 1$) nucleation.

Consequently, crystalline orientation factor at the condition $D_1^{\text{rot}}/\dot{K} \ll 1$ is determined by crystalline orientation factor at zero rotational diffusion constant, $f_{c,\delta=0}$, corrected by a term related to the correction in the crystalline orientation distribution in eqs.(90,91).

Numerical computations of amorphous and crystalline orientation factors are performed for polyethylene, and the results are shown in Fig.5 also for the asymptotic case of completely hindered rotational diffusion effect ($D_1^{\text{rot}}/\dot{K} = 0$). Amorphous orientation factor decreases monotonically to zero with increasing degree of transformation, X , and, consequently to eq.(86), crystalline orientation factor drops down considerably with increasing X to the asymptotic value equal to the value of initial amorphous orientation factor.

One concludes that rotational diffusion of single elements when not suppressed by kinetic effects of nucleation (low supercoolings), leads to high level crystalline orientation in system crystallized under orienting external forces. Suppression of the rotational diffusion effect by decreasing temperature and/or increasing the transformation rate results in lower crystalline as well as amorphous orientations comparing to the initial orientations produced by the orienting forces.

REFERENCES

1. J.Frenkel, Kinetic Theory of Liquids, Oxford University Press, London, 1946
2. D.Turnbull and J.C.Fisher, J.Chem.Phys., 17, 71, (1949)
3. F.C.Frank and M.Tosi, Proc.Royal Soc.(London), 263, 323, (1961)
4. A.Ziabicki and L.Jarecki, J.Chem.Phys. (in press)
5. J.D.Hoffman and J.I.Lauritzen, J.Res.NBS, 65A, 297, (1961)
6. A.Ziabicki and L.Jarecki, IFTB Reports 20/1981
7. A.Ziabicki, J.Chem.Phys., 65, 1638, (1977)

8. A.Ziabicki and L.Jarecki, IFTK Reports 1/1982
9. A.Ziabicki and L.Jarecki, Colloid Polymer Sci., 256, 332, (1978)
10. A.Ziabicki and L.Jarecki, The Theory of Molecular Orientation and Oriented Crystallization in High Speed Spinning in: "High Speed Melt Spinning", J.Wiley, New York (in press).
11. R.J.Roe and W.R.Krigbaum, J.Appl.Phys., 35, 2215, (1964)
12. B.Zimm, G.Roe, L.Epstein, J.Chem.Phys., 24, 279 (1956)

SUMMARY

The role of rotational diffusion of single amorphous elements in kinetics of oriented nucleation of new phase is discussed. A new theory of nucleation proposed recently for systems composed of asymmetric amorphous elements and exhibiting any degree of orientation is applied. The resultant nucleation rate is dependent on the orientation angle.

The angle-dependent kinetics of nucleation and the orientation distribution of single amorphous elements are coupled in the theory, and equation of continuity formulated in this paper for single elements takes into consideration rotational diffusion as well as kinetics of transformation. Forces inducing orientation of the elements are assumed to be potential, and rotational diffusion of clusters is neglected.

Effects of coupled rotational diffusion of amorphous elements and angle-dependent nucleation rate are discussed more details for two asymptotic cases. At the case of rotational diffusion predominating kinetic effects the system achieves stationary amorphous and crystalline orientations. Much higher degree of crystalline orientation in this case appears as an effect of dominating role of rotational diffusion in the process. Suppression of the role of rotational diffusion accompanying an increase in the transformation rate leads to the other asymptotic case, and the amorphous and crystalline orientation distributions appear to be non-stationary. Corresponding amorphous and crystalline orientation factors drop down monotonically with increasing degree of transformation. At the asymptotic case of totally reduced rotational diffusion effects crystalline orientation factor predicted in this paper for total transformation drops down to the value of initial amorphous orientation factor (at zero degree of transformation).

Numerical computations are performed for polyethylene.