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IN SYSTEMS OF ASYMMETRIC PARTICLES

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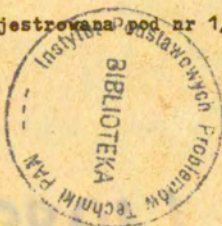


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INTRODUCTION

It has been noted in an earlier paper from this series¹, that orientability of asymmetric single elements affects nucleation kinetics and thermodynamics in the same way as dilution of the system by an inert component. The effective driving force for cluster growth in a dilute system of orientable particles includes an additional entropy term related to total molar fraction of single elements, C , and effectivity

coefficient of such elements, H

$$\tilde{\Delta F} = \Delta F_0 - (g-1) kT \ln(CH) \quad (1)$$

This result, which satisfies necessary thermodynamic conditions was guessed in¹, rather than systematically derived. The result, obtained from continualized and linearized form of the nucleation theory by Fisher and Turnbull² was different, and obviously approximate¹.

The effectivity coefficient H, or the fraction of single elements capable of being attached to the growing cluster was postulated in¹ in the form

$$H(\underline{\vartheta}) = w(\underline{\vartheta}) \Delta\omega \quad (2)$$

where $w(\underline{\vartheta})$ is orientation distribution density of single elements, and $\Delta\omega$ is "tolerance angle", i.e. the range of disorientation around the orientation of the growing cluster, $\underline{\vartheta}$. In other words, $H(\underline{\vartheta})$ is the probability that an element is oriented consistently with the growing cluster within the range $\Delta\omega$.

In the original paper¹, the "tolerance angle" $\Delta\omega$ was assumed a model parameter without any physical interpretation. Systematic derivation of eq.(1) was lacking and, last, not least, the thermodynamic sense of the driving force $\tilde{\Delta F}$, i.e. the driving force ΔF_0 for nucleation in an undiluted ($C=1$) system of symmetric, unorientable particles ($H=1$), completed with the additional entropy term was not clear. Extending our research on the theory of nucleation of asymmetric particles,

we have found it necessary to reexamine physical sense of the basic parameters of the nucleation theory, referring to the fundamentals of phenomenological and statistical thermodynamics. This applies, first of all to the driving forces (free energies) $\Delta\bar{F}$ and ΔF_0 . To derive eq.(1) we have moved from the continualized formalism of Fisher and Turnbull² to a more general, discrete theory of nucleation used, i.al. by Frank and Tosi³. It will be shown that eq.(1) results from strict derivation, if the discrete formalism is applied, thus confirming our earlier guess¹.

The following section and Appendix A are concerned with fundamentals of the discrete theory of nucleation in dilute systems of symmetric particles. Further sections and Appendix B deal with orientable particles and effects of their orientation on nucleation kinetics and thermodynamics. The parameter $\Delta\omega$ will be derived from statistical mechanics in Appendix B.

It should be noted that throughout this paper n_1 will be used for molar fraction of single elements (replacing C in ref.¹) and Δ for "tolerance angle" (instead of $\Delta\omega$ used in¹).

It should also be noted that above, and throughout all our papers on oriented nucleation, $\underline{\xi}$ denotes a set of angles describing completely state of orientation of the given particle. So, $\underline{\xi}$ is a pair of polar angles for axially symmetric particles, and a triad of Euler angles for a triaxial particle

$$\underline{\xi} = \left. \begin{array}{l} (\theta, \varphi) \text{ for cylindrical symmetry} \\ (\theta, \varphi, \psi) \text{ for triaxial symmetry} \end{array} \right\} \quad (3)$$

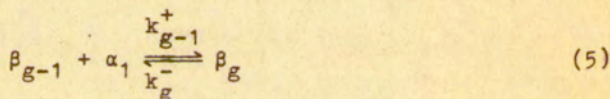
Similarly, $d\Omega$ is volume element in the appropriate orientation space

$$d\Omega = \left. \begin{array}{l} \sin\theta \, d\theta \, d\varphi \text{ for cylindrical symmetry} \\ \sin\theta \, d\theta \, d\varphi \, d\psi \text{ for triaxial symmetry} \end{array} \right\} \quad (4)$$

Hence, the total measure of the orientation space, $\Omega = \int d\Omega$ assumes values 4π and $8\pi^2$, respectively, for cylindrical and triaxial symmetry.

FUNDAMENTAL EQUATIONS OF NUCLEATION KINETICS

The formalism presented below is almost identical with known treatments of Frank and Tosi³, Lauritzen and Hoffman⁴ and many others. The new element is definition of the appropriate potential barriers in the rate constants k^+ , k^- . For a set of bimolecular reactions of growth and dissociation of clusters of size g , β_g , and single elements (atoms, molecules), of the mother phase, α_1



one can write the set of equations for fluxes j_g of clusters in the one-dimensional space of sizes g :

$$\left. \begin{array}{l} j_1 = k_1^+ n_1 \cdot n_1 - k_2^- n_2 \\ j_2 = k_2^+ n_2 \cdot n_1 - k_3^- n_3 \\ \dots\dots\dots \\ j_g = k_{g-1}^+ n_{g-1} \cdot n_1 - k_g^- n_g \end{array} \right\} \quad (6)$$

together with a continuity condition

$$dn_g/dt + j_{g+1} - j_g = 0 \quad (7)$$

In eqs.(6)-(7) k_g^+ , k_g^- denote, respectively, rate constants for growth and dissociation of g -size clusters, g - dimensionless cluster volume (number of single elements included in the cluster), and $n_g = N_g/(N_0 + N_1 + \sum_2^{\infty} N_g)$ molar fractions of g -clusters in the system. N_0 denotes the number of molecules of inert species (diluent) in the system, N_1 - the number of single elements participating in cluster growth reactions, and N_g - numbers of clusters with size g ($g = 2, 3, \dots$).

Formal solutions of eqs.(6)-(7) can be obtained in two special cases, for which cluster size distributions n_g are independent of time.

i. $j_g=0$ (thermodynamic equilibrium)

From the system of eqs.(6) results immediately equilibrium distribution of cluster sizes:

$$(n_g)_{eq} = (n_1)^g \prod_{i=2}^g (k_{i-1}^+/k_i^-) \quad (8)$$

Eq.(8) has a physical sense, i.e. the equilibrium distribution n_g is not divergent, only if the product on the right hand side vanishes at $g = \infty$.

n_1 in eq.(8) is also a resulting, equilibrium concentration (molar fraction) of single elements. The normalization

condition to be satisfied in the state of equilibrium is constant mass, i.e.

$$\sum_{g=1}^{\infty} g n_g = \text{const.}$$

which together with eq.(8) determines equilibrium fraction of single elements, n_1 .

ii. $j_g = j = \text{const.} > 0$ (steady state)

Simple operations performed on subsequent equations of the system (6) (cf.³) yield

$$k_1^+ n_1^2 - k_g^- n_g n_1 \prod_{i=2}^{g-1} (k_i^- / k_i^+ n_1) = j \left[1 + \sum_{k=2}^{g-1} \prod_{i=2}^k (k_i^- / k_i^+ n_1) \right] \quad (9)$$

Requiring that the resulting distribution of cluster sizes disappears at $g = \infty$

$$\lim_{g \rightarrow \infty} (n_g) = 0 \quad , \quad (10)$$

one obtains the steady-state flux

$$j_{st} = k_1^+ n_1^2 / [1 + \Sigma(2, \infty)] \quad (11)$$

and the corresponding steady-state distribution of cluster sizes

$$(n_g)_{st} = n_1^g \prod_{i=2}^g (k_{i-1}^+ / k_i^-) \Sigma(g, \infty) / [1 + \Sigma(2, \infty)] \quad (12)$$

where

$$\Sigma(r, s) = \sum_{k=r}^s \prod_{i=2}^k (k_i^- / k_i^+ n_1)$$

Eqs.(8),(11) and (12) provide formal solutions of the equilibrium and steady-state nucleation problems. Evaluation of these results requires that the rate constants k_g^+ , k_g^- are determined.

Unlike in the state of equilibrium, now the concentration of single elements, n_1 , is assumed a predetermined constant. In fact, constant (and steady-state) production of new nuclei is compatible with constant n_1 , only when such elements are supplied from an external source. Steady-state nucleation theory implies therefore, that clusters reaching some critical size split into single elements and these are added to the system.

Some information about the association and dissociation rate constants can be drawn out of the principles of chemical thermodynamics. It can be shown (cf. Appendix A) that the ratio of these constants in the conditions of thermodynamic equilibrium ($j_g = 0$) is solely determined by chemical potential of the transition $(\alpha_{g-1}, \beta_1) \rightarrow (\alpha_g)$

$$(k_g^- / k_{g-1}^+)_{eq} = \exp(\Delta\mu_g^0 / kT) \quad (13)$$

where (cf. eq.A11 in Appendix A)

$$\Delta\mu_g^0 = \Delta F_0(g) - \Delta F_0(g-1) \cong d \Delta F_0(g)/dg$$

The relation (13) derived for thermodynamic equilibrium, is commonly extended on steady-state conditions assuming that k_g^+/k_g^- are identical in the conditions of equilibrium and beyond. This assumption, like others involved in the nucleation theory (e.g. linear dependence of ΔF_0 on temperature) confine applications of the theory to the conditions not too far from equilibrium.

Both rate constants can be presented in the general form

$$k_g^{+,-} = \nu g^{\frac{2}{3}} \exp(-U_g^{\pm}/kT) \quad (14)$$

where ν is fundamental frequency of events leading eventually to reactions indicated in eq.(5), the factor $g^{\frac{2}{3}}$ (proportional to the surface area of the g -cluster) accounts for different number of sites on cluster surface accessible for reactions, and U_g^+ , U_g^- are potential barriers which must be overcome by reacting single elements. It is usually assumed that U_g^+ , U_g^- are linear combinations of the activation energy of self-diffusion in the system, responsible for transfer of single elements from, and to cluster surface ϵ , and the chemical potential of transition $\Delta\mu_g^0$. From eq.(13) and the assumption $g^{\frac{2}{3}} \cong (g-1)^{\frac{2}{3}}$ it follows that

$$kT \ln(k_{g-1}^+/k_g^-) \cong U_{g-1}^- = - \Delta\mu_g^0 \quad (15)$$

In the existing theories of nucleation appear various, and

rather arbitrary assumptions about the partition of $\Delta\mu_g^0$ between the two barriers. Writing

$$\left. \begin{aligned} U_{g-1}^+ &= \epsilon + z \Delta\mu_g^0 \\ U_g^- &= \epsilon - (1 - z) \Delta\mu_g^0 \end{aligned} \right\} \quad (16)$$

which satisfies the equilibrium condition (15), the partition coefficient, z , was assumed $\frac{1}{2}$ (ref.²), 0 (ref.³) or 1 (ref.⁴). All assumptions about the constant z lead to inconsistency at some values of $\Delta\mu_g^0$ and ϵ (negative potential barrier). Considering two situations presented in figure 1. it becomes evident that the partition of $\Delta\mu_g^0$ between U_{g-1}^+ and U_g^- should be different for positive (fig.1a) and negative (fig.1b) chemical potentials. In the first case, positive chemical potential affects the association transition (i.e. potential U_{g-1}^+), but there is no reason why it should have any effect on dissociation (potential U_g^-). In the case of negative $\Delta\mu_g^0$ (fig.1b) the reverse is true. The barrier to dissociation U_g^- must be increased and the more so, the deeper is the initial level (the larger $|\Delta\mu_i^0|$), while association (U_{g-1}^+) should not feel the final level, and $\Delta\mu_g^0$. Thus reasonable partition of $\Delta\mu_g^0$ seems to be one corresponding to the following values of z

$$z = \begin{cases} 1 & \text{for } \Delta\mu_g^0 > 0 \\ 0 & \text{for } \Delta\mu_g^0 \leq 0 \end{cases} \quad (17)$$

Consequently, we will use in further considerations rate constants in the form:

$$\left. \begin{aligned} k_{g-1}^+ &= \nu g^{\frac{3}{2}} \exp(-\epsilon/kT) \exp[-\frac{1}{2}(\Delta\mu_g^0 + |\Delta\mu_g^0|)/kT] \\ k_g^- &= \nu g^{\frac{3}{2}} \exp(-\epsilon/kT) \exp[\frac{1}{2}(\Delta\mu_g^0 - |\Delta\mu_g^0|)/kT] \end{aligned} \right\} \quad (18)$$

The fundamental frequency ν depends on the nature of the system undergoing transition. For gas systems, ν can be related to the frequency of binary collisions, for nucleation of vacancies in crystals to oscillations in the crystal lattice, etc. Using the relation (13) equilibrium cluster size distribution (eq.8) reduces to

$$(n_g)_{eq} = n_1^g \exp(-\sum_{i=2}^g \Delta\mu_i^0/kT) = n_1^g \exp[-\Delta F_0(g)/kT] \quad (19)$$

or, introducing a new potential

$$\tilde{\Delta F}(g) = \Delta F_0(g) - (g-1)kT \ln n_1 \quad (20)$$

n_g assumes the form of a Boltzmann distribution

$$(n_g)_{eq} = \exp[-\tilde{\Delta F}(g)/kT]. \quad (21)$$

$\tilde{\Delta F}$ includes the chemical potential of the transition

$$\Delta F_0(g) = \mu_g^0 - g \mu_1^0$$

plus an additional term related to the molar fraction of single elements, n_1 . As noted in¹ this additional entropy term can be interpreted as part of the free energy of mixing

of single elements with other species in the system. Its thermodynamic sense is now made absolutely clear in Appendix A. The derivation presented above proves that the correct form of the complete driving force for transition $\Delta\tilde{F}(g)$ is given by eq.(20) in contrast to the approximate expression

$$\Delta\tilde{F}(g) \cong (n_1 + 1) \Delta F_0(g)/2 - n_1 - g kT(1 - n_1)/n_1 \quad (20a)$$

obtained in¹ from the continualized and linearized nucleation theory⁴. Note that in eqs.(20,20a) n_1 should be compared with the product (CH) appearing in¹ and denoting the fraction of effective single elements.

Extending validity of the equilibrium relation between rate constants onto the steady-state case we obtain.

$$(n_g)_{st} = n_1 \exp[-\Delta\tilde{F}(g)/kT] \Sigma(g, \infty) / \Sigma(1, \infty) \quad (22)$$

In eq.(22) functions Σ assume the form

$$\Sigma(r, s) = \sum_{i=r}^s (k_1^+ / k_i^+) \exp[\Delta\tilde{F}(i)/kT]$$

Several ways can be employed to evaluate the infinite sum appearing in the steady-state flux (eq.12). Taking into account that the individual terms are controlled, first of all, by the exponential function $\exp(\Delta\tilde{F}/kT)$, while the exponent, $\Delta\tilde{F}(g)$, exhibits a maximum, one can approximate $\Sigma(1, \infty)$ by its maximum term

$$\Sigma(1, \infty) \cong k_1^+ \frac{1}{k_{g^*}^+} \exp(\Delta\tilde{F}/kT) \Big|_{g=g^*} \quad (23)$$

In this approximation, the steady-state flux (nucleation rate) results in the form

$$j_{st} = k_{g^*}^+ n_1^2 \exp(-\Delta\tilde{F}_{max}/kT) \quad (24)$$

Alternatively, the sum can be replaced by an integral, the exponent expanded in series around its maximum, truncated at the quadratic term, and integrated to yield (cf.⁵)

$$j_{st} = k_{g^*}^+ n_1^2 \exp(-\Delta\tilde{F}_{max}/kT) [2\pi kT / (-d^2\Delta\tilde{F}/dg^2)_{g^*}]^{\frac{1}{2}} \quad (25)$$

In any case, the exponential of $(\Delta\tilde{F}_{max}/kT)$ is the controlling term.

An important nucleation characteristic is the critical condition for the phase transition, i.e. the condition when the steady-state distribution, eq.(22) can no more be reached, and the distribution reaches the equilibrium form eq.(21). The necessary and sufficient condition for such a transition is divergent potential $\Delta\tilde{F}(g)$, i.e.

$$\lim_{g \rightarrow \infty} \Delta\tilde{F}(g)/kT = \infty \quad (26)$$

or

$$\lim_{g \rightarrow \infty} (\Delta\mu_g^0 - kT \ln n_1) = 0 \quad (27)$$

Equations (26, 27) determine critical conditions for phase transition, i.e. the relation between temperature T, and molar fraction of single elements, n_1 , for which the transition

becomes thermodynamically possible.

As evident from the above solutions, the two potentials, $\Delta F_0(g)$ and $\Delta \tilde{F}(g)$ play different roles in the nucleation theory. Concentration-independent potential, $\Delta F_0(g)$, and its derivative, $\Delta \mu_g^0$, controlled solely by the properties of pure components, determine partition of the thermodynamic contribution between the potential barriers to association and dissociation. Maximum of ΔF_0 with respect to g yields g_0^* , the critical point at which the chemical potential stops to contribute to the association constant k_{g-1}^+ and starts to control dissociation constant k_g^-

$$g_0^*: \Delta F(g_0^*) = \max; \quad \Delta \mu_{g_0^*}^0 = 0 \quad (28)$$

$$U_{g-1}^+ = \begin{cases} \epsilon + \Delta \mu_g^0 & \text{for } g \leq g_0^* \\ \epsilon & \text{for } g > g_0^* \end{cases} \quad (29)$$

An analogous relation holds for U_g^- . On the other hand, steady-state nucleation rate j_{st} , and the corresponding steady-state cluster size distribution are controlled by the complete potential, $\Delta \tilde{F}(g)$. Its maximum appearing at the cluster size, g^*

$$g^*: \Delta \tilde{F}(g^*) = \max.; \quad \Delta \mu_{g^*}^0 - kT \ln n_1 = 0 \quad (30)$$

controls j_{st} and $(n_g)_{st}$. Generally

$$g^* \geq g_0^* \quad (31)$$

and the rate constant $k_{g^*}^+$ appearing in eqs.(24,25) does not,

according to eq.(29) include chemical potential $\Delta\mu_{g^*}^0$:

$$k_{g^*}^+ = v g^{*3} \exp(-\epsilon/kT) \quad (32)$$

so that the steady-state nucleation rate is determined solely by the potential $\Delta\bar{F}(g)$.

NUCLEATION IN SYSTEMS OF ORIENTABLE PARTICLES

Nucleation equations derived in the preceding section concern systems composed of symmetric clusters and symmetric single elements i.e. particles for which no spatial orientation can be specified (fig.2a). For such systems kinetic considerations are based on the equations for fluxes, j_g , in which all kinetic elements are equally effective in association-dissociation reactions and in which appear total concentrations (molar fractions) of all species, n_g

$$j_g = k_{g-1}^+ n_{g-1} n_1 - k_g^- n_g \quad (33)$$

We will consider now systems in which single elements and/or clusters are asymmetrical and whose orientations in space can be distinguished.

Consider first a system of asymmetric, orientable clusters formed from symmetric, unorientable single elements (fig.2b). In such systems, nucleation can be separated into classes of clusters with different orientations, $\underline{\xi}$. Kinetic equation for a class of orientations $\underline{\xi}$, $\underline{\xi} + d\underline{\xi}$ can be written in the form

$$dj_g(\underline{\xi}) = k_{g-1}^+ dn_g(\underline{\xi}) \cdot n_1 - k_g^- dn_g(\underline{\xi}) \quad (34)$$

The first equation of the system, that for $g=2$, includes $dn_1(\underline{\xi})$. Since single elements were assumed unorientable, their orientation distribution $dn_1/d\underline{\xi}$ can be considered as uniform and equal to the reciprocal measure of the orientation space, Ω . Therefore

$$dn_1 = (dn_1/d\underline{\xi}) d\underline{\xi} = n_1/\Omega \quad (35)$$

and the first kinetic equation results in the form

$$dj_2(\underline{\xi}) = k_1^+(n_1^2/\Omega) d\underline{\xi} - k_2^- dn_2(\underline{\xi}) \quad (36)$$

Solving the system of equations (34) with eq.(36) for $g=2$ we arrive at the steady-state nucleation rate distribution

$$dj_g(\underline{\xi})/d\underline{\xi} = (1/\Omega)k_{g*}^+ n_1^2 \exp[-\Delta\tilde{F}(g^*, \underline{\xi})/kT] \quad (37)$$

where maximum term approximation has been used. For the sake of generality, the rate constants k_g^+, k_g^- were considered functions of orientation; hence also the free energy of transition ΔF_0 , the potential $\Delta\tilde{F} = \Delta F_0 - (g-1)kT \ln n_1$, and coordinates of its maximum,

$$g^*(\underline{\xi}) : \quad \partial\Delta\tilde{F}(g, \underline{\xi})/\partial g = 0 \quad (38)$$

are functions of orientation $\underline{\xi}$.

Similarly, for equilibrium distribution of clusters we obtain

$$\begin{aligned} dn_g(\underline{g})/d\underline{g}|_{eq} &= (1/\Omega) n_1^g \exp[-\Delta F_o(g, \underline{g})/kT] = \\ &= (n_1/\Omega) \exp[-\Delta \tilde{F}(g, \underline{g})/kT] \end{aligned} \quad (39)$$

Orientation dependence of the resulting nucleation characteristics is closely related to orientation-dependent energy of transition, ΔF_o . It is difficult, however, to name a process in which chemical potential of attaching one unorientable element to an orientable cluster, would depend on the orientation of the latter.

Even in the case of a dipole (multipole) cluster immersed in a linear directional force field (electrical, magnetical), chemical potential of the cluster would depend on its orientation, but the difference $\Delta \mu_g^o$ would not. Eliminating any orientation dependence from $\Delta \tilde{F}$, g^* and, $\Delta \tilde{F}^*$ in eqs.(37), (39), and integrating over the entire space of orientations Ω we arrive at the standard results obtained for unorientable particles in the previous section: eq.(21) for equilibrium cluster size distribution and eq.(24) for steady-state flux.

So, except for special situation when the potential of transition ΔF_o is orientation-dependent, nucleation in systems composed of asymmetric, orientable clusters with symmetric, unorientable single elements, does not introduce any new elements into the thermodynamic or kinetic characteristics of the nucleation process.

Combination of asymmetric clusters with asymmetric,

orientable single elements (fig.2c) offers a qualitatively new situation. Consider a class of clusters with orientation $\underline{\xi}$. Out of all n_1 single elements present in the system, only some are capable of reacting with clusters from the orientation class $\underline{\xi}$, viz. those whose orientations are consistent with those of clusters, i.e. $\underline{\xi}$. We will denote the fraction of such clusters $H(\underline{\xi})$. The fraction $H(\underline{\xi})$ of "consistently oriented" single elements, or the probability that a single element chosen at random is capable of reacting with clusters oriented at $\underline{\xi}$, cannot be based on the requirement that orientations of the cluster and the single element are strictly identical. For such a requirement, H would naturally be equal to zero. Therefore, in the earlier paper of this series¹ a model parameter called "tolerance angle" $\Delta\omega$ was introduced. (In this paper we will use a more adequate term "disorientation tolerance range" and Δ instead of $\Delta\omega$.) Single element is considered effective in the reactions of addition to clusters with orientation $\underline{\xi}$ if its orientation lies within the small, but finite, disorientation tolerance range Δ around $\underline{\xi}$. Disorientation tolerance range, introduced as an arbitrary parameter in¹ is now derived from statistical mechanical considerations in Appendix B. It is shown that Δ reduced by the measure of the entire orientation space Ω is related to the transition of rotational degrees of freedom of an asymmetric single element while in an uncombined state, into oscillatory degrees of freedom in the combined state after addition to the cluster. If $w(\underline{\xi})$ is normalized orientation distribution density of single elements in the system, the parameter $H(\underline{\xi})$ can be expressed as an integral of $w(\underline{\xi})$ over the disorientation tolerance range

around $\underline{\xi}$, $\Delta(\underline{\xi})$

$$H(\underline{\xi}) = \int_{\Delta(\underline{\xi})} w(\underline{\xi}) d\underline{\xi} ; \quad \int_{\Omega} w(\underline{\xi}) d\underline{\xi} = 1 \quad (40)$$

One can write alternatively

$$H(\underline{\xi}) = \Delta \cdot \langle w \rangle (\underline{\xi}) \quad (41)$$

where $\langle w \rangle (\underline{\xi})$ is average orientation density within the small tolerance range around $\underline{\xi}$. If Δ is small, and orientation density gradient $dw(\underline{\xi})/d\underline{\xi}$ not too large, the average orientation density can be replaced by point density at $\underline{\xi}$, $w(\underline{\xi})$

$$\Delta \ll \Omega : \quad H(\underline{\xi}) \approx \Delta \cdot w(\underline{\xi}) \quad (41a)$$

The latter, simplified form was proposed in¹, and will be used in numerical examples concerning oriented crystal nucleation in polyethylene later in this paper. However, the condition $\Delta/\Omega \ll 1$ is not always satisfied, and in some cases a complete formula (41) must be used. Such a situation occurs in crystal nucleation within ordered (liquid crystalline) domains where orientation distribution is extremely narrow and approaches delta-distribution. This problem will be considered at the end of this section.

Kinetic equations for a system of orientable clusters and orientable single elements assume for $g \geq 3$ the form

$$dj_g(\underline{\xi}) = k_{g-1}^+ dn_{g-1}(\underline{\xi}) n_1 \Delta \langle w \rangle (\underline{\xi}) - k_g^- dn_g(\underline{\xi}) \quad (42)$$

and for $g=2$

$$dj_2(\underline{\xi}) = k_1^+ n_1 w(\underline{\xi}) d\underline{\xi} n_1 \Delta \langle w \rangle(\underline{\xi}) - k_2^- dn_2(\underline{\xi}) \quad (43)$$

Assume, for a while, that orientation distribution of single elements is uniform

$$w(\underline{\xi}) = \langle w \rangle(\underline{\xi}) = 1/\Omega$$

Thus eqs.(42) assume the form

$$dj_g(\underline{\xi}) = k_{g-1}^+(\Delta/\Omega) dn_{g-1}(\underline{\xi}) n_1 - k_g^- dn_g(\underline{\xi}) \quad (44)$$

Eq.(43) transforms in the same way. It can be observed that eq.(44) is identical with eq.(34) and equivalent to eq.(33) derived for unorientable single elements but for a constant factor (Δ/Ω) at the addition rate constant k_{g-1}^+ . In other words, for a system of orientable, randomly distributed single elements the addition rate constant is reduced in the ratio (Δ/Ω) and the chemical potential of transition $\Delta\mu_g^0$ is correspondingly shifted, reducing the driving force for addition:

$$k_g^+ \rightarrow \hat{k}_g^+ = k_g^+(\Delta/\Omega) \quad (45)$$

$$\Delta\mu_g^0 \rightarrow \hat{\Delta}\mu_g^0 = \Delta\mu_g^0 - kT \ln(\Delta/\Omega) \quad (46)$$

$$\Delta F_0(g) \rightarrow \hat{\Delta}F_0(g) = \Delta F_0(g) - (g-1) kT \ln(\Delta/\Omega) \quad (47)$$

Since, generally, $(\Delta/\Omega) < 1$ the rate of cluster growth from

asymmetric particles is smaller than from symmetric elements. The chemical potential of addition of an asymmetric particle is increased by $-kT \ln(\Delta/\Omega)$ related to the entropy of disorientation of single elements.

Using modified rate constants, \hat{k}_g^+ , and chemical potentials, $\hat{\Delta}\mu_g^0$, one can solve the system of kinetic equations for an oriented system (i.e. for $dw/d\underline{g} \neq 0$):

$$\left. \begin{aligned} dj_2(\underline{g}) &= \hat{k}_1^+ n_1^2 w(\underline{g}) \langle w \rangle(\underline{g}) d\underline{g} \Omega - k_2^- dn_2(\underline{g}) \\ \dots\dots\dots \\ dj_g(\underline{g}) &= \hat{k}_{g-1}^+ dn_{g-1}(\underline{g}) n_1 \langle w \rangle(\underline{g}) \Omega - k_g^- dn_g(\underline{g}) \end{aligned} \right\} \quad (48)$$

The solution for thermodynamic equilibrium ($j_g=0$) reads

$$\begin{aligned} (dn_g/d\underline{g})_{eq} &= w(\underline{g}) n_1^g [\langle w \rangle(\underline{g}) \Omega]^{g-1} \exp[-\hat{\Delta}F_0(g)/kT] = \\ &= w(\underline{g}) n_1 \exp[-\tilde{\Delta}F(g, \underline{g})/kT] \end{aligned} \quad (49)$$

where appears a new, orientation-dependent potential

$$\tilde{\Delta}F(g, \underline{g}) = \hat{\Delta}F_0(g) - (g-1)kT \ln[n_1 \langle w \rangle(\underline{g}) \Omega] \quad (50)$$

Orientation distribution of the steady-state flux calculated in the maximum-term approximation (cf. eq. 24) results as

$$dj_{st}/d\underline{g} = \hat{k}_{g^*}^+ n_1^2 w(\underline{g}) \exp(-\tilde{\Delta}F_{max}/kT) \quad (51)$$

and in the integral approximation (cf. eq. 25)

$$dj_{st}/d\underline{\xi} = \hat{k}_{g^*}^+ n_1^2 w(\underline{\xi}) \exp(-\Delta F_{\max}^{\approx}/kT) \times \quad (52)$$

$$\times [2\pi kT/(-\partial^2 \Delta F^{\approx}/kT \partial g^2)]^{\frac{1}{2}}_{g^*}$$

In eqs.(51) and (52) $g^* = g^*(\underline{\xi})$ and $\Delta F_{\max}^{\approx} = \Delta F_{\max}^{\approx}(\underline{\xi})$ are solutions of the equation

$$(g^*, \Delta F_{\max}^{\approx}): \quad \partial \Delta F^{\approx}(g, \underline{\xi})/\partial g = 0 \quad (53)$$

Now, orientation dependence of the acting ΔF^{\approx} does not rely on the (dubious) effect of orientation on the chemical potential $\hat{\Delta}\mu_g^0$, but is controlled by non-uniform orientation distribution of single elements, $w(\underline{\xi})$. In the case of uniform distribution, $w(\underline{\xi}) = \langle w \rangle(\underline{\xi}) = 1/\Omega$, eqs.(49), (51) and (52) can be integrated over $\underline{\xi}$ to yield, respectively, fundamental equations (19), (24) and (25) with ΔF_0 modified by the orientability term $-(g-1)kT \ln(\Delta/\Omega)$.

Eqs.(49)-(53) present solutions for nucleation in homogeneous, oriented systems in which orientation distribution of single elements, $w(\underline{\xi})$ is non-uniform and constant throughout the nucleation process. Homogeneity means that in any volume element, macroscopically small but large compared with cluster size, function $w(\underline{\xi})$ is the same. Systems with domain structure (e.g. liquid crystals) do not satisfy this condition and cannot be described by the above equations. The case of locally ordered systems will be considered later in this section. Constant in time, and non-uniform orientation distribution of single elements can be achieved in several

different ways. One way is to impose constraints on kinetic elements and apply external deformation to the constrained system. Typical situation of this kind is crystallization of deformed crosslinked polymers, in which long flexible chains composed of statistical, asymmetric segments are partially stretched, producing non-uniform orientation distribution⁶. For a crosslinked system of polymer chains with Gaussian conformation statistics subjected to constant uniaxial extension λ , the resulting orientation distribution of chain segments expressed in polar coordinates assumes the form⁷

$$w(\theta, \varphi) = (1/4\pi) [1 + (1/5N_g)(\lambda^2 - 1/\lambda)(3\cos^2\theta - 1)/2 + (1/175N_g^2)(6\lambda^4 \dots)(35\cos^4\theta - 30\cos^2\theta + 3)/8 + \dots] \quad (54)$$

Another way is to apply directional force field to a fluid system (melt, solution) containing dipole, or multipole particles. Electric and magnetic fields provide natural examples. An important way of producing constant, non-uniform orientation distribution in fluids containing asymmetric particles (polymer solutions, suspensions) is steady-state irrotational hydrodynamic flow field (cf.⁸). In any such case, the existence of orientation-dependent particle-field interaction potential $U(\theta)$ leads to equilibrium (or steady-state) orientation distribution of the Boltzmann form

$$w(\theta) = C \exp[-U(\theta)/kT] ; \quad C = 1 / \int \exp[-U(\theta)/kT] \quad (55)$$

Examples of nucleation in oriented systems and their physical

consequences will be discussed later in this paper.

All the above discussed cases of oriented nucleation concerned homogeneous systems, i.e. ones which do not exhibit any local order, like liquid crystals. We will now briefly discuss nucleation in a system of ordered domains (figure 3). Consider a system of sub-systems (domains) small compared with the macroscopic sample, but large compared to a single cluster. Orientation of the main axis ("director") of each domain with respect to fixed coordinate system will be characterized by angles $\underline{\theta}$ and the distribution of directors of all domains in the system will be $w_d(\underline{\theta})$. We will also introduce orientation of a cluster, or single element with respect to the local coordinate system (based on the director as a main axis) $\underline{\eta}$; and the local orientation distribution of single elements within a domain, will be $w_l(\underline{\eta})$.

Nucleation equations will be defined in terms of the density of flux j_g in the orientation space $\underline{\theta} \times \underline{\eta}$. In other words, we will ask for the change in flux j_g (and nucleation rate) when orientation of the domain director changes by $d\underline{\theta}$ and orientation of cluster with respect to the director - by $d\underline{\eta}$

$$d^2 j_g(\underline{\theta}, \underline{\eta}) = j_g(\underline{\theta} + d\underline{\theta}, \underline{\eta} + d\underline{\eta}) - j_g(\underline{\theta}, \underline{\eta}) \quad (56)$$

$\underline{\theta}$ and $\underline{\eta}$ form two sets of orientation angles, independent of each other. The fundamental kinetic equations for $d^2 j_g(\underline{\theta}, \underline{\eta})$ assume now the form

$$d^2 j_g(\underline{\theta}, \underline{\eta}) = k_{g-1}^+ w_d(\underline{\theta}) d\underline{\theta} dn_{g-1}(\underline{\eta}) n_1 \langle w_l \rangle (\underline{\eta}) \Delta - k_g^- w_d(\underline{\theta}) d\underline{\theta} dn_g(\underline{\eta}) \quad (57)$$

Equations (59) are formally identical with eqs.(48) for the homogeneous case with the following correspondence of variables: the density of flux, $dj_g/d\hat{\varrho}$ in eqs.(48) is now replaced by density $d^2j_g/d\hat{\varrho} d\eta$; the present problem concerns orientation of clusters and single elements within a single domain, and their orientations η are related to the domain axis (director); in the homogeneous case (eqs.48) orientations of clusters and single elements $\hat{\varrho}$ were referred to the fixed coordinate system.

Formal solutions of eqs.(59) can be written down immediately. The equilibrium distribution density of clusters within a single domain

$$\begin{aligned} \left. \frac{dn_g(\eta)}{d\eta} \right|_{eq} &= w_1(\eta) n_1^g [\langle w_1 \rangle(\eta) \Omega]^{g-1} \exp[-\Delta\hat{F}_0(g)/kT] = \\ &= w_1(\eta) n_1 \exp[-\tilde{\Delta F}(g, \eta)/kT] \end{aligned} \quad (60)$$

where

$$\tilde{\Delta F}(g, \eta) = \Delta\hat{F}_0(g) - (g-1)kT \ln[n_1 \langle w_1 \rangle(\eta) \Omega] \quad (61)$$

The above result depends on the orientation of the domain with respect to the fixed coordinate system, $\hat{\varrho}$, only through (possible, but not very probable) orientation dependence of the density of single elements within domains, n_1 , or of the free energy of transition, $\Delta\hat{F}_0$. Steady-state flux density, calculated in the maximum-term approximation (cf.eq.24) assumes now the form

$$d^2j_{st}/d\hat{\varrho} d\eta = k_g^+ n_1^2 w_d(\hat{\varrho}) w_1(\eta) \exp(-\tilde{\Delta F}_{max}/kT) \quad (62)$$

where g^* and $\Delta F_{\max}^{\approx}$ are determined by the condition

$$\partial \Delta F^{\approx}(g, \underline{\eta}) / \partial g = 0 \quad (63)$$

An analogical expression for $d^2 j_{st} / d\underline{\theta} d\underline{\eta}$ in the integral approximation (cf. eq. 25) can also be written.

Eqs. (60) and (62), describe nucleation within a single domain. If we are interested in characteristics related to the entire system of many domains with director distribution $w_d(\underline{\theta})$, we should find orientation distribution densities of the equilibrium cluster size distribution and steady-state flux in the orientation space $\underline{\theta}$, with fixed coordinate system (cf. figure 3). These densities, $dn_g(\underline{\theta})/d\underline{\theta}$ and $dj_g(\underline{\theta})/d\underline{\theta}$ can be obtained by transformation of the local (intra-domain) nucleation characteristics using domain orientation distribution $w_d(\underline{\theta})$.

Two out of three orientations, $\underline{\theta}$, $\underline{\eta}$, and $\underline{\xi}$, are independent. We can eliminate e.g. orientation of the domain axis, $\underline{\theta}$, expressing it through orientation of a cluster in the fixed coordinate system, $\underline{\xi}$, and local orientation of the same cluster with respect to the domain axis, $\underline{\eta}$:

$$\left. \begin{aligned} \underline{\theta} &= \underline{\theta}(\underline{\xi}, \underline{\eta}) \\ d\underline{\theta} &= J(\underline{\xi}, \underline{\eta}) d\underline{\xi} \end{aligned} \right\} \quad (64)$$

where $J(\underline{\xi}, \underline{\eta})$ is Jacobian of the transformation; $d\underline{\theta}$, $d\underline{\xi}$ and $d\underline{\eta}$ are volume elements in the respective orientation spaces.

Application of the transformation (64) to eq. (62) and

integration over the other independent orientation, $\underline{\eta}$, yields the desired orientation dependence of the steady-state flux

$$dj_{st}(\underline{\xi})/d\underline{\xi} = \int \hat{k}_g^+ n_1^2 w_d[\underline{\xi}(\underline{\xi}, \underline{\eta})] w_1(\underline{\eta}) \times \exp[-\tilde{\Delta F}_{max}(\underline{\eta})/kT] J(\underline{\xi}, \underline{\eta}) d\underline{\eta} \quad (65)$$

To obtain the corresponding equilibrium distribution of cluster sizes, $dn_g(\underline{\xi})/d\underline{\xi}$, eq.(60) should be multiplied by the probability of finding domain with orientation $\underline{\xi}$, $w_d(\underline{\xi}) d\underline{\xi}$ transformed according to eqs.(64) and integrated over $\underline{\eta}$ to yield

$$dn_g(\underline{\xi})/d\underline{\xi} \Big|_{eq} = \int w_d[\underline{\xi}(\underline{\xi}, \underline{\eta})] w_1(\underline{\eta}) n_1 \times \exp[-\tilde{\Delta F}(g, \underline{\eta})/kT] J(\underline{\xi}, \underline{\eta}) d\underline{\eta} \quad (66)$$

Equations (65), (66) for nucleation in a system of oriented domains can be compared with analogous equations (49) and (51) for an oriented homogeneous system. Generally speaking, in the locally ordered systems global (average) nucleation characteristics depend both on the internal structure of the domains [local orientation distribution $w_1(\underline{\eta})$] and on the distribution of domain axes in the system [$w_d(\underline{\xi})$].

A few asymptotic solutions of eqs.(65), (66) are worth discussing.

1. $w_1(\underline{\eta}) = \text{const.} = 1/\Omega$. If single elements within a domain are randomly oriented, the governing potential $\tilde{\Delta F}(g, \underline{\eta})$ reduces to

$$\tilde{\Delta F}(g, \underline{\eta}) = \hat{\Delta F}_0(g) - (g-1)kT \ln n_1 \quad (67)$$

and $dn_g/d\underline{\vartheta}$, $dj_{st}/d\underline{\vartheta}$ become constants, independent of orientation of the cluster. The solutions for n_g and j_{st} are identical with those for a homogeneous, randomly oriented [$w(\underline{\vartheta}) = 1/\Omega$] system of asymmetric single elements [parameter Δ/Ω is included in $\hat{\Delta F}_0(g)$]. This is in fact a trivial case, since domains with random distribution of elements cease to be separate, distinguishable sub-systems.

ii. $w_d(\underline{\vartheta}) = \text{const.} = 1/\Omega$. If domains are internally ordered, but distribution of their directors is random (no external orienting field), the global nucleation characteristics $dn_g/d\underline{\vartheta}$ and $dj_{st}/d\underline{\vartheta}$ also become independent of orientation with respect to the fixed coordinate system, $\underline{\vartheta}$. However, the governing potential $\tilde{\Delta F}(g, \underline{\eta})$ depends on the domain structure, characterized by $w_1(\underline{\eta})$

$$\tilde{\Delta F}(g, \underline{\eta}) = \hat{\Delta F}_0(g) - (g-1)kT \ln[\langle w_1 \rangle(\underline{\eta})\Omega n_1] \quad (68)$$

Orientation-independent equilibrium distribution of cluster sizes

$$(n_g)_{eq} = n_1 \int w_1(\underline{\eta}) \exp[-\tilde{\Delta F}(g, \underline{\eta})/kT] d\underline{\eta}, \quad (69)$$

and steady-state flux

$$j_{st} = k_g^+ n_1^2 \int w_1(\underline{\eta}) \exp[-\tilde{\Delta F}_{max}(\underline{\eta})/kT] d\underline{\eta} \quad (70)$$

result as averages integrated for each domain over local orientation distribution $w_1(\underline{\eta})$. Note, that nucleation

characteristics for a system of randomly oriented ordered domains are different to those for a randomly oriented homogeneous system (case i.), and are to a large extent controlled by internal structure of each domain, characterized by $w_1(\underline{\eta})$.

iii. $w_d(\underline{\xi}) = \delta(\underline{\xi})$. Perfectly oriented system of domains, can be considered as a single domain oriented along the axes of the fixed coordinate system. In such a system, intra-domain orientations, $\underline{\eta}$, can be identified with orientations with respect to the fixed coordinate system $\underline{\xi}$

$$\underline{\eta} \rightarrow \underline{\xi}$$

and eqs.(65), (66) reduce to the results for oriented homogeneous system with single element distribution $w_1(\underline{\xi})$, eqs. (49),(51).

iv. $w_1(\underline{\eta}) = \delta(\underline{\eta})$. If the internal orientation within each domain is perfect, the asymptotic value of the potential $\Delta\tilde{F}(g, \underline{\eta})$ reduces to

$$\begin{aligned} \Delta\tilde{F}(g, \underline{\eta}) &= \Delta\hat{F}_0(g) - (g-1)kT \ln(n_1 \Omega / \Delta) = \\ &= \Delta F_0(g) - (g-1)kT \ln n_1 = \Delta\tilde{F}(g), \end{aligned}$$

i.e. to the value characteristic of the system of symmetric, unorientable particles (eq.20). Perfect orientation within the domains thus eliminates the thermodynamic and kinetic handicap of asymmetric particles related to the consistent orientation requirement, and characterized by the disorienta-

tion tolerance range Δ . Nucleation characteristics for case iv. are similar to those for a system of unorientable particles, eqs.(21),(24), but their orientation distribution is equal to that of the domains, $w_d(\underline{\xi})$:

$$\begin{aligned} (dn_g/d\underline{\xi})_{eq} &= w_d(\underline{\xi}) n_1^g \exp[(-\Delta F_o(g)/kT] = \\ &= w_d(\underline{\xi}) n_1 \exp[-\Delta \bar{F}(g)/kT] \end{aligned} \quad (71)$$

$$dj_{st}/d\underline{\xi} = w_d(\underline{\xi}) k_g^+ n_1^2 \exp[-\Delta \bar{F}_{max}/kT] \quad (72)$$

Physical consequences of the nucleation characteristics derived above will be discussed in the sections to follow.

SYMMETRY OF SINGLE ELEMENTS, ORIENTATION, AND CRITICAL TRANSITION TEMPERATURES

As shown in Appendix B, asymmetry (and orientability) of single elements affects the chemical potential for cluster growth reactions, $\Delta\mu_g^0$, introducing into it a temperature-dependent term related to the "disorientation tolerance range", Δ . For a random system of orientable elements, the appropriate chemical potential for the transition reads

$$\hat{\Delta}\mu_g^0 = \Delta\mu_g^0 - kT \ln(\Delta/\Omega) \quad (73)$$

while that for a class of clusters with orientation $\underline{\xi}$ in a system with non-uniform orientation distribution $w(\underline{\xi})$ becomes orientation-dependent (cf.also eq.41)

$$\Delta\mu_g^o(\underline{\varrho}) = \hat{\Delta\mu}_g^o - kT \ln \chi(\underline{\varrho}) = \Delta\mu_g^o - kT \ln[\Delta \cdot \langle w \rangle(\underline{\varrho})] \quad (74)$$

where $\chi(\underline{\varrho}) = \Omega \cdot \langle w \rangle(\underline{\varrho})$, and $\langle w \rangle(\underline{\varrho})$ is orientation distribution of single elements averaged over the "disorientation tolerance range", Δ .

The chemical potential for cluster growth within ordered domains is independent of orientation of the domain director, $\underline{\varrho}$, and of the corresponding director distribution, $w_d(\underline{\varrho})$, but is controlled by orientation of the cluster with respect to the main axis (director) of the domain $\underline{\eta}$, and by the local orientation distribution within the domain, $w_1(\underline{\eta})$.

$$\Delta\mu_g^o(\underline{\eta}) = \hat{\Delta\mu}_g^o - kT \ln[\Omega \langle w_1 \rangle(\underline{\eta})] \quad (75)$$

$\hat{\Delta\mu}_g^o$ appearing in eq.(75) and derived in eqs.(B18), (B19) describes a "random" domain and results from extrapolation of the chemical potential for ordered domains which, by definition, are always strongly oriented. Therefore $\hat{\Delta\mu}_g^o$, unlike $\Delta\mu_g^o$ for a homogeneous, randomly oriented system of orientable particles, does not describe any real system. Also, the disorientation tolerance parameter, Δ , unlike in a homogeneous system, is nearly independent of temperature (eqs. B20, B21), which makes thermodynamic relations for nucleation within domains similar in form to those for symmetric particles.

As shown in one of the preceding sections (eq.27), critical condition for the transition controlled by cluster growth with a chemical potential $\Delta\mu_g^o$ reads

$$\lim_{g \rightarrow \infty} \hat{\Delta\mu}_g^o(T) - kT \ln n_1 = 0 \quad (76)$$

We will discuss solutions of eq.(76) for critical nucleation temperatures, assuming undiluted system ($n_1=1$), using chemical potentials derived in Appendix B, and assuming that both, inter-, and intra-cluster vibrations exhibit energy small compared to kT

$$h\bar{\nu} \ll kT \quad (77)$$

This seems to be justified by the fact, that the vibrations are related to intermolecular forces in the new phase (crystal), rather than to first-order chemical bonds.

With the above assumptions, taking chemical potential for symmetric particles from eq.(B14) with approximation (77) we obtain the critical condition for temperature, T_{sym}

$$\Delta E^{\circ} - kT_{\text{sym}} \ln B - (3/2)kT_{\text{sym}} \ln(kT_{\text{sym}}) = 0 \quad (78)$$

where ΔE° and B are material constants, independent of temperature. An analogical expression can be derived using eqs.(74), and (B17), (77) for a homogeneous system of asymmetric particles with orientation distribution $w(\underline{\xi})$

$$\begin{aligned} \Delta E^{\circ} - kT_{\text{as}}(\underline{\xi}) \ln(BD) - (5/2)kT_{\text{as}}(\underline{\xi}) \ln[kT_{\text{as}}(\underline{\xi})] - \\ - kT_{\text{as}}(\underline{\xi}) \ln \chi(\underline{\xi}) = 0 \end{aligned} \quad (79)$$

For a homogeneous, randomly oriented system, $\chi = 1$, and eq.(79) reduces to

$$\Delta E^{\circ} - kT_{\text{as}} \ln(BD) - (5/2)kT_{\text{as}} \ln(kT_{\text{as}}) = 0 \quad (80)$$

In eqs.(79) and (80), D denotes another material constant related to the disorientation tolerance range

$$DkT = \Delta/\Omega \quad (81)$$

Note, that in the above equations uniaxial symmetry of single elements is implied (eq.B17). For triaxial single elements (eq.B16), Δ/Ω is proportional to $(kT)^{3/2}$ and the coefficient at the logarithmic term $kT_{as} \ln(kT_{as})$ should be 3, rather than 5/2. In the limiting case when orientation of all single elements is perfect, $w(\underline{\xi}) = \delta(\underline{\xi})$, $\chi(\underline{\xi}) = (\Omega/\Delta) \cdot \delta(\underline{\xi})$, and eq. (79) reduces to eq.(78) for symmetric particles. Consequently, the asymptotic relation reads

$$T_{as}(\underline{\xi}) = T_{sym} \cdot \delta(\underline{\xi}) \quad (82)$$

Critical transition temperature for a class of clusters growing within an ordered domain, all oriented at $\underline{\eta}$ with respect to the domain director, can be calculated from the equation derived from eqs.(75) and (B19)

$$\begin{aligned} \Delta E^0 - kT_{dom}(\underline{\eta}) \ln(B\Delta/\Omega) - (3/2)kT_{dom}(\underline{\eta}) \ln[kT_{dom}(\underline{\eta})] - \\ - kT_{dom}(\underline{\eta}) \ln[\Omega \langle w_1 \rangle(\underline{\eta})] = 0 \end{aligned} \quad (83)$$

The case of a "random domain", $w_1 = \text{const.}$, is unphysical. On the other hand, the limiting case when all single elements are perfectly parallel within each domain, $w_1(\underline{\eta}) = \delta(\underline{\eta})$ yields the critical condition equivalent to eq.(78) for symmetric

particles, and the asymptotic critical temperature

$$T_{\text{dom}}(\underline{\eta}) = T_{\text{sym}} \cdot \delta(\underline{\eta}) \quad (84)$$

The distribution of critical temperatures within domains, $T_{\text{dom}}(\underline{\eta})$ is not a direct physical observable. More important is the average temperature $\langle T_{\text{dom}} \rangle$ for each domain. This can be calculated by solving eq.(83) for $T_{\text{dom}}(\underline{\eta})$ and integrating with the distribution function $w_1(\underline{\eta})$

$$\langle T_{\text{dom}} \rangle = \int w_1(\underline{\eta}) T_{\text{dom}}(\underline{\eta}) d\underline{\eta} \quad (85)$$

Figure 4. presents critical transition temperatures T_{sym} , T_{as} , and $\langle T_{\text{dom}} \rangle$ calculated from eqs.(78),(80) and (85), plotted vs. disorientation tolerance parameter (Δ/Ω) at T_{sym} . Parameters chosen for the numerical example

$$\Delta E^0 = -6.7322 \cdot 10^{-13} \text{ erg}, \quad Bk^{3/2} = 2.3329 \cdot 10^{-9} \text{ K}^{-3/2}$$

correspond to transition enthalpy $\Delta H = -7.6766 \cdot 10^{-13}$ erg, and entropy $\Delta S = -1.6833 \cdot 10^{-15}$ erg/K. Consequently, the reference temperature for symmetric particles is $T_{\text{sym}} = 456.05$ K. These parameters do not describe any real system composed of symmetric particles, but were chosen to match some experimental data for crystallization of polyethylene to be discussed below. It can be observed that the critical temperature for randomly oriented homogeneous systems, T_{as} , is much more sensitive to disorientation tolerance range parameter (Δ/Ω) than the average critical temperature for transition within ordered

domains, $\langle T_{\text{dom}} \rangle$. The latter depends also on the local orientation distribution within the domain, $w_1(\eta)$ and approaches T_{sym} when local orientation is perfect.

For homogeneous systems, T_{as} drastically decreases when Δ/Ω is reduced. The values of the disorientation tolerance parameter are controlled, first of all, by size and shape of the single element. As shown in Appendix B, (Δ/Ω) for homogeneous systems with asymmetric single elements is proportional to the symmetry number of the single element, σ , and inversely proportional to its moment of inertia, I_1 (uniaxial case), or to the $(3/2)$ power of the mean moment of inertia \bar{I}_1 (triaxial case). Separating effects of size and shape as shown in eq.(B12) we obtain

$$\Delta/\Omega \sim \begin{cases} \sigma m_1^{-5/3} \xi^{-1} & \text{for uniaxial symmetry} \\ \sigma m_1^{-5/2} \xi^{-3/2} & \text{for triaxial symmetry} \end{cases} \quad (86)$$

where m_1 is mass of the single element, and ξ asymmetry parameter. ξ is minimum for spherically symmetrical particles and monotonically increases with absolute logarithm of axial ratio. This means that the parameter (Δ/Ω) decreases, and the orientation effects become stronger, when size (mass) of the single element increases, and/or when the elements become more asymmetrical (ξ increases). We have tried to calculate the parameter (Δ/Ω) for linear molecule of ethylene. Assuming the moment of inertia $I_1 = 4.24 \cdot 10^{-39} \text{ g} \cdot \text{cm}^2$, $\sigma = 2$, and vibration frequency $\bar{\nu}_e = 200 \text{ cm}^{-1}$, we obtain at $T = 103.97 \text{ K}$

(melting temperature⁹) $\Delta/\Omega = 0.821$ which is not far from unity. However, ethylene is a small molecule and only slightly elongated. For large, highly asymmetric single elements one can expect (Δ/Ω) values well below 0.1 and, consequently, transition temperatures much lower than those for systems composed of spherical particles. The data for crystallization of symmetric vs. asymmetric molecules collected by Ubbelohde⁹ confirm the general trend of increasing melting entropies, and decreasing melting temperatures for systems of rigid, highly asymmetric molecules. This effect seems to be specially important for crystallization of biopolymers, aromatic polyamides and similar rigid macromolecules.

We will turn to the different critical transition temperatures for various orientations of the growing crystals (clusters). As evident from eq.(79), in a homogeneous system of asymmetric elements with orientation distribution $w(\underline{\theta})$, the critical temperature $T_{as}(\underline{\theta})$ depends on crystal orientation; compared to a randomly oriented system (T_{as}), $T_{as}(\underline{\theta})$ can be elevated or depressed, dependently on the orientation, $\underline{\theta}$, and corresponding value of the parameter $\chi(\underline{\theta})$. We will calculate $T_{as}(\underline{\theta})$ for a model system in which $\chi(\underline{\theta})$ assumes the form

$$\chi(\theta, \varphi) = 1 + 5f_{or} [1 - (3/2)\sin^2\theta] \quad (87)$$

In eq.(87) cylindrical symmetry is assumed (χ does not depend on the angle φ) and f_{or} appearing as a constant is so called axial orientation factor

$$f_{or} = 1 - (3/2)\langle \sin^2\theta \rangle \quad (88)$$

Eq.(88) is a typical orientation dependence satisfying the conditions of uniaxial symmetry and applicable for not too high f_{or} values. For numerical calculations we have chosen the following data

$$\Delta E^0 = -6.7322 \cdot 10^{-13} \text{ erg}, \quad BDk^{5/2} = 2.2486 \cdot 10^{-12} \text{ K}^{-5/2}$$

what corresponds to experimental data for randomly oriented polyethylene¹⁰:

$$T_{as} = 415 \text{ K}, \quad \Delta H = -4.727 \cdot 10^{-13} \text{ erg}, \quad \Delta S = -1.139 \cdot 10^{-15} \text{ erg/K}$$

Figure 5. presents solution of eq.(79) with the above parameters and $\chi(\vartheta)$ from eq.(87). It is evident that even for relatively small average orientations in the system (orientation factor does not exceed 0.113) critical transition temperatures are considerably different for different orientation angles. At $\vartheta=0$ (direction of the orientation axis) critical temperatures $T_{as}(\vartheta)$ lie up to 20 deg above the temperature T_{as} for unoriented system. On the other hand, at $\vartheta = 90^\circ$ (direction perpendicular to orientation axis), $T_{as}(\vartheta)$ is depressed by 4-12 deg below that for a random system. All characteristics intersect in one point. This fact results from the specific form of the relation $\chi(\vartheta)$ and has no physical significance. The effect of crystal orientation on the critical nucleation (crystallization) temperature has been noted in our earlier paper¹. Differentiation of crystallization and melting temperatures among differently oriented crystals causes, that in a superheated, preoriented melt, gradually cooled down the

first crystals which are thermodynamically able to appear, are those, corresponding to some selected orientation (in the above case: crystals parallel to orientation axis, $\theta = 0$. Conversely, when oriented, crystallized system is gradually heated under conditions which guarantee constant orientation distribution of single elements (constant stress conditions, steady-state flow, constant orienting field), the first crystals to melt are those corresponding to minimum of $\chi(\theta)$ characteristic (here: at $\theta = 90^\circ$). This is an important effect specific for nucleation in oriented systems of asymmetric single elements. On the other hand, orientation of domains in an ordered system (fig.3) does not change the critical transition temperature, and all crystals can be formed and melt at a single temperature, $\langle T_{\text{dom}} \rangle$ dependent only on the internal structure of the domain [local distribution $w_1(\eta)$].

To investigate the effect of orientation distribution $w(\theta)$ in the entire range of possible distributions, i.e. from random to delta distribution, we will analyze maximum critical temperatures, $T_{\text{as}}(\theta = 0)$ for orientation factors f_{or} between 0 and 1. The orientation distribution which covers this range is

$$w(\theta, \varphi) = \frac{\sqrt{A} \exp(-A \sin^2 \theta)}{4\pi W(\sqrt{A})} \quad (39)$$

where

$$W(x) = e^{-x^2} \int_0^x e^{t^2} dt$$

The above distribution is also cylindrical and reduces to

$1/4\pi$ when $A = 0$ (random distribution) and continuously approaches $\delta(\theta)$ when $A = \infty$ (perfect orientation). It is easy to show that the orientation factor is a single-valued function of A

$$f_{or} = 1 - (3/2)\langle \sin^2\theta \rangle = \frac{3[\sqrt{A}-W(\sqrt{A})]}{4A W(\sqrt{A})} - \frac{1}{2} \quad (90)$$

Using orientation distribution $w(\theta, \varphi)$ from eq.(89) one can obtain the factor $\chi(\theta=0)$ as a function of disorientation tolerance range

$$\begin{aligned} \chi(\theta=0) &= 4\pi \int_0^\delta w(\theta, \varphi) \sin\theta \, d\theta / \int_0^\delta \sin\theta \, d\theta = \\ &= \frac{1}{1 - \cos\delta} \left[1 - \exp(-A \sin^2\delta) \frac{W(\sqrt{A} \cos\delta)}{W(\sqrt{A})} \right] \end{aligned} \quad (91)$$

where

$$\cos\delta = 1 - \Delta/\Omega$$

Figure 6. presents $T_{as}(\theta=0)$ as a function of the orientation distribution parameter A for three different (Δ/Ω) ratios. In all cases, critical nucleation temperature starts with T_{as} for a random system at $A = 0$, and asymptotically approaches the limit for symmetric particles, T_{sym} at $A = \infty$.

Figures 5. and 6. illustrate three important features of oriented nucleation:

- the critical transition temperature T_{as} is a function of cluster orientation in the system, (fig.5),

- at given orientation, say $\theta = 0$, T_{as} is a functional of the orientation distribution $w(\theta)$ (fig.6),

- the sensitivity to orientation is controlled by disorientation tolerance parameter (Δ/Ω) which is a molecular constant.

In the field of polymer crystallization, effect of orientation in the amorphous phase on the incipient crystallization, and melting temperatures, is widely recognized¹¹. Different crystallization temperatures for differently oriented crystals are supported only by indirect evidence¹²:

An interesting observation was reported by an anonymous author during the conference¹³. Some carotenoides with large, rigid molecules were crystallized from solution. Crystallization in quiescent solutions could not be achieved; when the solutions were pressed through a porous membrane, however, the material crystallized immediately past the membrane. The interpretation of this observation seems straightforward: low crystallizability of randomly oriented (quiescent) solutions of large, asymmetric molecules is due to dilution ($kT \ln n_1$ term in the critical condition eq.76) as well as to the high absolute entropy of crystallization [factor $kT \ln(\Delta/\Omega)$] related to rotational degrees of freedom. Flow of the solution through the membrane orients molecules and aligns them parallel to the flow direction ($\theta = 0$); high value of $\chi(\theta=0)$ elevates critical nucleation temperature $T_{as}(0)$ above the room temperature, and makes crystallization possible. This provides additional evidence for the fact, that application of orienting fields can considerably modify critical transition temperatures in homogeneous systems composed of asymmetric particles. On the other hand, orientation of domains in locally

ordered systems does not influence critical transition temperatures.

NUCLEATION RATE PARAMETERS

Thermodynamic effects discussed in the preceding section are closely related to kinetics of nucleation in the conditions of supercooling (supersaturation). For a homogeneous system of orientable elements with orientation distribution function $w(\underline{\vartheta})$ the active driving force for nucleation $\Delta F \approx$ is strongly orientation-dependent

$$\Delta F \approx(\underline{\vartheta}, g) = \hat{\Delta F}_0(g) - (g-1)kT \ln[n, \chi(\underline{\vartheta})] \quad (92)$$

where

$$\chi(\underline{\vartheta}) = \langle w \rangle(\underline{\vartheta}) \cdot \Omega$$

If the free energy of a g -cluster, $\hat{\Delta F}_0(g)$, can be presented as a sum of a surface ($\sim g^{\frac{2}{3}}$) and a bulk term ($\sim g$), then

$$\hat{\Delta F}_0(g) = a (g^{\frac{2}{3}} - 1) + b (g-1) \quad (93)$$

and the total driving force $\Delta F \approx$ assumes a similar form

$$\Delta F \approx(\underline{\vartheta}, g) = a (g^{\frac{2}{3}} - 1) + \tilde{b}(\underline{\vartheta}) \cdot (g-1) \quad (94)$$

where

$$\tilde{b}(\underline{\vartheta}) = b - kT \ln[n, \chi(\underline{\vartheta})]$$

Coordinates of the maximum of $\Delta F \approx$ vs. g which control nucleation kinetics result in the form

$$\left. \begin{aligned} g^*(\vartheta) &= (2a/3b)^3 = (8/27) \{a/[kT \ln(n_1\chi) - b]\}^3 \\ \tilde{\Delta F}_{\max}(\vartheta) &= \tilde{\Delta F}[\vartheta, g^*(\vartheta)] = (4/27) a^3/b^2 - (a+b) = \\ &= (4/27) a^3/[kT \ln(n_1\chi)]^2 - [a+b - kT \ln(n_1\chi)] \end{aligned} \right\} \quad (95)$$

All these characteristics depend on orientation, ϑ , and on the orientation distribution $w(\vartheta)$ through the parameter $\chi(\vartheta)$. If we consider an undiluted ($n_1=1$) and randomly oriented system ($\chi=1$) the absolute value of the driving force

$$\tilde{\Delta F}(g) = \hat{\Delta F}(g) = \Delta F_0(g) - kT(g-1) \ln(\Delta/\Omega) \quad (96)$$

is reduced as compared to that for a system of symmetric elements $[\Delta F_0(g)]$. Consequently, the critical cluster size, g^* , and the maximum free energy $\tilde{\Delta F}_{\max}$ for systems of asymmetric elements are larger than the corresponding characteristics for symmetric elements (g_0^* , and $\Delta F_{0,\max}$, respectively). As a result of this, nucleation rate in systems of asymmetric elements will be generally slower than that in symmetric particles.

For oriented systems of asymmetric particles [$w(\vartheta) \neq \text{const.}$, $\chi(\vartheta) \neq 1$] all the kinetic characteristics become orientation-dependent. Nucleation rate j_{st} , slower than that for symmetric particles, assumes maximum values at the orientation angles ϑ where orientation distribution of single elements [$w(\vartheta)$, and hence $\chi(\vartheta)$] are maximum. Similarly differentiated are also parameters $g^*(\vartheta)$ and $\tilde{\Delta F}_{\max}(\vartheta)$. To illustrate these effects we have calculated from eq.(95) angular distribution of the

critical parameters g^* , $\Delta F_{\max}^{\approx}$, for polyethylene, using the following material constants¹⁰

$$\text{heat of fusion, } \Delta h = 2.9 \cdot 10^9 \text{ erg/cm}^3$$

$$\text{melting temperature, } T_m^0 = 415 \text{ K} = 141.8^\circ\text{C}$$

$$\text{mean surface energy density, } \bar{\sigma} = (\sigma_e \sigma_s^2)^{1/3} = 22.24 \text{ erg/cm}^2.$$

Assuming crystallization temperature $T_{\text{cr}} = 365 \text{ K} = 91.8^\circ\text{C}$, $n_1 = 1$, and volume of a single kinetic element (statistical chain segment) $v_0 = 1.63 \cdot 10^{-22} \text{ cm}^3$, the material parameters in eqs. (93), (94) reduce to

$$a = 4\pi\bar{\sigma}(3v_0/4\pi)^{2/3} = 3.209 \cdot 10^{-13} \text{ erg}$$

$$b = \Delta h(T_{\text{cr}} - T_m^0)v_0/T_m^0 = -5.695 \cdot 10^{-14} \text{ erg}$$

Consequently, the critical cluster size, and critical free energy for an unoriented [$\langle w \rangle = 1/\Omega$, $\chi = 1$] and undiluted system ($n_1 = 1$) amount to:

$$g^*(\chi = 1) = 53$$

$$\Delta F_{\max}^{\approx}(\chi = 1) = 1.246 \cdot 10^{-12} \text{ erg} = 24.73 \text{ kT}_{\text{cr}}$$

Figures 7. and 8. present angular dependence of the critical cluster size, g^* , and the reduced critical free energy $\Delta F_{\max}^{\approx}$ at $T_{\text{cr}} = 365 \text{ K}$ calculated from eqs.(95) for an undiluted system, with uniaxial orientation of single elements (χ from eq.87). It is evident that even at relatively small degrees of orientation in the amorphous phase, f_{or} , both the kinetic parameters are strongly modified as compared to

ones for a randomly oriented system: in the range of small orientation angles, where orientation distribution of single elements, $w(\theta)$, and the parameter $\chi(\theta)$ is maximum, g^* and $\Delta\bar{F}$ are strongly reduced; in the range of angles close to 90° (perpendicular to orientation axis) the critical parameters are even stronger elevated. The consequence of this, is angular differentiation of the nucleation rate distribution, presented in Figure 9. The characteristic plotted in Figure 9. is nucleation rate distribution reduced with the respective characteristic for a randomly oriented system, $dj_{st}/d\theta|_{\chi=1}$. Using eq.(52), the reduced characteristic can be presented in the form

$$\frac{dj_{st}/d\theta}{dj_{st}/d\theta|_{\chi=1}} = \chi(\theta) [g^*(\theta)/g^*(\chi=1)]^{2/3} \times \exp\{[\Delta\bar{F}_{max}(\chi=1) - \Delta\bar{F}_{max}(\theta)]/kT\} \quad (97)$$

Example calculations have been performed for undiluted, uniaxially oriented polyethylene (χ from eq.87), crystallizing at $T_{cr} = 365$ K. It can be seen from Figure 9 that the orientation effects are quite dramatic: nucleation rate for crystals oriented parallel to orientation axis ($\theta=0$) increases, and that for perpendicular crystals is reduced by many orders of magnitude. This means that, with the exception for nearly randomly oriented systems ($f_{or} \approx 0$) nucleation of crystals is practically limited to the angular range close to orientation axis of the system; this range is the narrower

the higher is orientation factor in the amorphous phase, f_{or} . The observable consequence of this fact is crystal orientation distribution $W_{cr}(\vartheta)$ discussed below.

ORIENTATION DISTRIBUTION OF CRYSTALS VS. AMORPHOUS ELEMENTS.

The theory of crystal orientation developed by the present authors⁸ predicts strong effects related to the kinetics of crystal nucleation from asymmetric elements. If other effects, viz. thermal motions, orientation-dependent free energy, and convectional rotation of crystals in a flowing fluid can be neglected, the kinetically controlled crystal orientation distribution, $W_{cr}(\vartheta)$ reduces to the normalized nucleation rate distribution

$$W_{cr}(\vartheta) = (dj_{st}/d\vartheta) / \int (dj_{st} d\vartheta) d\vartheta \quad (98)$$

Using the integral approximation for nucleation rate (eq.52) eq.(98) assumes the form

$$W_{cr}(\vartheta) = \text{const. } w(\vartheta) [g^*(\vartheta)]^{2/3} \exp[-\tilde{\Delta F}_{max}(\vartheta)/kT] \quad (99)$$

and using the maximum-term formula, eq.(51)

$$W_{cr}(\vartheta) = \text{const. } w(\vartheta) \exp[-\tilde{\Delta F}_{max}(\vartheta)/kT] \quad (100)$$

Using $\tilde{\Delta F}(g, \vartheta)$ from eq.(94) and the critical parameters g^* and $\tilde{\Delta F}_{max}$ derived in the preceding section, eq.(99) reduces to

$$W_{cr}(\underline{\xi}) = \frac{[w(\underline{\xi})/\chi(\underline{\xi})][kT \ln(n_1\chi) - b]^{-2} \exp\{-4a^3/27 kT[kT \ln(n_1\chi) - b]^2\}}{\int [w(\underline{\xi})/\chi(\underline{\xi})][kT \ln(n_1\chi) - b]^{-2} \exp\{-4a^3/27 kT[kT \ln(n_1\chi) - b]^2\} d\underline{\xi}}$$

(101)

Eq.(100) for maximum-term approximation reduces to a similar form, without the pre-exponential term $[kT \ln(n_1\chi) - b]^{-2}$ in the numerator and under the integral.

$\chi(\underline{\xi}) = \Omega \langle w \rangle(\underline{\xi})$ being roughly proportional to the distribution of single elements, $w(\underline{\xi})$, kinetically controlled crystal orientation distribution is a strong functional of $w(\underline{\xi})$. This is evident in Figure 10. showing crystal orientation distribution for polyethylene crystallized at $T_{cr} = 365$ K from a uniaxially oriented amorphous material. In all cases, crystal orientation distribution is much sharper than the original distribution of the amorphous segments.

This fact is widely recognized in oriented crystallization, e.g. in high-speed spinning of polyester¹⁴, or crystallization of rubbers under tension¹⁵. It occurs that crystallization from oriented amorphous phase is the most effective way of producing highly oriented crystals. Physical nature of this phenomenon is related to selective nucleation (and growth) of those kinetic elements (segments) which have orientations close to the direction of the orientation axis of the system, and whose concentration is the highest in the system. Fifteen years ago, Krigbaum and Roe¹⁶, realizing this fact, proposed that crystal orientation distribution should be a power function of the amorphous orientation distribution,

the exponent being equal to the critical cluster size, in the unoriented state g_0^*

$$W_{cr}(\phi) = [w(\phi)]^{g_0^*} / \int [w(\phi)]^{g_0^*} d\phi \quad (102)$$

The Krigbaum and Roe expression is not consistent with our prediction derived from the oriented nucleation theory (eq.101) However, using maximum-term approximation, eq.(51) we can present our results in a form similar to that of Krigbaum and Roe

$$W_{cr}(\phi) = \frac{[w(\phi)/\langle w \rangle(\phi)] [\langle w \rangle(\phi)]^{g^*(\phi)} \exp\{-[ag^{2/3}(\phi) + bg^*(\phi)]/kT\}}{\int [w(\phi)/\langle w \rangle(\phi)] [\langle w \rangle(\phi)]^{g^*(\phi)} \exp\{-[ag^{2/3}(\phi) + bg^*(\phi)]/kT\} d\phi} \quad (103)$$

Comparing eqs.(102) and (103) it becomes evident that the error in the Krigbaum and Roe treatment lies in assuming a constant, critical cluster size, g_0^* , instead of the actual, orientation-dependent value $g^*(\phi)$, and in the implicit identification of the averaged distribution $\langle w \rangle(\phi)$ with the local distribution, $w(\phi)$. Putting $\langle w \rangle = w$, and $g^*(\phi) = g_0^* = \text{const.}$ our eq.(103) reduces to the Krigbaum-Roe result. Figure 11. presents comparison of the amorphous segment distribution, $w(\phi)$, and two crystal distributions, $W_{cr}(\phi)$, calculated from eqs.(101) and (102). Both crystal orientations are much sharper than the original amorphous distribution $w(\phi)$, but the assumption of a constant critical cluster size, g_0^* ,

in the Krigbaum-Roe treatment overestimates the effect of selection of appropriately oriented elements leading to too sharp a crystal distribution. In one of our earlier papers⁸, comparing kinetically-controlled crystal orientation with the predictions of Krigbaum and Roe¹⁶ we have come to a different conclusion. Our earlier comparison, however, used an incorrect reference state: the experimental parameters for polyethylene crystallization, were completed with the disorientation tolerance parameter, $kT \ln(\Delta/\Omega)$, while, in fact this parameter is automatically included in the enthalpy and entropy of crystallization of an unoriented polymer composed of asymmetric elements. Consequently, our predictions for crystal orientation distribution published in⁸ were overestimated, and that much more than those of Krigbaum and Roe.

FINAL REMARKS

The present paper had several aims. First, it corrected some inconsistencies and errors involved in our earlier papers on the theory of nucleation: elucidated the thermodynamic nature of the chemical potential, $\Delta\mu_g^0$, and the thermodynamic driving force, $\Delta F(g)$, $\Delta\bar{F}(g)$, and produced a consistent formula for the potential barrier for the kinetic rate constants, k_g^+ , k_g^- . Second, it presented a thorough discussion of the thermodynamic and kinetic effects of an external field on the nucleation involving asymmetric single elements. The nature of the "disorientation tolerance angle", Δ , has been elucidated using a simple statistical mechanical model, and difference between homogeneous, and locally ordered (domain) systems shown.

An external orienting field in a homogeneous system composed of asymmetric kinetic elements affects critical transition temperatures, nucleation rates, and the resulting crystal orientation distribution. On the other hand, in nucleation from a domain (liquid crystal) structure it is the internal, not the external field which controls the thermodynamic parameters of the transition liquid crystal \rightarrow crystal. Consequently, the critical nucleation temperature is insensitive to orientation of the domains in the system, and the latter is not enhanced in the form of crystal orientation distribution.

The results included in this paper are confined to a system of isolated, rigid, asymmetric molecules, like those of biopolymers, aromatic polyamides etc. One can expect that different results will be obtained for flexible polymer chains, composed of many jointed asymmetric segments. In particular, orientation effects can be expected to be very different for various crystallization morphologies, viz. many-chain bundle like crystallization vs. cooperative, regular chain-folding.

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APPENDIX A

EQUILIBRIUM CONCENTRATIONS IN CLUSTER GROWTH REACTIONS
AND THE CHEMICAL POTENTIAL OF CLUSTER GROWTH $\Delta\mu_g^0$

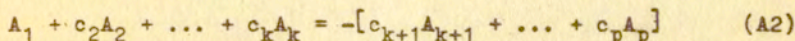
Consider a system composed of p components, each represented by N_i molecules. The total free energy of the system can be presented formally as a sum of two contributions

$$F(N_i) = \sum_{i=1}^p N_i \mu_i^0 + kT \sum_{i=1}^p N_i \ln n_i, \quad (A1)$$

the first related to chemical potentials of the pure components, μ_i^0 , the second - to the entropy of mixing.

$n_i = N_i / \sum_1^p N_i$ denotes molar fraction of the i -th component.

Consider chemical reaction between the components A_i of the system



or

$$-\sum_{i=1}^p c_i A_i = 0; \quad c_1 = 1 \quad (A3)$$

where c_i denote stoichiometric coefficients, or the proportions in which individual components enter the reaction. It should be noted that in the convention of eqs.(A2,A3) coefficients c_i from the right-hand side of the reaction ("products") are negative, those from the left-hand side ("substrates") - positive. In the conditions of reaction, the stoichiometric coefficients provide $(p-1)$ equations relating

changes dN_1 of the number of molecules of the individual components one with another. Consequently, the condition of thermodynamic equilibrium in a reacting system

$$F(N_1, N_2, \dots, N_p) = \text{minimum} \quad (A4)$$

can be found from minimization of F with respect to the number of molecules of any single, reacting component, say N_1

$$\begin{aligned} dF/dN_1 &= \partial F/\partial N_1 + \\ &+ (\partial F/\partial N_2)(dN_2/dN_1) + \dots + (\partial F/\partial N_p)(dN_p/dN_1) = 0 \end{aligned} \quad (A5)$$

After differentiation, taking into account that $c_i = dN_i/dN_1$, $\mu_i = \partial F/\partial N_i$

$$\sum_i c_i \mu_i = \sum_i c_i \mu_i^0 + kT \sum_i c_i \ln n_i = 0 \quad (A6)$$

or

$$\prod_i (n_i)^{c_i} = \exp\left[-\sum_i c_i \mu_i^0/kT\right] \quad (A7)$$

Applying eq.(A7) to the cluster growth reaction

$$\beta_{g-1} + \alpha_1 = \beta_g$$

we obtain

$$\frac{n_g}{n_{g-1} n_1} = \exp[-(\mu_g^0 - \mu_{g-1}^0 - \mu_1^0)/kT] \quad (A8)$$

At the same time, in the conditions of equilibrium ($j_g=0$) from the kinetic equations of nucleation (eq.6) results

$$\frac{n_g}{n_{g-1} n_1} = k_{g-1}^+ / k_g^- \quad (A9)$$

Hence, the ratio of rate constants is determined by the difference of chemical potentials in pure components between the product (g -cluster) and the substrates ($g-1$ cluster and single element)

$$k_{g-1}^+ / k_g^- = \exp(-\Delta\mu_g^0 / kT) \quad (A10)$$

where $\Delta\mu_g^0 = \mu_g^0 - (\mu_{g-1}^0 + \mu_1^0)$. It is easy to observe that the sum of consecutive potentials μ_1^0 for individual growth reactions yields the total potential of transition $\Delta F_0(g)$ used throughout any nucleation theory

$$\Delta F_0(g) = \sum_{i=2}^g \Delta\mu_i^0 = \mu_g^0 - g \cdot \mu_1^0 \quad (A11)$$

APPENDIX B

CHEMICAL POTENTIAL OF TRANSITION $\Delta\mu_g^0$, DISORIENTATION TOLERANCE RANGE, Δ , AND MOLECULAR PARAMETERS

To derive the chemical potential of transition and related characteristics from statistical mechanics we will consider a simple model composed of non-interacting particles in a box

of volume V . Free energy of the system, F , can be related to the partition functions f_i for individual types of particles

$$F = -kT \ln Z \quad (B1)$$

$$Z = \prod_i (f_i^{N_i} / N_i!) \quad (B2)$$

where N_i are numbers of i -type particles. Chemical potential of the i -th component, μ_i , results from differentiation of eqs.(B1,B2)

$$\mu_i = \partial F / \partial N_i = -kT \ln(f_i / N_i) \quad (B3)$$

and the chemical potential of the i -th component in the pure state, μ_i^0 (cf.eq.A1 in Appendix A)

$$\mu_i^0 = \mu_i - kT \ln(N_i / \sum N_i) = -kT \ln(f_i / \sum N_i) \quad (B4)$$

Hence, for the reaction of addition of a single element to $(g-1)$ cluster we obtain

$$\exp(-\Delta\mu_g^0/kT) = (f_g / f_{g-1} f_1) \sum N_i \quad (B5)$$

where $\Delta\mu_g^0 = \mu_g^0 - (\mu_{g-1}^0 + \mu_1^0)$. We will assume that the partition functions for individual particles, f_i , are multiplicative combinations of the partition functions for translation, f_i^t , rotation, f_i^r , vibration, f_i^v , and electron energy, f_i^e

$$f_i = \exp(-E_i^0/kT) f_i^t f_i^r f_i^v f_i^e \quad (B6)$$

where

$$f_i^t = V(m_i kT/2\pi h^2)^{3/2} \quad (B7)$$

$$f_i^r = \begin{cases} 1 & \text{for spherically symmetric particles} \\ (2 I_i kT/h^2)/\sigma & \text{for particles with uniaxial symmetry} \\ (2 \bar{I}_i kT/h^2)^{3/2} \sqrt{\pi}/\sigma & \text{for particles with triaxial symmetry} \end{cases} \quad (B8)$$

$$f_i^v = \prod_{k=1}^s [1 - \exp(-h\nu_k/kT)]^{-1} \quad (B9)$$

E_i^0 is zero energy level, from which partition functions are calculated, m_i and I_i are, respectively, mass and moment of inertia of the i -th particle, k and h are Boltzmann and Planck constants, σ - symmetry number for rotation, ν_k characteristic frequency of vibration. For a triaxial particle, the mean moment of inertia, $\bar{I}_i = (I_{11}I_{21}I_{31})^{1/3}$.

In the expression for the partition function of vibration, s is the number of degrees of freedom left for vibration. If the particle is composed of n_A atoms, and r is the number of degrees of freedom used for rotation, then

$$s = 3 n_A - 3 - r \quad (B10)$$

$r = 0$ for spherically symmetric particles, 2 - for uniaxial particles (two degrees of freedom), and 3 - for triaxial particles.

We will consider now two cases demonstrated in figures 2b, and 2c.

Case 2b : addition of a spherically symmetric single element to a triaxial cluster.

Substitution of the appropriate components of the partition function into eq.(B5) yields

$$\exp(-\Delta\mu_g^0/kT) = \left(\frac{m_g \bar{I}_g}{m_{g-1} \bar{I}_{g-1}} \right)^{3/2} (\Sigma N_i/V) \cdot (2\pi h^2/m_1 kT)^{3/2} \times$$

$$\times \prod_{k=1}^3 [1 - \exp(-h\nu_k/kT)]^{-1} \frac{r_g^e}{r_{g-1}^e r_1^e} \cdot \exp(-\Delta E_g^0/kT) \quad (B11)$$

where

$$\Delta E_g^0 = E_g^0 - E_{g-1}^0 - E_1^0 - kT$$

is related to the heat of melting. There is no reason to expect that electron energy of the system is considerably changed on addition of a single element to the growing cluster. Hence we will put

$$r_g^e / r_{g-1}^e r_1^e \approx 1$$

The ratio of masses, (m_g/m_{g-1}) can be replaced by the ratio of cluster sizes

$$m_g/m_{g-1} = g/(g-1)$$

Moment of inertia, I_g (\bar{I}_g) can be presented as a function of mass, m_g , and dimensionless shape coefficient, ξ_g

$$I_g = \text{const. } \rho^{-\frac{2}{3}} m_g^{5/3} \xi_g \quad (\text{B12})$$

(ρ = density). Assuming that the shape coefficient ξ_g does not change considerably from a (g-1) to a g-cluster, we obtain

$$I_g/I_{g-1} = [g/(g-1)]^{5/3} \xi_g/\xi_{g-1} \approx [g/(g-1)]^{5/3} \quad (\text{B13})$$

and finally, the expression for equilibrium constant (eq.B11) reduces to

$$\begin{aligned} \exp(-\Delta\mu_g^0/kT) &= (\sum N_i/V)(2\pi h^2/m_1 kT)^{3/2} [g/(g-1)]^4 \times \\ &\times \exp(-\Delta E_g^0/kT) \prod_{k=1}^3 [1 - \exp(-h\nu_k/kT)]^{-1} \end{aligned} \quad (\text{B14})$$

Case 2c : addition of an asymmetric single element to a triaxial cluster.

Using partition functions from eqs.(B7)-(B9) and approximations mentioned in case 2b, we obtain for the triaxial single element (with mean moment of inertia, \bar{I}_1) instead of eq.(B14)

$$\exp(-\hat{\Delta\mu}_g^0/kT) = \frac{\sigma}{\sqrt{\pi}} (\sum N_i/V) (\pi h^4/m_1 \bar{I}_1 k^2 T^2)^{3/2} \times \quad (B15)$$

$$\times [g/(g-1)]^4 \exp(-\Delta E_g^0/kT) \prod_{k=1}^6 [1 - \exp(-h\nu_k/kT)]^{-1}$$

The "disorientation tolerance angle" Δ/Ω results from division of eqs.(B15) and (B14) sidewise

$$\Delta/\Omega = \hat{k}_{g-1}^+/k_{g-1}^+ = \exp[-(\Delta\mu_g^0 - \Delta\mu_g^0)/kT] = \quad (B16)$$

$$= (\sigma/\sqrt{\pi})(h^2/2 \bar{I}_1 kT)^{3/2} \prod_{k=1}^3 [1 - \exp(-h\nu_k/kT)]^{-1}$$

Alternatively, for a uniaxially symmetric single element with moment of inertia I_1 ,

$$\Delta/\Omega = \sigma(h^2/2 I_1 kT) \prod_{k=1}^2 [1 - \exp(-h\nu_k/kT)]^{-1} \quad (B17)$$

The above considerations all concerned homogeneous systems, not too densely packed, in which free molecular rotations were allowed. Moving to systems with local order (figure 3) in which individual liquid-crystalline domains contain densely packed, and nearly parallel single elements and clusters, free rotation of molecular units is no more possible and must be replaced by low-energy vibrations (rocking,

libration). This fact affects the disorientation tolerance Δ , and the related chemical potential of transition $\Delta\mu_g^0$.

Case 3. addition of uniaxial single elements to triaxial cluster within a densely packed domain

Partition functions f_1' for all components are products of functions for translation, low-energy vibration (mean frequency $\bar{\nu}_e$) of the entire molecule, internal vibrations (mean frequency $\bar{\nu}_i$), and electronic energy which does not change on transition. The equilibrium constant results in the form:

$$\begin{aligned} \exp(-\Delta\mu_g^0/kT) &= (\sum N_i/V)(2\pi h^2/m_1 kT)^{3/2} [g/(g-1)]^{3/2} \times \\ &\times \exp(-\Delta E_g^0/kT) \prod_{k=1}^2 [1 - \exp(-h\nu_{ek}/kT)] \times \\ &\times \prod_{k=1}^5 [1 - \exp(-h\nu_{ik}/kT)]^{-1} \end{aligned} \quad (B18)$$

If vibration energies $h\nu_{ek}$, $h\nu_{ik}$ are small compared to kT eq.(B18) reduces to

$$\begin{aligned} \exp(-\Delta\mu_g^0/kT) &\cong (\sum N_i/V)(2\pi kT/m_1 \bar{\nu}_i^2)^{3/2} \times \\ &\times [g/(g-1)]^{3/2} \exp(-\Delta E_g^0/kT) (\bar{\nu}_e/\bar{\nu}_i)^2 \end{aligned} \quad (B19)$$

Comparing eq.(B18) with eq.(B14) for the equilibrium constant in a homogeneous system of symmetric, unorientable single elements and freely rotating clusters, we obtain the dis-

orientation tolerance parameter Δ

$$\begin{aligned} \Delta/\Omega &= \exp[-(\Delta\mu_g^0 - \Delta\mu_g^0)/kT] = \\ &= [(g-1)/g]^{5/2} \prod_{k=1}^2 \frac{[1 - \exp(-h\nu_{ek}/kT)]}{[1 - \exp(-h\nu_{ik}/kT)]} \end{aligned} \quad (B20)$$

or, in the approximation (B19)

$$\Delta/\Omega \cong [(g-1)/g]^{5/2} (\bar{\nu}_e/\bar{\nu}_1)^2 \quad (B21)$$

Since $\bar{\nu}_e$ is generally smaller than $\bar{\nu}_1$, $\Delta/\Omega < 1$.

As evident from eqs.(B19),(B20) the molecular mechanism responsible for the appearance of the factor (Δ/Ω) is the change in the energy of internal vibrations within the cluster (i.e. within crystal lattice, if "crystal - liquid crystal" transition is considered), $\bar{\nu}_1$, into low-energy external vibrations (rocking, libration) within ordered domains (frequency $\bar{\nu}_e$).

On the other hand, comparing eqs.(B20) and (B17) for the parameter (Δ/Ω) in locally ordered, vs. homogeneous systems, we obtain

$$\frac{(\Delta/\Omega)_{\text{dom}}}{(\Delta/\Omega)_{\text{hom}}} = (2 I_1 kT/\sigma h^2) [(g-1)/g]^{5/2} \prod_{k=1}^2 [1 - \exp(-h\nu_{ek}/kT)] \quad (B22)$$

and in the approximation (B21)

$$\frac{(\Delta/\Omega)_{\text{dom}}}{(\Delta/\Omega)_{\text{hom}}} = [(g-1)/g]^{5/2} (2I_1/\sigma kT \bar{v}_e^2) \quad (\text{B23})$$

Eqs.(B22)(B23) characterize change in the equilibrium constant (and chemical potential of transition $\Delta\mu_g^0$) when a system with local order is replaced by a homogeneous system of freely rotating single elements. The ratios (B22),(B23) should be greater than unity, and the more so, the larger is moment of inertia of the single element, I_1 , and the lower is energy of "external" vibrations within the ordered domain, \bar{v}_e . Naturally, restrictions on the transition from a dilute homogeneous system of freely rotating elements are stronger, (and absolute transition entropy larger) than these characteristics for a transition from densely packed pre-ordered domains with suppressed freedom of particle rotation.

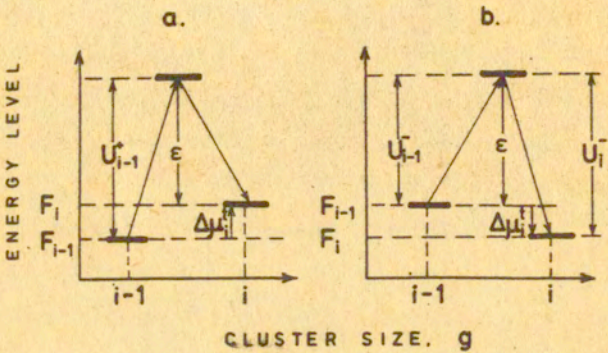


Fig. 1. Energy levels in the process of transition:
 $(i-1)$ -cluster \rightarrow i -cluster.

a. $\Delta\mu_i^0 > 0$; b. $\Delta\mu_i^0 < 0$

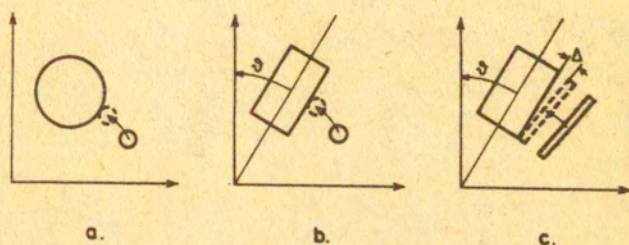


Fig. 2. Process of growth of a cluster.

- a. addition of a spherical single element to a spherical cluster,
- b. addition of a spherical single element to an asymmetric cluster,
- c. addition of an asymmetric single element to an asymmetric cluster

ξ - orientation of cluster axis, Δ - disorientation of the single element.

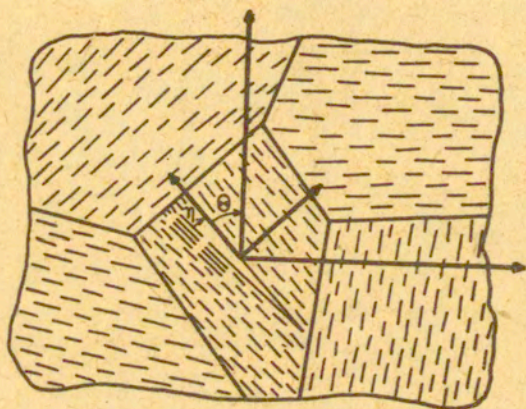


Fig. 3. Crystal nucleation within a domain in a locally ordered (nematic) system θ - orientation of the domain director with respect to macroscopic axis of the system, η - orientation of cluster (crystal) with respect to the domain director.

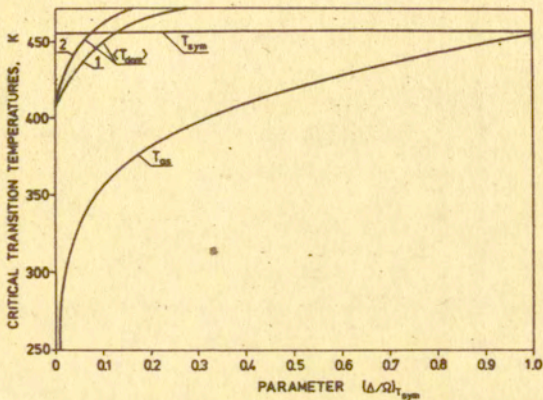


Fig. 4. Critical transition temperatures for spherically symmetric (T_{sym}), and asymmetric (T_{as}) single elements, in homogeneous, randomly oriented systems, and average transition temperatures for intra-domain transitions $\langle T_{dom} \rangle$. Intra-domain orientation parameter, $f_{or} = 0.839$ (curve 1), and $f_{or} = 0.923$ (curve 2).

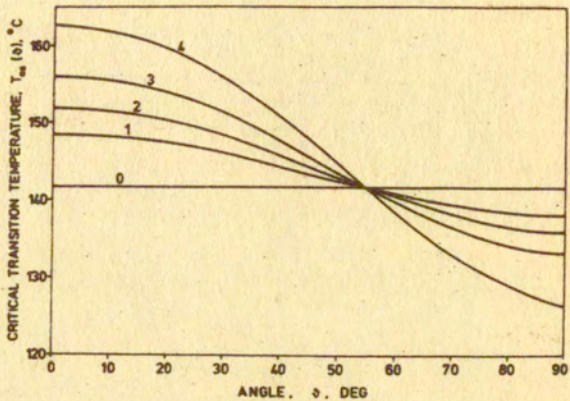


Fig. 5. Critical transition temperature for uniaxially oriented polyethylene as a function of orientation angle ϕ . Orientation factor for single elements:

curve	f_{or}
0	0 (randomly oriented system)
1	0.0315
2	0.0496
3	0.0717
4	0.1122

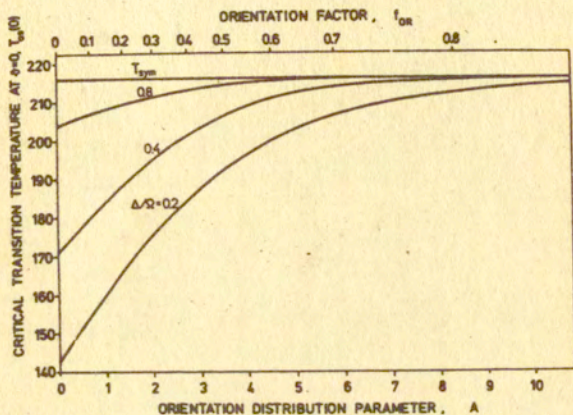


Fig. 6. Critical transition temperature at $\delta = 0$, $T_{as}(0)$, as a function of orientation distribution parameter, A (orientation factor f_{or}) for a uniaxially oriented system. Disorientation tolerance parameter (Δ/Ω) indicated.

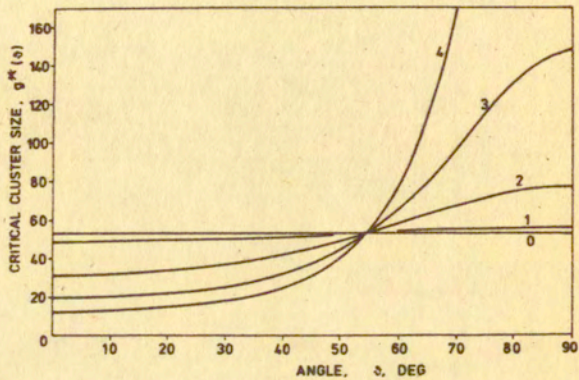


Fig. 7. Critical cluster size, g^* , for uniaxially oriented polyethylene crystallized at $T_{cr} = 365$ K as a function of orientation angle ϕ .

curve	f_{or}
0	0
1	0.0070
2	0.0496
3	0.1122
4	0.1998

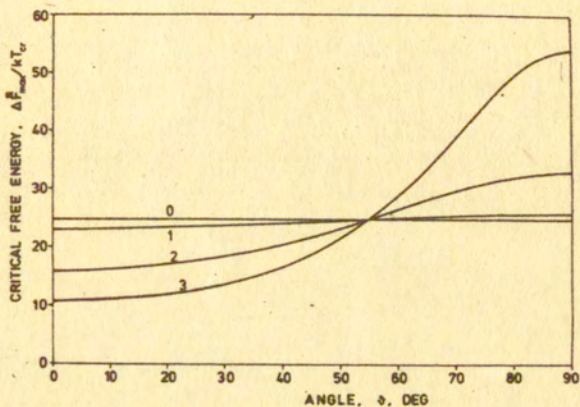


Fig. 8. Critical free energy of transition, $\Delta F_{cr}/kT_{cr}$, for uniaxially oriented polyethylene crystallized at $T_{cr} = 365$ K, vs. orientation angle ϕ .

curve	f_{or}
0	0
1	0.0070
2	0.0496
3	0.1122

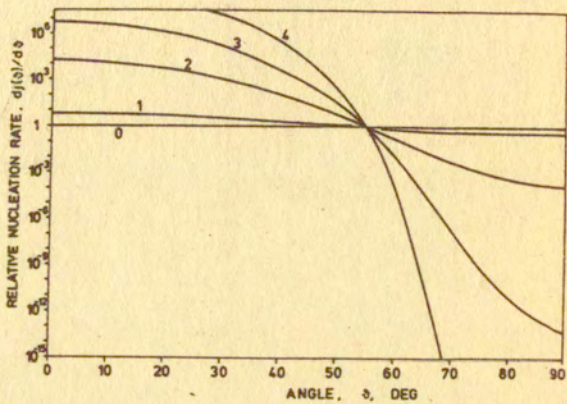


Fig. 9. Reduced nucleation rate distribution $(dj_{st}/d\theta)/(dj_{st}/d\theta)_{\chi=1}$ for uniaxially oriented polyethylene crystallized at $T_{cr} = 365$ K, vs. orientation angle θ .

curve	f_{or}
0	0
1	0.0070
2	0.0496
3	0.1122
4	0.1998

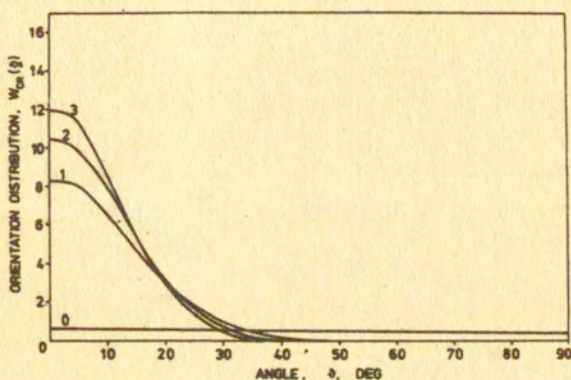


Fig.10. Kinetically-controlled crystal orientation distribution, $W_{cr}(\theta)$ resulting in a uniaxially oriented polyethylene in crystallization at $T_{cr} = 365$ K.

curve	f_{or} in the amorphous phase
0.	0.0496, amorphous distribution $w(\theta)$
1	0.0315, crystal distribution, $W_{cr}(\theta)$
2	0.0496, crystal distribution, $W_{cr}(\theta)$
3	0.0717, crystal distribution, $W_{cr}(\theta)$