

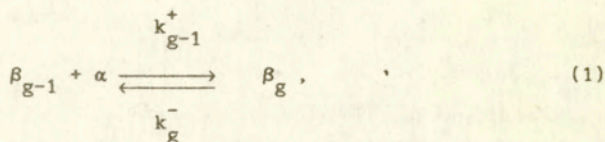
DIFFUSION OF SINGLE ELEMENTS AND STERIC CONSTRAINTS IN
KINETIC THEORY OF NUCLEATION AND CRYSTALLIZATION

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Introduction

It is widely assumed in the kinetic theories of nucleation [1-9] that the following bimolecular reactions:



for $g=2,3,4,\dots$, between cluster β_{g-1} and single element α dominate other types of possible reactions of growth. The index g indicates size of the cluster. It is assumed that the reactions are controlled by intrinsic, chemical rate constants of addition, k_{g-1}^+ , and dissociation, k_g^- . Bimolecular reactions between two clusters, as well as the reactions involving more than two kinetic elements, are neglected. They are less frequent because of much lower probability of collisions between clusters and reduced mobility of the clusters as compared to the mobility of single elements.

Kinetic models of nucleation and crystal growth assume rate constants proposed by transition state model [10-12]. Free energy barrier controlling the rate constants in the model concerns short-range motion within an average intermolecular distance, where the particles involved in the reaction collide.

Sanchez [9] pointed out that in the viscous media (condensed polymer solutions, polymer melts), short-range motion over the free energy barrier is strongly affected by relatively high friction forces, and the rate constants proposed by Kramers [13,14] should be used. The rate constants derived by Kramers converge to the constants of the transition state method in the limit of low viscosity, and in the limit of high viscosity they converge to similar constants with free energy barrier enhanced by activation energy of viscous motion. In the polymer melts, the molecular viscous friction of short-range transport over the free energy barrier is high, and it reduces the rate constants by a factor of $10^{-1} - 10^{-4}$ [9].

The rate constants proposed by Kramers account for effective friction of the molecular motion over the free energy barrier, i.e. for short-range diffusion effects only. Turnbull and Fisher [4] also emphasized that their model of nucleation which next was used as a basic model in kinetic theories of nucleation and crystallization, does not account for long-range diffusion effects. The authors [4] account for "free energy of activation for short-range diffusion of atoms or molecules moving a fraction of an atomic distance across an interface to join a new lattice. However, long-range diffusion is to be expected in phase transformations that involve more than one component".

Under the conditions of nucleation, the clusters are scattered in the matrix of single elements of the mother phase. In a solution, the kinetic elements involved in the reaction of cluster growth are scattered between the solvent particles. Because of much reduced probability of cluster-cluster collision in comparison to cluster-single element collision, the system under nucleation can be treated as composed of a set of isolated, non-interacting clusters, each one surrounded by high number of single elements involved in "diffusive" interactions with the particular cluster. The "diffusive" interactions concern long-range diffusion of single elements, induced by consumption (or delivery) of the elements by the cluster, due to the reaction (1). It is assumed that other types of interactions between single elements and the clusters can be neglected, except for the addition-dissociation process which occurs at the cluster surface.

In the solution, at the condition of non-zero net rate of the addition-dissociation reaction (1), a non-zero concentration gradient of single elements is created in the surroundings of the cluster. The gradient of concentration induces an effective flow of single elements towards or out of the cluster. The gradient induced flow should affect the rate of the reaction, and it is expected to be controlled by the intrinsic rate constants, k_g^+ , k_g^- , as well as by long-range diffusion, mainly diffusion of single elements which are more mobile than the clusters are.

The aim of this paper is to formulate the equations for diffusion of single elements in the surroundings of the cluster involved in the bimolecular reaction (1) in solution, as well as to predict effects of finite long-range diffusion of the elements on the kinetics of nuclea-

tion and crystal growth. The equation of diffusion will be derived for orientable single elements, subjected to external orienting forces and/or to macroscopic solvent flow which can also induce molecular orientation. The equation of diffusion will account for translational and rotational motion of single elements. Steric limitation, related to required compliant orientation of reacting substrats, are taken into account at the boundary conditions.

Coupling between finite diffusion rate of single elements and the intrinsic rate constants of addition and dissociation reaction (1) is expected, which should results in reduced, effective rate constants of the reaction. In the kinetics of nucleation and crystallization one should expect stronger rate reduction effects for faster reactions.

The kinetic equations

In the kinetic theories of nucleation and crystal growth, the bimolecular reaction (1) is assumed to be controlled by the intrinsic, chemical rate constants, k_{g-1}^+ , k_g^- , taken for the conditions close to the equilibrium. At the conditions close to equilibrium, influence of long-range diffusion can be neglected, and the process should be controlled practically by the intrinsic rate constants. Effective coupling with long-range diffusion is expected at the conditions markedly departing from the equilibrium, and it will be taken into account by determining effective rate constants for the reaction (1).

Then the effective flux of growth of the clusters β_g in the solution should read

$$j_g = k_{g-1}^{\text{eff},+} n_{g-1} c_{\text{eq}} - k_g^{\text{eff},-} n_g \quad (2)$$

where $k_{g-1}^{\text{eff},+}$, $k_g^{\text{eff},-}$ denote the effective rate constants of addition and dissociation, resulting from coupling of the reaction with long-range diffusion of single elements. n_g denotes concentration density of number of clusters of size g , c_{eq} - degree of concentration of single elements at equilibrium, normalized to unity for pure, undiluted amorphous system.

In the case of orientable single elements and nucleation under external orienting forces, the flux of cluster growth depends on the orientation of the growing cluster in the external force field [15,16]. Kinetic theory of nucleation in the system of orientable single elements, formulated originally with neglected effects of diffusion, should consider also long-range diffusion of single elements. Obviously, translational and rotational diffusion should be taken into account. The flux of cluster growth should be controlled by the effective rate constants, accounting for translational and rotational diffusion. Then, the originally proposed flux of clusters growth [15,16] should be considered as controlled by the effective, angle-dependent rate constants, $k_{g-1}^{\text{eff},+}(\underline{\theta})$, $k_g^{\text{eff},-}(\underline{\theta})$:

$$dj_g(\underline{\theta}) = k_{g-1}^{\text{eff},+}(\underline{\theta}) dn_{g-1}(\underline{\theta}) c_{\text{eq}} - k_g^{\text{eff},-}(\underline{\theta}) dn_g(\underline{\theta}) \quad (3)$$

Here $dn_g(\underline{\theta})$ denotes number of clusters of size g in unit volume, and

oriented within differential $d\theta$ of the angular space at the angle θ . For uniaxial clusters, the orientation angle is specified by two polar angles, $\underline{\theta} = (\theta, \phi)$, and $d\underline{\theta} = \sin\theta d\theta d\phi$. c_{eq} is concentration of single elements at equilibrium, normalized to unity for pure amorphous system. $dj_g(\underline{\theta})$ is number of clusters of size g produced in unit time and unit volume, and oriented within the differential angle $d\underline{\theta}$ at the orientation angle $\underline{\theta}$.

In the theory proposed earlier [15,16], with neglected effects of long-range translational and rotational diffusion, the rate constant for the reaction of addition is postulated in the following form with a factor $\Delta/4\pi$ responsible for steric constraints

$$k_{g-1}^+(\underline{\theta}) = (\Delta/4\pi) k_{g-1}^{0,+}(\underline{\theta}) \quad (4)$$

Δ denotes solid tolerance angle range which accounts for the stereospecificity of the reaction of addition. Uniaxial single elements (e.g. rodlike particles) are considered. 4π is total solid angle of the angular space for uniaxial single element. The factor $\Delta/4\pi$ is fraction of the total solid angle occupied by the tolerance angle range. $k_{g-1}^{0,+}$ is angle-dependent rate constant with the steric effect eliminated. Ratio of the rate constants is controlled by orientation-dependent thermodynamic driving force [16], according to

$$k_{g-1}^+(\underline{\theta})c_{eq}/k_{g-1}^-(\underline{\theta}) = \exp[-\delta\mu_g(\underline{\theta})/kT] \quad (5)$$

where $\delta\mu_g(\underline{\theta})$ is free enthalpy of cluster formation in solution, corresponding to the addition of one single element to the cluster of size $g-1$, oriented at the angle $\underline{\theta}$, and it reads [16]

$$\delta\mu_g(\underline{\theta}) = \delta\mu_g^0 + U_g(\underline{\theta}) - U_{g-1}(\underline{\theta}) + kT \ln \frac{1}{4\pi c} \int_{eq}^{\Omega} \exp[-U_1(\underline{\theta})/kT] d\underline{\theta}, \quad (6)$$

$\delta\mu_g^0 = \mu_g^0 - (\mu_{g-1}^0 + \mu_1^0)$ is change in free enthalpy in pure, unoriented system; μ_1^0 , μ_g^0 are pure component chemical potentials of single element and the cluster of size g , respectively, at the absence of external orienting forces. $U_1(\underline{\theta})$, $U_g(\underline{\theta})$ are orientation-dependent potential energies of single element, and the cluster of size g , respectively, in the external potential force field. Integration in formula (6) occurs over the total range Ω of the orientation angle of single element.

One should emphasize that eqs.(5,6) were derived for equilibrium, Boltzmann orientation distribution of single elements, and with the assumption of relatively small rotational mobility of clusters in comparison with the mobility of single elements.

The kinetic model of nucleation will be expanded in this paper for the effects of long-range diffusion of single elements on the rate constants. Translational and rotational diffusion will be taken into account, as well as steric, angular constraints in the basic addition-dissociation reaction of the nucleation process.

Long-range diffusion

It is assumed that single elements of the mother phase in solution are subjected to external orienting forces, e.g. permanent or induced

electric dipoles in electric field, rodlike particles in uniaxial elongational flow of the solvent, etc. Furthermore, any single element in the solution undergoes translational and rotational Brownian motion.

Let unit vector \underline{e} indicates orientation of the main axis of single element, and $c(\underline{r}, \underline{e}, t)$ denotes concentration distribution function of single elements at the point \underline{r} of the space of translation, for the orientation vector \underline{e} , at the time t . Let $U(\underline{r}, \underline{e})$ be constant in time potential energy of single element in the external force field. In general, the potential energy U depends on the position of the center of mass of the element in the space of translation, \underline{r} , and on the orientation in the external force field, \underline{e} . For the sake of simplicity, uniaxial force field will be taken into consideration. Then, the potential energy U depends on the scalar product $\underline{e} \cdot \underline{e}_U$, where \underline{e}_U is unit vector indicating orientation of the external force field.

For non-interacting Brownian particles, at the total balance of forces and torques, the equation of motion leads to the following expressions for the velocity of translational (\underline{v}) and rotational ($\underline{\omega}$) motion of single elements [17,18]

$$\underline{v} = - \underline{D}^{tr} \text{grad} (\ln c + U/kT) + \underline{v}_0 \quad (7)$$

$$\underline{\omega} = - D^{\text{rot}} \underline{\mathcal{R}} (\ln c + U/kT) + \underline{\omega}_0 .$$

$\underline{\omega}$ is velocity vector of rotation around the axis perpendicular to the main axis of the rodlike particle. \underline{v}_0 and $\underline{\omega}_0$ are convective, translational and rotational velocities of single element, respectively, related to the flow of the solvent. \underline{D}^{tr} denotes tensor of translational diffusion, D^{rot} is constant of rotational diffusion of single element

around the axis perpendicular to the main axis. $U(\underline{r}, \underline{e}) + kT \ln c(\underline{r}, \underline{e}, t)$ is thermodynamic driving force for translation and rotation diffusion of single elements in the external force field. The entropic term $kT \ln c$ controls translational and rotational Brownian motion. \underline{R} denotes rotational operator for the rotational motion

$$\underline{R} = \underline{e} \times \frac{\partial}{\partial \underline{e}} \quad (8)$$

and it plays the same role, as the gradient operator grad does for translational motion.

Uniform orienting force field, as well as uniform macroscopic flow of the solvent, are assumed for further discussion, i.e.

$$\text{grad } U = \text{const}, \quad \text{and} \quad \underline{R} U = \underline{f}(\underline{e} \cdot \underline{e}_U) \quad (9)$$

where $\underline{f}(\underline{e} \cdot \underline{e}_U)$ is a vector being a function of cosine of the angle between the axis of single element, \underline{e} , and the axis of the external force field, \underline{e}_U . Then the orienting force acting on single elements depends on orientation of the element, and it is uniform in the space of translation:

For uniform flow of the solvent, translational velocity of the solvent convection, \underline{v}_0 , can be expressed by macroscopic velocity gradient tensor, \underline{K}

$$\underline{v}_0(\underline{r}) = \underline{K} \cdot \underline{r} \quad (10)$$

where tensor \underline{K} is constant in the space of translation.

The rate $\underline{\omega}_0$ of rotation convection of single element in the flow

field reads [18,19]:

- for slender rod particle

$$\underline{\omega}_0 = \underline{e} \times \underline{K} \cdot \underline{e} \quad , \quad (11)$$

- for spheroid of aspect ratio p

$$\underline{\omega}_0 = \underline{e} \times (p^2 \underline{K} - \underline{K}^T) \cdot \underline{e} / (p^2 + 1) \quad (12)$$

For an irrotational solvent flow, $\underline{K}^T = \underline{K}$, and it can be expressed by a scalar function [20], called a potential of the flow, ϕ_s

$$\underline{K} = - \text{grad} (\text{grad} \phi_s) \quad (13)$$

Introducing potential energy U_s of single element, related to the macroscopic potential flow of the solvent

$$U_s(\underline{r}, \underline{e}) = kT [\phi_s(\underline{r}) / \|\underline{D}^{\text{tr}}\| + Z_p \phi_s(\underline{e}) / D^{\text{rot}}] \quad , \quad (14)$$

equation of diffusion of single elements assumes the following form

$$\begin{aligned} \partial c / \partial t = & \|\underline{D}^{\text{tr}}\| \text{div} [(\underline{D}^{\text{tr}} / \|\underline{D}^{\text{tr}}\|)(\text{grad} c + c \text{grad} U/kT) + c \text{grad} U_s \\ & + D^{\text{rot}} \underline{X} \cdot [\underline{X} c + c \underline{X} (U + U_s)/kT] \quad . \end{aligned} \quad (15)$$

Z_p is a shape function of single element. For slender rodlike elements $Z_p = 1$, and for uniaxial spheroids of aspect ratio p [19]

$$Z_p = (p^2 - 1) / (p^2 + 1) \quad (16)$$

The boundary conditions

Uniaxial single elements diffuse in solution towards or out of the cluster in the effect of addition-dissociation reaction (1). An isolated single cluster involved in the bimolecular reaction, and suspended in the solution is considered. Separation of clusters in the system, particularly at the initial stages of the nucleation process, should be good enough to satisfy the assumption. Then, the diffusion of single elements in the system can be approximated by diffusion in the infinite continuum with single cluster embedded. This approximation applies when the average distance between neighboring clusters is higher than the range of substantial changes in the concentration of single elements. The range of substantial changes in the concentration is estimated *a posteriori* from the solution of the equation of diffusion for the model of single cluster in the infinite surroundings.

For the sake of simplicity, the cluster is approximated by spherical body of radius R with reactive surface. Reactivity of the surface should exhibit stereospecificity typical for reactions involving uniaxial elements. Boundary condition for the equation of diffusion (15) at the reactive surface is related to the addition-dissociation reaction, and it is postulated in the form

$$n \cdot \vec{L}_{tr} |_{r=R} \partial v_c = k^+(\underline{r}, \underline{e}; \underline{e}_c) c(\underline{r}, \underline{e}) - k^-(\underline{r}, \underline{e}; \underline{e}_c) \quad (17)$$

where

$$j_{tr} = \underline{D}^{tr} v_1^{-1} (\text{grad } c + c \text{ grad } U/kT) + \|\underline{D}^{tr}\| v_1^{-1} c \text{ grad } U_s/kT \quad (17a)$$

$v_1^{-1} c(\underline{r}, \underline{e})$ is density of number of single elements in the space of translation and rotation. v_1 denotes volume occupied by one single element. Eq.(17) is similar to the boundary condition introduced by Solc and Stockmayer [21] for irreversible chemical reactions, and by Schmitz and Schurr [22] for reversible reactions.

The term on the left hand side of eq.(17) is radial component of the flux density of translation diffusion at the point \underline{r} on the cluster surface, ∂V_c . Rotation diffusion, as well as transversal component of translation diffusion can be neglected [21]. \underline{n} denotes unit vector, normal to the cluster surface at the point $\underline{r} \in \partial V_c$. The boundary condition says that radial component of the flux of diffusion of single elements at the surface is totally balanced by the reaction. The reaction is controlled by rate coefficients $k^+(\underline{r}, \underline{e}; \underline{e}_c)$, $k^-(\underline{r}, \underline{e}; \underline{e}_c)$, and by the concentration $c(\underline{r}, \underline{e})$ of single elements at the point \underline{r} at the surface. The rate coefficients used are surface and angular densities of addition and dissociation rate constants. \underline{e}_c is unit vector (used as parameter) indicating orientation of the reactive surface. Unit vector \underline{e}_c indicates orientation of single element, most favored for the reaction of addition. For further discussion, the reaction favored direction, \underline{e}_c , as well as orientation-dependent rate coefficients are assumed to be uniform over the total reactive surface, i.e independent of the surface point \underline{r} .

Angular dependence of the rate constants is postulated in the boundary condition (eq.17), and it should result from both, orientation-dependent potential energy of substrats involved in the reaction, and from steric constraints related to the orientation of single elements, favored by the reaction. As far as steric constraints are concerned, kinetics of the reaction is assumed to be sensitive to mutual orientation of the substrats, i.e. to the scalar product $\underline{e} \cdot \underline{e}_c$.

At the absence of external forces, steric limitations alone determine angular dependence of the rate coefficients. The steric constraints can be characterized by a scalar function $\chi(\underline{e} \cdot \underline{e}_c)$, dependent on the mutual orientation of the substrats involved in the reaction, and defined

$$\chi(\underline{e} \cdot \underline{e}_c) = k^+(\underline{e} \cdot \underline{e}_c) / k^+(\underline{e} \cdot \underline{e}_c = 1) \quad , \quad (18)$$

where k^+ is rate coefficient for the reaction of addition at the absence of external forces, dependent on the mutual orientation of the substrats. Then, the function of steric constraints χ is angular density of the addition rate constant, reduced by value of the rate constant for the reaction favored direction, at the absence of any external forces. It is expected that $\chi(\underline{e} \cdot \underline{e}_c) \leq 1$, what means that the favored direction \underline{e}_c is characterized by the highest value of the rate coefficient for the reaction of addition.

At the lack of any steric constraints, the function of steric constraints $\chi=1$. Then, the rate coefficients are uniform in the space of orientation (for example spherical single elements forming spherical

clusters).

The function χ may be postulated as continuous, or a step function [16,21,22]. The following step function

$$\chi(\underline{e} \cdot \underline{e}_c) = \begin{cases} 1 & \text{for } 0 \leq \arccos|\underline{e} \cdot \underline{e}_c| \leq \Delta\theta \\ 0 & \text{for } \Delta\theta \leq \arccos|\underline{e} \cdot \underline{e}_c| \leq \pi/2 \end{cases} \quad (19)$$

allows for addition of single elements oriented only within the zenithal tolerance angle range $\Delta\theta$. The tolerance angle range $\Delta\theta$ was introduced in the kinetic theory of nucleation, first as a model parameter [15], and next physical interpretation was assigned to it [16]. With the definition of the steric constraints function (eq.19), the solid tolerance angle range reads $\Delta = 1 - \cos(\Delta\theta)$. For narrow tolerance angle range ($\Delta\theta/\pi \ll 1$), the solid angle range $\Delta \cong (\Delta\theta)^2/2$.

It is assumed that the external potential forces, inducing orientation of single elements, do not affect the function of steric constraints χ . It is convenient for further considerations to use normalized function of steric constraints $\chi(\underline{e} \cdot \underline{e}_c) / \int \chi \, d\underline{e}$.

Steric constraints for the reaction of dissociation are assumed to be controlled by the same mechanisms as for the reaction of addition, and common function χ is taken for both reactions. Then, the boundary condition (eq.17) is postulated in the following form with steric constraints specified

$$\frac{n}{V} \cdot \int_{\underline{r} \in \partial V_c} \underline{j} = [k^+ 4\pi c(\underline{r}, \underline{e}) - k^-] v_1 \chi(\underline{e} \cdot \underline{e}_c) / \int \chi \, d\underline{e} \quad (20)$$

The rate coefficients $k^\pm = k^\pm(\underline{e}; \underline{e}_c)$ depend on the orientation of single element and the cluster in the external force field. For the systems of spherical single elements and clusters (no steric constraints and orientation effects) the steric function $\chi/\int \chi \, d\epsilon = 1/4\pi$, and the rate coefficients $k^\pm = k^{0,\pm}$ are surface densities of the addition and dissociation rate constants.

For the conditions close to the equilibrium of the reaction (1), the ratio of the rate coefficients is controlled by thermodynamic driving force $\hat{\delta}\mu_g^0$, and it reads

$$k^+/k^- = \exp(-\hat{\delta}\mu_g^0/kT) \quad (21)$$

where

$$\hat{\delta}\mu_g^0 = \delta\mu_g^0 + \delta U_c(g, \underline{e}_c) - U_1(\underline{e}) \quad (22)$$

$\delta\mu_g^0$ is pure component free enthalpy of addition of single element to the cluster of size $g-1$, at the absence of any external force field and solvent particles. $\delta U_c = U_c(g, \underline{e}_c) - U_c(g-1, \underline{e}_c)$ is change in potential energy of the cluster in the external potential force field due to growth of the cluster by one single element. U_c denotes potential energy of cluster of size g , oriented at \underline{e}_c . U_1 is potential energy of single element, $U_1 = U + U_s$, and it is the sum of potential energy of the element in the external force field and the potential energy related to the solvent flow. In general, $\hat{\delta}\mu_g^0$ depends on the cluster size g , orientation \underline{e}_c of the cluster, and orientation \underline{e} of single element in the external force field. The pure component chemical potential $\delta\mu_g^0$ does

not include any entropic term related to the degree of dilution of single elements. The concentration distribution c should be normalized to $1/4\pi$ for undiluted amorphous system, at the absence of any external orienting field.

At the equilibrium, concentration distribution of single elements at the reactive surface reads

$$c(\underline{r} \in \partial V_c, \underline{e}) = c_{eq} \exp[-U_1(\underline{e})/kT] / \int \exp[-U_1/kT] d\underline{e} \quad (23)$$

and

$$k^+ 4\pi c / k^- = \exp(-\delta\mu_g/kT) \quad (24)$$

$\delta\mu_g$ is free enthalpy of the cluster growth per one single element in oriented and diluted system

$$\delta\mu_g = \delta\mu_g^0 + \delta U_c(g, \underline{e}_c) + kT \ln(Z/c_{eq}) \quad (25)$$

where

$$Z = (1/4\pi) \int \exp[-U_1(\underline{e})/kT] d\underline{e} \quad (26)$$

For undiluted system, $c_{eq}=1$, and at the absence of any external potential the statistical sum $Z=1$.

The absolute rate coefficients for the addition-dissociation reaction can be formulated using the following formula, proposed earlier [23]

$$k^\pm(\underline{e}; \underline{e}_c) = (kT/h)n_s \exp(-E/kT) \exp\left[\mp \frac{1}{2} (\hat{\delta}\mu_g^0 \pm |\hat{\delta}\mu_g^0|)/kT\right], \quad (27)$$

where n_s' is surface density of active sites on the cluster surface. E is activation energy for short-range transport of single element over the potential barrier at the cluster surface. Eq.(27) accounts for thermodynamic barrier $\hat{\delta}\mu_g^0$ in the reaction of addition only if $\hat{\delta}\mu_g^0 > 0$, and in the reaction of dissociation only if $\hat{\delta}\mu_g^0 < 0$. The absolute rate constants given by eq.(27) correspond to the kinetic models of chemical reactions proposed by the state transition method [10-12], or by Kramers [13,14] for small and high viscosity media. In the limit of high viscosity polymer media, WLF-type term should appear in eq.(27) in addition to the Arrhenius-type transport term [9].

At a distance far from the reacting cluster, concentration distribution c will be approximated by the Boltzmann distribution. Then, the boundary condition at the infinity reads:

$$\lim_{r \rightarrow \infty} c(\underline{r}, \underline{e}) = c_{eq} \exp[-U_1(\underline{e})/kT] / \int \exp[-U_1/kT] d\underline{e} \quad (28)$$

Any physical initial condition can be assumed, depending upon the problem to be solved. For the purpose of this paper where stationary nucleation is considered, stationary solution of the diffusion problem is needed, and the initial condition is not a subject of main interest.

Results and discussion

To solve the diffusion equation (15), zero of the coordinate system is shifted to the center of the cluster. It is assumed that all forces acting on single elements and the cluster are nearly balanced by the viscous friction forces. Then, the equation of diffusion, expressed in the coordinate system connected with center of the cluster, holds the form of eq.(15) for any uniform external force field, and for any uniform flow field of the solvent. Translational and rotational mobility of the cluster is much reduced in comparison with the mobility of single elements, i.e. $\|D_c^{tr}\|/\|D^{tr}\| \ll 1$, and $\|D_c^{rot}\|/D^{rot} \ll 1$, where "c" indicates the diffusion tensors of the cluster, and $\|\cdot\|$ denotes scalar measure of the diffusion tensors. Then, the tensors of translational and rotational diffusion in eq.(15), relative to the cluster, can be approximated by the diffusion tensors of single elements.

In general, solution of the diffusion equation (15) assumes the following form [18]

$$c(\underline{r}, \underline{e}, t) = c^{st}(\underline{r}, \underline{e}) \left[1 + \sum_{i=1}^{\infty} \gamma_i(\underline{r}, \underline{e}) \exp(-\lambda_i t) \right] \quad (29)$$

where the eigenvalues λ_i are positive, and c^{st} is a stationary solution. The solution converges to the stationary one with increasing time, $t/\lambda_1 \rightarrow \infty$, and the coefficients γ_i are controlled by the initial and the boundary conditions.

The stationary distribution $c^{st}(\underline{r}, \underline{e})$ satisfies the following stationary form of the diffusion equation:

$$L c^{st} = 0 \quad (30)$$

with the boundary conditions given by eqs.(20,28). L is a linear, second order differential operator, given by right-hand side of eq.(15), and controlled by the potential of the external forces, and by the macroscopic flow of the solvent.

In general, stationary solution of the diffusion equation can be expressed in the form

$$c^{st}(\underline{r}, \underline{e}) = c_{eq} \psi(\underline{r}, \underline{e}) \exp[-U_1(\underline{e})/kT] / \int \exp[-U_1(\underline{e})/kT] d\underline{e}, \quad (31)$$

The dimensionless function $\psi(\underline{r}, \underline{e})$ shows deviation of the concentration distribution of single elements from the equilibrium one, due to net consumption (or delivery) of single elements by the cluster surface. ψ converges to unity with increasing distance from the cluster to infinity. At the equilibrium, $\psi=1$ everywhere, and the orientation distribution of single elements is Boltzmann and uniform in the space of translation.

Analytical and numerical discussion of the deviation function ψ is given in a separate paper [24] for square cosine orienting potential, typical for uniaxial single elements in uniaxial potential solvent flow or for induced dipoles in electric field.

Example numerical computations of the deviation of the concentration distribution from the equilibrium one are performed for two values of the chemical rate constants, $k^+ = \|\underline{r}^{tr}\|/Rv_1$ and $k^+ = 10\|\underline{D}^{tr}\|/Rv_1$, and for fixed diffusional characteristic $D^{rot}R^2/\|\underline{D}^{tr}\| = 0.01$. The tole-

rance angle range is assumed to be $\Delta\theta = 5^\circ$. The computed values of the deviation from the equilibrium, $1-\psi$, expressed in qc_{eq} units, are plotted in Figs. 1a,b vs. distance from the cluster center, r/R . The distance $r/R=1$ corresponds to the cluster surface. The plots are shown for several angles of orientation, θ , of single elements with respect to the favored direction of the reaction. q is a parameter related to the thermodynamic driving force of the reaction

$$q = 1 - \exp(\delta\mu_g/kT) . \quad (32)$$

For the conditions of effective forward reaction ($\delta\mu_g < 0$), the thermodynamic factor $0 < q \leq 1$. Then, the depression of concentration distribution from the equilibrium one is predicted by the model. For $\delta\mu_g > 0$, the factor q is negative, and the effective backward reaction (melting) leads to the concentration of single elements exceeding the equilibrium state.

Figs. 1a,b show strongest deviation of the concentration from the equilibrium distribution for single elements oriented along the favored direction of the reaction, and within the tolerance angle range, $\Delta\theta=5^\circ$. The deviation is strongest at the cluster surface, and it increases considerably with increasing the rate constant of the reaction of addition (from $-0.3qc_{eq}$ in Fig. 1a to $-0.8qc_{eq}$ in Fig. 1b). The Figures show also that the concentration deviation is much smaller for the elements oriented outside the $\Delta\theta$ -range. Radial gradient of the concentration on the cluster surface is non-zero only for the elements oriented within the $\Delta\theta$ -range, and it is zero for the elements oriented outside the range. It results from the steric constraints introduced in the boundary condition for the cluster surface.

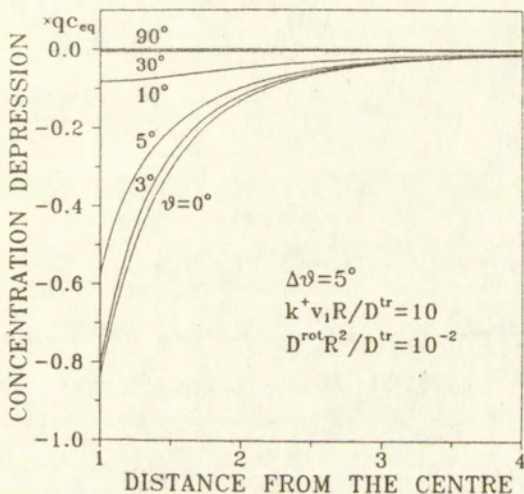
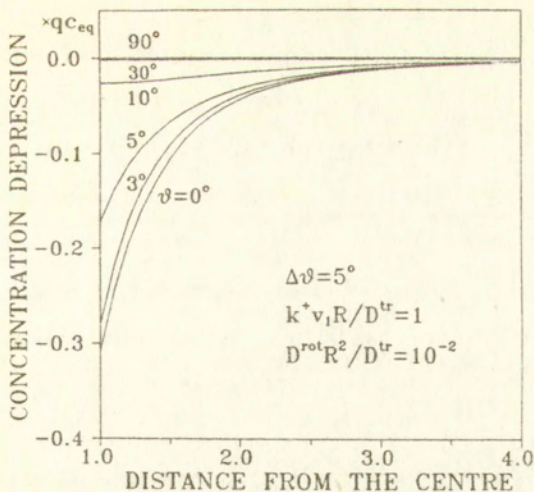


Fig. 1.

Concentration depression of single elements from the equilibrium vs. distance from the cluster center, r/R , for various orientation angles of single elements. The tolerance angle range $\Delta\vartheta = 5^\circ$, and value of the reduced rotational diffusion constant is fixed.

(a) reduced rate constant $k^+v_1R/\|D^{tr}\| = 1$.

(b) $k^+v_1R/\|D^{tr}\| = 10$.

Radius of a sphere surrounding the cluster where deviation of the concentration from the equilibrium exceeds 10% of $q_{c_{eq}}$ (i.e. $|1-\psi|/q_{c_{eq}} > 0.1$) is predicted for $2R-3R$ in a wide range of the reaction and diffusion rates, as well as steric constraints. R is radius of the cluster. The conclusion justifies a posteriori the assumption of the system of isolated clusters embedded in a matrix of single elements and the solvent particles. For the most severe kinetic and steric regimes, the radius does not exceed $10R$ at the 10%-criterion assumed.

It has been shown [24] that kinetics of the process, with long-range diffusion and steric effects taken into consideration, is controlled by a dimensionless, reduced rate constant α^+/α^* , and by the thermodynamic factor q (eq.32). The dimensionless rate constant is

$$\alpha^+ = k^+ v_1 R / \|D\|^{tr} \quad (33)$$

The factor α^* is responsible for effectivity of the rate constant and results from long-range diffusion (rotational and translational), and steric constraints. The factor can be computed using the following formula [24]

$$1/\alpha^* = \sum_{n=0}^{\infty} \frac{\kappa_n(\Delta\theta)}{1 + [2n(2n+1)D^{rot} R^2 / \|D\|^{tr}]^{1/2}} \quad (34)$$

where the coefficients $\kappa_n(\Delta\theta)$ are related to the steric constraint, and they can be computed using the following recurrent formula

$$\kappa_n(\Delta\theta) = \frac{(n-1)(2n-1)(4n+1)}{n(2n+1)(4n-3)} \kappa_{n-1}(\Delta\theta) + \frac{(4n-1)(4n+1)}{2n(2n+1)} (1+\cos\Delta\theta) P_{2n-1}(\cos\Delta\theta) \quad (35)$$

where $\kappa_0(\Delta\theta)=1$, and P_n denotes Legendre polynomial. In general, the parameter α^* is a function of reduced rotational diffusion constant, $D^{\text{rot}}R^2/\|\underline{D}^{\text{tr}}\|$, and the tolerance angle range, $\Delta\theta$.

Fig.2 shows the rate effectivity parameter, α^* , computed from eqs.(34,35) and plotted vs. the tolerance angle range, $\Delta\theta$, for different values of the reduced rotational diffusion constant, $D^{\text{rot}}R^2/\|\underline{D}^{\text{tr}}\|$. For lack of any steric constraints ($\Delta\theta=90^\circ$), α^* equals to unity, and rotational diffusion does not affects the parameter. With sharpening the steric constraints, i.e. with decreasing $\Delta\theta$ to zero, rotational diffusion affects the parameter α^* the stronger the narrower is $\Delta\theta$ range. It is seen in Fig.2 that the effect of steric constraints vanish with increasing reduced rotational diffusion constant to infinity, and α^* tends then to unity. Steric effect becomes strongly pronounced for rotational diffusion much hindered in comparison with translational motion. Then, for $D^{\text{rot}}R^2/\|\underline{D}^{\text{tr}}\| \ll 1$, the rate effectivity parameter $\alpha^* \approx 1-\cos\Delta\theta$. For narrow tolerance angle range, $\Delta\theta/\pi \ll 1$, and for strongly hindered rotation, $\alpha^* \approx (\Delta\theta)^2$, where $\Delta\theta$ is expressed in radians. For example, at the tolerance angle range $\Delta\theta=5^\circ$, the parameter α^* assumes values in the range from about unity at high values of the reduced rotational diffusion constant, to about 4×10^{-3} at rotational diffusion totally hindered. One concludes that diffusional and steric effects in the kinetics of the reaction are coupled, and they are

predicted for several orders of magnitude at strong diffusional and steric constraints.

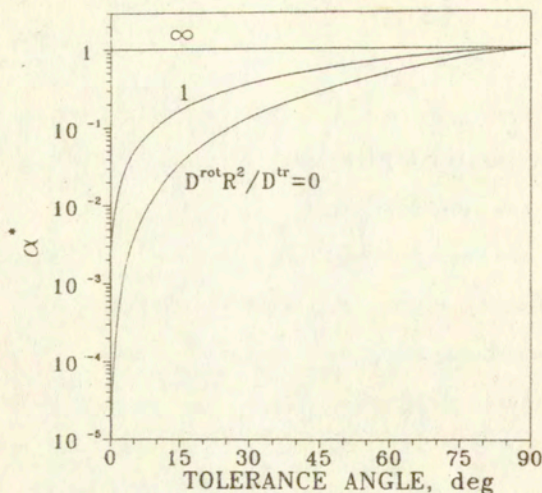


Fig.2.

Rate effectivity parameter α^* plotted vs. tolerance angle range $\Delta\theta$ for: totally hindered rotational diffusion, an intermediate value, and infinite rotational diffusion constant.

The effective rate constants, accounting for simultaneous rotational and translational long-range diffusion at steric constraints present, read [24]

$$k^{\text{eff}, \pm} = \frac{4\pi R^2 k^{\pm}}{1 + \alpha^* / \alpha} \quad (36)$$

where the rate constant of addition, k^+ , was redefined to satisfy $k^+ c_{\text{eq}}^- / k^- = \exp(-\delta\mu/kT)$, where $\delta\mu$ is free enthalpy of addition of single element to the cluster in solution (eq.23).

For the case of slow reactions and/or relatively fast rotational diffusion ($\alpha^+/\alpha^* \ll 1$), the effective rate constants converge to chemical rate constants

$$k^{\text{eff},\pm} \cong 4\pi R^2 k^\pm \quad (37)$$

The intrinsic chemical rate constant for the reaction of addition, k^+ , already includes equilibrium steric factor [16]. It means that $k^+ = (1-\cos\Delta\theta) k^{0,+}$, where $k^{0,+}$ is taken for corresponding reaction involving spherical elements, without steric constraints.

For fast reactions and/or relatively slow rotational diffusion ($\alpha^+/\alpha^* \gg 1$), the effective rate constants converge to Smoluchowski-type rate constant, multiplied by the rate effectivity factor α^* :

$$k^{\text{eff},+} \cong 4\pi R \parallel \underline{D}^{\text{tr}} \parallel \alpha^*, \quad (38)$$

$$k^{\text{eff},-} \cong 4\pi R \parallel \underline{D}^{\text{tr}} \parallel (k^-/k^+) \alpha^*.$$

For lack of any steric constraints, or relatively fast rotational diffusion of single elements ($\alpha^* = 1$), formula (38) for the reaction of addition assumes the form of classical Smoluchowski rate constant, proposed in diffusion limited aggregation (D.L.A.) model [25,26]. For totally hindered rotational diffusion, the rate effectivity parameter $\alpha^* = 1 - \cos(\Delta\theta)$, and the Smoluchowski rate constant is reduced the stronger, the sharper is the steric restriction.

Nucleation and crystal growth rates

The effective rate constants (eq.36), when applied in the kinetic theory of nucleation and crystal growth, lead to nucleation and crystal growth rates reduced by the coupled effects of long-range diffusion and steric constraints. Following the formal procedure of Frank and Tosi [6], and using the effective rate constants, one obtains the following expression for the nucleation rate

$$\dot{N} = (1 + k_g^{+*} v_1 R^* / \|\underline{D}\|^{tr} \alpha^*)^{-1} \dot{N}_0 \quad (39)$$

where \dot{N}_0 is nucleation rate predicted by the classical theory with neglected effects of long-range diffusion. k_g^{+*} is surface density of intrinsic (chemical) rate constant of the reaction of addition to the cluster of critical size g^* , and R^* denotes radius of the critical cluster. Formula (39) is proposed for unoriented systems, and the classical nucleation rate, \dot{N}_0 , reads

$$\dot{N}_0 = (g^{2/3})^* (kT/h) n \exp(-E/kT) c_{eq}^2 \exp(-\Delta F^*/kT) \quad (40)$$

where n is number of single elements in unit volume of the melt. c_{eq} is equilibrium value of the concentration of single elements, normalized to unity in undiluted, amorphous state. $(g^{2/3})^*$ is a surface factor [4,8,16], proportional to the surface of the critical cluster. ΔF^* is free enthalpy of critical cluster formation in the dilute system [15,16]

$$\Delta F^* = \mu_g^0 - g \mu_1^0 - (g-1)kT \ln c_{eq} \quad (41)$$

g^* is number of single elements forming cluster of critical size, and μ_g^0 , μ_1^0 are pure component chemical potentials of the critical cluster and single element, respectively.

For the systems under influence of external orienting forces, application of Frank and Tosi procedure [16], with the effective rate constants (eq.36) taken into consideration, leads to the following expression for angular distribution of the nucleation rate

$$d\dot{N}(\underline{e})/d\underline{e} = (1 + k_g^+ v_1 R^* / \|\underline{D}\| \alpha^*)^{-1} [d\dot{N}_0(\underline{e})/d\underline{e}] \quad (42)$$

where $d\dot{N}_0(\underline{e})/d\underline{e}$ is angular distribution of the nucleation rate with the effects of long-range diffusion neglected. According to the earlier model proposed for nucleation under external orienting forces [16]

$$d\dot{N}_0(\underline{e})/d\underline{e} = (g^{2/3})^* (kT/h) n \exp(-E/kT) c_{eq}^2 w_{eq}(\underline{e}) \exp[-\Delta F^*(\underline{e})/kT] \quad (43)$$

where

$$\Delta F^*(\underline{e}) = \mu_g^0 - g \mu_1^0 + U_c(g^*, \underline{e}) - U_1(\underline{e}) + (g-1)kT \ln (Z/c_{eq}) \quad (44)$$

For zero external potential, free enthalpy barrier ΔF^* converges to eq.(41) valid for the system in isotropic state. $w_{eq}(\underline{e})$ is normalized Boltzmann orientation distribution of single elements, controlled by the potential energy, $U_1(\underline{e})$.

The rate constant, k_g^{*} , appearing in the reduction factor $(1+k_g^{*}v_1R^*/\|D_{tr}\|\alpha^*)^{-1}$, is not controlled by the chemical potential of the reaction, but only by the transport activation energy E [16,23], in the case of not too high potential energy of the cluster, i.e. for $-\delta U_c(g, \underline{e}) < kT \ln(Z/c_{eq})$. Then, one obtains $k_g^{*} = (kT/h) \exp(-E/kT)$.

The kinetic theory of crystal growth, proposed by Frank and Tosi [6] with the intrinsic rate constants $k_0^{*}=k_1^{*}=k_2^{*}=k_3^{*}=\dots$, $k_1^{-}=k_2^{-}=k_3^{-}=\dots$ defined according to the transition state method [11-14] or according to Kramers [23], leads to the following expression for the steady-state crystal growth rate in unoriented systems

$$G_0 = g^{2/3} k_0^{+} c_{eq} [1 - \exp(\delta\mu/kT)] / [2 - \exp(\delta\mu/kT)] \quad (45)$$

The rate of crystal growth, resulting from the effective rate constants (eq.36), is given by the following formula

$$G = (1+k_0^{+} v_1 R^* / \|D_{tr}\| \alpha^*)^{-1} G_0 \quad (46)$$

which is classical Frank and Tosi growth rate, G_0 , reduced by the factor resulting from long-range diffusion at steric constraints present. The growth rate reduction factor is controlled, except for diffusion and steric constraints, also by the initial rate constant of addition, k_0^{+} , for the first step, and by the dimension of the growing crystal, R .

For preoriented systems, with external orienting forces acting, the growth rate of a crystal oriented at the direction \underline{e} can be also described by eqs.(45,46), but with orientation-dependent driving force $\delta\mu$ of the process

$$\delta\mu(\underline{e}) = \delta\mu^0 + \delta U_c(\underline{e}) + kT \ln(Z/c_{eq}) \quad (47)$$

The rate reduction factor, resulting from the effects of long-range translational and rotational diffusion at steric constraints present, is similar in its form for nucleation and crystal growth rates (cf. eqs.(39,42,46) in unoriented and oriented systems. For slow process ($k^+ v_1 R / \parallel \underline{D}^{tr} \parallel \alpha^* \ll 1$), the rate reduction factor is close to unity, and the nucleation and crystal growth rates can be described by the classical model, with long-range diffusion neglected (eqs.40,43,45).

But for relatively fast process ($k^+ v_1 R / \parallel \underline{D}^{tr} \parallel \alpha^* \gg 1$), the rate reduction factor is much lower than unity, and it approximately equals to $\parallel \underline{D}^{tr} \parallel \alpha^* / k^+ v_1 R$. Then the diffusion limited aggregation (D.L.A.) conditions are approached, and the appropriate kinetic equations should read:

- nucleation rate in unoriented systems (D.L.A. limit)

$$\dot{N} = (g^{1/3})^* \parallel \underline{D}^{tr} \parallel (nc_{eq})^2 \alpha^* \exp(-\Delta F^* / kT) \quad (48)$$

- angular distribution of the nucleation rate in preoriented systems (D.L.A. limit)

$$d\dot{N}(\underline{e})/d\underline{e} = (g^{1/3})^* \parallel D_{\parallel}^{tr} \parallel (nc_{eq})^2 \alpha^* w_{eq}(\underline{e}) \exp[-\Delta F^*(\underline{e})/kT] \quad (49)$$

-growth rate of crystal oriented at \underline{e} in unoriented or oriented systems (D.L.A. limit)

$$G(\underline{e}) = g^{1/3} \parallel D_{\parallel}^{tr} \parallel nc_{eq} \alpha^* [1 - \exp(\delta\mu(\underline{e})/kT)] / [2 - \exp(\delta\mu(\underline{e})/kT)]. \quad (50)$$

$g^{1/3}$ is a factor proportional to linear dimension of the cluster of size g . For spherical cluster, $g^{1/3} = 4\pi R$, and $(g^{1/3})^* = 4\pi R^*$ where R^* is radius of the cluster of critical size. For uniaxial single elements, $\parallel D_{\parallel}^{tr} \parallel = (D_{\parallel}^{tr} + 2D_{\perp}^{tr})/3$. nc_{eq} is number of single elements per unit volume of the solution at the equilibrium. α^* is the rate effectivity factor (eqs.34,35), resulting from long-range rotational and translational diffusion at steric constraints present, $\alpha^* = \alpha^* (D^{rot} R^2 / \parallel D_{\parallel}^{tr} \parallel, \Delta\theta)$.

Obviously, long-range diffusion effects which are of kinetic nature, do not affect the thermodynamic barrier for the kinetics of nucleation and crystal growth. The rate reduction factor appears as a preexponential factor, and it ranges from unity for slow processes, to its D.L.A. limit equal to $\parallel D_{\parallel}^{tr} \parallel \alpha^* / k^+ v_1 R$ for fast processes.

Example computations of the rate reduction factor were performed. Figs.3a,b illustrate the effects of reduced rotational diffusion of single elements on the rate reduction factor, $(1 + k^+ v_1 R / \parallel D_{\parallel}^{tr} \parallel \alpha^*)^{-1}$, computed for various intrinsic rate constants of the reaction of addition, and various values of the tolerance angle range. The general conclusion is that with decreasing the constant of reduced rotational diffusion, the rate reduction factor decreases by several orders of

magnitude, depending upon intrinsic rate constant, k^+ , and tolerance angle range, $\Delta\theta$.

In particular, Fig.3a shows the rate reduction factor plotted vs. the reduced rotational diffusion constant, $D^{\text{rot}}R^2/\|\underline{D}^{\text{tr}}\|$, for several values of the dimensionless rate constant of the reaction of addition, $k^+v_1R/\|\underline{D}^{\text{tr}}\|$, ranging from 10^{-4} to 10^2 , and the tolerance angle range is fixed to $\Delta\theta=5^\circ$. Strongest reduction of the nucleation and crystal growth rates by a factor of 10^{-4} are predicted for highest values of $k^+v_1R/\|\underline{D}^{\text{tr}}\|$, taken for the computations as 10^2 , and for lowest values of the reduced rotational diffusion constant. For slow reactions, characterized by $k^+v_1R/\|\underline{D}^{\text{tr}}\| < 10^{-2}$, the rate reduction factor is close to unity, and does not vary considerably with increasing rotational mobility of single elements.

Fig.3b shows the rate reduction factor, computed for fixed value of the rate parameter, $k^+v_1R/\|\underline{D}^{\text{tr}}\|=1$, and plotted vs. the reduced rotational diffusion constant, for various values of the tolerance angle range. It is predicted that for lack of any steric constraints ($\theta=90^\circ$), rotational mobility of single elements do not affect kinetics of the process at all. But with narrowing the tolerance angle range, the role of rotational diffusion of single elements becomes pronounced the stronger the sharper is the steric constraint. Let say, for $\Delta\theta=5^\circ$ and smaller, the theory predicts reduction of the kinetics by several orders of magnitude, and the rate reduction factor assumes the values of the order from 10^{-2} at $\Delta\theta=5^\circ$, to 10^{-4} at $\Delta\theta=.1^\circ$, for a low value of the reduced rotational diffusion constant. With increasing rotational mobility of single elements, the rate reduction factor converges to the value obtained at the lack of steric restrictions.

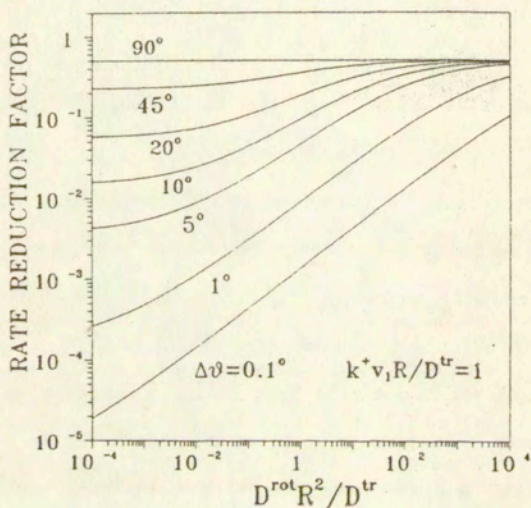
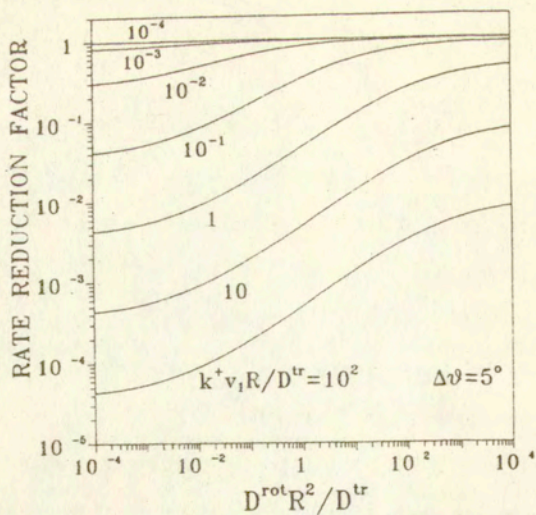


Fig. 3.

Rate reduction factor $(1 + k^+ v_1 R / \parallel \underline{D}^{\text{tr}} \parallel \alpha^*)^{-1}$ plotted vs. reduced rotational diffusion constant $D^{\text{rot}} R^2 / \parallel \underline{D}^{\text{tr}} \parallel$ for:

(a) several values of reduced rate constant $k^+ v_1 R / \parallel \underline{D}^{\text{tr}} \parallel$, $\Delta\theta = 5^\circ$.

(b) several values of $\Delta\theta$, and $k^+ v_1 R / \parallel \underline{D}^{\text{tr}} \parallel = 1$.

It is obvious that even at the lack of steric constraints, or at the limit of infinite value of the reduced rotational diffusion constant, the rate reduction factor is still lower than unity because of finite translational diffusion. It results in diffusion limited kinetics also for spherical single elements, at relatively fast reaction and/or strongly hindered translational motion. This case corresponds to the classical results of Smoluchowski [25], and Collins and Kimball [26], obtained in the D.L.A. model for spherical elements. At the lack of steric constraints, the rate reduction factor converges to unity for slow reactions, and/or for relatively fast translational diffusion of single elements. This is also seen in Fig.4a at the tolerance angle range $\Delta\theta=90^\circ$, for several values of the intrinsic reaction rates taken for computations.

Figs.4a,b illustrate effect of steric constraints on the rate reduction factor. One concludes that the steric effects are pronounced the stronger the narrower is the tolerance angle range. Fig.4a shows plots of the rate reduction factor, $(1+k^+v_1R/\|\underline{D}^{tr}\|\alpha^*)^{-1}$, vs. the tolerance angle range, $\Delta\theta$, computed for fixed value of the reduced rotational diffusion constant, $D^{rot}R^2/\|\underline{D}^{tr}\| = 1$, for several values of the intrinsic rate parameter, $k^+v_1R/\|\underline{D}^{tr}\|$, ranging from 10^{-4} to 10^2 . It is seen from the plots that steric effects reduce kinetics of the processes by the factor of 10^{-2} , with decreasing the tolerance angle range from 90° to a value of few degrees. Steric effects are less pronounced for slow reactions where the rate reduction factor is close to unity, and only very narrow tolerance angle range is able to reduce the kinetics considerably.

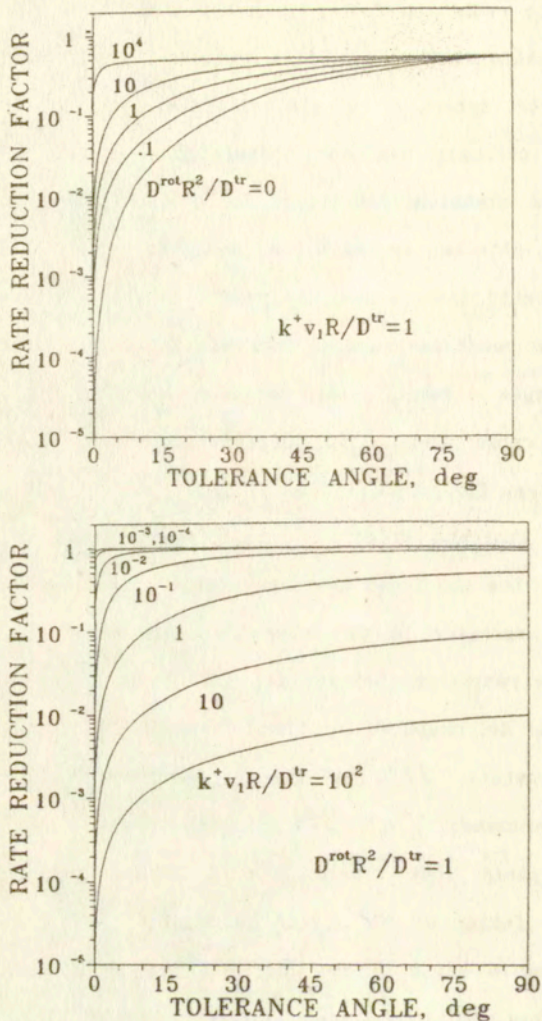


Fig. 4

Rate reduction factor $(1+k^+v_1R/\|D^{tr}\|\alpha^*)^{-1}$ plotted vs. tolerance angle range $\Delta\theta$ for:

- (a) several values of reduced rate constant, and fixed value of reduced rotational diffusion constant.
- (b) several values of reduced rotational diffusion constant, and fixed value of the reduced rate constant.

In the case of lack of steric limitations where rotational diffusion also does influence the kinetics, the rate reduction factor assumes values lower than unity, and its values are the lower, the faster is the reaction. In this case, long-range translational diffusion is the only kinetics limiting factor, typical for the D.L.A. model in the systems of spherical elements.

Fig.4b shows rate reduction factor vs. tolerance angle range plots, computed for several values of the reduced rotational diffusion constant $D^{\text{rot}} R^2 / \parallel \underline{D}^{\text{tr}} \parallel$ in the range from 0 to 10^4 , at fixed reaction rate $k^+ v_1 R / \parallel \underline{D}^{\text{tr}} \parallel = 1$. In the range of weak steric restrictions ($\Delta\theta$ close to 90°), rotational diffusion of single elements does not influence the kinetics, and the rate reduction factor is controlled mainly by translational diffusion. With decreasing the tolerance angle range to small values, the role of rotational diffusion becomes substantial. For zero rotational mobility, the lowest rate reduction factor is predicted which assumes values of 10^{-3} , 10^{-4} for the tolerance angle range of few degrees. The model predicts that the considerably high reduction in the rates, resulting from sharp steric restrictions, can be compensated by increasing rotational mobility of single elements. For high values of the reduced rotational diffusion constant, in the range of sharp steric constraints, the rate reduction factor converges to the value predicted for weak steric constraints, and the classical Smoluchowski model can be applied. But at limited rotational mobility and steric limitations present, the rates can be substantially reduced in comparison to the values predicted by the Smoluchowski model.

The dimension of the cluster, R , is one of the parameters affecting the rate of nucleation and crystal growth. In fact, the cluster dimension appears in the dimensionless variables of the model, as combined with kinetic characteristics of diffusion and intrinsic rate constants. Then, the influence of the cluster dimension on the kinetics can not be omitted. The dependence of the rate reduction factor on the radius of the cluster was exemplarily computed for fixed constants of translational and rotational diffusion, $\|D^{tr}\|=10^{-9}$ cm²/s, $D^{rot}=10^7$ /s, and for fixed tolerance angle range, $\Delta\theta=5^\circ$. The computed plots are presented in Fig.5 for several values of the intrinsic rate constant of addition, in the range from zero to $k^+v_1=1$ cm/s. Results of the computations show that the rate reduction factor decreases with increasing radius of the cluster. The effects of cluster size on the kinetics are more pronounced for bigger clusters. For the radius of the cluster within the range from few Angstrom units up to 1,000 , the rate reduction factor drops down by more than one order of magnitude for fast reactions, for the assumed parameters of diffusion at the computations. For slow processes, the effect of cluster size can be neglected. The conclusion is, that also cluster dimension, besides long-range diffusion and steric limitations, is a factor reducing the rates of nucleation and crystal growth.

Conclusions

The intrinsic chemical rate constants, defined by the transition state method [10-12], or by Kramers [13,14], account for the effects of short-range transport over the potential barrier within the range of a fraction of interatomic distance. Steric constraints reduce the equilibrium rate constants of the reaction of addition already on the level of short-range transport, because only a portion of the configurations of the cluster and single element at the collision satisfy steric conditions of the reaction [16]. Then, the intrinsic rate constants of sterically constrained reactions account for steric effects, but in the sense of the short-range mechanism. This reduces kinetics of the process by a factor equal to the fraction of the total solid angle occupied by the tolerance angle range. The reduction in the kinetics can be interpreted as an effect of dilution of the number of configurations favoring the reaction in the total number of all possible configurations at the collision.

The intrinsic rate constants are rate determining for the case of slow reactions and/or fast diffusional mobility of the elements involved in the reaction. Then, the kinetic theories of nucleation and crystal growth, based on the rate constants of the transition state method (or Kramers) can be used for slow reaction unoriented and oriented systems. The range of slow reactions is scaled by the rate effectivity parameter α^* , introduced in this paper, and dependent on mutual translational and rotational diffusion of single elements at steric constraints present. This parameter provides criterion of applicability of the classical kinetic theory of nucleation.

In the case of fast reactions and/or limited diffusional mobility of single elements, the effects of long-range diffusion and steric constraints should be taken into consideration.

The effective rate constants of the reaction of addition and dissociation, accounting for the effects of long-range diffusion at steric constraints present, has been applied in the kinetic theory of phase transformation. Translational and rotational diffusion of single elements has been taken into consideration. The effective rate constants converge to the intrinsic rate constants for slow reactions and for fast rotational diffusion of single elements. In the limit of fast reactions, the effective rate constants converge to Smoluchowski-type rate constant multiplied by the rate effectivity factor α .

The effects of long-range diffusion lead to the reduction of the addition and dissociation rate constants, as well as kinetics of nucleation and crystal growth. The rate reduction factor is dependent on translational and rotational diffusion constants, as well as steric constraints characterized by the tolerance angle range.

The rate reduction by the effects of long-range diffusion, at steric constraints present, is estimated numerically for several orders of magnitude at strong diffusional and steric limitations. The role of rotational diffusion appears to be substantial for strong steric constraints. But for weak steric constraints the effects are small, and can be neglected. The role of steric constraints becomes substantial for strongly hindered rotational mobility at narrow tolerance angle range. The effects of steric constraints can be compensated by rotational diffusion of single elements, if the constant of rotational diffusion assumes relatively high values. In the case of relatively

fast rotational mobility and/or weak steric limitations, the intrinsic rate constants and translational diffusion only play the decisive role in the kinetics of the process.

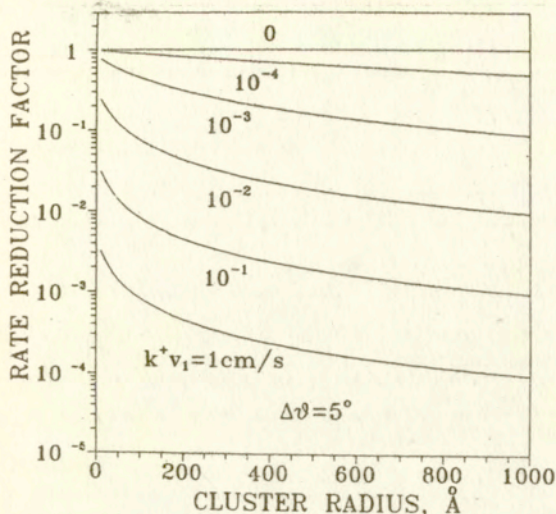


Fig. 5. Rate reduction factor $(1+k^+v_1R/\|\underline{D}^{\text{tr}}\|\alpha^*)^{-1}$ plotted vs. radius of the cluster R , in Angstrom units, for several values of surface density of the S_{rate} constant k^+ , and fixed values of: $D^{\text{rot}}=10^7\text{s}^{-1}$, $\|\underline{D}^{\text{tr}}\|=10^2\text{cm}^2/\text{s}$, and the tolerance angle range $\Delta\theta=5^\circ$.

References

1. Volmer M, Weber A (1926) Z Physic Chemie 119: 277
2. Kaishev R, Stransky IN (1934) Z Physic Chemie B 26: 317
3. Becker R, Doering W (1935) Ann Phys 24:719, (1938) ibid 32: 128
4. Turnbull D, Fisher JC (1949) J Chem Phys 17: 71
5. Frenkel J (1946) Kinetic Theory of Liquids, Oxford Univ Press, London
6. Frank FC, Tosi M (1960) Proc Roy Soc A 263: 323
7. Lauritzen JI, Hoffman JD (1960) J Res NBS 65 A: 73
8. Ziabicki A (1968) J Chem Phys 48: 4368

9. Sanchez IC (1974) J Macromol Sci-Revs Macromol Chem C 10: 113
10. Pelzer H, Wigner E (1932) Z Phys Chem B 15: 445
11. Eyring H (1935) J Chem Phys 3: 107
12. Glasstone S, Laidler KJ, Eyring H (1941) The Theory of Rate Processes, McGraw-Hill Book Inc, New York
13. Kramers HA (1940) Physica 7: 284
14. Chandrasekhar S (1943) Rev Mod Phys 15: 1
15. Ziabicki A (1977) J Chem Phys 66: 1638, (1986) *ibid* 85:3042
16. Ziabicki A, Jarecki L (1982) Inst Fund Technol Res Report no 1 Warsaw
17. Kirkwood JG, Auer PL (1951) J Chem Phys 19: 281
18. Doi M, Edwards SF (1986) The Theory of Polymer Dynamics, Clarendon Press, Oxford
19. Jeffery GB (1922) Proc Roy Soc, London A102: 161
20. Kramers HA (1946) J Chem Phys 14: 415
21. Solc K, Stockmayer WH (1971) J Chem Phys 54: 2981
22. Schmitz KS, Schurr JM (1972) 76: 534
23. Ziabicki A, Jarecki L (1984) J Chem Phys 80: 5751
24. Jarecki L, to be published
25. Smoluchowski MW (1917) Z Physic Chem 92: 129
26. Collins FC, Kimball GE (1949) J Colloid Sci 4: 425
27. Ziabicki A, Jarecki L, to be published