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Effects of translational and rotational diffusion on the association in kinetic model of nucleation

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Abstract: Kinetics of an association and dissociation of single elements with the effects of translational and rotational diffusion and angular limitations is discussed. Separated clusters embedded in a solution of orientable single elements are considered.

Steady-state positional and angular distribution of single elements is calculated from the equation of translational–rotational diffusion and the boundary conditions proposed for orientation-limited association. Although spherical orientable elements are assumed, the model can be used for non-spherical particles with aspect ratios close to unity.

Diffusion-limited rate constants of association and dissociation are proposed which depend on translational and rotational diffusion constants of single elements, the tolerance angle of the association, and the cluster size.

Effective concentration of single elements and effective rate constants are expressed by the equilibrium and diffusion-limited rate constants. Effects of finite diffusion rates and finite tolerance angle are discussed.

The equations of the kinetic model of nucleation are modified due to the diffusion-limited rate of the association.

Key words: Diffusion-limited association – translational and rotational diffusion – angular limitations – nucleation

Introduction

Bimolecular reactions of association and dissociation between clusters and single elements are considered as a fundamental process in kinetic theories of crystal nucleation and crystallization. Net frequency of the reaction between an individual cluster of size g and single elements in a solution is expressed by the formula

$$J_g = k_g^+ n_1 - k_g^- , \qquad (1)$$

where the index g denotes number of single elements in the cluster (cluster volume), k_g^+, k_g^- are association and dissociation rate constants, n_1 – concentration of single elements. Such an approach of individual cluster reacting with single elements is adequate for nucleation where concentration of clusters is much lower than concentration of single elements, and separation of clusters in the system is high enough to neglect cluster–cluster collisions.

Concentration of single elements has been usually approximated by its equilibrium value, i.e., the value at zero net rate of the reaction or at infinite diffusion rate of the elements. In fact, at non-zero net rate of the reaction, at limited rate of the diffusion, a non-uniform distribution of single elements around the cluster is created. Then, an effective concentration of single elements, n_1^{eff}, should be used in Eq. (1) instead of its equilibrium value, particularly for fast reactions and slow diffusion. Considering that single elements which participate in collisions and in the association–dissociation process come from the nearest cluster surroundings, the effective concentration should be the one in the cluster surface rather than its equilibrium value.

The effective concentration is expected to depend on long-range diffusion of single elements, and the role of the diffusion should be the higher, the faster the reaction and the slower the diffusion. Long-range translational diffusion should be considered for solutions of spherical elements, while translational and rotational diffusion should be considered for pure melts, as well as for solutions of asymmetric, orientable elements. The rate constants k_g^+, k_g^- include only short-range diffusion through the free energy barrier at the cluster surface [1, 2], and they are affected by activation energy of the transport.

The role of long-range diffusion of single elements in aggregation was discussed by Smoluchowski [3], Collins and Kimball [4], Waite [5] for a system of spherical elements, and an irreversible process. An effective rate constant of association which accounts for finite rate of diffusion reads [6]

$$k_g^{\mathrm{eff}\,+} = \frac{k_g^+}{1 + k_g^+/k_g^{\mathrm{D}}} . \tag{2}$$

The corresponding effective concentration of single elements reads

$$n_1^{\mathrm{eff}} = \frac{n_1^{\mathrm{eq}}}{1 + k_g^+/k_g^{\mathrm{D}}} , \tag{3}$$

where n_1^{eq} is the equilibrium concentration of single elements, k_g^{D} denotes a diffusion-limited rate constant, which for spherical cluster of radius $R(g)$ reads [3,4]

$$k_g^{\mathrm{D}} = 4\pi R(g) D^{\mathrm{tr}} , \tag{4}$$

where D^{tr} is the translational diffusion constant of single elements.

Steric constraints and the role of translational and rotational diffusion were discussed by Solc and Stockmayer [7, 8], Schmitz and Schurr [9–11], and others for chemical reactions. Steric limitations in those models result from non-uniform distribution of reactivity on the surface of the reacting particles. The aim was to find an explanation for considerable reduction in observable rates of enzyme-substrate reactions in comparison with the values predicted by the Smoluchowski formula (4).

The effective rate constant and effective concentration proposed in the models [7–11] assume the form of Eqs. (2, 3), but with the rate constant of the reaction and the diffusion-limited rate constant in the following form

$$k^+ = k^{0+} \frac{\Delta}{4\pi} \tag{5}$$

$$k^{\mathrm{D}} = k^{0\mathrm{D}} A(D^{\mathrm{tr}}, D^{\mathrm{rot}}, \Delta) , \tag{6}$$

where k^{0+}, $k^{0\mathrm{D}}$ are, respectively, the rate constant and the diffusion-limited rate constant for spherical molecules without steric constraints of the reaction, Δ denotes an angle range of mutual orientations enabling the reaction at a collision, and $\Delta/4\pi$ is the fraction of such mutual configurations. The diffusion-limited rate constant (Eq. (6)) is reduced by a factor A dependent on translational and rotational diffusion constants of the reactants, and on the tolerance range, Δ. The factor A was computed in the quoted papers and its values are much below unity for narrow tolerance range.

The aim of this paper is to propose an expression for effective concentration of single elements, and effective and diffusion-limited rate constants for association and dissociation of single elements in crystal nucleation with angular limitations. It will allow to account for orientational and diffusional limitations in the kinetic model of crystal nucleation.

The model assumptions

A single-cluster approximation valid for a system of well separated aggregates is assumed. The system is considered as a set of isolated clusters, where each one is surrounded by an infinite solution of single elements. The approximation is valid for the stages of nucleation where concentration of the clusters is much lower than concentration of single elements. Validity of the approximation can be confirmed by estimating radial range of substantial influence of the process on the distribution of single elements.

It is assumed that orientable elements are spherical and orientation of each one is defined by a unit vector $\boldsymbol{e}$. This model applies to nearly-spherical molecules with negligible deviation of the diffusion tensors (translational and rotational) from spherical symmetry. The elements are subjected to aggregation where a cluster of orientation-ordered single elements is formed.

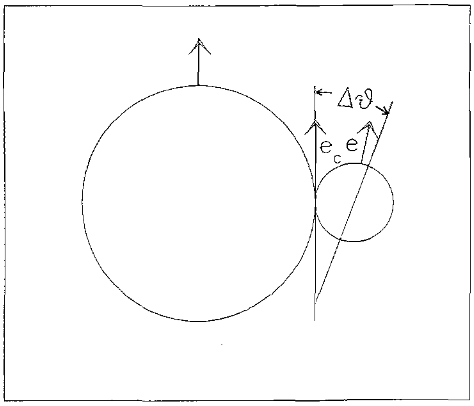

Fig. 1. The cluster and a single element at the collision with a mutual orientation within the tolerance angle range, $\Delta\vartheta$.

Spherical aggregate of radius R is assumed where the vectors $\boldsymbol{e}$ of single elements are oriented uniaxially inside the cluster. A unit vector $\boldsymbol{e}_c$ is assigned to the aggregate, and it is related to orientational order of the elements inside the cluster. The vector $\boldsymbol{e}_c$ defines favorable orientation of single elements for the association (Fig. 1).

Reaction of association and dissociation between the aggregate and single elements, modified by a condition of compliant orientation is assumed. Any collision of an element with the cluster can be effective only if the angle between the vectors $\boldsymbol{e}$ and $\boldsymbol{e}_c$ does not exceed a tolerance angle $\Delta\vartheta$ (Fig. 1). The tolerance angle, introduced here as a model parameter, is of physical nature [12].

At non-zero net rate of the association–dissociation process, a non-zero radial and angular gradients of the distribution of single elements arise around the cluster. The non-uniformity of the distribution results from limited rates of translational and rotational diffusion of the elements, and from limited tolerance angle. Radial and angular gradients should be stronger, the faster the reaction, and the slower the diffusion. The coupling between the association-dissociation process and the diffusion is expected to lower the effective rate of the process. At narrow tolerance angle, the role of the diffusion can be substantial.

Translational and rotational diffusion of the aggregate is neglected in comparison with the diffusion of single elements

$$\frac{D_g^{\mathrm{tr}}}{D^{\mathrm{tr}}} \ll 1, \qquad \frac{D_g^{\mathrm{rot}}}{D^{\mathrm{rot}}} \ll 1 \,, \tag{7}$$

where D^{tr}, D^{rot}, D_g^{tr} , D_g^{rot} are the constants of translational and rotational diffusion of single elements and g-size cluster.

The diffusion equation and the boundary conditions

Let $n_1(\boldsymbol{r}, \boldsymbol{e}, t)$ be distribution density of single elements in three-dimensional space of translational motion and two-dimensional space of rotational motion, in a solution, at an instant of time t. Position of the center of mass of an element is given by the vector $\boldsymbol{r}$, and $\boldsymbol{e}$ is a unit vector specifying orientation of the element. The distribution n_1 is normalized to the total number of single elements in the system

$$\int\int n_1(\boldsymbol{r}, \boldsymbol{e}, t)\, d^3 r\, d^2 e = N_1(t) \,. \tag{8}$$

Angular distribution of single elements at point $\boldsymbol{r}$ reads

$$w(\boldsymbol{r}, \boldsymbol{e}, t) = \frac{n_1(\boldsymbol{r}, \boldsymbol{e}, t)}{\int n_1(\boldsymbol{r}, \boldsymbol{e}, t)\, d^2 e} \,, \tag{9}$$

where $d^2 e = \sin\vartheta\, d\vartheta\, d\varphi$ is a differential element of the space of orientation, and ϑ, φ are spherical angles of the unit vector $\boldsymbol{e}$.

Kinetic equations of translational and rotational motion of single elements in the absence of an external force field read [13, 14]

$$\boldsymbol{v} = -D^{\mathrm{tr}} \nabla \ln n_1(\boldsymbol{r}, \boldsymbol{e}, t) \tag{10}$$

$$\boldsymbol{\omega} = -D^{\mathrm{rot}} \mathcal{R} \ln n_1(\boldsymbol{r}, \boldsymbol{e}, t) \,, \tag{11}$$

where $\boldsymbol{v}$, $\boldsymbol{\omega}$ are, respectively, translational and rotational velocity vectors. The motion is driven by positional and angular gradients of the distribution. $\mathcal{R}$ is the rotational operator in the space of orientation [14]

$$\mathcal{R} = \boldsymbol{e} \times \frac{\partial}{\partial \boldsymbol{e}} \,, \tag{12}$$

which is analogous to the gradient operator ∇ in the space of translation.

Equation of continuity for the distribution n_1 reads

$$\frac{\partial n_1}{\partial t} = -\nabla \cdot n_1 \boldsymbol{v} - \mathcal{R} \cdot n_1 \boldsymbol{\omega} \,, \tag{13}$$

and from Eqs. (10, 11), one obtains

$$\frac{\partial n_1}{\partial t} = D^{\mathrm{tr}}\nabla \cdot \nabla n_1 + D^{\mathrm{rot}}\mathcal{R} \cdot \mathcal{R} n_1 \,. \tag{14}$$

Interactions between the elements and the aggregate are neglected in the diffusion range. The elements interact with the clusters at the collision only where the association–dissociation process takes place. The interactions at the cluster surface, leading to the "oriented" aggregation will be accounted for by introduction of the tolerance angle in the boundary condition.

The cluster surface is uniform in the model, and the unit vector $\boldsymbol{e}_{\mathrm{c}}$ assigned to the cluster defines for single elements the direction of association and dissociation at any point of the surface, with the tolerance angle $\Delta\vartheta$. In other words, the vector $\boldsymbol{e}_{\mathrm{c}}$ shows orientation of single elements desired by the cluster, and it is fixed for any point at the cluster surface. A spherical boundary surface of radius $R = R_{\mathrm{g}} + R_1$ is taken where R_{g}, R_1 are radii of the cluster and a single element, respectively. The origin of an external coordinate system is chosen at the center of mass of the cluster. Then, at any point of the boundary $|\boldsymbol{r}| = R$, one postulates the following boundary condition

$$-\frac{\boldsymbol{r}}{R} \cdot \boldsymbol{j}_{\mathrm{tr}}(\boldsymbol{r}, \boldsymbol{e}, t) = k^{+}(\boldsymbol{e}; \boldsymbol{e}_{\mathrm{c}})\, n_1(\boldsymbol{r}, \boldsymbol{e}, t) - k^{-}(\boldsymbol{e}; \boldsymbol{e}_{\mathrm{c}}) \,, \tag{15}$$

where $-\boldsymbol{r}/R$ is a unit vector normal to the surface at $|\boldsymbol{r}| = R$, and oriented towards the center of the cluster, and k^{+}, k^{-} are rate coefficients of association and dissociation dependent on orientation of single element with respect to the cluster vector $\boldsymbol{e}_{\mathrm{c}}$. Vector $\boldsymbol{e}_{\mathrm{c}}$ appears in Eq. (15) as a parameter.

The boundary condition assumes that the diffusional flux of single elements at the cluster surface is consumed by the association–dissociation process. The lefthand side of Eq. (15) is the radial component of translational flux density of the elements with orientation $\boldsymbol{e}$ at the cluster boundary. The translational flux density reads

$$\boldsymbol{j}_{\mathrm{tr}}(\boldsymbol{r}, \boldsymbol{e}, t) = -D^{\mathrm{tr}}\nabla n_1(\boldsymbol{r}, \boldsymbol{e}, t) \,. \tag{16}$$

Contribution of rotational flux to the boundary condition can be neglected [7].

The dependence of the rate coefficients on the orientation vector $\boldsymbol{e}$ results from the interactions between the elements and the cluster at the collision. The following step-wise coefficients of the association and dissociation are proposed

$$k^{+}(\boldsymbol{e}; \boldsymbol{e}_{\mathrm{c}}) = \hat{k}^{+}\chi(\boldsymbol{e} \cdot \boldsymbol{e}_{\mathrm{c}}) \tag{17}$$

$$k^{-}(\boldsymbol{e}; \boldsymbol{e}_{\mathrm{c}}) = \frac{\hat{k}^{-}}{\int \chi(\boldsymbol{e} \cdot \boldsymbol{e}_{\mathrm{c}})\, d^2\boldsymbol{e}}\, \chi(\boldsymbol{e} \cdot \boldsymbol{e}_{\mathrm{c}}) \,,$$

where $\hat{k}^{+}$, $\hat{k}^{-}$ are rate constants per unit cluster surface, at no orientational restrictions. The function $\chi(\boldsymbol{e} \cdot \boldsymbol{e}_{\mathrm{c}})$ is introduced to account for a limited tolerance angle, and it is assumed in the following step-wise form (Fig. 2)

$$\chi(\boldsymbol{e} \cdot \boldsymbol{e}_{\mathrm{c}}) = \begin{cases} 1 & \text{for} \quad 0 \leqslant \arccos |\boldsymbol{e} \cdot \boldsymbol{e}_{\mathrm{c}}| \leq \Delta\vartheta \\ 0 & \text{for} \quad \Delta\vartheta < \arccos |\boldsymbol{e} \cdot \boldsymbol{e}_{\mathrm{c}}| \leq \pi/2 \end{cases}, \tag{18}$$

where $\boldsymbol{e} \cdot \boldsymbol{e}_{\mathrm{c}} = \cos\vartheta$ is the scalar product, ϑ is an angle between the orientation vectors of the cluster and a single element, and $\Delta\vartheta$ is the tolerance angle. The function $\chi(\boldsymbol{e} \cdot \boldsymbol{e}_{\mathrm{c}})$ is taken as common for association and dissociation, assuming that angular limitations are controlled by the same interactions for both directions of the process. The rate coefficient of dissociation (Eq. 17) assumes uniform distribution of dissociation of the elements within the tolerance angle range $\int \chi\, d^2\boldsymbol{e}$.

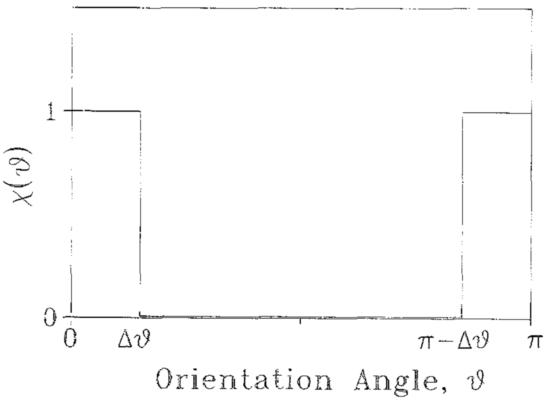

Fig. 2. Step-wise function $\chi(\vartheta)$ characterizing angular range of the association–dissociation process.

From Eqs. (16, 17), the boundary condition Eq. (15) reads

$$\frac{D^{\mathrm{tr}}}{R}\boldsymbol{r}\cdot\nabla_{|\boldsymbol{r}|=R}\, n_1(\boldsymbol{r},\boldsymbol{e},t) = \left[\hat{k}^{+} n_1(\boldsymbol{r},\boldsymbol{e},t) - \frac{\hat{k}^{-}}{\int\chi(\boldsymbol{e}\cdot\boldsymbol{e}_{\mathrm{c}})\,d^2\boldsymbol{e}}\right]\chi(\boldsymbol{e}\cdot\boldsymbol{e}_{\mathrm{c}}) \,. \tag{19}$$

$$|\boldsymbol{r}| = R$$

In the case of no orientational limitations, $\Delta\vartheta = \pi/2$, the angular distribution of single elements is uniform

$$n_1(\boldsymbol{r},\boldsymbol{e},t) = \frac{n_1(\boldsymbol{r},t)}{4\pi}\,, \tag{20}$$

and

$$\int\chi(\boldsymbol{e}\cdot\boldsymbol{e}_{\mathrm{c}})\,d^2\boldsymbol{e} = 4\pi\,. \tag{21}$$

Then, Eq. (19) reduces to the following form

$$\frac{D^{\mathrm{tr}}}{R}\boldsymbol{r}\cdot\nabla_{|\boldsymbol{r}|=R}\, n_1(\boldsymbol{r},t) = \hat{k}^{+} n_1(\boldsymbol{r},t) - \hat{k}^{-} \tag{22}$$

$$|\boldsymbol{r}| = R\,,$$

where $\hat{k}^{+}$, $\hat{k}^{-}$ are surface densities of the rate constants. For irreversible process, Eq. (22) reduces to the form proposed by Collins and Kimball [4].

Surfaces densities of the rate constants will be presumed in the following form proposed earlier in ref. [15]

$$\hat{k}^{+} = \nu n_{\mathrm{s}} v \exp\left(-\frac{E_{\mathrm{D}}}{kT}\right)\exp\left(-z\frac{\delta f_{\mathrm{g}}^{0}}{kT}\right) \tag{23}$$

$$\hat{k}^{-} = \nu n_{\mathrm{s}} v \exp\left(-\frac{E_{\mathrm{D}}}{kT}\right)\exp\left[(1-z)\frac{\delta f_{\mathrm{g}}^{0}}{kT}\right], \tag{24}$$

where

$$z = \tfrac{1}{2}\left[1 + \mathrm{sign}(\delta f_{\mathrm{g}}^{0})\right], \tag{25}$$

and ν is frequency of thermal motion, n_{s} is surface density of active centers at the cluster surface, v is volume per single element in the pure component, E_{D} is activation energy of transport of a single element through the cluster surface layer, and $\delta f_{\mathrm{g}}^{0}$ is free energy of the cluster growth by one element in pure melt, with lack of orientational limitations of association

$$\delta f_{\mathrm{g}}^{0} = \mu_{\mathrm{g}}^{0} - \mu_{\mathrm{g}-1}^{0} - \mu_{1}^{0}\,, \tag{26}$$

where μ_{g}^{0}, μ_{1}^{0} are pure-component chemical potentials of g-size cluster and a single element, respectively.

For negative free energy of the aggregate growth, $\delta f_{\mathrm{g}}^{0} < 0$, the factor z equals zero, and for positive one, $\delta f_{\mathrm{g}}^{0} > 0$, it is unity. Then, the free energy barrier appears for association if $\delta f_{\mathrm{g}}^{0}$ is positive, and for dissociation if it is negative.

At infinite distance from the cluster, the boundary condition assumes the original concentration of single elements

$$\lim_{r\to\infty}\int n_1(\boldsymbol{r},\boldsymbol{e},t)\,d^2\boldsymbol{e} = n_1^{\mathrm{eq}}\,, \tag{27}$$

where n_1^{eq} is volume density of single elements, undisturbed by the process.

The diffusion equation expressed in a dimensionless form reads

$$\frac{\partial\psi}{\partial\tau} = \nabla^2\psi + \frac{D^{\mathrm{rot}}R^2}{D^{\mathrm{tr}}}\boldsymbol{\mathcal{R}}^2\psi\,, \tag{28}$$

and it is obtained from Eq. (14) by the following substitutions

$$\boldsymbol{\varrho} = \frac{\boldsymbol{r}}{R}, \qquad \tau = \frac{D^{\mathrm{tr}}}{R^2}t \tag{29}$$

$$n_1(\boldsymbol{\varrho},\boldsymbol{e},t) = \frac{n_1^{\mathrm{eq}}}{4\pi}\psi(\boldsymbol{\varrho},\boldsymbol{e},t)\,, \tag{30}$$

where $\psi(\boldsymbol{\varrho},\boldsymbol{e},\tau)$ is a dimensionless distribution function. For the undisturbed, equilibrium distribution, ψ equals unity. The gradient operator in Eq. (28) is defined in dimensionless space of translation, $\boldsymbol{\varrho}$, and $\nabla^2 = \nabla\cdot\nabla$, $\boldsymbol{\mathcal{R}}^2 = \boldsymbol{\mathcal{R}}\cdot\boldsymbol{\mathcal{R}}$.

The boundary conditions for the distribution ψ read – at the cluster surface, $\varrho = 1$:

$$\left.\frac{\partial\psi}{\partial\varrho}\right|_{\varrho=1} = \frac{R\hat{k}^{+}}{D^{\mathrm{tr}}}\left(\psi - \frac{4\pi\hat{k}^{-}}{\hat{k}^{+}n_0\int\chi(\boldsymbol{e}\cdot\boldsymbol{e}_{\mathrm{c}})\,d^2\boldsymbol{e}}\right)\chi(\boldsymbol{e}\cdot\boldsymbol{e}_{\mathrm{c}})\,; \tag{31}$$

– at infinity, $\varrho \to \infty$:

$$\lim_{\varrho\to\infty}\frac{1}{4\pi}\int\psi(\boldsymbol{\varrho},\boldsymbol{e},\tau)\,d^2\boldsymbol{e} = 1\,. \tag{32}$$

Solution of Eq. (28) can be expressed as the sum of a steady state term, ψ^{st}, and a transient term, u

$$\psi(\boldsymbol{\varrho},\boldsymbol{e},\tau) = \psi^{\mathrm{st}}(\boldsymbol{\varrho},\boldsymbol{e}) + u(\boldsymbol{\varrho},\boldsymbol{e},\tau)\,. \tag{33}$$

Then, Eq. (28) and the boundary conditions split into

- the steady-state equations:

$$(\nabla^2 + \mathscr{D}\mathscr{R}^2)\psi^{\mathrm{st}} = 0 \tag{34}$$

$$\frac{\partial \psi^{\mathrm{st}}}{\partial \varrho}\bigg|_{\varrho=1} = \alpha^+\left(\psi^{\mathrm{st}}(\varrho = 1, e) - \frac{\hat{k}^-}{\hat{k}^+ n_0 X_{00}}\right) \times \frac{\chi(e \cdot e_c)}{X_{00}} \tag{35}$$

$$\lim_{\varrho \to \infty} \frac{1}{4\pi} \int \psi^{\mathrm{st}}(\varrho, e)\, d^2 e = 1 \ , \tag{36}$$

- and the transient equations:

$$\frac{\partial u}{\partial \tau} = (\nabla^2 + \mathscr{D}\mathscr{R}^2) u \tag{37}$$

$$\frac{\partial \psi}{\partial \varrho}\bigg|_{\varrho=1} = \alpha^+ u(\varrho = 1, e)\frac{\chi(e \cdot e_c)}{X_{00}} \tag{38}$$

$$\lim_{\varrho \to \infty} \frac{1}{4\pi} \int u(\varrho, e, \tau)\, d^2 e = 0 \ , \tag{39}$$

where $\mathscr{D}$ is a dimensionless parameter

$$\mathscr{D} = \frac{D^{\mathrm{rot}} R^2}{D^{\mathrm{tr}}} \ , \tag{40}$$

and α^+ – a dimensionless parameter:

$$\alpha^+ = \frac{\hat{k}^+ X_{00} R}{D^{\mathrm{tr}}} \ , \tag{41}$$

where

$$X_{00} = \frac{1}{4\pi} \int \chi(e \cdot e_c)\, d^2 e = 1 - \cos \Delta\vartheta \tag{42}$$

is the fraction of the total solid angle (4π) covered by the tolerance angle.

Discussion in this paper concerns the steady-state distribution.

The steady-state solution

The distribution ψ^{st} is spherically symmetric in the space of transition, ϱ, and uniaxially symmetric in the space of orientation, e, with respect to the cluster axis e_c. Uniaxial symmetry of the distribution of orientation results from uniaxial symmetry of the association–dissociation process, introduced by the function $\chi(e \cdot e_c)$ in the boundary condition. Then, ψ^{st} is a function of the distance ϱ from the cluster center and of the angle ϑ between the cluster and a single element where $\cos\vartheta = e \cdot e_c$. Then, Eq. (34) reduces to

$$\left[\varrho^{-2}\frac{\partial}{\partial \varrho}\left(\varrho^2 \frac{\partial}{\partial \varrho}\right) + \mathscr{D}\sin^{-1}\vartheta \frac{\partial}{\partial \vartheta}\left(\sin\vartheta \frac{\partial}{\partial \vartheta}\right)\right] \times \psi^{\mathrm{st}} = 0 \ , \tag{43}$$

and the solution can be expressed by the following series expansion in zero-order spherical harmonics

$$\psi^{\mathrm{st}}(\varrho, \vartheta) = \sum_{j=0}^{\infty} b_j(\varrho) \frac{Y_j(\vartheta)}{Y_0} \ , \tag{44}$$

where b_j are the expansion coefficients dependent on the distance ϱ, and

$$Y_j(\vartheta) = \left(\frac{2j+1}{4\pi}\right)^{1/2} P_j(\vartheta) \ . \tag{45}$$

Substitution of Eq. (44) to Eq. (43) results in the following set of equations for the coefficients $b_j(\varrho)$

$$\left[\varrho^{-2}\frac{\mathrm{d}}{\mathrm{d}\varrho}\left(\varrho^2 \frac{\mathrm{d}}{\mathrm{d}\varrho}\right) - j(j+1)\mathscr{D}\right] b_j(\varrho) = 0 \tag{46}$$

$$j = 0, 1, 2, \ldots,$$

and the solutions satisfying the boundary conditions read

$$b_j(\varrho) = \delta_{j0} - a_j \frac{\alpha^+}{\varrho} \exp[-(j(j+1)\mathscr{D})^{1/2}(\varrho - 1)] \times \left[1 - \exp\left(\frac{\delta f_g}{kT}\right)\right] \tag{47}$$

$$j = 0, 1, 2, \ldots,$$

where δ_{j0} is Kronecker's symbol, and

$$\delta f_g = \delta f_g^0 - kT \ln\left(c_1^{\mathrm{eq}} X_{00}\right) \ , \tag{48}$$

where $c_1^{\mathrm{eq}} = n_1^{\mathrm{eq}} v$ is an undisturbed fraction of single elements in the solution, and $c_1^{\mathrm{eq}} X_{00}$ is the fraction of single elements oriented within the tolerance angle range, undisturbed by the aggregation process. For pure melt, $c_1^{\mathrm{eq}} = 1$, and with lack of any orientational limitations, $X_{00} = 1$, the free energy of association $\delta f_g = \delta f_g^0$.

The coefficients a_j depend on the parameters α^+, $\mathscr{D}$, and on the tolerance angle range $\Delta\vartheta$

$$a_j = a_j\left(\alpha^+, \mathscr{D}, \Delta\vartheta\right), \tag{49}$$

and they are solutions of the following set of algebraic equations

$$\sum_{j=0}^{\infty} B_{ij} a_j = \frac{X_{i0}}{X_{00}} \qquad i = 0, 1, 2, \ldots, \tag{50}$$

where

$$B_{ij} = [1 + (j(j+1)\mathscr{D})^{1/2}]\,\delta_{ij} + \alpha^+ \frac{X_{ij}}{X_{00}}, \tag{51}$$

and X_{ij} are the following integrals dependent on the tolerance angle

$$X_{ij}(\Delta\vartheta) = 2\pi \int_0^{\pi} Y_i(\vartheta)\,\chi(\vartheta)\,Y_j(\vartheta)\sin\vartheta\,\mathrm{d}\vartheta. \tag{52}$$

The set of Eqs. (50) is obtained by integrating both sides of the boundary condition Eq. (35) with spherical harmonics. The integrals X_{ij} vanish for odd values of $i + j$, and result in $a_j = 0$ for odd j. The integral $X_{00} = 1 - \cos\Delta\vartheta$. At $\Delta\vartheta = \pi/2$, $X_{00} = 1$, and the tolerance range covers total solid angle. At narrow tolerance angle, $\Delta\vartheta \ll \pi/2$, the integral $X_{00} \cong (\Delta\vartheta)^2/2$.

Substituting coefficients $b_j(\varrho)$ in the form of Eq. (47), and considering that a_j vanish for odd j, the steady-state solution reads

$$\begin{aligned}\psi^{\mathrm{st}}(\varrho, \vartheta) ={}& \\ & 1 - \frac{\alpha^+}{\varrho}\left[1 - \exp\left(\frac{\delta f_{\mathrm{g}}}{kT}\right)\right] \\ & \times \sum_{j=0}^{\infty} a_{2j} \exp\left[(2j(2j+1)\mathscr{D})^{1/2}(\varrho - 1)\right] \\ & \times \frac{Y_{2j}(\vartheta)}{Y_0},\end{aligned} \tag{53}$$

where the coefficients a_{2j} depend on the parameters $\alpha^+, \mathscr{D}$, and on the tolerance angle range $\Delta\vartheta$.

The coefficients a_{2j} should be computed from Eq. (50). Their asymptotic solutions can be determined analytically for $\alpha^+ \ll 1$ (slow association and/or fast translational diffusion of single elements), as well as for $\mathscr{D} \ll 1$ and for $\mathscr{D} \gg 1$.

Assuming Einstein–Stokes formulae for the diffusion constants, the parameter $\mathscr{D}$ is proportional to the square of the ratio of the cluster boundary radius R to a single element radius R_1:

$$\mathscr{D} = \frac{D^{\mathrm{rot}} R^2}{D^{\mathrm{tr}}} = \frac{3}{4}\left(\frac{R}{R_1}\right)^2. \tag{54}$$

Nevertheless, the range of $\mathscr{D} \ll 1$ will be discussed to see the role of finite constant of rotational diffusion in comparison with a hypothetical state of hindered rotational motion. The case of $\mathscr{D} \gg 1$ is realistic for large aggregates.

For $\alpha^+ \ll 1$:

$$a_{2j} = [1 + (2j(2j+1)\mathscr{D})^{1/2}]^{-1} \frac{X_{2j,0}}{X_{00}}. \tag{55}$$

For $\mathscr{D} \ll 1$:

$$a_{2j} = \frac{1}{1 + \alpha^+/X_{00}} \frac{X_{2j,0}}{X_{00}}. \tag{56}$$

For $\mathscr{D} \gg 1$:

$$a_{2j} = \frac{1}{1 + \alpha^+}\,\delta_{2j,0}, \tag{57}$$

and the tolerance angle does not affect the solution.

The following relationship should be used to check the solution for $\mathscr{D} \ll 1$

$$\sum_{j=0}^{\infty} X_{2i,2j} X_{2j,0} = X_{2i,0} \qquad i = 0, 1, 2, \ldots, \tag{58}$$

valid for the 0–1 step function $\chi(\vartheta)$ for which $\chi^2(\vartheta) = \chi(\vartheta)$.

For intermediate values of the parameters α^+ and $\mathscr{D}$, the coefficients a_{2j} should be computed. Example computations are performed for several values of α^+ and $\mathscr{D}$, at a fixed tolerance angle range, $\Delta\vartheta = 5°$. The distributions computed for the boundary surface $\varrho = 1$ from Eqs. (50, 53) are

$$\psi^{\mathrm{st}}(\varrho = 1, \vartheta) = 1 - \alpha^+\left[1 - \exp\left(\frac{\delta f_{\mathrm{g}}}{kT}\right)\right] \times \sum_{j=0}^{\infty} a_{2j} \frac{Y_{2j}(\vartheta)}{Y_0}, \tag{59}$$

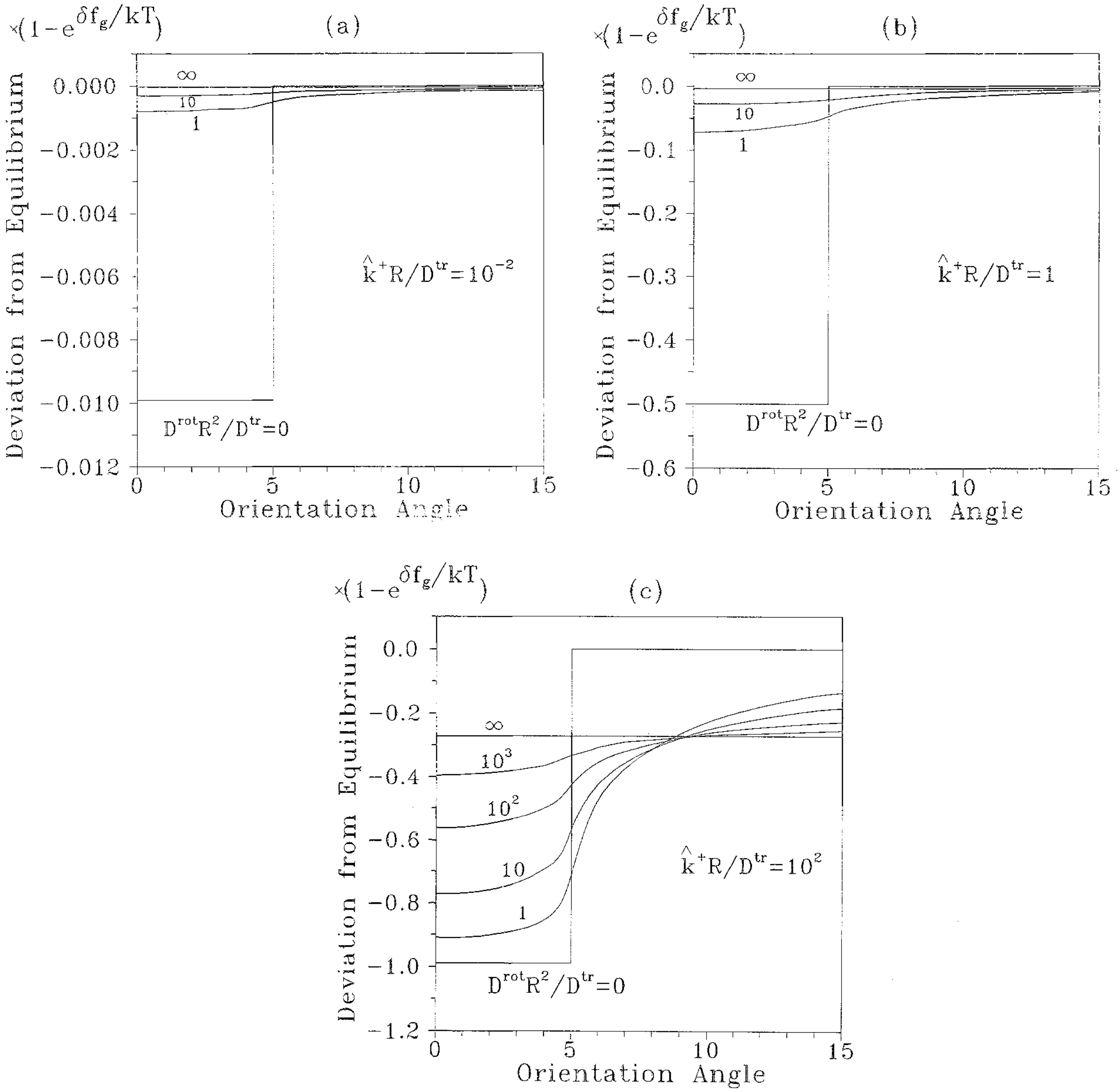

Fig. 3. Deviation of the distribution from equilibrium, $\psi^{st}(\varrho = 1, \vartheta) - 1$, at the cluster surface, plotted vs. orientation angle ϑ (in degrees) for several values of $D^{rot}R^2/D^{tr}$, and $\Delta\vartheta = 5^0$. a) $\hat{k}^+R/D^{tr} = 10^{-2}$, b) $\hat{k}^+R/D^{tr} = 1$, c) $\hat{k}^+R/D^{tr} = 10^2$.

and are plotted in Figs. 3a, b, c vs. orientation angle ϑ for $\alpha^+/X_{00} = 10^{-2}$, 1, 10^2, and $\Delta\vartheta = 5°$. The plots show deviation of ψ^{st} at the boundary surface from its equilibrium value (unity) for several values of $\mathscr{D}$ between zero and infinity. The deviation increases with increasing α^+, and it is substantially affected by $\mathscr{D}$.

For a hypothetical state of inhibited rotational motion of single elements, $\mathscr{D} \to 0$, the following step-wise angular distribution at the cluster surface is predicted from Eqs. (56, 59),

$$\psi^{st}(\varrho = 1, \vartheta) = 1 - \left[1 - \exp\left(\frac{\delta f_g}{kT}\right)\right] \times \frac{\alpha^+/X_{00}}{1 + \alpha^+/X_{00}} \chi(\vartheta) . \tag{60}$$

In this case, the elements with compliant orientation are consumed or released by the cluster, while

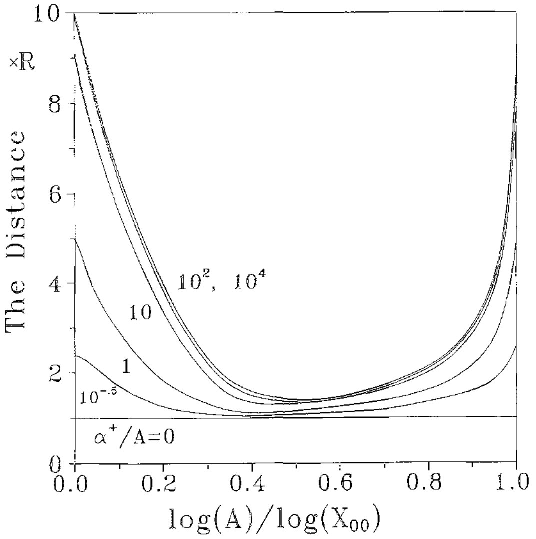

Fig. 4. Distance from the cluster center where the deviation of the distribution from equilibrium is reduced by 90%, plotted vs. $\log A/\log X_{00}$ for various association rates α^+/A, (A is defined by Eq. (71)).

the elements outside the tolerance angle range do not participate in the process at all.

For $\mathscr{D} \gg 1$, Eqs. (57, 59) lead to the following asymptotic formula

$$\psi^{\mathrm{st}}(\varrho = 1, \vartheta) = 1 - \left[1 - \exp\left(\frac{\delta f_g}{kT}\right)\right]\frac{\alpha^+}{1+\alpha^+}\,, \tag{61}$$

and the angular distribution is uniform.

One estimates from computations performed for a wide range of α^+ and $\mathscr{D}$ that the deviation of the distribution from the undisturbed distribution at infinity reduces by 90% within the distance range $R - 2R$ from the cluster surface (Fig. 4). Even at extreme values of α^+ and $\mathscr{D}$, the radial range of the reduction does not exceed $10R$. This provides criterion for validity of the assumption of isolated clusters embedded in an infinite solution of single elements.

Kinetics of the association–dissociation process

Total net frequency of association and dissociation of single elements by one g-size cluster reads

$$J_g = \iint \left[\hat{k}^+ n_1(\varrho = 1, \boldsymbol{e}) - \frac{\hat{k}^-}{\int \chi(\boldsymbol{e}\cdot\boldsymbol{e}_c)\, d^2\boldsymbol{e}}\right] \times \chi(\boldsymbol{e}\cdot\boldsymbol{e}_c)\, d^2\boldsymbol{e}\, d\sigma \tag{62}$$

or

$$J_g = \iint D^{\mathrm{tr}}\, \nabla_{|\varrho=1}\, n_1(\varrho, \boldsymbol{e}) \cdot d\sigma\, d^2\boldsymbol{e}\,. \tag{63}$$

Equations (62, 63) are obtained by integrating both sides of the boundary condition (Eq. (19)) over the orientations of single elements ($d^2\boldsymbol{e}$), and over the cluster surface ($d\sigma$).

For steady-state distribution (Eq. (53)), the total flux calculated from Eq. (62) reads

$$J_g = 4\pi R^2 \hat{k}^+ X_{00}\, n_1^{\mathrm{eq}}\left[1 - \exp\left(\frac{\delta f_g}{kT}\right)\right] \times \left(1 - \alpha^+ \sum_{j=0}^{\infty} a_{2j}\frac{X_{2j,0}}{X_{00}}\right). \tag{64}$$

From Eqs. (50, 51) for $i = 0$, one obtains the following relation

$$1 - \alpha^+ \sum_{j=0}^{\infty} a_{2j}\frac{X_{2j,0}}{X_{00}} = a_0\,. \tag{65}$$

Then, the flux J_g includes only the coefficient a_0

$$J_g = 4\pi R^2 \hat{k}^+ X_{00} n_1^{\mathrm{eq}}\left[1 - \exp\left(\frac{\delta f_g}{kT}\right)\right] a_0\,. \tag{66}$$

From Eqs. (55–57), the asymptotic coefficients read

$$a_0 = 1 \qquad \text{for } \alpha^+ \ll 1 \tag{67}$$

$$a_0 = \frac{1}{1 + \alpha^+/X_{00}} \qquad \text{for } \mathscr{D} \ll 1 \tag{68}$$

$$a_0 = \frac{1}{1 + \alpha^+} \qquad \text{for } \mathscr{D} \gg 1\,. \tag{69}$$

For intermediate values of the parameters α^+ and $\mathscr{D}$, a_0 should be computed from the set of Eqs. (50). The computed values well fit the following formula

$$a_0 = \frac{1}{1 + \alpha^+/A}\,, \tag{70}$$

where the factor A is the following function of $\mathscr{D}$ and the tolerance angle $\Delta\vartheta$

$$1/A = \sum_{i=0}^{\infty} \frac{X_{2i,0}^2(\Delta\vartheta)/X_{00}^2(\Delta\vartheta)}{1 + (2i(2i+1)\mathscr{D})^{1/2}}\,. \tag{71}$$

For $\mathscr{D} \ll 1$ the parameter $A = X_{00} = 1 - \cos\Delta\vartheta$ (cf. Eq. (58)), and for $\mathscr{D} \to \infty$, $A \to 1$.

Using recurrent formulae for Legendre polynomials in the integrals $X_{2i,0}$, Eq. (71) assumes

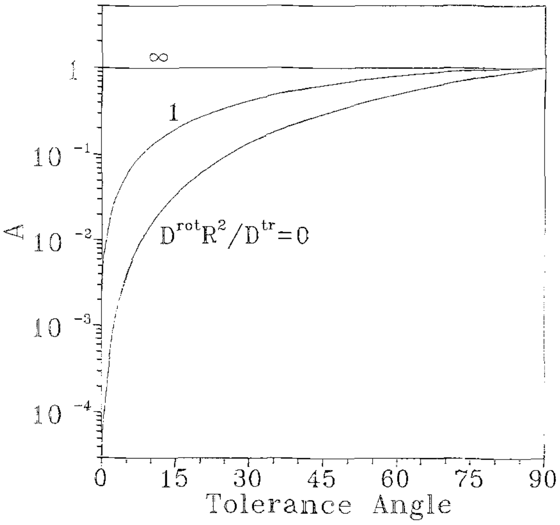

Fig. 5. The factor A plotted vs. tolerance angle (in degrees), $\Delta\vartheta$, for $D^{\mathrm{rot}}R^2/D^{\mathrm{tr}} = 0$, 1, and infinity.

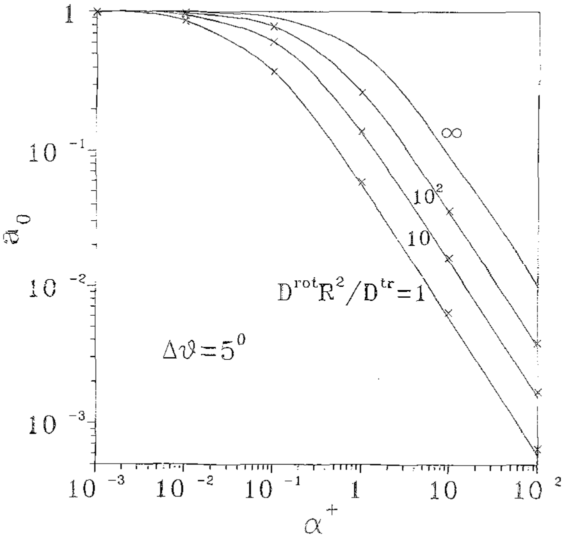

Fig. 6. The coefficient a_0 plotted vs. α^+ for several values of $D^{\mathrm{rot}}R^2/D^{\mathrm{tr}}$, at $\Delta\vartheta = 5°$. The plots are evaluated from Eq. (70), while the marked points are computed using 200 equations of the set (50).

the following form

$$1/A = \sum_{i=0}^{\infty} \frac{(4i+1)\,\kappa_{2i}^2(\Delta\vartheta)}{1+(2i(2i+1)\,\mathscr{D})^{1/2}}\,, \tag{72}$$

where κ_{2i} depend on the tolerance angle $\Delta\vartheta$. They can be evaluated using the following recurrent formula

$$\kappa_{2i} = \frac{(i-1)(2i-1)}{i(2i+1)}\,\kappa_{2(i-1)} + \frac{(4i-1)}{2i(2i+1)}\,(1+\cos\Delta\vartheta)\,P_{2i-1}(\cos\Delta\vartheta) \tag{73}$$

$$i = 1, 2, 3, \ldots$$

$$\kappa_0 = 1$$

where P_{2i-1} denotes odd Legendre polynomials.

Figure 5 shows plots of the factor A vs. tolerance angle $\Delta\vartheta$ computed for $\mathscr{D} \to 0$, for $\mathscr{D} = 1$, and for $\mathscr{D} \to \infty$, using 200 terms in the sum in Eq. (72). A formula for the factor A, published earlier (ref. [16], Eq. (43)) contains an error where κ_{2i} should be in the square power.

The coefficient a_0 proposed by Eq. (70) converges to the asymptotic solutions given by Eqs. (67–69), and it fits the computed values for intermediate values of α^+ and $\mathscr{D}$. The computations of a_0 were performed from the set of Eqs. (50) for several values of the tolerance angle between 5° and 180°, for several values of α^+ between 10^{-3} and 10^3, and for $\mathscr{D}$ between 1 and 10^3. A set of 200 equations was taken for computations. For this number of equations, the computed values of a_0 differ by no more than 2–3 per cent from the values obtained from a set of 100 equations, and convergence of the numerical solution is satisfactory in this range.

Figure 6 shows the plots of a_0 vs. α^+ predicted by Eq. (70) for $\mathscr{D} = 1$, 10, 10^2, and infinity, at the tolerance angle $\Delta\vartheta = 5°$. The values of a_0 computed directly from Eqs. (50) using a set of 200 equations are marked by the points. Deviations of the computed values from the values predicted by Eq. (70) are very small, thus indicating good agreement between the proposed formula and the computed solutions. The agreement is even better for wider tolerance angle (plots not shown).

Substituting a_0 in the form of Eq. (70), the total frequency of the process reads

$$J_{\mathrm{g}} = 4\pi R^2 \hat{k}^+ X_{00} n_1^{\mathrm{eq}} \left[1 - \exp\left(\frac{\delta \mathrm{f_g}}{kT}\right)\right] \frac{1}{1+\alpha^+/A}$$

$$= 4\pi R^2 (\hat{k}^+ X_{00} n_1^{\mathrm{eq}} - \hat{k}^-)\,\frac{1}{1+\alpha^+/A}\,. \tag{74}$$

The above formula can be derived also starting from Eq. (63).

Total frequency of the process given by Eq. (74) can be expressed by an effective concentration of the elements, n_1^{eff}, and the overall rate constants of association and dissociation, k_g^+, k_g^-

$$J_g = k_g^+ n_1^{\mathrm{eff}} - k_g^- \ , \tag{75}$$

where

$$k_g^+ = 4\pi R^2 \hat{k}^+ X_{00} \ , \qquad k_g^- = 4\pi R^2 \hat{k}^- \tag{76}$$

or by the effective rate constants, $k_g^{\mathrm{eff}+}$, $k_g^{\mathrm{eff}-}$, and the equilibrium concentration, n_1^{eq}

$$J_g = k_g^{\mathrm{eff}+} n_1^{\mathrm{eq}} - k_g^{\mathrm{eff}-} \ . \tag{77}$$

The effective concentration reads

$$n_1^{\mathrm{eff}} = \frac{1 + (\alpha^+/A)\exp(\delta f_g/kT)}{1 + \alpha^+/A} n_1^{\mathrm{eq}} \ . \tag{78}$$

At $\delta f_g = 0$, the effective concentration equals n_1^{eq}. At $\delta f_g < 0$ (net growth) the effective concentration is below the equilibrium value, while at $\delta f_g > 0$ (net dissociation) it is above n_1^{eq}.

The effective rate constants read

$$k_g^{\mathrm{eff}\pm} = \frac{1}{1 + \alpha^+/A} k_g^{\pm} \ . \tag{79}$$

For a slow process, satisfying the condition $\alpha^+/A \ll 1$, Eqs. (78, 79) reduce to

$$n_1^{\mathrm{eff}} = n_1^{\mathrm{eq}} \qquad k_g^{\mathrm{eff}\pm} = k_g^{\pm} \ , \tag{80}$$

and kinetics of the process can be described using the equilibrium rate constants and the equilibrium concentration of the elements. No diffusion control is predicted for this case.

For fast reactions, $\alpha^+/A \gg 1$

$$n_1^{\mathrm{eff}} = n_1^{\mathrm{eq}} \exp\left(\frac{\delta f_g}{kT}\right) , \tag{81}$$

and the effective rate constants assume the following diffusion-limited forms

$$k_g^{\mathrm{eff}+} \to k_g^{\mathrm{D}+} = 4\pi R(g) D^{\mathrm{tr}} A(\mathscr{D}, \Delta\vartheta) \tag{82}$$

$$k_g^{\mathrm{eff}-} \to k_g^{\mathrm{D}-} = 4\pi R(g) D^{\mathrm{tr}} A(\mathscr{D}, \Delta\vartheta) \frac{k_g^-}{k_g^+} \ . \tag{83}$$

For fast irreversible reactions ($k_g^- = 0$), Eqs. (77, 82, 83) lead to

$$J_g = 4\pi R D^{\mathrm{tr}} A n_1^{\mathrm{eq}} \ . \tag{84}$$

The factor A reduces the role of translational diffusion in the diffusion-limited rate constants due to finite rotational diffusion rate of the elements and finite tolerance angle.

At $\mathscr{D} \to \infty$, or $\Delta\vartheta = \pi/2$, the parameter $A \to 1$, and Eq. (84) reduces to the following formula

$$J_g = 4\pi R D^{\mathrm{tr}} n_1^{\mathrm{eq}} \ , \tag{85}$$

known as Smoluchowski formula for diffusion-limited aggregation, derived for spherical elements without angular limitations of the aggregation.

The effective association and dissociation rate constants, as well as the effective concentration of the elements, can be expressed by the equilibrium rate constants, k_g^+, k_g^-, and by the diffusion-limited rate constant, $k_g^{\mathrm{D}+}$.

$$k_g^{\mathrm{eff}\pm} = \frac{k_g^{\pm}}{1 + k_g^+/k_g^{\mathrm{D}+}} \tag{86}$$

$$n_1^{\mathrm{eff}} = \frac{1 + (k_g^+/k_g^{\mathrm{D}+})\exp(\delta f_g/kT)}{1 + k_g^+/k_g^{\mathrm{D}+}} n_1^{\mathrm{eq}} \ . \tag{87}$$

Application to crystal nucleation

Kinetic models of nucleation [17–19] assume bimolecular reactions of association and dissociation between the clusters and single elements as dominating in the process. Effects of finite diffusion rate of single elements and angular limitations can be included in the models using effective rates of association and dissociation of the elements, derived in this paper. One assumes that average distance between clusters is high, and the system can be considered as a set of individual, non-interacting clusters embedded in an infinite solution of single elements.

Effective frequency of association of the elements by a g-size cluster is given by the association term in Eq. (75), and it equals $k_g^+ n_1^{\mathrm{eff}}(g)$, while the frequency of dissociation equals k_g^-.

The net flux of growth of the clusters of size g from the clusters of size $g - 1$ in a unit volume of the system reads

$$j_g = k_{g-1}^+ n_1^{\mathrm{eff}}(g-1) n_{g-1} - k_g^- n_g \ , \tag{88}$$

where n_g is the number of g-size clusters in a unit volume, and $n_1^{\mathrm{eff}}(g-1)$ is the effective concentration of single elements at the cluster of size $g - 1$.

Equation of continuity for time-dependent distribution $n_g(t)$ of the clusters' size g in the system reads

$$\frac{\partial n_g}{\partial t} = -(j_{g+1} - j_g)\,. \tag{89}$$

Considering cluster size as a continuum variable g, and taking into account linear terms of the expansions over g, the following ratio reads

$$\frac{k^+_{g-1} n_1^{\mathrm{eff}}(g-1)}{k_g^-} = 1 - \frac{\delta f_g/kT}{1 + k_g^+/k_g^{\mathrm{D}+}} + \cdots, \tag{90}$$

and a linearized form of the flux (Eq. (88)) reads

$$j(g) = -k_g^- \left(\frac{\partial n}{\partial g} + n\frac{\delta f_g/kT}{1 + k_g^+/k_g^{\mathrm{D}+}}\right), \tag{91}$$

where $n(g, t)$ is time-dependent distribution of the cluster size. Growth of the clusters can be considered as a diffusion in the space of cluster sizes with a driving force. The driving force is free energy of association per one element, reduced by the factor $1 + k_g^+/k_g^{\mathrm{D}+}$ resulting from limited translational and rotational diffusion rates of single elements, and from limited tolerance angle.

Following Eq. (91), the equation of continuity for the distribution of the clusters, accounting for the finite diffusion rates and tolerance angle, assumes the form of a Fokker–Planck equation

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial g}\left[k_g^- \left(\frac{\partial n}{\partial g} + n\frac{\delta f_g/kT}{1 + k_g^+/k_g^{\mathrm{D}+}}\right)\right] \tag{92}$$

For a slow association, $k_g^+/k_g^{\mathrm{D}+} \ll 1$, Eq. (92) reduces to the form proposed by the kinetic models of nucleation without the effects of long-range diffusion. For fast association, $k_g^+/k_g^{\mathrm{D}+} \gg 1$, the role of thermodynamic driving force of aggregation is considerably reduced by the finite diffusion rates, translational and diffusional, and by the tolerance angle.

Conclusions

The deviations of the angular distribution of single elements at the cluster surface, and the effective concentration of the elements from equilibrium (cf. Eqs. (59, 78)) are proportional to $\exp(\delta f_g/kT) - 1$, where δf_g is free energy of association per one element. The concentrations decrease below their equilibrium values for negative δf_g, and increase for positive one, and the effect is the stronger, the higher the association rate constant.

Highest deviation of the orientation distribution from equilibrium is predicted for elements oriented within the tolerance angle range, and it is affected by rotational diffusion.

The role of rotational diffusion is controlled by the factor $\mathscr{D} = D^{\mathrm{rot}}R^2/D^{\mathrm{tr}}$, dependent also on the cluster radius. For a hypothetical case of $\mathscr{D} \to 0$ (hindered rotational motion), a step-wise orientation distribution at the cluster surface is predicted where the elements oriented outside of the tolerance angle do not participate in the association process. In this regime, considerable influence of the tolerance angle on the distribution is expected, while for $\mathscr{D} \to \infty$ no effect of the tolerance angle on the distribution is predicted.

For the association discussed in this paper, the parameter $\mathscr{D}$ is higher than unity ($R > R_1$, cf. Eq. (54)). Nevertheless, Schmitz and Schurr [10, 11] considered translational and rotational diffusion for steric chemical reactions on a small, immobile hemi-sphere ($R \ll R_1$) localized on a plain where $\mathscr{D}$ was much lower than unity, and their results are consistent with the results obtained in this paper for the case of small $\mathscr{D}$.

For slow association, $\alpha^+/A \ll 1$, an equilibrium form of the kinetic equation of the process, expressed by the equilibrium rate constants and equilibrium concentration of single elements, is valid. For fast association, $\alpha^+/A \gg 1$, the diffusion-limited rate constants are proportional to the constant of translational diffusion, D^{tr}, and to the factor $A \le 1$ dependent on the tolerance angle and on the parameter $\mathscr{D}$. The factor A reduces effectivity of translational diffusion of single elements due to limited tolerance angle and limited diffusion rates of single elements. It assumes the following asymptotic values: $A = 1$ for $\mathscr{D} \to \infty$, and $A = 1 - \cos\Delta\vartheta$ for $\mathscr{D} \to 0$. The narrower the tolerance angle range $\Delta\vartheta$, the smaller the lower bound of A, and the higher the reduction of the effectivity of translational diffusion.

Effective association and dissociation rate constants as well as effective concentration of single elements are expressed by the equilibrium and diffusion-limited rate constants. They allow to formulate kinetic equations for the association–dissociation process by the equilibrium and diffusion-limited rate constants.

A linear flux of growth of clusters in a solution subjected to nucleation, and a Fokker–Planck equation for the distribution of the cluster size include effects of finite diffusion rates of single elements. The flux of growth of the clusters, as well as the distribution of the cluster sizes in the system are controlled by the thermodynamic driving force of association, reduced by the factor $1 + k_g^+/k_g^{D+}$ which accounts for the effects of the diffusion. For a slow association, the factor can be assumed as unity, while for a fast process, a considerable reduction of the role of the thermodynamic driving force is predicted due to limited diffusion rates.

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