Colloid Polym Sci (1995) 273:138–149

ORIGINAL CONTRIBUTION

L. Jarecki

Effects of diffusion-controlled association in kinetic model of crystal nucleation in external orienting field

Received: 4 March 1994
Accepted: 11 July 1994

Abstract Translational and rotational diffusion equation of orientable single elements in external orienting potential field is used to discuss effective rate of association and dissociation during cluster growth. First and second harmonic terms of orientation-dependent potential energy of single elements are taken into consideration. Tolerance angle accounting for orientational limitations for association is introduced.

Effective rate of association of single elements is derived with first-order correction for the effects of orienting potential. Net rate of cluster growth depends on orientation in the field, and it is controlled by long-range diffusion (rotational and translational) of single elements. Influence of diffusion is higher, the narrower the tolerance angle and the faster the association.

At slow association, long-range diffusion does not influence the process, the growth of a cluster is controlled by thermodynamic, orientation-dependent potential of the species involved in the process.

Effective rate constants of association and dissociation, as well as effective concentration of single elements are derived as functions of orientation angle in the field.

The Fokker–Planck equation is proposed for the distribution of cluster size in external orienting potential, with the effects of finite translational and rotational diffusion of single elements, for the case of non-polar clusters.

Dr. L. Jarecki
Institute of Fundamental Technological Research
Polish Academy of Sciences
Swietokrzyska 21
00-049 Warsaw, Poland

Key words Translational and rotational diffusion – kinetics of association and nucleation – orienting field – steric limitations

Introduction

Rate of association in the systems of orientable elements is affected by long-range translational and rotational diffusion of single elements, particularly at fast association and slow diffusion. The effects of finite rate of rotational diffusion are proportionally stronger as the orientational limitations of association [1–6] are sharper, and effective concentration of single elements in the process deviates from the concentration at equilibrium.

Kinetics of association of single elements in the process of crystal nucleation with orientational limitations and effects of finite diffusion rate, in the absence of external orienting forces, has been discussed in ref. [6]. Net frequency of the process has been expressed by:

1) association and dissociation rate constants, $k_g^{\pm}$, and an effective concentration of single elements, n_1^{eff}

$$J_g = k_g^+ n_1^{\mathrm{eff}} - k_g^- , \tag{1}$$

where g indicates the number of single elements in the cluster, or

2) effective rate constants, $k_g^{\mathrm{eff}\,\pm}$, and equilibrium concentration of single elements, n_1^{eq}

$$J_g = k_g^{\mathrm{eff}\,+} n_1^{\mathrm{eq}} - k_g^{\mathrm{eff}\,-} \,. \tag{2}$$

The effective rate constants and effective concentration of the elements in Eqs. (1, 2) are controlled by the constants of translational and rotational diffusion of single elements, D^{tr}, D^{rot}, free energy of association of an element by the cluster, δf_g, and a tolerance angle, $\Delta\vartheta$, representing orientational limitations of association.

For spherical clusters, the effective rate constants and effective concentration of single elements read [6]

$$k_g^{\mathrm{eff}\,\pm} = \frac{k_g^{\pm}}{1 + k_g^{+}/k_g^{\mathrm{D}}}\,, \quad n_1^{\mathrm{eff}} = \frac{1 + (k_g^{+}/k_g^{\mathrm{D}})\exp\left[\dfrac{\delta f_g}{kT}\right]}{1 + k_g^{+}/k_g^{\mathrm{D}}}\, n_1^{\mathrm{eq}}\,, \tag{3}$$

where k_g^{D} is diffusion-limited rate constant of association by g-size cluster

$$k_g^{\mathrm{D}} = 4\pi R_g D^{\mathrm{tr}} A(D^{\mathrm{rot}} R_g^2/D^{\mathrm{tr}}, \Delta\vartheta)\,; \tag{4}$$

R_g is the cluster radius, $0 < A \leq 1$ depends on the diffusion constants, the cluster size, and the tolerance angle.

External orienting forces affect free energy of cluster growth, the rate constants, orientation distribution, and effective concentration of single elements. Finite rate of rotational diffusion of single elements is expected to affect kinetics of crystal nucleation in orienting fields, particularly in the case of narrow tolerance angle.

Model assumptions

A solution of single elements in external orienting field is considered. It is assumed that the elements are nearly spherical in shape, and that they associate and orient in the field as uniaxial particles. One assumes that single elements form spherical clusters, where the elements are ordered uniaxially inside each cluster. Let unit vector $\mathbf{e}_{\mathrm{C}}$ be the direction of orientation of the elements inside a cluster, unit vector $\mathbf{e}$ denote orientation of a single element in the solution, and unit vector $\mathbf{e}_{\mathrm{U}}$ indicate direction of the field (Fig. 1).

Compliant orientation of a single element and of the cluster is required for association. One assumes that any collision of single element with the cluster can be effective for the angle between $\mathbf{e}$ and $\mathbf{e}_{\mathrm{C}}$ vectors not exceeding the tolerance angle $\Delta\vartheta$. The tolerance angle, introduced as a model parameter, is of physical nature and has been estimated by statistical mechanical considerations in ref. [7].

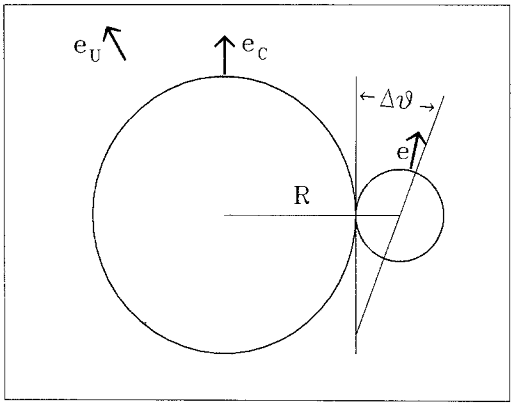


Fig. 1. Oriented cluster and a single element at collision in an external orienting field. $\Delta\vartheta$ denotes tolerance angle of association. Unit vector e_{U} indicates direction of the field

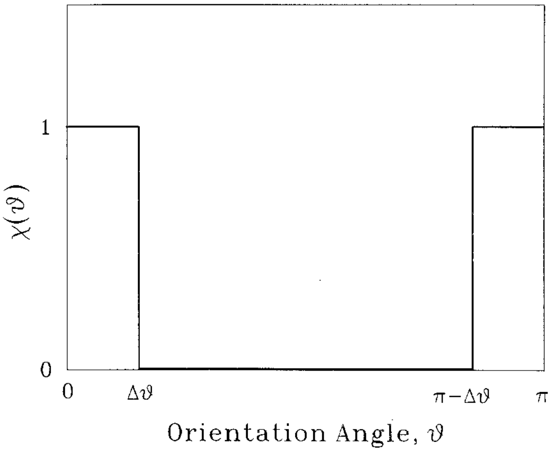


Fig. 2. Step-wise function, $\chi(\vartheta)$, characterizing angular range of association-dissociation process

The following step function, unity within the tolerance angle and zero elsewhere, is introduced to characterize the tolerance angle

$$\chi(\vartheta) = \begin{cases} 1 & \text{for } 0 \leq \vartheta \leq \Delta\vartheta \text{ and } \pi - \Delta\vartheta \leq \vartheta \leq \pi \\ 0 & \text{elsewhere}\,, \end{cases} \tag{5}$$

where $\cos\vartheta = \mathbf{e}\cdot\mathbf{e}_{\mathrm{C}}$, and ϑ is the angle of disorientation of the element. Sensitivity of association to the disorientation angle ϑ is taken into account by introducing orientation-dependent rate constants equal to zero for ϑ exceeding the tolerance angle, $\Delta\vartheta$. Eq. (5) represents axial symmetry of orientational limitations of association.

Each cluster in the system is considered to be embedded in an infinite solution of single elements. Such an assumption is valid for crystal nucleation where average distance between clusters formed in the liquid phase is high enough. Validity of this approximation can be verified by comparing the range of substantial changes of the distribution of single elements, predicted by the model, with an average cluster-to-cluster distance. It has been shown in ref. [6] that deviation of the distribution from its equilibrium value decreases by 90% within the distance R-2R from the cluster surface, in a wide range of diffusion and rate constants. R is the distance between centers of the cluster and single element at the collision. At extreme values of the kinetic constants, the distance does not exceed 10R.

It is assumed that translational and rotational diffusion of a g-size cluster, D_g^{tr}, D_g^{rot}, can be neglected because of much reduced cluster mobility in comparison with mobility of single elements

$$\frac{D_g^{\mathrm{tr}}}{D^{\mathrm{tr}}} \ll 1 , \quad \frac{D_g^{\mathrm{rot}}}{D^{\mathrm{rot}}} \ll 1 . \tag{6}$$

Equation of diffusion and the boundary conditions

Let n_1 ($\mathbf{r}$, $\mathbf{e}$, t) be distribution density of number of single elements in the space of translations, $\mathbf{r}$, and orientations, $\mathbf{e}$, around the cluster, in the instant of time t. Orientation distribution of the elements is

$$w_1(\mathbf{r}, \mathbf{e}, t) = \frac{n_1(\mathbf{r}, \mathbf{e}, t)}{\int n_1(\mathbf{r}, \mathbf{e}, t) d^2\mathbf{e}} , \tag{7}$$

where $d^2\mathbf{e} = \sin\theta d\theta d\Phi$, and θ, Φ are spherical angles of unit vector $\mathbf{e}$ in an external coordinate system. The coordinate system is chosen to be oriented with its Oz axis along the direction of the field, $\mathbf{e}_{\mathrm{U}}$, and with its origin fixed at the cluster center.

Equation of continuity for the distribution n_1 is

$$\frac{\partial n_1}{\partial t} = D^{\mathrm{tr}} \nabla \cdot \nabla n_1 + D^{\mathrm{rot}} \mathscr{R} \cdot \left[\mathscr{R} n_1 + n_1 \mathscr{R} \frac{U_1(\mathbf{e})}{kT} \right] , \tag{8}$$

where U_1 ($\mathbf{e}$) is orientation-dependent potential energy of single elements in the field, $\mathscr{R}$ is rotational operator

$$\mathscr{R} = \mathbf{e} \times \frac{\partial}{\partial \mathbf{e}} . \tag{9}$$

Translational flux of single elements is controlled by statistical forces, and the external potential contributes to the rotational flux only.

Interactions between the cluster and the elements are neglected in the range of diffusion. Single elements interact with the cluster at the collision, and the interactions will be accounted for in the boundary condition for the cluster surface.

The boundary condition for the cluster surface assumes that at any point of the surface, $|\mathbf{r}| = R$, the flux of single elements with orientation $\mathbf{e}$ balances the flux of association-dissociation reaction with the cluster

$$-\frac{\mathbf{r}}{R} \cdot \mathbf{j}_{\mathrm{tr}}(\mathbf{r}, \mathbf{e}, t) = k^+(\mathbf{e}; \mathbf{e}_{\mathrm{C}})\, n_1(\mathbf{r}, \mathbf{e}, t) - k^-(\mathbf{e}; \mathbf{e}_{\mathrm{C}}) \tag{10}$$

$-\mathbf{r}/R$ is unit vector normal to the cluster surface, and origin of the coordinate system is fixed at the cluster center. Diffusional mobility of the cluster is neglected, and relative translational and rotational diffusion of single elements to the cluster is represented by the constants of self-diffusion. The left-hand side of Eq. (10) is the radial component of translational flux of elements with orientation $\mathbf{e}$

$$\mathbf{j}_{\mathrm{tr}} = -D^{\mathrm{tr}} \nabla n_1(\mathbf{r}, \mathbf{e}, t) , \tag{11}$$

and contribution of rotational flux of the elements can be neglected for geometrical reasons [1], $k^{\pm}$ ($\mathbf{e}$; $\mathbf{e}_{\mathrm{C}}$) are coefficients of association and dissociation which depend on orientation $\mathbf{e}$. Orientation of the cluster, $\mathbf{e}_{\mathrm{C}}$, appears as a parameter. Cluster surface is assumed to be uniform, with fixed favored direction of association at any point of the surface, $\mathbf{e}_{\mathrm{C}}$.

At the infinite distance from the cluster, the distribution is undisturbed, and it reads

$$\lim_{r \to \infty} \int n_1(\mathbf{r}, \mathbf{e}, t) d^2\mathbf{e} = n_1^{\mathrm{eq}} , \tag{12}$$

where n_1^{eq} is the number of single elements per unit volume of the solution at equilibrium.

Dependence of the kinetic coefficients $k^{\pm}$ on orientation $\mathbf{e}$ of single elements results from orientation-dependent potential energy of the elements and the cluster in the field, as well as from interactions between the elements and the cluster resulting in angular limitations of association.

For the purpose of this paper, the following step-wise coefficients of association and dissociation are proposed [6]

$$k^+(\mathbf{e}; \mathbf{e}_{\mathrm{C}}) = \hat{k}^+(\mathbf{e}; \mathbf{e}_{\mathrm{C}})\, \chi(\mathbf{e} \cdot \mathbf{e}_{\mathrm{C}})$$

$$k^-(\mathbf{e}; \mathbf{e}_{\mathrm{C}}) = \hat{k}^-(\mathbf{e}; \mathbf{e}_{\mathrm{C}}) \frac{\chi(\mathbf{e} \cdot \mathbf{e}_{\mathrm{C}})}{\int \chi(\mathbf{e} \cdot \mathbf{e}_{\mathrm{C}}) d^2\mathbf{e}} , \tag{13}$$

where χ is step function defined by Eq. (5), and taken as common for association and dissociation. $\hat{k}^{\pm}$ are rate constants of association and dissociation per unit cluster surface, with the lack of orientational limitations. One assumes that orientational limitations are controlled by the same mechanisms for both directions of the process.

Then, Eq. (10) assumes the following form

$$\frac{D^{\mathrm{tr}}}{R} \mathbf{r} \cdot \nabla n_1 = \left[\hat{k}^+(\mathbf{e}; \mathbf{e}_{\mathrm{C}}) n_1 - \frac{\hat{k}^-(\mathbf{e}; \mathbf{e}_{\mathrm{C}})}{\int \chi(\mathbf{e} \cdot \mathbf{e}_{\mathrm{C}}) d^2\mathbf{e}} \right] \chi(\mathbf{e} \cdot \mathbf{e}_{\mathrm{C}})$$

$$|r| = R \tag{14}$$

Surface densities of the rate constants are taken in the following form [6, 12]

$$\hat{k}^{+}(\mathbf{e};\mathbf{e}_{\mathrm{C}}) = \nu n_{\mathrm{s}} v \exp\left(-\frac{E_{\mathrm{D}}}{kT}\right)\exp\left[-f\,\frac{\delta\mu_{\mathrm{g}}(\mathbf{e};\mathbf{e}_{\mathrm{C}})}{kT}\right] \tag{15}$$

$$\hat{k}^{-}(\mathbf{e};\mathbf{e}_{\mathrm{C}}) = \nu n_{\mathrm{s}} \exp\left(-\frac{E_{\mathrm{D}}}{kT}\right)\exp\left[(1-f)\,\frac{\delta\mu_{\mathrm{g}}(\mathbf{e};\mathbf{e}_{\mathrm{C}}}{kT}\right], \tag{16}$$

where

$$f = \frac{1}{2}\left[1 + \mathrm{sgn}\left(\delta\mu_{\mathrm{g}}(\mathbf{e};\mathbf{e}_{\mathrm{C}})\right)\right]. \tag{17}$$

ν is frequency of thermal motion, n_{s} is surface density of active centers on the cluster surface, v is volume per single element in pure component, E_{D} is activation energy of transport in the boundary region, $\delta\mu_{\mathrm{g}}(\mathbf{e};\mathbf{e}_{\mathrm{C}})$ is pure-component free energy of association of single element oriented at $\mathbf{e}$ by g-size cluster oriented at $\mathbf{e}_{\mathrm{C}}$ in the field

$$\delta\mu_{\mathrm{g}}(\mathbf{e};\mathbf{e}_{\mathrm{C}}) = \delta\mu_{\mathrm{g}}^{0} + U_{\mathrm{g}}(\mathbf{e}_{\mathrm{C}}) - [U_{\mathrm{g}-1}(\mathbf{e}_{\mathrm{C}}) + U_{1}(\mathbf{e})], \tag{18}$$

where $\delta\mu_{\mathrm{g}}^{0}$ is standard free energy of association at zero external field with the lack of orientational limitations of association, U_1, U_{g} are, respectively, potential energy of single element and of the cluster.

Steady-state solution

The steady-state equation of diffusion obtained from Eq. (8) is expressed in the following dimensionless form

$$\nabla^2\psi + \frac{D^{\mathrm{rot}}R^2}{D^{\mathrm{tr}}}\left[\boldsymbol{\mathscr{R}}^2\psi + \boldsymbol{\mathscr{R}}\,\frac{U_1(\mathbf{e})}{kT}\cdot\boldsymbol{\mathscr{R}}\psi\right] = 0\,, \tag{19}$$

where $\psi(\boldsymbol{\varrho},\mathbf{e})$ is a dimensionless distribution function of single elements, Laplace operator ∇^2 is defined in dimensionless space of translations, $\boldsymbol{\varrho}$. The following definitions are used:

$$n_1(\mathbf{r},\mathbf{e}) = n_1^{\mathrm{eq}} w_1^{\mathrm{eq}}(\mathbf{e})\,\psi(\boldsymbol{\varrho},\mathbf{e}) \tag{20}$$

and

$$\boldsymbol{\varrho} = \mathbf{r}/R\,,\quad \tau = D^{\mathrm{tr}}t/R^2\,. \tag{21}$$

$$w_1^{\mathrm{eq}}(\mathbf{e}) = (4\pi\mathscr{Z})^{-1}\exp\left[-\frac{U_1(\mathbf{e})}{kT}\right] \tag{22}$$

is the Boltzmann orientation distribution of single elements where

$$\mathscr{Z} = \frac{1}{4\pi}\int\exp\left[-\frac{U_1(\mathbf{e})}{kT}\right]d^2\mathbf{e}\,. \tag{23}$$

Then, the boundary conditions read

$$\left.\frac{\partial\psi}{\partial\varrho}\right|_{\varrho=1} = \frac{\hat{k}^{+}R}{D^{\mathrm{tr}}}\left[\psi - \frac{\hat{k}^{-}}{\hat{k}^{+}n_1^{\mathrm{eq}}w_1^{\mathrm{eq}}\int\chi(\mathbf{e}\cdot\mathbf{e}_{\mathrm{C}})\,d^2\mathbf{e}}\right]\chi(\mathbf{e}\cdot\mathbf{e}_{\mathrm{C}}) \tag{24}$$

$$\lim_{\rho\to\infty}\int\psi(\boldsymbol{\varrho},\mathbf{e})\,w_1^{\mathrm{eq}}(\mathbf{e})\,d^2\mathbf{e} = 1 \tag{25}$$

Introducing the following small parameter for the potential energy term in Eq. (19),

$$\varepsilon = \frac{\sup|U_1(\mathbf{e})|}{kT} \ll 1\,, \tag{26}$$

an expansion method will be applied for the solution. Sup $|U_1(\mathbf{e})|$ is the superior value of potential energy of a single element in the space of orientations. One assumes that U_1 is confined to the first and second harmonic term

$$U_1(\mathbf{e}) = U_1^{(1)}Y_1(\mathbf{e}\cdot\mathbf{e}_U) + U_1^{(2)}Y_2(\mathbf{e}\cdot\mathbf{e}_U)\,, \tag{27}$$

where $\mathbf{e}\cdot\mathbf{e}_U = \cos\theta$ specifies orientation of the single element's axis $\mathbf{e}$ in the field, $U_1^{(i)}$ are expansion coefficients.

Distribution function ψ is spherical in the space of translations, and it is a function of the distance from the cluster center, ϱ, and of orientation $\mathbf{e}$. Steady-state distribution, expanded over small parameter, reads

$$\psi(\varrho,\mathbf{e}) = \sum_{i=0}\varepsilon^i\psi_i(\varrho,\mathbf{e})\,, \tag{28}$$

where ψ_i satisfy the following equations

$$i = 0 \quad (\nabla^2 + \mathscr{D}\mathscr{R}^2)\psi_0 = 0$$

$$i \geq 1 \quad (\nabla^2 + \mathscr{D}\mathscr{R}^2)\psi_{\mathrm{i}} = \mathscr{D}\boldsymbol{\mathscr{R}}\mathscr{U}\cdot\mathscr{R}\psi_{i-1} \tag{29}$$

Boundary conditions for the first two terms read

$$\left.\frac{\partial\psi_0}{\partial\varrho}\right|_{\varrho=1} = \frac{\hat{k}^{0+}R}{D^{\mathrm{tr}}}\left[\psi_0 - \frac{\hat{k}^{0-}\mathscr{Z}}{\hat{k}^{+}X_{00}(\Delta\vartheta)\,n_1^{\mathrm{eq}}}\right]\chi(\mathbf{e}\cdot\mathbf{e}_{\mathrm{C}}) \tag{30}$$

$$\left.\frac{\partial\psi_1}{\partial\varrho}\right|_{\varrho=1} = \frac{\hat{k}^{0+}R}{D^{\mathrm{tr}}}[\psi_1 - \delta\mathscr{U}_{\mathrm{g}}(\mathbf{e}_{\mathrm{C}})\psi_0]\,\chi$$

$$+ [f^{0}\mathscr{U}_1(\mathbf{e}) + (1-f^{0})\,\delta\mathscr{U}_{\mathrm{g}}(\mathbf{e}_{\mathrm{C}})]\left.\frac{\partial\psi_0}{\partial\varrho}\right|_{\varrho=1}$$

$$\lim_{\varrho\to\infty}\psi_i = \delta_{i0}\,, \tag{31}$$

where $\hat{k}^{0\pm}$ are zero-field surface densities of the rate constants with lack of orientational limitations of association, f^{0} denotes the factor f taken for zero field (cf. Eqs. (17, 18)), δ_{i0} is the Kronecker's symbol.

$$\mathscr{U}_1(\mathbf{e}) = U_1(\mathbf{e})/\sup|U_1| \quad \delta\mathscr{U}_{\mathrm{g}} = (U_{\mathrm{g}} - U_{\mathrm{g}-1})/\sup|U_1| \tag{32}$$

are, respectively, dimensionless potential energy of single element and change of potential energy of g-size cluster during growth by one element, reduced by superior value of potential energy of single element.

$$\mathscr{D} = \frac{D^{\mathrm{rot}} R^2(g)}{D^{\mathrm{tr}}} \tag{33}$$

is the reduced constant of rotational diffusion of single element, and

$$X_{00}(\Delta\vartheta) = \int X(\mathbf{e}\cdot\mathbf{e}_{\mathrm{C}})\, d^2\mathbf{e}/4\pi = 1 - \cos\Delta\vartheta \tag{34}$$

is the fraction of the total solid angle occupied by the tolerance angle. For narrow tolerance angle, X_{00} can be approximated by $(\Delta\vartheta)^2/2$, and it equals unity for lack of orientational limitations.

The zero-order term is expressed by an expansion over zero-order even spherical harmonics, $Y_{2j}(\mathbf{e}\cdot\mathbf{e}_{\mathrm{C}})$

$$\psi_0(\varrho, \mathbf{e}) = \sum_{j=0}^{\infty} n_{2j}(\varrho)\frac{Y_{2j}(\mathbf{e}\cdot\mathbf{e}_{\mathrm{C}})}{Y_0} . \tag{35}$$

The expansion coefficients are functions of the distance from the cluster center, ϱ

$$b_{2j}(\varrho) = \delta_{j0} - a_{2j}\frac{\alpha^{+}}{\varrho}\exp\left[-(2j(2j+1)\mathscr{D})^{\frac{1}{2}} \times(\varrho - 1)\right]\left[1 - \exp\left(\frac{\delta f_{\mathrm{g}}}{kT}\right)\right],$$

$$b_{2j+1}(\varrho) = 0 \tag{36}$$

where

$$\alpha^{+} = \hat{k}^{0+} X_{00}(\Delta\vartheta) R(g)/D^{\mathrm{tr}} \tag{37}$$

is reduced surface density of the association rate constant at zero external field, and

$$\delta f_{\mathrm{g}} = \delta\mu_{\mathrm{g}}^{0} - kT\ln[X_{00}(\Delta\vartheta)c_1^{\mathrm{eq}}] + kT\ln\mathscr{L} , \tag{38}$$

where $c_1^{\mathrm{eq}} = v n_1^{\mathrm{eq}}$ is volume fraction of single elements in the system. Coefficients a_{2j} are functions of the reduced association rate constant, reduced rotational diffusion constants of single elements, and the tolerance angle [6]

$$a_{2j} = a_{2j}(\alpha^{+}, \mathscr{D}, \Delta\vartheta) , \quad a_{2j+1} = 0 . \tag{39}$$

First-order correction term

The first-order correction term is expressed by the following series expansion in spherical harmonics, $Y_j^m(\mathbf{e}\cdot\mathbf{e}_{\mathrm{C}}, \varphi)$

$$\psi_1(\varrho, \mathbf{e}) = \sum_{j=0}^{\infty}\sum_{m=-j}^{j} b_{jm}(\varrho)\frac{Y_j^m(\mathbf{e}\cdot\mathbf{e}_{\mathrm{C}}, \phi)}{Y_0} . \tag{40}$$

Using potential energy U_1 and the zero-order term ψ_0 given by Eqs. (27, 35), the following set of equations is obtained for $b_{jm}(\varrho)$

$$\frac{d^2 b_{jm}}{d\varrho^2} + \frac{2}{\varrho}\frac{db_{jm}}{d\varrho} - \mathscr{D}j(j+1) = \mathscr{D}\sum_{i=1}^{2}\mathscr{U}_1^{(i)} f_{jm}^{(i)}(\varrho)\, \overset{*}{Y}{}_i^m(\mathbf{e}_{\mathrm{C}}\cdot\mathbf{e}_{\mathrm{U}}, \Phi) \tag{41}$$

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

$m = -j, -j+1, \ldots, j-1, j ,$

where

$$\mathscr{U}_1^{(i)} = \frac{U_1^{(i)}}{\sup|U_1|} \tag{42}$$

are dimensionless coefficients of the single element's potential energy, and functions $f_{jm}^{(i)}(\varrho)$ are shown in the Appendix (Eqs. (A1–A9)). Scalar product $\mathbf{e}_{\mathrm{C}}\cdot\mathbf{e}_{\mathrm{U}} = \cos\theta$, and (θ, Φ) are spherical angles of orientation of the cluster axis $\mathbf{e}_{\mathrm{C}}$ with respect to the direction of the field, $\mathbf{e}_{\mathrm{U}}$. The pair of spherical angles (θ, Φ) should be distinguished from (ϑ, φ) denoting orientation of a single element's axis $\mathbf{e}$ with respect to the cluster. $\overset{*}{Y}{}_i^m(\theta, \Phi)$ are conjugate spherical harmonics. Orientation angle θ of the cluster axis in the field will be used below in this paper instead of scalar product $\mathbf{e}_{\mathrm{C}}\cdot\mathbf{e}_{\mathrm{U}}$.

Solution of Eq. (41) reads

$$b_{jm} = C_{jm}\frac{\alpha^{+}}{\varrho}\exp[(j(j+1)\mathscr{D})^{\frac{1}{2}}(\varrho - 1)] + \alpha^{+}\left[1 - \exp\left(\frac{\delta f_{\mathrm{g}}}{kT}\right)\right]\sum_{i=1}^{2}\mathscr{U}_1^{(i)} g_{jm}^{(i)}(\varrho)\, \overset{*}{Y}{}_i^m(\theta, \Phi) , \tag{43}$$

where $g_{jm}^{(i)}(\varrho)$ are listed in the Appendix (Eqs. (A10–A18)), and the constants C_{jm}, determined from boundary condition for the cluster surface, read

$$C_{kn} = \left[1 - \exp\left(\frac{\delta f_{\mathrm{g}}}{kT}\right)\right]\left[\delta_{n0} d_k \not{f}^{0}\, \delta\mathscr{U}_{\mathrm{g}}(\theta) + \sum_{i=1}^{2}(a_{kn}^{(i)} - \not{f}^{0} d_{kn}^{(i)})\mathscr{U}_1^{(i)}\, \overset{*}{Y}{}_i^n(\theta, \Phi)\right] + \delta_{n0} a_k \exp\left(\frac{\delta f_{\mathrm{g}}}{kT}\right)\delta\mathscr{U}_{\mathrm{g}}(\theta) \tag{44}$$

$|n| = 0, 1, 2$

$k = |n|, |n|+1, |n|+2, \ldots .$

$$C_{kn} = 0 \quad \text{for } |n| \geq 3 \tag{45}$$

Coefficients d_k, $a_{kn}^{(i)}$, $d_{kn}^{(i)}$ are solutions of the following sets of equations

$$\sum_{j=0}^{\infty} B_{mj0} d_j = [1 + (m(m+1)\mathscr{D})^{\frac{1}{2}}]\, a_m \tag{46}$$

$$\sum_{j=|n|}^{\infty} B_{mjn}\, a_{jn}^{(i)} = \frac{dg_{mn}^{(i)}}{d\varrho|_{\varrho=1}} - \alpha^{+} \sum_{j=|n|}^{\infty} g_{jn}^{(i)}(\varrho=1)\,\frac{X_{jm}^{nn}}{X_{00}} \qquad (47)$$

$$\sum_{j=|n|}^{\infty} B_{mjn}\, d_{jn}^{(i)} = h_{mn}^{(i)} \qquad (48)$$

$$i = 1, 2, 3, \ldots .$$
$$n = 0, 1, 2\ .$$

Factors $h_{mn}^{(i)}$ are listed in the Appendix (Eqs. (A20–A26)), and components of the matrix $\mathbf{B}_n$ read

$$B_{mjn} = [1 + (m(m+1)\mathscr{D})^{\frac{1}{2}}]\,\delta_{mj} + \alpha^{+}\,\frac{X_{mj}^{nn}(\Delta\vartheta)}{X_{00}(\Delta\vartheta)}\,, \qquad (49)$$

where

$$X_{mj}^{nn}(\Delta\vartheta) = 2\pi \int_{-1}^{1} Y_m^n(\vartheta,\varphi)\,\chi(\vartheta)\,\overset{*}{Y}{}_i^n(\vartheta,\varphi)\,d(\cos\vartheta)\ . \qquad (50)$$

Equations (46–48) have been solved numerically. For $n \geq 3$, Eqs. (47, 48) are uniform, and then $a_{kn}^{(i)} = 0$, $d_{kn}^{(i)} = 0$.

Net rate of association

Net rate of association is given by total flux of single elements at the cluster surface, and for g-size cluster it can be expressed by the following formula

$$J_g(\mathbf{e}_C) = \int\!\!\int \left[\hat{k}^{+}(\mathbf{e};\mathbf{e}_C)\,n_1 - \frac{\hat{k}^{-}(\mathbf{e};\mathbf{e}_C)}{\int \chi(\mathbf{e}\cdot e_C)\,d^2 e} \right] \chi(\mathbf{e}\cdot\mathbf{e}_C)\,do\,d^2\mathbf{e}$$
$$= \int\!\!\int D^{\mathrm{tr}}(\nabla_{|\varrho=1} n_1 \cdot d^2\boldsymbol{\sigma})\,d^2\mathbf{e}\ . \qquad (51)$$

Equation (51) is obtained by integrating both sides of the boundary condition (Eq. 14) over total cluster surface ($d\sigma$) and total orientation space of single elements ($d^2\mathbf{e}$). Net rate of association is the function of cluster orientation $\mathbf{e}_C$ in the field.

For steady-state distribution of single elements, the net rate of association reads

$$J_g(\mathbf{e}_C) = 4\pi R(g)\,D^{\mathrm{tr}}\,n_1^{\mathrm{eq}} \int w_1^{\mathrm{eq}}(\mathbf{e})\,\frac{\partial}{\partial\varrho_{|\varrho=1}}\,\psi(\varrho,\mathbf{e};\mathbf{e}_C)\,d^2\mathbf{e}\ , \qquad (52)$$

and its expanded form is

$$J_g(\mathbf{e}_C) = J_{g,0} + \sum_{i=1} \varepsilon^i J_{g,i}(\mathbf{e}_C)\ . \qquad (53)$$

The zero-order term in Eq. (53) is isotropic, and it reads (cf. Eqs. (64–66) in ref. [6])

$$J_{g,0} = 4\pi R^2(g)\,\hat{k}^{0+} X_{00}(\Delta\vartheta)\,n_1^{\mathrm{eq}} \left[1 - \exp\left(\frac{\delta f_g}{kT}\right)\right] a_0/\mathscr{L}\ , \qquad (54)$$

The first-order correction term is orientation-dependent, and it assumes the following form

$$J_{g,1} = -4\pi R^2(g)\,\hat{k}^{0+} X_{00}(\Delta\vartheta)\,n_1^{\mathrm{eq}}\,C_{00}(\theta)/\mathscr{L}\ , \qquad (55)$$

where

$$C_{00}(\theta) = \left[1 - \exp\left(\frac{\delta f_g}{kT}\right)\right] \Bigg[d_0\,\mathscr{f}^{0}\,\delta\mathscr{U}_g(\theta) + \sum_{i=1}^{2} (a_{00}^{(i)} - \mathscr{f}^{0} d_{00}^{(i)})\,\mathscr{U}_1^{(i)}\,Y_i(\theta) \Bigg] + \exp\left(\frac{\delta f_g}{kT}\right) a_0\,\delta\mathscr{U}_g(\theta)\ , \qquad (56)$$

and

$$a_0 = [1 + \alpha^{+}/A(\mathscr{D},\Delta\vartheta)]^{-1} = \left[1 + \frac{\hat{k}^{0+} X_{00} R}{D^{\mathrm{tr}} A}\right]^{-1} . \qquad (57)$$

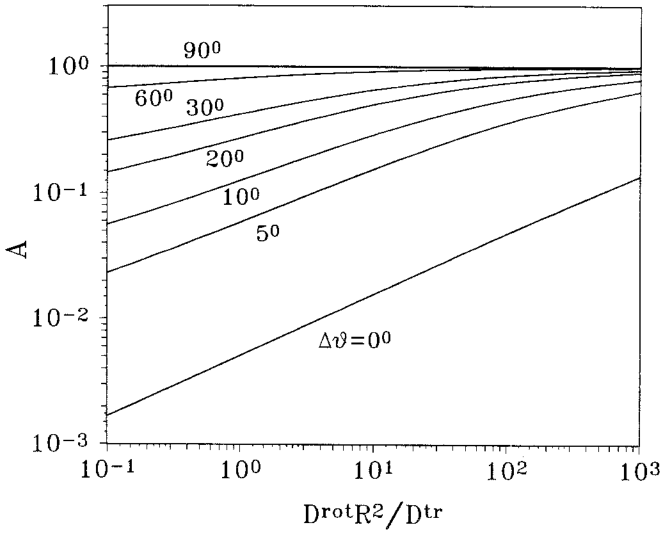
Factor A in Eq. (57) has been derived in ref. [6], and it is given by Eqs. (A27, A30) in the Appendix. Figure 3 shows plots of A vs. $\mathscr{D} = D^{\mathrm{rot}} R^2/D^{\mathrm{tr}}$ for several values of the tolerance angle. The values of A are between zero and unity. For narrow tolerance angle A is much smaller than unity, and it approaches unity for $\Delta\vartheta \to \pi/2$ or $\mathscr{D} \to \infty$.

For odd j, the constants $a_j = 0$, and from Eqs. (47, 48, A10, A20) one obtains

$$a_{00}^{(1)} = d_{00}^{(1)} = 0\ . \qquad (58)$$

The coefficients $a_{00}^{(2)}$, d_0, and $d_{00}^{(2)}$ have been computed using Eqs. (46–48). Figure 4 shows plots of $a_{00}^{(2)}/a_0\,(1 - \alpha^{+} a_0)$ vs. α^{+}/A computed from Eq. (47) for $\mathscr{D} = 10^{-1}, 1, 10, 10^2$, and

Fig. 3 Plots of A vs. $\mathscr{D} = D^{\mathrm{rot}} R^2/D^{\mathrm{tr}}$ computed for several values of the tolerance angle $\Delta\vartheta$



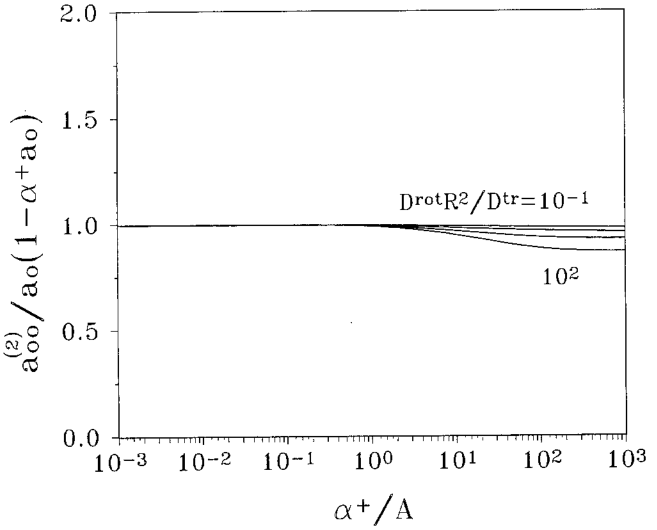


Fig. 4. Plots of $a_{00}^{(2)}/[a_0(1-\alpha^+ a_0)]$ vs. α^+/A computed for $D^{\mathrm{rot}}R^2/D^{\mathrm{tr}} = 10^{-1}$, 1, 10, 10^2, $\Delta\vartheta = 5^0$

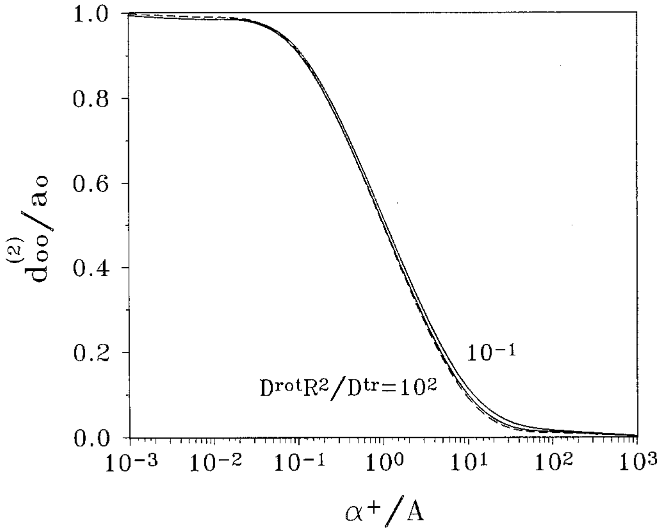


Fig. 6. Plots of $d_{00}^{(2)}/a_0$ vs. α^+/A computed for $D^{\mathrm{rot}}R^2/D^{\mathrm{tr}} = 10^{-1}$, 10^2, and $\Delta\vartheta = 5^0$. Dashed curve indicates plot of $a_0 = (1 + \alpha^+/A)^{-1}$

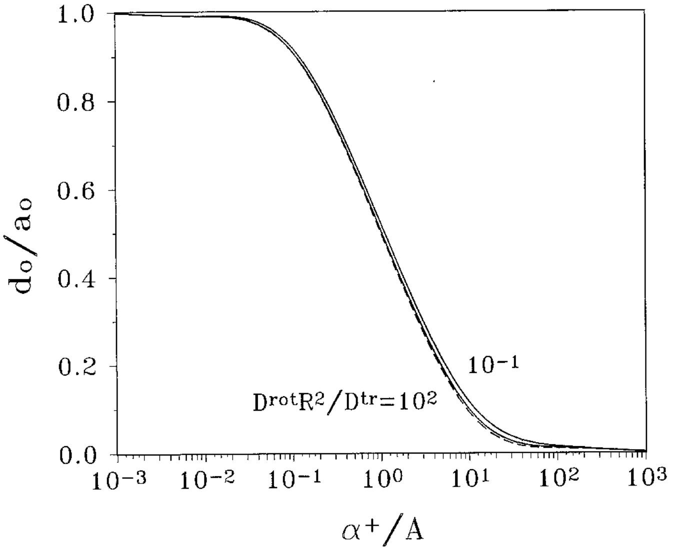


Fig. 5. Plots of d_0/a_0 vs. α^+/A computed for $D^{\mathrm{rot}}R^2/D^{\mathrm{tr}} = 10^{-1}$, 10^2, and $\Delta\vartheta = 5^0$. Dashed curve indicates plot of $a_0 = (1 + \alpha^+/A)^{-1}$

$\Delta\vartheta = 5^0$. The computed values are close to unity, and in this range one can approximate

$$a_{00}^{(2)} \cong a_0(1-\alpha^+ a_0)\,. \tag{59}$$

The plots of d_0/a_0 and $d_{00}^{(1)}/a_0$ vs. α^+/A, computed from Eqs. (46, 48), are shown in Figs. 5 and 6 for $\mathscr{D} = 10^{-1}$, $\mathscr{D} = 10^2$, and $\Delta\vartheta = 5^0$. The plots almost overlap in the figures, and they overlap with the plot of a_0 shown by dashed curves. For intermediate values of $\mathscr{D}$, the computed values also overlap (the plots are not shown). Then, d_0 and $d_{00}^{(2)}$ will be approximated by

$$d_0 \cong d_{00}^{(2)} \cong a_0^2\,. \tag{60}$$

Using zero- and first-order correction terms (Eqs. (54, 55)) and the coefficients given by Eqs. (56–60), the steady-state net rate of association is

$$J_g(\theta) = J_{g,0}\left[1 - \frac{1+(1-A)\alpha^+/A}{1+\alpha^+/A}\,\frac{U_1^{(2)}}{kT}\,Y_2(\theta) - \not{f}^0\,\frac{\delta U_g(\theta) - U_1^{(2)}Y_2(\theta)}{(1+\alpha^+/A)kT}\right] - 4\pi R^2 \hat{k}^{0-}\,\frac{\delta U_g(\theta)}{(1+\alpha^+/A)kT}\,. \tag{61}$$

Factor $\not{f}^0$ equals zero for positive net rate of association at zero field, $J_{g,0} > 0$, and it is unity for negative one.

Equation (61) predicts that the first harmonic term of single element's potential energy, $U_1^{(1)}$, does not contribute at all to angular dependence of the net flux of association. This is a consequence of axial symmetry of orientational limitations of association defined by Eq. (5). Such a symmetry corresponds to formation of non-polar clusters in polar fluid where parallel and anti-parallel orientations of single elements are accepted by a growing cluster with equal weights. Second harmonic term, $U_1^{(2)}$, which corresponds, for example, to induced effects in an electric field, contributes to orientational dependence of the flux, as well as does the change of potential energy of the cluster during growth, δU_g.

The conclusion is in agreement with experimental observations of growth of non-polar phase in crystallizing poly(vinylidene fluoride) in electric field. It has been observed that contribution of the field to angular differentiation of crystallization rate of non-polar phase was negligible, as results from weak induced effects [13, 14]. Orientation of permanent dipoles in the amorphous matrix does not cause any angular anisotropy of the association process.

Net rate of association is enhanced by the field for the range of cluster orientations where the second term of single elements' potential energy, and the change of potential energy of cluster during growth are negative ($U_1^{(2)} Y_2(\theta) < 0$, $\delta U_g(\theta) < 0$), and it is reduced elsewhere.

At a temperature at which zero-field net flux of association, $J_{g,0}$, vanishes, a non-zero net flux of association (or dissociation) is induced by the field, and it is governed by the change of potential energy of cluster during growth, δU_g:

$$J_g(\theta) = -4\pi R^2 \hat{k}^{0-} \frac{\delta U_g(\theta)}{(1+\alpha^+/A)kT} . \tag{62}$$

At this zero-field equilibrium melting temperature, the field induces positive net flux (association) in the range of cluster orientations where the cluster potential energy decreases during growth, $\delta U_g(\theta) < 0$, and negative one (dissociation) in the range where $\delta U_g(\theta) > 0$. Finite diffusion rates and orientational limitations of association reduce effects of the field by the factor of $(1+\alpha^+/A)^{-1}$.

For fast reversible association and narrow tolerance angle ($\alpha/A \gg 1$)

$$J_g(\theta) = 4\pi R D^{\mathrm{tr}} A n_1^{\mathrm{eq}} \left[1 - (1-A) \frac{U_1^{(2)}}{kT} Y_2(\theta) \right.$$
$$\left. - \exp\left(\frac{\delta f_g}{kT}\right) \left(1 - (1-A) \frac{U_1^{(2)}}{kT} Y_2(\theta) + \frac{\delta U_g(\theta)}{kT}\right) \right] \Big/ \mathscr{X} \tag{63}$$

For fast irreversible process, $\delta f_g \to -\infty$, Eq. (63) reduces to

$$J_g(\theta) = 4\pi R D^{\mathrm{tr}} A n_1^{\mathrm{eq}} \left[1 - (1-A) \frac{U_1^{(2)}}{kT} Y_2(\theta) \right] \Big/ \mathscr{X} . \tag{64}$$

Equation (68) shows diffusion limited aggregation (DLA) formula for the case of external orientation field and uniaxial symmetry of orientational limitations of association. The DLA rate is enhanced by the field in the range of orientations where the second harmonic term of single element's potential energy is negative, and it is reduced in the range where the term is positive.

For narrow tolerance angle ($A \ll 1$), Eq. (64) reads

$$J_g(\theta) = 4\pi R D^{\mathrm{tr}} A n_1^{\mathrm{eq}} \left[1 - \frac{U_1^{(2)}}{kT} Y_2(\theta) \right] \Big/ \mathscr{X} . \tag{65}$$

For lack of any orientational limitation of association ($A = 1$), Eq. (64) reduces to the following isotropic form

$$J_g = 4\pi R D^{\mathrm{tr}} n_1^{\mathrm{eq}} / \mathscr{X} , \tag{66}$$

which for zero external field ($\mathscr{X} = 1$) assumes the well known Smoluchowski DLA formula.

Effective rate constants and effective concentration

Net rate of association of single elements by g-size cluster, expressed by orientation-dependent, effective rate constants, $k_g^{\mathrm{eff}\,\pm}(\theta)$, and equilibrium concentration of single elements, n_1^{eq}, reads

$$J_g(\theta) = k_g^{\mathrm{eff}\,+}(\theta)\, n_1^{\mathrm{eq}} - k_g^{\mathrm{eff}\,-}(\theta) , \tag{67}$$

where

$$k_g^{\mathrm{eff}\,+}(\theta) = \frac{4\pi R^2 \hat{k}^+ X_{00}}{1+\alpha^+/A} [1 - \xi(\theta)] / \mathscr{X} \tag{68}$$

$$k_g^{\mathrm{eff}\,-}(\theta) = \frac{4\pi R^2 \hat{k}^-}{1+\alpha^+/A} \left[1 - \xi(\theta) + \frac{\delta U_g(\theta)}{kT} \right], \tag{69}$$

and

$$\xi(\theta) = \frac{1 + (1-A)\alpha^+/A}{1+\alpha^+/A} \frac{U_1^{(2)}}{kT} Y_2(\theta)$$
$$+ \not{f}^{0} \frac{\delta U_g(\theta) - U_1^{(2)} Y_2(\theta)}{(1+\alpha^+/A)kT} . \tag{70}$$

At slow associations ($\alpha^+/A \ll 1$), the effective rate constants reduce to equilibrium rate constants:

$$k_g^+(\theta) = 4\pi R^2 \hat{k}^{0+} X_{00} \left[1 - \frac{U_1^{(2)}}{kT} Y_2(\theta) \right.$$
$$\left. - \not{f}^{0} \frac{\delta U_g(\theta) - U_1^{(2)} Y_2(\theta)}{kT} \right] \Big/ \mathscr{X} \tag{71}$$

$$k_g^-(\theta) = 4\pi R^2 \hat{k}^{0-} \left[1 + (1 - \not{f}^{0}) \frac{\delta U_g(\theta) - U_1^{(2)} Y_2(\theta)}{kT} \right] . \tag{72}$$

In this case of slow association, the effective rate constants are not influenced by long-range diffusion, and they are controlled by thermodynamic factors.

Net rate of association, expressed by an effective, orientation-dependent concentration of single elements, $n_1^{\mathrm{eff}}(\theta)$, and by the equilibrium rate constants, reads

$$J_g(\theta) = k_g^+(\theta) n_1^{\mathrm{eff}}(\theta) - k_g^-(\theta) , \tag{73}$$

where n_1^{eff} accounts for the effects of finite diffusion rate, and it reads

$$\frac{n_1^{\mathrm{eff}}(\theta)}{n_1^{\mathrm{eq}}} = \frac{1}{1+\alpha^+/A}\left[1 - \exp\left(\frac{\delta f_{\mathrm{g}}}{kT}\right)\left[1 + \frac{\alpha^+/A}{1+\alpha^+/A}\right.\right.$$
$$\left.\left.\times\left(A\,\frac{U_1^{(2)}}{kT}\,Y_2(\theta) + \not{f}^{0}\,\frac{\delta U_{\mathrm{g}}(\theta) - U_1^{(2)}\,Y_2(\theta)}{kT}\right)\right]\right.$$
$$\left. + \exp\left(\frac{\delta f_{\mathrm{g}}}{kT}\right)\left[1 + \frac{\alpha^+/A}{1+\alpha^+/A}\,\frac{\delta U_{\mathrm{g}}(\theta)}{kT}\right]\right. . \tag{74}$$

For slow association, Eq. (74) reduces to $n_1^{\mathrm{eff}} = n_1^{\mathrm{eq}}$. At zero external field it reduces to the form derived in ref. [6].

The ratio α^+/A in the above formulae can be expressed by the ratio of the equilibrium rate constant of association at zero field, k_{g}^{0+}, and the DLA rate constant at zero field, $k_{\mathrm{g}}^{\mathrm{D}}$

$$\alpha^+/A = k_{\mathrm{g}}^{0+}/k_{\mathrm{g}}^{\mathrm{D}}\,, \tag{75}$$

where

$$k_{\mathrm{g}}^{0+} = 4\pi R^2(g)\,\hat{k}^{0+}X_{00}(\varDelta\vartheta), \quad k_{\mathrm{g}}^{\mathrm{D}} = 4\pi R(g)\,D^{\mathrm{tr}}A(\mathscr{D}, \varDelta\vartheta)\,. \tag{76}$$

Crystal nucleation

In kinetic models of crystal nucleation, the clusters can be considered as isolated one from another in the system, and the effective rate constants and effective concentration of single elements, derived in this paper, can be used.

Frequency of association of single elements by a g-size cluster in the system is $k_{\mathrm{g}}^+ n_1^{\mathrm{eff}}(g)$, and that of dissociation is k_{g}^-. Then, net flux of growth of clusters of size g from clusters of size $g-1$ in a unit volume of the system is

$$j_{\mathrm{g}} = k_{\mathrm{g}-1}^+ n_1^{\mathrm{eff}}(g-1)\,n_{\mathrm{g}-1} - k_{\mathrm{g}}^- n_{\mathrm{g}}\,, \tag{77}$$

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

Equation of continuity for the distribution of cluster sizes reads

$$\frac{\partial n_{\mathrm{g}}}{\partial t} = -(j_{\mathrm{g}+1} - j_{\mathrm{g}})\,. \tag{78}$$

For continual variable g, the ratio

$$k_{\mathrm{g}-1}^+ n_1^{\mathrm{eff}}(g-1)/k_{\mathrm{g}}^- = 1 - \frac{\delta f_{\mathrm{g}} + \delta U_{\mathrm{g}}(\theta)}{(1 + k_{\mathrm{g}}^+/k_{\mathrm{g}}^{\mathrm{D}})kT} + \cdots \tag{79}$$

and linearized form of orientation-dependent flux of growth of the clusters in the field reads

$$j(g, \theta, t) = -k_{\mathrm{g}}^-(\theta)\left(\frac{\partial n}{\partial g} + n\,\frac{\delta f_{\mathrm{g}} + \delta U_{\mathrm{g}}(\theta)}{(1 + k_{\mathrm{g}}^+/k_{\mathrm{g}}^{\mathrm{D}})kT}\right), \tag{80}$$

where $n\,(g, \theta, t)$ is time- and orientation-dependent distribution of cluster sizes in the system.

Equation of continuity for the distribution of clusters, n, assumes the following form of a Fokker–Planck equation

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial g}\left[k_{\mathrm{g}}^-(\theta)\left(\frac{\partial n}{\partial g} + n\,\frac{\delta f_{\mathrm{g}} + \delta U_{\mathrm{g}}(\theta)}{(1 + k_{\mathrm{g}}^+/k_{\mathrm{g}}^{\mathrm{D}})kT}\right)\right], \tag{81}$$

where orientation-dependent thermodynamic driving force of the process, $\delta f_{\mathrm{g}} + \delta U_{\mathrm{g}}(\theta)$, is reduced by $1 + k_{\mathrm{g}}^+/k_{\mathrm{g}}^{\mathrm{D}}$. For fast association, the role of the thermodynamic force can be considerably reduced by finite diffusion rate of single elements and narrow tolerance angle.

For slow association ($k_{\mathrm{g}}^+/k_{\mathrm{g}}^{\mathrm{D}} \ll 1$), Eq. (81) is controlled by pure thermodynamic driving force. Orientational dependence of the thermodynamic force results from potential energy of clusters in the field.

Conclusions

Net rate of association in external orienting field is orientation-dependent. The rate of the process is reduced by the finite rate of long-range translational and rotational diffusion of single elements, particularly for fast reactions and narrow tolerance angles.

The role of external field in the kinetics of association is affected by the diffusion and depends on the rate of association, translational and rotational diffusion constants of single elements, and the tolerance angle.

For slow associations, long-range diffusion of single elements does not influence the process, and net rate of the process is expressed by orientation-dependent equilibrium rate constants (Eqs. (71, 72)), and by equilibrium concentration of single elements. To satisfy the condition of slow reactions, the rate of association should be the slower, the slower the translational diffusion of single elements, the smaller the ratio $D^{\mathrm{rot}}R^2/D^{\mathrm{tr}}$, and the narrower the tolerance angle.

For fast processes, translational and rotational diffusion of single elements and the tolerance angle influence orientation distribution of single elements and kinetics of cluster growth (dissociation) in external orienting fields.

For narrow tolerance angle and not too high values of $D^{\mathrm{rot}}R^2/D^{\mathrm{tr}}$ (i.e., for $A \ll 1$) potential energy of single elements contributes significantly to orientational dependence of the effective rate constants of association and dissociation, and $\xi(\theta)$ equals $U_1^{(2)}\,Y_2(\theta)/kT$ in Eqs. (68, 69).

For lack of orientational limitations of association, or for very large clusters (i.e., for $A \cong 1$), potential energy of single elements does not influence orientational dependence of the effective rate constants, and $\xi(\theta)$ equals zero.

The only orientation-dependent contribution of the field comes from potential energy of the cluster, $\delta U_g(\theta)$.

Finite rate of translational and rotational diffusion, as well as orientational limitations of association reduce effective rate of cluster growth in the range of orientation angle where the second harmonic term of the single element's potential energy is positive, $U_1^{(2)} Y_2(\theta)) > 0$, and enhance it in the range where $U_1^{(2)} Y_2(\theta) < 0$. The first harmonic term of the potential energy does not contribute to orientational dependence of the growth rate of nonpolar clusters.

The model used in this paper allows for formulation of the equations of kinetic theory of crystal nucleation in external orienting field with the effects of finite translational and rotational diffusion of single elements and angular limitations of association. Equation of continuity for the distribution of clusters in the system has a form of diffusion equation in the space of cluster sizes with orientation-dependent thermodynamic driving force. The role of the thermodynamic force in this equation is reduced by $1 + k_g^{0+}/k_g^{D}$, dependent on the association rate constant, rate of translational and rotational diffusion of single elements, and tolerance angle. Angular dependence of thermodynamic driving force of the process results only from the orientation-dependent potential energy of clusters in the field.

Appendix

Functions $f_{jm}^{(i)}(\varrho)$ read
– for odd j

$$f_{j0}^{(1)} = \left[\frac{(j+1)(j+2)}{(2j+3)^{\frac{1}{2}}} b_{j+1}(\varrho) - \frac{j(j-1)}{(2j-1)^{\frac{1}{2}}} b_{j-1}(\varrho) \right] \frac{1}{(2j+1)^{\frac{1}{2}}} \tag{A1}$$

$$f_{1,\pm 1}^{(1)} = -\left[\frac{j+2}{(2j+3)^{\frac{1}{2}}} b_{j+1}(\varrho) + \frac{j-1}{(2j-1)^{\frac{1}{2}}} b_{j-1}(\varrho) \right] \times \left(\frac{j(j+1)}{2(2j+1)} \right)^{\frac{1}{2}} \tag{A2}$$

$$f_{jm}^{(1)} = 0 \quad \text{for } |m| \geq 2 \tag{A3}$$

$$f_{jm}^{(2)} = 0 \tag{A4}$$

– for even j

$$f_{jm}^{(1)} = 0 \tag{A5}$$

$$f_{j0}^{(2)} = \left[\frac{(j+1)(j+2)(j+3)}{(2j+3)(2j+5)^{\frac{1}{2}}} b_{j+2}(\varrho) + \frac{j(j+1)(2j+1)^{\frac{1}{2}}}{(2j-1)(2j+3)} b_j(\varrho) - \frac{(j-2)(j-1)j}{(2j-1)(2j-3)^{\frac{1}{2}}} b_{j-2}(\varrho) \right] \frac{3}{(2j+1)^{\frac{1}{2}}} \tag{A6}$$

$$f_{j,\pm 1}^{(2)} = -\left[\frac{(j+2)(j+3)}{(2j+3)(2j+5)^{\frac{1}{2}}} b_{j+2}(\varrho) - \frac{3(2j+1)^{\frac{1}{2}}}{2(2j-1)(2j+3)} b_j(\varrho) + \frac{(j-2)(j-1)}{(2j-1)(2j-3)^{\frac{1}{2}}} b_{j-2}(\varrho) \right] \left(\frac{6j(j+1)}{2j+1} \right)^{\frac{1}{2}} \tag{A7}$$

$$f_{j,\pm 2}^{(2)} = \left[\frac{j+3}{(2j+3)(2j+5)^{\frac{1}{2}}} b_{j+2}(\varrho) - \frac{3(2j+1)^{\frac{1}{2}}}{(2j-1)(2j+3)} b_j(\varrho) - \frac{j-2}{(2j-1)(2j-3)^{\frac{1}{2}}} b_{j-2}(\varrho) \right] \times \left(\frac{3(j-1)j(j+1)(j+2)}{2(2j+1)} \right)^{\frac{1}{2}} \tag{A8}$$

$$f_{jm}^{(2)} = 0 \quad \text{for } |m| \geq 3\,, \tag{A9}$$

where $b_j(\varrho)$ are coefficients of zero-order solution.

Introducing $\beta_j = [j(j+1)\mathscr{D}]^{\frac{1}{2}}$, functions $g_{jm}^{(i)}(\varrho)$ read
– for odd j

$$g_{j0}^{(1)} = -\frac{1}{\varrho}\left[\frac{j+2}{(2j+3)^{\frac{1}{2}}} a_{j+1}\, e^{-\beta_{j+1}(\varrho-1)} + \frac{j-1}{(2j-1)^{\frac{1}{2}}} a_{j-1}\, e^{-\beta_{j-1}(\varrho-1)} \right] \frac{1}{2(2j+1)^{\frac{1}{2}}} \tag{A10}$$

$$g_{j,\pm 1}^{(1)} = \frac{1}{\varrho}\left[\frac{j+2}{(j+1)(2j+3)^{\frac{1}{2}}} a_{j+1}\, e^{-\beta_{j+1}(\varrho-1)} - \frac{j-1}{j(2j-1)^{\frac{1}{2}}} a_{j-1}\, e^{-\beta_{j-1}(\varrho-1)} \right] \left(\frac{j(j+1)}{2(2j+1)} \right)^{\frac{1}{2}} \tag{A11}$$

$$g_{jm}^{(1)} = 0 \quad \text{for } |\mathrm{m}| \geq 2 \tag{A12}$$

$$g_{jm}^{(2)} = 0 \tag{A13}$$

– for even j

$$g_{jm}^{(1)} = 0 \tag{A14}$$

$$\begin{aligned} g_{j0}^{(2)} = -\frac{1}{\varrho}\Bigg[& \frac{(j+1)(j+2)(j+3)}{(2j+3)^2(2j+5)^{\frac{1}{2}}}\, a_{j+2}\, e^{-\beta_{j+2}(\varrho-1)} \\ & -\frac{(2j+1)^{\frac{1}{2}}}{(2j-1)(2j+3)}\, a_j\, \beta_j\, e^{-\beta_j(\varrho-1)} \\ & +\frac{(j-2)(j-1)j}{(2j-1)^2(2j-3)^{\frac{1}{2}}}\, a_{j-2}\, e^{-\beta_{j-2}(\varrho-1)}\Bigg]\frac{3}{2(2j+1)^{\frac{1}{2}}} \end{aligned} \tag{A15}$$

$$\begin{aligned} g_{j,\pm 1}^{(2)} = \frac{1}{\varrho}\Bigg[& \frac{(j+2)(j+3)}{(2j+3)^2(2j+5)^{\frac{1}{2}}}\, a_{j+2}\, e^{-\beta_{j+2}(\varrho-1)} \\ & +\frac{3(2j+1)^{\frac{1}{2}}}{2(2j-1)(2j+3)j(j+1)} \\ & \times a_j\, \beta_j\, e^{-\beta_j(\varrho-1)} - \frac{(j-2)(j-1)}{(2j-1)^2(2j-3)^{\frac{1}{2}}}\, a_{j-2} \\ & \times e^{-\beta_{j-2}(\varrho-1)}\Bigg]\left(\frac{3j(j+1)}{2(2j+1)}\right)^{\frac{1}{2}} \end{aligned} \tag{A16}$$

$$\begin{aligned} g_{j,\pm 2}^{(2)} = -\frac{1}{4\varrho}\Bigg[& \frac{j+3}{(2j+3)^2(2j+5)^{\frac{1}{2}}}\, a_{j+2}\, e^{-\beta_{j+2}(\varrho-1)} \\ & +\frac{3(2j+1)^{\frac{1}{2}}}{(2j-1)(2j+3)j(j+1)}\, a_j\, \beta_j\, e^{-\beta_j(\varrho-1)} \\ & +\frac{j-2}{(2j-1)^2(2j-3)^{\frac{1}{2}}}\, a_{j-2}\, e^{-\beta_{j-2}(\varrho-1)}\Bigg] \\ & \times\left(\frac{6(j-1)j(j+1)(j+2)}{2j+1}\right)^{\frac{1}{2}} \end{aligned} \tag{A17}$$

$$g_{jm}^{(2)} = 0 \quad \text{for } |m| \geq 3\,, \tag{A18}$$

where a_j are coefficients of zero-order solution, $a_j = 0$ for odd j.

When the constants C_{kn} has been derived, the following integral appears, which for potential energy given by Eq. (27) reads

$$\begin{aligned} \iint \mathscr{U}_1(\mathbf{e}\cdot\mathbf{e}_C)\,\frac{\partial\psi^{(0)}}{\partial\varrho_{|\varrho=1}}\, Y_0^0\, \overset{*}{Y}{}_k^n(\mathbf{e}\cdot\mathbf{e}_C)\, d^2\,\mathbf{e} = & \left[1-\exp\left(\frac{\delta f_g}{kT}\right)\right] \\ \times \sum_{i=1}^{2} \mathscr{U}_1^{(i)}\, \overset{*}{Y}{}_i^n(\mathbf{e}_C\cdot\mathbf{e}_U, \Phi)\, h_{kn}^{(i)}\,, & \end{aligned} \tag{A19}$$

where

$$\begin{aligned} h_{k0}^{(1)} = \Bigg[& \frac{k+1}{(2k+3)^{\frac{1}{2}}}(1+\beta_{k+1})\,a_{k+1} \\ & +\frac{k}{(2k-1)^{\frac{1}{2}}}(1+\beta_{k-1})\,a_{k-1}\Bigg]\frac{1}{(2k+1)^{\frac{1}{2}}} \end{aligned} \tag{A20}$$

$$\begin{aligned} h_{k,\pm 1}^{(1)} = -\Bigg[& \frac{1}{(2k+3)^{\frac{1}{2}}}(1+\beta_{k+1})\,a_{k+1} - \frac{1}{(2k-1)^{\frac{1}{2}}} \\ & \times(1+\beta_{k-1})\,a_{k-1}\Bigg]\left(\frac{k(k+1)}{2(2k+1)}\right)^{\frac{1}{2}} \end{aligned} \tag{A21}$$

$$h_{kn}^{(1)} = 0 \quad \text{for } |n| \geq 2 \tag{A22}$$

$$\begin{aligned} h_{k0}^{(2)} = \Bigg[& \frac{3(k+1)(k+2)}{2(2k+3)(2k+5)^{\frac{1}{2}}}(1+\beta_{k+2})\,a_{k+2} \\ & +\frac{k(k+1)(2k+1)^{\frac{1}{2}}}{(2k-1)(2k+3)}(1+\beta_k)\,a_k \\ & +\frac{3k(k-1)}{2(2k-1)(2k-3)^{\frac{1}{2}}}(1+\beta_{k-2})\,a_{k-2}\Bigg] \\ & \times\frac{1}{(2k+1)^{\frac{1}{2}}} \end{aligned} \tag{A23}$$

$$\begin{aligned} h_{k,\pm 1}^{(2)} = \Bigg[& -\frac{k+2}{(2k+3)(2k+5)^{\frac{1}{2}}}(1+\beta_{k+2})\,a_{k+2} \\ & +\frac{(2k+1)^{\frac{1}{2}}}{(2k-1)(2k+3)}(1+\beta_k)\,a_k \\ & +\frac{k-1}{(2k-1)(2k-3)^{\frac{1}{2}}}(1+\beta_{k-2})\,a_{k-2}\Bigg] \\ & \times\left(\frac{3k(k+1)}{2(2k+1)}\right)^{\frac{1}{2}} \end{aligned} \tag{A24}$$

$$\begin{aligned} h_{k2}^{(2)} = \Bigg[& \frac{1}{(2k+3)(2k+5)^{\frac{1}{2}}}(1+\beta_{k+2})\,a_{k+2} \\ & -\frac{2(2k+1)^{\frac{1}{2}}}{(2k-1)(2k+3)}(1+\beta_k)\,a_k \\ & +\frac{1}{(2k-1)(2k-3)^{\frac{1}{2}}}(1+\beta_{k-2})\,a_{k-2}\Bigg] \\ & \times\left(\frac{3(k-1)k(k+1)(k+2)}{8(2k+1)}\right)^{\frac{1}{2}} \end{aligned} \tag{A25}$$

$$h_{kn}^{(2)} = 0 \qquad \text{for } |n| \geq 3 \tag{A26}$$

a_k are coefficients of zero-order solution.

The factor A is

$$A^{-1} = \sum_{i=0}^{\infty} \frac{(4i+1)\,\kappa_{2i}^2(\varDelta\vartheta)}{1+(2i(2i+1)\mathscr{D})^{\frac{1}{2}}}\,, \tag{A27}$$

where

$$\kappa_{2i} = \frac{X_{2i,0}(\Delta\vartheta)}{(4i+1)X_{00}(\Delta\vartheta)} \qquad \text{(A28)}$$

$$X_{2i,0}(\Delta\vartheta) = 2\pi \int_{-1}^{1} Y_{2i}(\cos\vartheta)\,\chi(\vartheta)\,Y_0\,d(\cos\vartheta)\,. \qquad \text{(A29)}$$

κ_i $(\Delta\vartheta)$ can be computed using the following recurrent formula [6]

$$\kappa_0 = 1$$

$$\kappa_{2i} = \frac{(i-1)(2i-1)}{i(2i+1)}\kappa_{2(i-1)} + \frac{4i-1}{2i(2i+1)}(1+\cos\Delta\vartheta)\,P_{2i-1}(\cos\Delta\vartheta) \qquad \text{(A30)}$$

References

1. Solc K, Stockmayer WH (1971) J Chem Phys 54:2982
2. Solc K, Stockmayer WH (1973) Intern J Chem Kinetics 5:733
3. Schmitz KS, Schurr JM (1972) J Phys Chem 76:534
4. Schurr JM, Schmitz KS (1975) J Phys Chem 80:1934
5. Jarecki L (1991) Colloid Polym Sci 269:777
6. Jarecki L (1994) Colloid Polym Sci 272:784
7. Ziabicki A, Jarecki L (1994) J Chem Phys 101:2267
8. Kirkwood JG, Auer PL (1951) J Chem Phys 19:281
9. Doi M, Edwards SF (1986) In: Theory of polymer dynamics, Clarendon Press
10. Smoluchowki MW (1917) Z Physik Chem 29:129
11. Collins FC, Kimball GE (1949) J Colloid Sci 4:425
12. Ziabicki A, Jarecki L (1984) J Chem Phys 80:5751
13. Marand HL, Stein RS (1988) J Polym Sci (Phys) 26:1361
14. Sajkiewicz P, J Polym Sci (Phys) (1994) 32:313