On the elastic contribution to crystal growth in complex environments

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Based on a number of experimental studies, we propose to consider how elastic interactions between a crystal and its surroundings change crystal growing conditions. To aim to do this, we analyze the influence of some nonequilibrium modification of the Gibbs–Thomson thermodynamic condition, prescribed at the crystal boundary, on some properties of a kinetic model of protein crystal growth in a mass-convection regime. Next, to draw the physical picture more realistically, we study the influence of a certain stochastic perturbation on the crystal growth rate. To fulfill the task we apply the description of crystal growth in terms of nonequilibrium thermodynamics at a mesoscopic level. The proposed model offers a quite comprehensive picture of the formation of modern organic crystalline materials such as non-Kossel crystals.

1 Introduction

Elastic strains appearing in the region of contact of a surface of the growing crystal and its surroundings may significantly influence growing behavior [1]. This phenomenon can be important in case of macro-molecular (e.g. polymers, proteins) clusters and/or crystals, because of their, very often, complex spatial structure. Linear or folded chains [2] are very susceptible to deformations under the influence of even small external forces. Such strains cause the crystal surface to expand or shrink, deformations can be superficial as well as deep, ca. few lattice constants. Specifically, for some macromolecules it is possible to obtain some auxetic effects that may lead to untypical deformational behavior of growing objects [3, 4]. In particular, addition of the elastic contribution to the equilibrium Gibbs–Thomson boundary condition [5] extends its range of applicability [1, 6], changing effectively the crystal surface under growth. It also enables us to study e.g. the protein (non-Kossel[1]) crystal growth under a larger variety of supersaturation regimes [1, 7], mostly where one refers to the fact that the Gibbs–Thomson boundary regime describes appropriately crystal growth under small supersaturations [6]. As a consequence, adding the elastic contribution would mimic an increase or a decrease of the particle concentration at the crystal boundary. Such an addition, even if considered as a small perturbation to the equilibrium boundary condition, drives the system out of equilibrium, though close to it. Moreover, it offers a chance of introducing the nucleation mechanism, for example, in a way reminiscent of Burton–Cabrera–Frank defect-driven growth of crystals [8]. Thus, surface elastic phenomena may influence significantly the growing rate of the crystal. Additional forces emerging at the surface of the growing crystal mean that we can observe

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[1] As coined by Chernov [1], non-Kossel crystals are defined as complex structures with serveral molecules per unit cell in inequivalent positions.
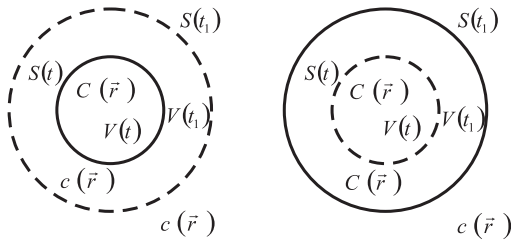
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Fig. 1 Two consecutive snapshots showing, in two instants t and $t_1 > t$, respectively (from left to right), the mass conservation effect.

competition between the elastic strain field and the surface tension. If the elastic contribution was constant with time, then we would have an equilibrium condition at the surface. In the case when the elastic contribution is not constant with time but is proportional to the relative edge length (1D case), surface area (2D case) or volume of the growing crystal (3D case), the growing conditions dramatically change with time, leading the system out of equilibrium. These changes relate not only to the growth rate but also to the free energy of the system and to the diffusion function of the growing objects, see Section 4 of this paper.

The main goal of this work is to show how the d-dimensional elastic contribution, where $d = 1, 2, 3$, influences the crystal growth conditions in a mass-convection regime [9, 10]. In Section 2, we state explicitly the mass conservation law in its most general as well as application – specific forms. This section is included mostly for recapping the working Eq. (2), without explaining the details which have been published elsewhere [9–11]. In Section 3, a deterministic view of the mass-convection driven crystal growth, with elastic constraints on the crystal boundary, is presented. In Section 4, an influence of a certain (application-rich) stochastic perturbation on the crystal growth rate, has been provided. Section 5 serves as the conclusion.

2 Mass conservation law

Consider growth of a spherical object by aggregation of particles from the external environment, see Fig. 1. (For possible limitations of the spherical approximation applied to growing phenomena in complex milieus, see [1], and refs. therein.)

The particles stick to the surface of the object in a location corresponding to the minimum energy configuration. The aggregated particles become a part of the object and migrate, in an electrostatic double layer, presumably of the Stern type [12], surrounding the object under growth. Let us assume that $C(\boldsymbol{r})$ is the nucleus density (we assume that the nucleus is homogeneous and its density $C(\boldsymbol{r}) = C = \text{const}$ [11]), $c(\boldsymbol{r})$ is the surrounding concentration field, $\boldsymbol{r}$ represents a particle position and S defines the surface of the object. At time t the object has the volume $V(t)$ (the surface $S = S(t)$) which increases to $V(t_1)$ (the surface $S = S(t_1)$) for time $t_1 > t$. The rate of change of the mass in the volume $V(t_1)$ equals the net mass flux through the surface $S(t_1)$: $\dfrac{\Delta m}{\Delta t} = \displaystyle\int_{S(t_1)} \boldsymbol{j}[c(\boldsymbol{r})] \cdot \mathrm{d}\boldsymbol{S}$, where

$\Delta m = m(t_1) - m(t)$, $\Delta t = t_1 - t$, $\boldsymbol{j}[c(\boldsymbol{r})]$ is the flux of particles which depends on $c(\boldsymbol{r})$, and $\mathrm{d}\boldsymbol{S}$ is an inward normal to the surface $S(t_1)$. We can write down the mass conservation law for the growing object [9, 10]:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int_{V(t)} [C(\boldsymbol{r}) - c(\boldsymbol{r})] \, \mathrm{d}V = \int_{S(t)} \boldsymbol{j}[c(\boldsymbol{r})] \cdot \mathrm{d}\boldsymbol{S} \,, \tag{1}$$

where the limit $\Delta t \to 0$ is taken, $\boldsymbol{j}[c(\boldsymbol{r})] = c(\boldsymbol{r}) \, \boldsymbol{v}(\boldsymbol{r})$ and $\boldsymbol{v}(\boldsymbol{r})$ is the incoming matter velocity vector field.

Let us make readily use of sphere symmetry [11]. Let us then assume that initially at $t = 0$ the growing object is an ideal sphere of radius R_0. At time $t > 0$ the radius of the growing sphere is equal to $R = R(t)$. Because of the symmetry, the evolution Eq. (1) considerably simplifies and takes the form:

$$[C - c_s(R)] \frac{\mathrm{d}R}{\mathrm{d}t} = c_s(R) \, v(R) \,, \tag{2}$$

where $c_s(R)$ is the surface concentration, and $v(R)$ is the incoming matter velocity, both taken at distance R from sphere center [9, 11]. Equation (2) will further be used both in deterministic, elastic-contribution free and elastic-contribution involved, as well as in stochastic contexts.

3   A simple deterministic view of mass-convection crystal growth

The concentration $c_s(R)$, prescribed at the boundary $S(t)$, was derived under the assumption of local thermodynamic equilibrium near the boundary. It has the form of the well-known linearized Gibbs–Thomson relation [5, 9, 10]:

$$c_s(R) = c_0(1 + \Gamma K_1) , \tag{3}$$

provided that Γ is the so-called Gibbs–Thomson or capillary constant, which is usually of the order of $10\ nm$ for lysozyme crystal [1]. Here $K_1 = 2/R$ is twice the mean curvature [11] and c_0 is an equilibrium concentration for the planar surface, practically for $R \gg R_0$. A plausible extension is to add a Gauss curvature term, $K_2 = 1/R^2$, which refers to possible variations of the (crystal) surface tension with local curvatures, such as those created by sparsely located molecular rows [1], cf. the so-called Tolman correction to surface tension [12, 13].

After putting Eq. (3) into Eq. (2) we get the following growth rule:

$$\frac{dR}{dt} = \sigma_R^{(\varepsilon=0)} v_{mi} , \tag{4}$$

where

$$\sigma_R^{(\varepsilon=0)} = \sigma \frac{R + 2\Gamma}{R - R_c} . \tag{5}$$

Here $\sigma = c_0/(C - c_0)$ and $R_c = 2\sigma\Gamma$ is a critical nucleus' radius. σ is an equivalent of the bulk supersaturation's[2] characteristic of the crystal growth, when the crystal is fed by diffusion, typically over long distances from the crystallization center [9, 11]. We must emphasize that $C - c_0$ is not a global driving force of the crystal growth, since C which is always bigger than c_0 is known to be inactive during the process. A chemical potential's difference between the external bath and the crystal is pointed out to be the main driving force. We have to notice formally that the growth occurs only when $R > R_c$. In our model we do not take the nucleation stage into consideration, so R is always bigger then R_c. Moreover R_c is of the order of 10^{-11} m and single lysozyme radius is of the order of 10^{-9} m. v_{mi} is now a parameter – it represents a characteristic Frenkel-type velocity of macroions arriving at crystal surface [9, 12]. In general, v_{mi} may change in the course of time t.

The solution of Eq. (4) can be written in an implicit form as [9]:

$$R - R_0 - (R_c - 2\Gamma) \ln \frac{R + 2\Gamma}{R_0 + 2\Gamma} = \sigma v_{mi} t , \tag{6}$$

which is, in general, a nonlinear solution. However, for mature stages of growth (large t-s) and under the given set of the idealized growing conditions just considered, from Eqs. (4) and (5) a simple asymptotic solution can be given, namely:

$$R \sim t , \tag{7}$$

which, in turn, leads to the conclusion that the growth rate, $V_{gr} = dR/dt$, must be constant in the long-time limit.

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[2] Except that the original Gibbs–Thomson condition suffers from its obvious limitations, that are curvature-dependent, see Eq. (3), it is hardly applicable to crystallization under high bulk supersaturation [1, 6, 7].

If the elastic contribution, denoted by y_μ, enters via the boundary condition, the Gibbs–Thomson relation (Eq. (3)) can be modified as [14, 15]:

$$c_s(R) = c_0(1 + \Gamma K_1 + y_\mu),\tag{8}$$

where y_μ is the positive or negative elastic term. To determine when the y_μ is positive or negative we have to consider how the proteins can attach to the surface of the growing crystal. Speaking in the most general terms a protein is a chain of the hydrophobic and hydrophilic aminoacids. Particles which are at the surface are typically exposed with their hydrophilic sides to the water-based solution. When the space between the incoming particle and the surface of the growing crystal is water-free (in practice: water-poor), the protein can make durable adhesive bonds with the crystal on the whole contact line. When the crystal is fed by the incoming biomolecular material, the surface becomes stretched. The distance between the bonding points increases and for the same reason the effective (working) surface increases too. This effect leads to an increase of the surface concentration, $c_s(R)$, thus $y_\mu > 0$. In the case when the incoming proteins become attached to the growing surface so that their hydrophilic parts are exposed to the crystal's surface, incoming water molecules would form a kind of bubble. Water pressure pushes out an unpinned part of the protein which is between the bonding points. This in turn results in a decrease of the distance between these points. This effect leads to a decrease of the surface concentration, $c_s(R)$, because the effective (working) surface area decreases, thus $y_\mu < 0$. This phenomenon is similar to the relaxation effect. Both scenarios are pH and salt concentration dependent, because the ionic strength of the solution influences the depth of the electrostatic double layer and the electrostatic interactions between particles in the solution [1, 7]. Moreover

$$y_\mu = \varepsilon_\mu \Delta y^{(\mu)},\tag{9}$$

where $\mu = 1, 2, 3$ specify different elastic-contribution influenced mechanisms in our model. Thus μ characterizes a spatial dimension-dependent nucleation, where the nucleation occurs at the crystal boundary. ε_μ, being positive, or in auxetic systems, negative, is a dimensionless and system-dependent elastic parameter. $\Delta y^{(\mu)}$ represents an elastic dimensionless displacement, coming, in general, from Hook's law. From our modeling this can be of: linear ($\mu = 1$), surfacional ($\mu = 2$) or volumetric ($\mu = 3$) character. The latter has already been proposed by Schmelzer & Gutzow [14, 15], but for an external diffusion field, feeding the crystal. The two first cases ($\mu = 1, 2$) are our proposal to model surface nucleation phenomena in the spirit of Burton–Cabrera–Frank type rationale [1, 6, 8], mostly in protein crystal growth [7, 16, 17]. Notice here that our relation (8), though taken for the surface concentration, is from a mathematical point of view of the same type as that adopted in [6], originally borrowed from [7], from the rate of step propagation during crystal growth. However, in all three cases, we propose to consider a mass-convection regime, where the mass-convection is modeled either in a deterministic (this section) or in a stochastic manner (next section). Typically a 2D nucleation mechanism, especially for biomolecular crystals, is considered most frequently [7, 16, 17], but specifically one may also expect more exceptional situations, such as a 1D nucleation by molecular rows, taking place on kinks [6], arising on the crystal boundary [18, 19], or a 3D nucleation [14, 15], in which the full possibility (3D interspace) is explored near the crystal surface by a penetrating (locally diffusive) external field [9]. We have to stipulate that $y_\mu > -\Gamma K_1$ because if $y_\mu < -\Gamma K_1$ it would be possible to get a negative surface concentration $c_s(R)$, i.e. an unphysical case. This constitutes the first (from below) limitation of y_μ. Moreover, note that addition of the elastic contribution, y_μ, also changes locally the chemical potential of the crystal [6]. Thus, it also changes the overall crystallization driving force [1, 6, 7].

Let us now assume in more detail that a tensional modification of the Gibbs–Thomson thermodynamic condition $c_s(R)$ can be considered in three cases, cf. Eq. (9) above.

First, let us add an elastic contribution y_μ proportional to the (relative) overall nucleus' edge (kink) length so that when the kinks in Burton–Cabrera–Frank mechanism dominate the surface development [1], $\mu = 1$ (1D case): $c_s(R) = c_0(1 + \Gamma K_1 + y_1)$, where $y_1 = \varepsilon_1 L_{\text{eff}}$; here $L_{\text{eff}} = \Delta y^{(1)} = (L - L_0)/L_0$, L and L_0 are the circumferences of the nucleus at time t and t_0 respectively, ε_1 is a constant, which de-

pends upon the elastic as well as the shear moduli of the crystal, see [1, 7, 15, 19] for many types of non-Kossel crystals. In the case of (ideal) spherical symmetry we can write that $y_1 = \varepsilon_1 (R - R_0)/R_0$.

Secondly, let us add the elastic contribution y_μ proportional to the (relative) overall nucleus' surface area. The most typical growing mechanism is the surface nucleation mechanism (2D case). In this case the elastic contribution can be related to Grinfeld instability [20]. If some atomic layers are not complete, they can expand or shrink. The atomic layers of the adsorbate can do so, since their lattice parameter thus approaches its natural value. Therefore we can expect them to split through a modulation of the surface. The free energy per unit area contains three contributions: (i) the capillary energy due to chemical bonds which are broken when forming the surface; (ii) the energy gained due to the relaxation in the undulating region which is proportional to the height of this region, to the average strain and to the external stress; (iii) the energy concentrated below the undulating region, with its density being proportional to the square average strain through an elastic constant. For this scenario: $c_s(R) = c_0 (1 + \Gamma K_1 + y_2)$, where $y_2 = \varepsilon_2 S_{\text{eff}}$; here $S_{\text{eff}} = \Delta y^{(2)} = (S - S_0)/S_0$, S and S_0 are the surface areas of the nucleus at time t and t_0, respectively; ε_2 – a constant, see above. Here we can also write that $y_2 = \varepsilon_2 (R^2 - R_0^2)/R_0^2$.

Finally, a full three dimensional mechanism (3D case) can be of interest [14, 15]. If the origin of the evolution of the elastic strains in crystal growth consists of the difference between the average volume per number of particles in the two phases, crystal and solution, then the total energy of elastic deformation can be characterized by the Young's modulus and Poisson's ratio of the matrix (the environment in which growth takes place) and the crystal. For this scenario: $c_s(R) = c_0 (1 + \Gamma K_1 + y_3)$, where $y_3 = \varepsilon_3 V_{\text{eff}}$ (ε_3 – a constant, see above; for *pret-a-porter* formula for ε_3, cf. relation (3.3) in [14]); here $V_{\text{eff}} = \Delta y^{(3)} = (V - V_0)/V_0$, V and V_0 is the volume of the nucleus at time t and t_0, respectively. As above, we can also write that $y_3 = \varepsilon_3 (R^3 - R_0^3)/R_0^3$.

For $\varepsilon_\mu \neq 0$ ($\mu = 1, 2, 3$), based on Eq. (4) and Eq. (8) one obtains σ_R on the right-hand side of (4) as follows:

$$\sigma_R^{(\varepsilon \neq 0)} = \sigma \frac{R + 2\Gamma + Ry_\mu}{R - R_c - \sigma Ry_\mu}. \tag{10}$$

Now, we have to notice that the growth occurs only when $R > R_c + \sigma Ry_\mu$, thus $y_\mu < \frac{1}{\sigma} - \frac{2\Gamma}{R}$. This constitutes a 2nd (from above) limitation of y_μ. Taking both limitations mentioned into account we finally state that $y_\mu \in \left(-\frac{2\Gamma}{R}, \frac{1}{\sigma} - \frac{2\Gamma}{R} \right)$. Thus, for readily mature growing stages, when $t \gg 1$ ($R \gg R_0$), $\frac{2\Gamma}{R}$ takes on very small values (no curvature dependence, practically), so that $y_\mu \in \left(0, \frac{1}{\sigma} \right)$. But $\frac{1}{\sigma} \equiv \frac{C - c_0}{c_0}$ is typically taken to be about 1000 in our modeling, which fits with the increase of the surface concentration $c_s(R)$, Eq. (8). However, it may still cause some problems with the announced negative entering the boundary condition by the elastic contribution, y_μ, possibly overriding the basic condition of non-negativity of the surface concentration. Thus, in this case, we have to apply the decrease of the surface concentration for immature stages of crystal growth instead. It suits, however, biomolecular crystallization because of the smaller linear sizes the crystals generally assume while growing [1, 7, 19].

We can also consider the case when the elastic contribution y_μ is small and assumed to be constant in time, $y_\mu \approx y_c = \text{const}$, as if it was almost d- and R-independent [11, 14, 15]. It is, in our opinion possible if: (i) because of some screening effects that do not favor the growth the system pits due to strong pining with the ambient phase close to a starting position, i.e. when $|R^\mu - R_0^\mu|$ does not change much, $0 < |R^\mu - R_0^\mu| \ll 1$; (ii) the system enters the readily mature growing stage, so that in practice $R^\mu - R_0^\mu \simeq R^\mu$, and $(R/R_0)^\mu$ remains unchanged to a sufficiently good accuracy. Otherwise, the approximate implicit solution (11) does not work, and a full analytical solution must be provided. The solution of Eq. (4), but now with $\sigma_R^{(\varepsilon \neq 0)}$ put in on the right-hand side of Eq. (4) and with $y_\mu \approx y_c$, is given by a
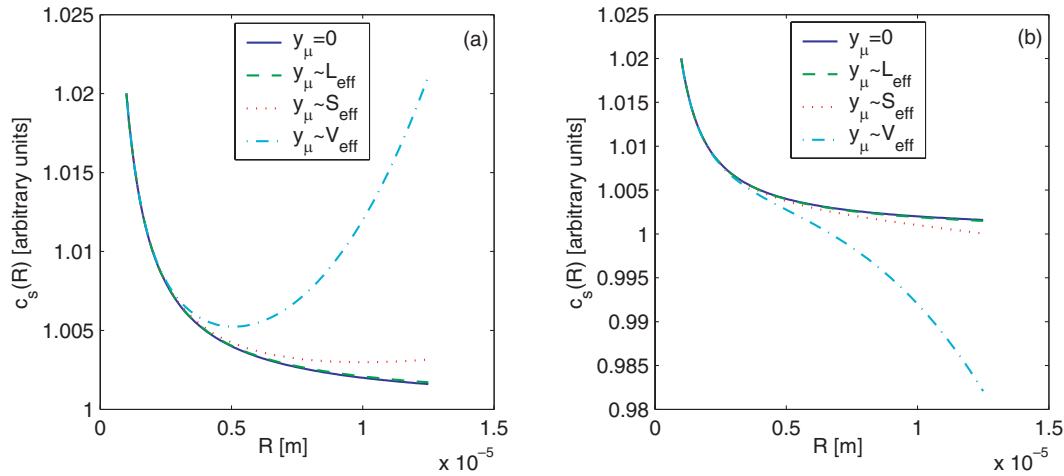
Fig. 2 (online colour at: www.pss-b.com) Surface concentration $c(R)$ vs. crystal radius R for 1D, 2D and 3D (a) positive and (b) negative elastic contributions marked by dashed lines, plotted on the basis of Eqs. (3) and (8) ($\varepsilon_\mu = 0.00001$, $c_0 = 1$ [arbitrary units], $\Gamma = 1 \times 10^{-8}$ m, $R_0 = 1 \times 10^{-6}$ m, $v_{mi} = 5 \times 10^{-5}$ m/s). The continuous line is drawn for the elastic free reference contribution, see inset. y_μ is limited and depends on μ, so it is impossible to plot reasonably all three cases ($\mu = 1, 2, 3$) on the one graph and this leads sometimes to unphysical situations, especially for positive elastic contribution, in particular when an increase of $c_s(R)$ at a corresponding R can be seen.

nonlinear implicit form:

$$(R - R_0)\,(1 + y_c)\,(1 - \sigma y_c) - (R_c - 2\Gamma)\ln \frac{R + 2\Gamma + R y_c}{R_0 + 2\Gamma + R_0 y_c} = \sigma v_{mi}(1 + y_c)^2 t \,, \qquad (11)$$

though the asymptotic solution is again linear, i.e. $R \sim t$, for $t \gg 1$, because the left-hand and the right-hand sides of Eq. (11), when compared to Eq. (6), are, except for a shifted argument in the logarithm, only multiplied by some constants. (Note, formally, that (11) becomes (6) for $y_c = 0$.)

Figure 2 shows surface concentration profiles for 1D, 2D and 3D with (a) positive and (b) negative elastic contributions. We can see that for $y_\mu = 0$ (no elastic contribution) surface concentration goes to a constant value. If $y_\mu \neq 0$ we have a nonequilibrium condition at the surface, where a departure from the equilibrium is measured directly by y_μ. We can observe competition between the curvature term ΓK_1 from Eq. (3) and the elastic part of the Gibbs–Thomson condition y_μ. For the 3D case we see that the elastic term starts predominating very early, especially when compared to the 1D and 2D cases.

Figure 3 shows growth based characteristics for 1D, 2D and 3D elastic contributions, respectively. We can see that for $y_\mu = 0$ (no elastic contribution) growth rate goes to a constant value (Eq. (7)), whereas for $y_\mu \neq 0$ it does not, i.e. it suffers from a monotonic departure from the constancy.

Taking into account that the asymptotic solutions of Eq. (6) and (11) are: $R \sim t$, we can expect that the growth rate, $V_{gr} = dR/dt$, as a function of time t, $V_{gr}(t)$, in long-time limit, will have the same characteristic as the one presented in Fig. 3.

If we consider the above mentioned limitations for y_μ, we can eventually expect that the elastic contribution will go to a constant value. The surface concentration, and in consequence, the growth rate will go to some constant value too. (We are of the opinion that from a technological point of view one would anticipate the constancy of crystal growth rate as an advantage.) Moreover, note a striking similarity of the curves presented in Figs. 2 and 3, witnessing the fact that the growth characteristics are markedly dominated by the (growing) surface profiles.

4 A stochastic view of mass-convection crystal growth

In order to study the influence of statistics of fluctuations [7, 16, 17] on kinetics of the growth process of biomolecular crystals, one has at least to specify Gaussian fluctuations $V_r(t)$ [10], i.e., their correlation
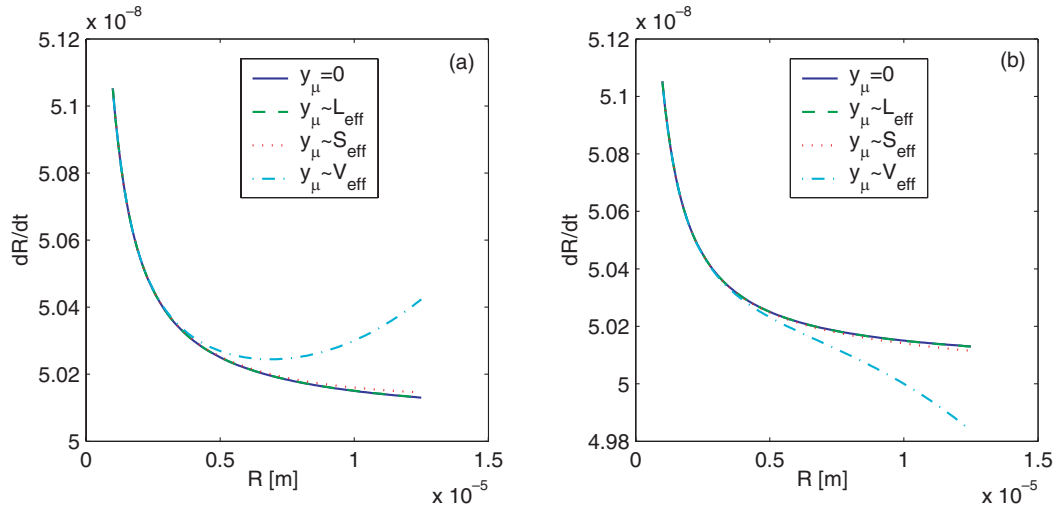
Fig. 3 (online colour at: www.pss-b.com)   Growth rate dR/dt vs. crystal radius R for 1D, 2D and 3D (a) positive and (b) negative elastic contributions marked by dashed lines, plotted on the basis of Eqs. (4), (5) and (10) ($\varepsilon_\mu = 0.00001$, $C = 1000$ [arbitrary units], $c_0 = 1$ [arbitrary units], $\Gamma = 1 \times 10^{-8}$ m, $R_0 = 1 \times 10^{-6}$ m, $v_{mi} = 5 \times 10^{-5}$ m/s). The continuous line is drawn for the elastic free reference contribution, see inset. y_μ is limited and depends on μ, so it is impossible to plot reasonably all three cases ($\mu = 1, 2, 3$) on the one graph and this leads sometimes to unphysical situations, cf. legend to Fig. 2.

function K. The nature and origin of fluctuations of different types is a core issue in biomolecular crystallization [6, 7, 16, 17, 19]. The simplest model assumes that fluctuations are uncorrelated, i.e. the correlation time is zero, but this idealization is never exactly realized, and therefore velocity fluctuations of the non-zero correlation time have to be considered.

A stochastic modification to Eq. (4) can simply be expressed as

$$\frac{dR}{dt} = V_r(t)\, \sigma_R^{(\varepsilon \neq 0)} , \qquad (12)$$

where $\langle V_r(t) \rangle = 0$ and $\langle V_r(t) V_r(s) \rangle = K(|t - s|)$ [10], meaning that the nonzero time-dependent correlations K within the macroion velocity field are assumed [9, 10]. In [10] one may find an extensive theoretical survey of some important K functions, and their impact on the growth rate. Equation (12) is related to its generalized Fokker–Planck partial differential equation [10] with corresponding initial and boundary conditions (IBC-s) [21, 22]:

$$\frac{\partial P(R,t)}{\partial t} = \frac{\partial}{\partial R}\left(\frac{D(R,t)}{k_B T} \frac{\partial \Phi}{\partial R} P(R,t) + D(R,t)\frac{\partial P(R,t)}{\partial R} \right), \qquad (13)$$

where the energy (sometimes referred to as the entropic potential [22])

$$\Phi = k_B T \ln [\sigma_R^{(\varepsilon \neq 0)}] , \qquad (14)$$

and the overall diffusion function

$$D(R,t) = D(t)\,[\sigma_R^{(\varepsilon \neq 0)}]^2 , \qquad (15)$$

while $D(t)$ comes from the correlations K above as $D(t) = \int_0^t K(s)\,ds$ after applying the fluctuation-

dissipation theorem [22]. As is expected, $P(R, t)$ stands for a probability density of finding a crystal of radius R at time t. Let us formally note that the matter flux

$$J(R, t) = -\left(\frac{D(R, t)}{k_B T} \frac{\partial \Phi}{\partial R} P(R, t) + D(R, t) \frac{\partial P(R, t)}{\partial R} \right), \tag{16}$$

for a given temperature T is explicitly crystal radius R, and time t, dependent. For it, the left boundary condition is of reflective type, $J(R_0, t) = 0$. Another condition for $P(R_0)$ is given by the delta Dirac function, see [10]. It matches exactly the requirement for the boundary condition demanded by nonequilibrium thermodynamics at the mesoscopic level [22]. Thus the IBC-s are well prescribed. An explicit time dependence of $D(R, t)$ reveals the process to be non-Markovian [10, 21]. Moreover, bear in mind that the free energy Φ assumes a classical Boltzmann' form, i.e. it is supposed to be of exclusively entropic character; as was mentioned such an entropic character comes from the competition of curvature-driven surface tension as well as elastic effects within the growing layer [7]. As an example of the contribution of the mentioned before auxetic effect(s) one could invoke here the so-called stretch-densified crystals [23]. It is the situation that a biomolecule, or a 'coherent' group of them, is at a given time instant t electrostatically pinned to the crystal surface. At a subsequent time instant $t_1 > t$ a growing event may accidentally occur, thus stretching the 'entropy connector' [2], so that it causes a drop in the density of the crystal material locally; otherwise, a non-auxetic (or typical) growing event occurs, and the overall event (assumed always as being realized with a possible structural rearrangement thereafter) will contribute to a positivity of the Poisson's coefficient value, cf. [23].

The obtained equation, Eq. (13), offers a description of crystal growth in terms of nonequilibrium thermodynamics at a mesoscopic level [22, 24]. It opens up some new possibilities in understanding the phenomenon under study. First, the process is described as a two-state process, in which its two neighboring physical states are separated by an energetic barrier, Φ, which is a surmountable barrier for the matter flux $J(R, t)$. We now know that this barrier depends in a logarithmic fashion on $\sigma_R^{(\varepsilon \neq 0)}$, given by Eq. (10), similarly to the one given in [22] for complex matter agglomerations, such as polycrystals or bubbles. It is depicted, as a dependence of $\Phi(R)$, in Fig. 4. From it, we may see that the energy barrier is different for different types of mechanisms involved. We also see that it is lower when the negative contribution enters the generalized boundary condition, Eq. (8). Thus, the auxetic-type effect [3, 4] arising at the crystal boundary may play a beneficial role here.
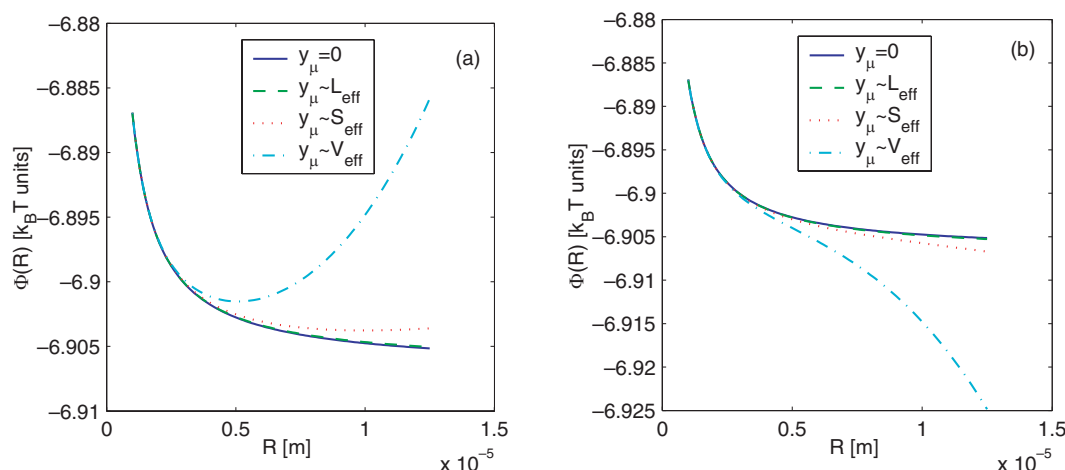

Fig. 4 (online colour at: www.pss-b.com)   Free energy vs. crystal radius for 1D, 2D and 3D (a) positive and (b) negative elastic contributions marked by dashed lines, plotted on the basis of Eqs. (14) and (10) ($\varepsilon_\mu = 0.00001$, $C = 1000$ [arbitrary units], $c_0 = 1$ [arbitrary units], $\Gamma = 1 \times 10^{-8}$ m, $R_0 = 1 \times 10^{-6}$ m, $v_{mi} = 5 \times 10^{-5}$ m/s). The continuous line is drawn for the elastic free reference contribution, see inset. y_μ is limited and depends on μ, so it is impossible to plot reasonably all three cases ($\mu = 1, 2, 3$) on the one graph and this leads sometimes to unphysical situations, cf. legend to Fig. 2.

Then, we are able to describe the process in a more realistic way, based on experimentally observed [16, 17] correlations $K(|t - s|)$. It is feasible to derive, relying either on a theoretical model or simulation, or at best on an experiment [7], the diffusion function, given by a Green–Kubo [5, 22, 24] type formula.

There is a quite substantial lack in the literature of biomolecular crystal growth that concerns a determination of the velocities of macroions near the crystal surface [18, 19]. However, there exists a large amount of experimental data, that indicates a constant growth rate, V_{gr}, of the crystal, cf. Eq. (7), as the case expressing a most favorable (toward steadiness) tendency for the process to go on, mostly when $t \gg 1$ is fulfilled [1, 19]. Therefore, our choice of the velocity correlation field must be a power-law correlation, because it is the only possibility in the proposal offered in [10], which reproduces well the asymptotic solution, Eq. (7). In [10] such a correlation is offered in an explicit form. It leads, after making use of the fluctuation-dissipation theorem (Green–Kubo formula), to [10]:

$$D(t) = \frac{A\tau_c}{1-\gamma}\left[\left(1 + \frac{t}{\tau_c}\right)^{1-\gamma} - 1\right],$$ (17)

where τ_c is the correlation time of the velocity fluctuations (we take $\tau_c = 1$ [10]), and A is a positive constant (for simplicity we take $A = 1$).

To be in the "realm of action" of Eq. (7) (constant speed for the crystal growth), we have to put in an additional requirement, that is $0 < \gamma \ll 1$, see Eq. (71) in [10]. This means that the correlation exponent, γ, must be not only from $(0, 1)$, but at best possibly close to 0. This way we postulate that the velocity correlations decrease in time in a power-law fashion (see Eq. (17) and apply the Green–Kubo formula), but also they have to go extremely slowly in time. $D(t)$ must now go almost linearly in time, especially when $t \gg 1$, cf. Eq. (17). This view is consistent with an observation that crystallization of biomolecular objects typically goes relatively slowly in time [1, 7, 18, 19]. Moreover, notice that both $R = R(t)$ and $D = D(t)$ go almost linearly in this correlational regime, see Eqs. (7) and (17). Thus, we may argue, that in some cases discussed by this paper, such a (correlated) slowing down of the process can be due to the elastic contribution [1, 6, 14, 15], i.e. when $\varepsilon_\mu \neq 0$. Such a physically-motivated picture may contribute to a more realistic description of the growing phenomenon in complex environments, mostly, when biomolecules get crystallized.

Figure 5 shows the time evolution of the diffusion function $D(R, t)$ vs. crystal radius with positive elastic contribution $y_\mu > 0$. We can see that for $\gamma = 0.9$ the diffusion coefficient D starts to evolve from a certain different value than for $\gamma = 0.1$ and increases more slowly in time. In the case when elastic contribution $y_\mu < 0$, Fig. 6, we can see that for $\gamma = 0.9$ the diffusion coefficient decreases more slowly in time than for $\gamma = 0.1$. In the latter, we see a natural way of making the surmountable barrier smaller, i.e., accessible for the matter flux $J(R, t)$. Thus the elastic contribution may distinctly help in facilitating the (protein) crystal growth.

5 Conclusions

In the present study, we have confirmed that growth significantly depends on the elastic contribution proposed to be active at the crystal boundary [1, 6, 7, 14, 15, 19, 20]. It also visibly depends upon the temporal velocity correlations near the interface [9, 10].

In particular, we have found that:

– Addition of the elastic contribution apparently mimics either an increase or a decrease of the magnitude of the molecular concentration at the boundary. In comparison with the elastic-contribution free case, it either facilitates or impedes the process, respectively (Figs. 2 and 3).

– The deterministic view is as incomplete. A first thought modification toward physical reality is to propose multiplicative fluctuations, $V_r(t)$, expecting the time correlations within the velocity field, near the interface, to occur. (Full space-time correlations are still a challenge here.)
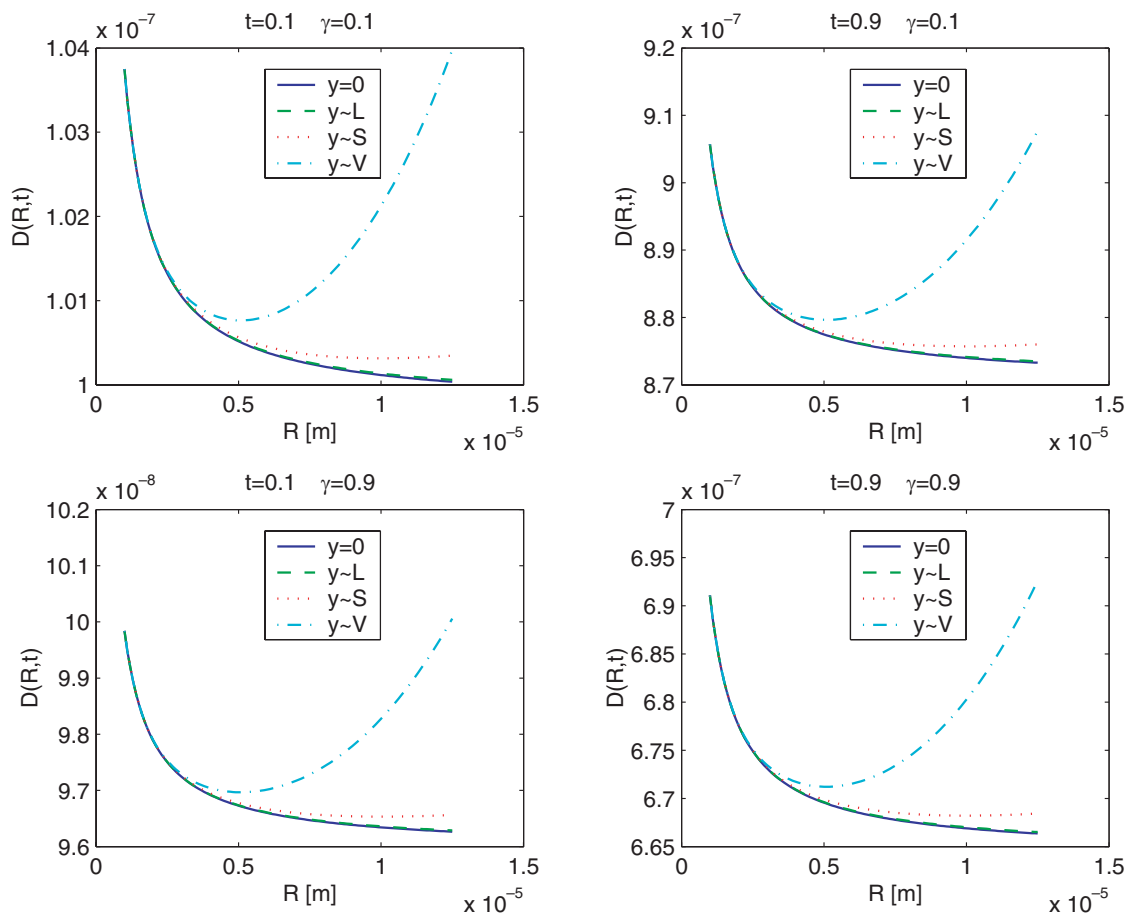
Fig. 5 (online colour at: www.pss-b.com)   Time evolution of a diffusion function vs. crystal radius for $\gamma = 0.1$ and $\gamma = 0.9$ for $t = 0.1, 0.9$ with positive elastic contribution, plotted on the basis of Eqs. (17), (15) and (10) ($C = 1000$ [arbitrary units], $c_0 = 1$ [arbitrary units], $\Gamma = 1 \times 10^{-8}$ m, $R_0 = 1 \times 10^{-6}$ m, $v_{\mathrm{mi}} = 5 \times 10^{-5}$ m/s, $\tau_c = 1$). The values of $\gamma = 0.1$ or $\gamma = 0.9$ do not formally obey the requirement of $0 < \gamma \ll 1$ (see text) but are taken as such exclusively for visualization purposes; see legend to Fig. 6 too. The inset marks the type of the surface nucleation mechanism involved, see text. y_μ is limited and depends on μ, so it is impossible to plot reasonably all three cases ($\mu = 1, 2, 3$) on the one graph and this leads sometimes to unphysical situations, cf. legend to Fig. 2.

– The above observation leads to a quite comprehensive[3] nonequilibrium thermodynamics view [25], well established on the mesoscopic (crystal magnitude) level [21, 24]. This view leads to: (i) unambiguous determination of the free energy (Boltzmann) form, Φ, as logarithm of $\sigma_R^{(\varepsilon \neq 0)}$, first involved in the deterministic growth rate equation, cf. Eqs. (4), (5) and (10); (ii) clear factorization of the diffusion function $D(R, t)$ into a product $D(t)\,[\sigma_R^{(\varepsilon \neq 0)}]^2$ which may help in deeper, mostly analytic, exploration of the problem. To some extent, this may contribute to the full space-time correlation problem, where the space distances are measured in terms of the crystal radii, R-s (Fig. 4). While analyzing the behavior presented in Figs. 1 and 6, one may anticipate some characteristic "turning points" viz deflection regions of R from which $y_\mu \neq 0$ starts dominating over the case of $y_\mu = 0$, containing the curvature term without the elastic contribution, cf. Eq. (3). Note, however, that one has to be careful because of the limitations of the proposed approach and unphysical effects that may emerge when the parametric window is not chosen

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[3] We use the term 'quite comprehensive' since we are aware of certain limitations of the Gibbs–Boltzmann–Onsager nonequilibrium thermodynamics [5, 22, 24, 25], mostly those concerning the usage of the Green–Kubo formula, with a possible entrance to some chaotic regime [26].
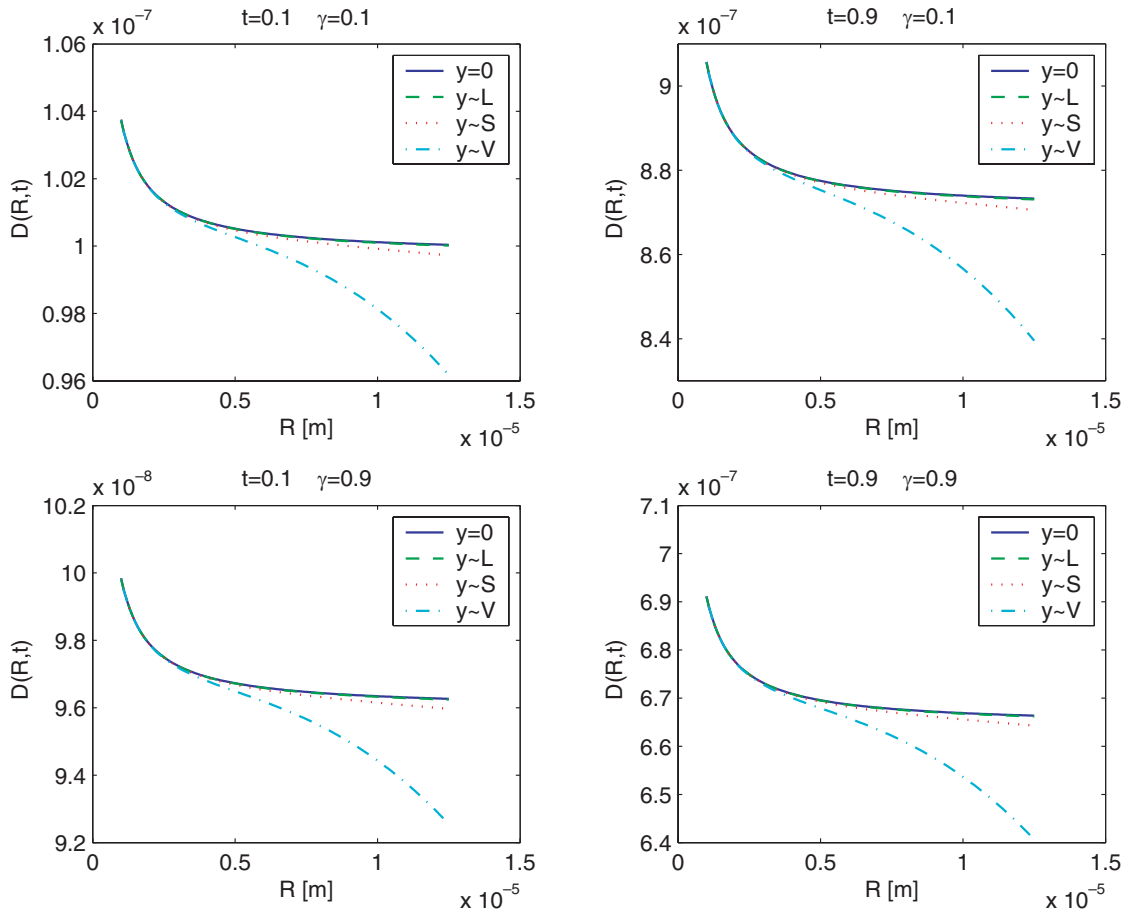
Fig. 6 (online colour at: www.pss-b.com)   Time evolution of a diffusion function vs crystal radius for $\gamma = 0.1$ and $\gamma = 0.9$ for $t = 0.1, 0.9$ with negative elastic contribution, plotted on the basis of Eqs. (17), (15) and (10) ($C = 1000$ [arbitrary units], $c_0 = 1$ [arbitrary units], $\Gamma = 1 \times 10^{-8}$ m, $R_0 = 1 \times 10^{-6}$ m, $v_{mi} = 5 \times 10^{-5}$ m/s, $\tau_c = 1$). The inset marks the type of the surface nucleation mechanism involved, see text.

appropriately, cf. legends to the figures presented. The formalism of mesoscopic nonequilibrium thermodynamics shows how to couple effectively the main crystal-boundary and external field effects together in a proper working manner, see Figs. 5 and 6.

– $D(t)$ is a signature of time correlations involved in the crystal growth; $\sigma_R^{(\varepsilon \neq 0)}$ represents the elastic contribution, as well as the surface tension's fingerprint. From the applicational viewpoint $D(t)$ of a power-law viz superdiffusive type with a characteristic exponent γ [10] is of interest (Figs. 5–6).

– The elastic contribution can be proposed as being either 'additive' (+), i.e. related to an elastic expansion of biomolecules, or 'subtractive' (–) viz related to an elastic contraction of biomolecules, i.e. leading to the generalized Gibbs–Thomson boundary condition applied throughout this study, Eq. (8). This means different behaviors, as if they were in auxetics or other "percolative" (composite, foams) materials, because our ε_μ, being in fact elastic-mechanism dependent (the Poisson ratio involving [3]), can as in auxetics [23], eventually take on either positive or negative values, thus causing the adequate changes in surface concentration, cf. stretch-densified crystal or some smectic liquid crystals [2, 23].

– To sum up, the overall (bio)molecular crystal growth picture that emerges from our modeling is as follows. Due to nonlinear damping with time, the biomolecule velocity, $v_{mi} = v_{mi}(t)$, such that for $K(0) = \langle V_r(t) V_r(s) \rangle|_{t=s} \simeq v_{mi}^2(t)$. According to our assumption about K (for $t \gg 1$) one infers $v_{mi}^2(t) \propto t^{-\vartheta}$, where the external matrix parameter, ϑ, is linearly related to γ in our model. Near the crystal surface one

encounters such damping presumably due to the elastic constraints, which can either strengthen or weaken the general curvature-dependent conditions of Gibbs–Thomson type, see preceding sections. A final, and quite comprehensive picture, which arises from our modeling could be formulated as follows: When an experimentalist tries to optimize the process toward having it kept with a constant rate, Eq. (7), he has to allow that: (i) the entropic, Boltzmann-like, potential Φ (Eq. (14)) will drive the system; (ii) the molecules that do feed eventually the growing object are going to perform a superdiffusional motion in interface's region, Eq. (17), so that one is placed in the realm of the so-called anomalous, fractal-like or dispersive, kinetics [27], in which any existence of a characteristic time scale is prohibited. The overall diffusion function, Eq. (15), which naturally decreases in the course of the process, completes the mesoscopic nonequilibrium thermodynamics picture drawn [10, 22, 24, 25].

– Last but not least, let us state that our model can be seen as an alternative theoretical view of the non-Kossel crystal growth, offered here in terms of elasticity and stochastic character of the surrounding nearby field, feeding the crystal. While the former proposal seems to be a not entirely new conceptual challenge [14, 15], because the screw dislocation-driven growth is described by the well known Burton–Cabrera–Frank model [8, 20], the latter looks promising, since it contributes to a quite comprehensive crystal growth picture by elucidating certain fluctuation effects coming mostly from experiment [7, 10 16, 17]. These are now seen not as an intrinsic feature, attributed to the growth layer dynamics [7], but they are understood in terms of stochastic dynamics of the interface between the crystal surface and a nearby contacting milieu, characteristic of a well-described fluctuating velocity field [9, 10].

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