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A Kinetic Model of Protein Crystal Growth in Mass Convection Regime

Based on experimentally motivated assumptions, a new kinetic model of protein crystallization by mass-convection than by bulk diffusion is proposed. It is assumed that the charged-mass conservation law is being fulfilled, and that the attractive potential is of (screened) electrostatic nature. The role of the double-layer surrounding the crystal under growth is indicated, and the thermodynamic conditions responsible for the association of protein macroions to a growing and charged nucleus are specified. Moreover, by replacing the dielectric constant of the solution by the dielectric constant of the solvent (water) times a Debye-Hückel exponential term, it is possible to take into account the influence of water on the behavior of the system, potentially with hydrophobic effects involved. The study is, in fact, based on a combined concept in which the Burton-Cabrera-Frank and Mullins-Sekerka-Langer-Chernov mechanisms supplement each other. The role of fluctuations in the studied process is also examined.

Keywords: protein crystals, mass-convection, electrolytes, growth kinetics, double-layer

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1. Introduction

Biological molecules dissolved under suitable processing conditions in aqueous solutions are capable of constituting crystals. There exist many experimental and some theoretical studies devoted to the crystal growth of large molecule crystals. This problem is of special interest because, if one were able to control the basic factors influencing the kinetics, one would clearly prefer to design properly structural arrangements arising during growth (cf. CHERNOV 1997, and references therein). These, in turn, are very necessary to continue the general task, undertaken nowadays by crystallographers, to reveal many new molecular structures, mostly by *X*-ray diffraction (for details see DRENTH 1999).

The aim of this paper is to outline some basic features of a simple kinetic model designed to capture the main points that must be taken into consideration while describing the growth process in complex polyelectrolytes. The notion involving such really complex kinetic circumstances can be termed as ionic association phenomenon in weakly nonideal classical plasma (BALESCU 1975) for which subsequent sub-notions of Debye-Hückel potential (Poisson electrostatic equation) as well as Bjerrum specific length are of use (SAFRAN 1999). Specifically, we offer an alternative model to those reviewed by CHERNOV (1997), in particular by: (i) formulating a deterministic (kinetic) model with linear radius versus time dependence and with short time logarithmic departure from linearity; (ii) presenting a novel phenomenological derivation for the speed of a protein in the double-layer, the role of which cannot be underestimated in modeling growth; (iii) sketching a linear instability analysis slightly different from that of Mullins-Sekerka approach (MULLINS, SEKERKA 1963), which

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yields similar and physically valuable results; (iv) introducing a reasonable as well as possibly simple stochastic perturbation of the protein speed, due to e.g. thermal agitation and possible overproduction of hydrogen bonds under physical circumstances met in the double-layer.

The structure of the paper is as follows. First, we make use of charged-mass conservation law and propose a simplified equation for crystalline evolution that, for the sake of clarity, will be presented for an ideal sphere immersed in a water-based electrolyte. Then, the physical meaning of the quantities involved in the principal but simplified equation is briefly explained. Next, we discuss an important limiting kinetic factor associated with the speed of an individual (charged) protein molecule trying to join electrostatically some oppositely charged part(s) of the surface of the growing crystal while wandering at random along the surface and being "trapped" by the electrostatic double-layer, surrounding the growing object. Finally, a linear (small) departure from the spherical ideality, cf. the perennially alive linear instability analysis (MULLINS, SEKERKA 1963), is discussed. We also introduce a simple stochastic perturbation of the deterministic rate of the protein crystal growth, just by reconsidering some results reported earlier (GADOMSKI, LUCZKA 1993). The present study seems to be quite novel from the conceptual viewpoint, but mathematical details need not be repeated here. Consequently some important steps towards presenting our model will be emphasized whereas certain remaining will be quoted just for the sake of brevity, since they have been published elsewhere.

2. The Model

For simplicity, consider a spherical nucleus of density C, immersed in an electrolyte consisting typically of H_2O dipoles, protein molecules (e.g. lysozyme, one of the most studied biomolecules), and some precipitants like Na^+ and Cl^- ions. Let us assume that under given thermodynamic conditions (pH, temperature T, etc.) the nucleus can be characterized by its surface charge density s_n and that the net charge of the protein molecule is designated by Q_P. Let us further assume that the solution can be characterized by its dielectric constant e. After the induction (incubation) period, the nucleus starts to grow by incorporating protein molecules. This serves as an evidence that:

(i) the charged-mass conservation law must be readily fulfilled (LANGER 1980; CHERNOV 1984);

(ii) there should be a mechanism that is responsible for the incorporation of the molecules.

The growth mechanism is as follows. On a non-local scale it is purely of electrostatic nature, and is associated with attracting charged protein molecules to the crystal surface with a constant electrostatic force F_e to the spots that are oppositely charged. This is so because mostly the bigger and quite movable Cl^- ions do change the balance of charges at the crystal surface, and participate in the screening effect on it. It should be noted that, in practice, it would be sufficient to pick up a protein molecule at a distance longer than the double-layer width. Moreover, the sign of the charge of protein molecules depends on pH value; but for lysozyme molecules for example, for typical crystallization conditions $pH \approx 4.5$, they are positively charged. Some attraction of small charged molecular aggregates, like dimers or trimers, is also not excluded during the above process. The smaller and slowly moving Na^+ ions "stay apart", and do not influence much the overall electrostatic behavior (DRENTH, HAAS 1998). On a local scale, in the double-layer surrounding the crystal (ADAMSON 1963), some interesting things happen. For example, within that 'electrostatic realm', characterized by the equilibrium concentration $2 \times c_0$ (Fig. 1), we observe a competition between surface diffusion characterized by the (Arrhenius) diffusion time t_D and electrostatic association

process well described by the Debye-Hückel scenario as well as a Bjerrum-like characteristic length L_B (SAFRAN 1999; BALESCU 1975). Thus, the growth rate is limited by a prefactor v_i, which can be represented by the ratio of L_B and t_D, respectively.

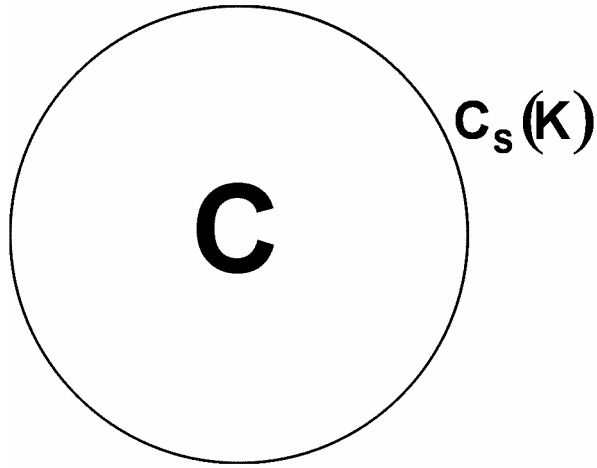

Fig. 1: Two-dimensional cross section of the sphere of the density C, surrounded by a (mono)layer, not depicted here, of the solution concentration. $c_s = c_s(K)$. See text for details.

Taking the above ideas into account and referring to our earlier works (GADOMSKI et al. 1993; GADOMSKI, LUCZKA 1993) for the details of the derivations, one can propose the following equation for the evolution of the sphere of radius R in the electrolyte:

$$\frac{dR}{dt} = v_i \times \frac{s\,R + R_c}{R - R_c}, \tag{1}$$

where $R \equiv R(t)$ (t is the time), $s = c_0/(C - c_0)$ is termed a dimensionless supersaturation parameter, and $R_c = 2\Gamma s$ stands for the critical nucleus radius; for $s = 0$, one expects $dR/dt = 0$, because the right-hand side of (1) is equal to $s \times v_i(R + 2\ \Gamma)/(R - R_c)$. Here Γ is the so-called Gibbs-Thomson or capillary constant, which is usually of the order of 10 nm for lysozyme crystals; e.g. for smectics A one can have $\Gamma \approx 100$ nm. This parameter reflects, roughly speaking, a depth associated with the action (influence) of surface tension, and the surface tension, in turn, is known as a thermodynamic quantity causing the crystal surface to be smooth.

We summarize here the main points of the derivation of Eq. (1). First, we take the mass of the growing object in two consecutive time steps, t and t_1, where $t_1 > t$, expressed via the corresponding densities of the object and of the surrounding field, respectively. Second, we take the difference between the masses, Δm, and construct the quotient $\Delta m/\Delta t$, where $\Delta t = t_1 - t$. Then we go into the limit $\Delta t \to 0$, or $t \to t_1$. Further, we make use of the observation that $\Delta m/\Delta t = \mathbf{J}$, where $\mathbf{J}$ is the global flux taken at the object surface. The above procedure is called here the mass conservation law. Then, we make use of the (spherical) symmetry of the object under growth, assume its density to be constant, utilize the Gibbs-Thomson thermodynamic and curvature-dependent internal boundary condition

(see below), and apply the formula for the convective flux, which on a local level reads $\mathbf{j}(r) = \mathbf{v}(r)c(r)$, where $\mathbf{v}(r)$ is a position (r) dependent velocity and $c(r)$ represents the concentration at the vicinity of the surface. Following the above procedure, one arrives at Eq. (1) (GADOMSKI et al. 1993). Clearly, growth proceeds when $R > R_c$ for any t value, when $R(t=0) > R_c$ holds, i.e. there cannot be any singularity at $R = R_c$; cf. Eq. (1). Usually, $s << 1$, which means that we are dealing with dilute solutions. However, according to our standpoint, this dilution is mostly manifested in the double-layer or, equivalently, in the very vicinity of the crystal. This condition is compensated by the fact that typically $v_i >> dR/dt$, which seems to be natural, for large t, because the crystal grows much slower than an individual protein molecule (macroion) can move!

3. Results and discussion

The solution of Eq. (1) can be written implicitly as

$$R - R_0 - (R_c + 2\Gamma)\ln\frac{R + 2\Gamma}{R_0 + 2\Gamma} = s\, v_i t\,, \tag{2}$$

which is, in general, a nonlinear solution. In Eq. (2) R and R_0 are the crystal radii at time t and $t = 0$, respectively. However, for mature stages of growth (large t) and under the given set of growth conditions, a simple asymptotic solution can be given, namely

$$R \propto t\,, \tag{3}$$

which, in turn, leads to the conclusion that the growth rate V_{gr} is constant, (i.e. $V_{gr} = dR/dt \to \text{const}$) for the time interval mentioned. This conclusion has been confirmed by experimental studies (KAM et al. 1978; PUSEY et al. 1986; CHERNOV 1997), mostly applied to lysozyme. This kind of physical scenario also suits crystal growth from lysozyme-water solutions, as presented in the literature (CHERNOV 1997). It should be noted that kinetic relation (3) characterizes equally well polymeric spherulites (GADOMSKI, LUCZKA 1993).

As seen from Eq. (2), the main rate-limiting factor appears to be the product of $s \times v_i$. Let us look a bit at s. This quantity is much better defined for diffusion-controlled systems, and it reads: $s_D = (c_\infty - c_0)/(C - c_0)$ (LANGER 1980, CHERNOV 1984), where c_∞ represents the (diffusive) bulk concentration. Note that we have in our model a certain equivalent of supersaturation not well comparable to most of the studies referred to (CHERNOV 1997). It is based on the relative difference between some inner crystal mass characteristics, i.e. its density C as well as the equilibrium solution concentration c_0 at the crystal vicinity. Truly speaking, they both are kinetically passive, and thus s is not related with driving force. On the contrary, s_D is related with the driving force by means of a concentration difference $c_\infty - c_0$, where c_∞ is kinetically active throughout the diffusion-controlled process. Such a reasoning can, *mutatis mutandis*, be applied to the definition of R_c, though for a diffusion-controlled process it also depends upon the way in which the spherical ideality is perturbed.

Thus a spherical harmonics index of the perturbing function appears additionally (MULLINS, SEKERKA 1963). In our case, one simply notes that $s_D = s$ when

$$c_\infty = 2 \times c_0 , \tag{4}$$

which can be interpreted as the first signature of the double-layer, and its quite firm presence in our model, recalling that condition $s << 1$ holds in the double-layer.

Let us now inspect more closely the second rate-limiting factor, namely v_i, which is, within the realm of our approximation, a time-independent quantity. From elementary electrostatics (HALLIDAY, RESNICK 1962), utilizing the Gauss (1st Maxwell) law for a charged conductor, we know that the attractive force F_e (see above) may be given by

$$F_e = \frac{s_n \times Q_P}{e_0 e} , \tag{5}$$

where s_n is the surface charge, Q_P is the net charge of the protein molecule, e_0 is the dielectric constant of the vacuum and e is the dielectric constant of solution. Within the validity of overdamped regime approximation, the speed v_i may be expressed as

$$v_i = F_e / g , \tag{6}$$

where g (here $g >> 1$) denotes a damping constant closely related to the viscosity h of the solution in the "static" monolayer adjacent to the crystal surface. The relation between g and h may be given by

$$g = 2 \ r_P \times h , \tag{7}$$

where r_P is the protein radius. Here it was assumed that the adjacent monolayer is at least of the order of the diameter of the protein molecule. Note again an implicit notification of the double-layer because the diameter of lysozyme is of the order of 3 nm.

Applying the Einstein-Smoluchowski relation (ROZENFELD et al. 1998), using the definition of surface charge density $s_n = Q_n / S_n$ (where S_n stands for the crystal area $\approx L_D^2$; L_D is the linear dimension of the growing surface) as well as reasonably postulating a (surface) diffusional natural scaling like

$$t_D = d_0 \times L_D^2 , \tag{8}$$

with a characteristic surface diffusion time denoted by t_D, one obtains

$$v_i = L_B / t_A , \tag{9}$$

where L_B and t_A will be specified below. Here it is assumed that $e = e_{H_2O} \times \exp(-2k r_P)$ where k is the inverse Debye length, i.e. the length on which an incident electrostatic field

decreases by $1/e$, where $e \approx 2.71$ (the Napier constant). This means that the dielectric "constant" e, characterizing the solution ("structured" water), can be expressed by the solvent (pure or "unstructured" water) dielectric constant and the well-known Debye-Hückel exponential term. However, in general, one may also use the Kirkwood approximation for e taking into account the hydrophobic effect clearly present in the electrolyte.

From the above it turns out that the Bjerrum-like length $\mathrm{L}_B = Q_n Q_P / e_0 e_{\mathrm{H_2O}} k_B T$, which means that a characteristic charge and a temperature dependent length characterizing the solvent, has to be identified while studying the problem. Formula (9) is derived under the condition that $d_0 \times D_0 = (3p)^{-1}$ because the Einstein-Smoluchowski formula $D = k_B T / 6ph r_P$ is valid for spherically symmetric objects for any diffusion coefficient D expressed by: $D = D_0 \times \exp(-E_A b)$ (cf. SKULSKI 1999), where E_A represents the activation energy for the surface diffusion process and $b = 1/k_B T$ is the inverse thermal energy (k_B is the Boltzmann constant). Formula (9) looks like the well-known Frenkel formula for the mean velocity of a molecule immersed in a fluid, though its derivation is quite different; cf. scaling relation (8) as well as the application of the above mentioned structured water concept.

To complete this phenomenological derivation we finally express L_B and t_A as follows (see Eq. (9)):

$$L_B = \mathrm{L}_B \times \exp(-2k r_P), \tag{10}$$

and

$$t_A = t_D \times \exp(E_A b), \tag{11}$$

which implies that an Arrhenius-type formula (11) has been obtained, though some extensions, due to the so-called Vogel-Fulcher-Tammann behavior in complex fluids cannot be excluded a priori (SKULSKI 1999, and references therein). Note that the phenomenological derivation performed above is, to our knowledge, for the first time applied to protein crystallization from solution.

Now, we determine the validity of our approximation for the proteins containing spherical agglomerate, growing in a water-based electrolyte. As stated before, the condition

$$v_i >> V_{gr}, \tag{12}$$

describes well the kinetic limitations of the process in question. Then from Eqs. (9)-(11), one may write explicitly for large time

$$\mathrm{L}_B >> V_{gr} \times t_{DE}, \tag{13}$$

where both surface diffusion and screening electrostatic events determine the association of proteins with charged crystal surface. This picture looks very consistent with what has been claimed (CHERNOV 1997). It also supports, to a certain extent, the thermodynamic concept of transient nucleation for protein crystal growth (HAAS, DRENTH 2000), since presence of the solution realm, "encapsulating" the nucleus under growth considered there can be identified with the existence of the double-layer in our model. The overall association time t_{DE} is

simply given by

$$t_{DE} = t_D \times \exp\left(b\, E_A + 2k r_P\right), \tag{14}$$

where we recall again that k is the inverse Debye length, and k^{-1} is closely related to the Bjerrum length L_B (SAFRAN 1999). It may be noted that the elementary surface diffusion time t_D is a pre-exponential factor in Eq. (14), $t_D < t_{DE}$.

Two additional important aspects of the problem under study should be emphasized. First, the case when a departure from spherical ideality is taken into consideration. Within the approximations (13)-(14), in our model there is a possibility to incorporate such a perturbation. It can be done by substituting R in Eq. (1) by

$$r = R + d\,F\left(f, q\right), \tag{15}$$

where typically (for the mature stages of the growing process, which is usually of technological importance)

$$\left|F\left(f, q\right) d/R\right| << 1. \tag{16}$$

Here d stands for the perturbation amplitude. The perturbation procedure is realized by assuming bound functions $F\left(f, q\right)$ (KESSLER et al. 1988) as the real surface representatives, like the spherical harmonics, Weierstrass functions or others (MULLINS, SEKERKA 1963; SETHIAN, STRAIN 1992; GADOMSKI, TRAME 1999). For a sufficiently mature stage of the growing process ($R(t) >> R_c$), it leads to a simple exponential behavior of the amplitude, i.e.

$$d\left(t\right) \propto \exp\left(-t/t_d\right), \tag{17}$$

where $t_d = R_l^2 / v_i R_c$, ($R_c = 2s\Gamma$ and R_l is a particular radius value taken for some sufficiently large instant measured). The value of the instant is supposed to determine readily the lower bound limit of the time zone from which the so-called large times may commence. This is certainly our approximation. However we recall again that we make use of our kinetic limit, namely $v_i >> dR/dt$, and $s << 1$.

Formula (17) is similar to the formula for d provided for purely diffusional growth (MULLINS, SEKERKA 1963; LANGER 1980; GADOMSKI et al. 1993; GADOMSKI, TRAME 1999), where some exponential decay is also observed. It is in a rather minor contrast to the well known Mullins-Sekerka linear instability analysis for which: (i) a growing object is immersed in a stationary (bulk) diffusional field; (ii) the growth rate V_{gr} drops in time algebraically, with an exponent one-half, since the crystal radius $R \propto \sqrt{t}$ for sufficiently large t ; (iii) the perturbation amplitude $d \equiv d\left(t\right)$ does not attain an optimal behavior but diminishes exponentially with time. The main difference between convection and diffusion-limited crystal growth concerns with point (ii), because in our model there is no decrease in V_{gr} with time but $V_{gr} \to \text{const}$. Another quantitative difference could be that the time constants for the damping out of the amplitude $d\left(t\right)$ can be different for both these

processes; see t_d (it can take quite large values). Moreover, in our analysis growth of $d(t)$ with time is not possible while in the classical Mullins-Sekerka instability analysis this may occur (MULLINS, SEKERKA 1963). The idea of perturbing the sphere and performing the linear stability analysis is also consistent with surface diffusion model of Burton, Cabrera and Frank (BCF model), which describes the evolution of crystalline heterostructures (PIMPINELLI, VILLAIN 1998; KITTEL 1996) and protein crystal growth (CHERNOV 1997). Note that the BCF model also leads to a constant crystal growth rate, i.e. $V_{gr} \to \text{const}$.

Another thing of equal importance is a stochastic perturbation, which can be included in our model by means of a simple observation that, instead of Eq. (1), one considers

$$\frac{dR}{dt} = \left(v_i + V(x,t)\right) \times \frac{s\,R + R_c}{R - R_c}, \tag{18}$$

where $V(x,t)$ denotes a spatio-temporal noisy perturbation of the temporal behavior of the system. To propose some reasonable and physically justified characteristics of the noise $V(x,t)$ is always a problem. It was assumed earlier (GADOMSKI, LUCZKA 1993) that

$$V(x,\ t) = V(t), \tag{19}$$

where $V(t)$ conforms to the so-called Gaussian white noise (non-correlated fluctuations)

$$\langle V(t) \rangle = 0 \quad \text{and} \quad \langle V(t)V(t\ ') \rangle = 2D\delta(t - t'). \tag{20}$$

Here D stands for the noise intensity ($t \neq t'$), according to the fluctuation–dissipation theorem equivalent to the diffusion coefficient (BALESCU 1975), and $\delta(t-t')$ represents the Dirac function; for lysozyme in water $D \approx 10^{-6}$ cm^2/s , which is certainly a very small value. We observed that by increasing the noise intensity the main temporal characteristics of the growing process are changed quite drastically (cf. Eqs. (2) and (3)). This means that growth switches over from purely mass-convectional behavior (Eq. (3)) to the diffusional one, i.e.

$$R \propto t^{1/2}, \tag{21}$$

which is rather characteristic for small-particle crystallization processes taking place in solutions or melts, and sometimes in some 'noisy' (reactive) macromolecular solutions (YAMAKAWA 1971). It conforms well to our case since the speed of each individual protein can easily be perturbed. For example, the easier one can reach it, the more thermally agitated the system can be. This leads to the following consequences: perturbation of hydrophobic behavior near the interface, additional production of hydrogen bonds, activation of otherwise 'lazy' ions (Na^+) repelling the protein, etc.

To check the physical validity of our model let us propose to evaluate a characteristic length l_{cr} of the crystal for stable growth (CHERNOV 1997). Let us do it specifically for lysozyme. The comparison is based on the kinetics of the crystal growth described by the BCF model (CHERNOV 1997).

In the BCF model adapted to protein crystallization the kinetic coefficient of a crystal face taken as a whole is $V_{gr} = b_{st}p$, where the vicinal slope p is typically equal to 10^{-2}.

Here b_{st} is the kinetic coefficient for the movement of steps and p is an average step density normalized by the step height. Therefore, $V_{gr} \approx 10^{-6} - 10^{-5}\,\mathrm{cm/s}$ because the measured value of b_{st} is about $5\times10^{-5}\,\mathrm{cm/s}$ for lysozyme. In the BCF model the lysozyme diffusivity is $D \approx 10^{-6}\,\mathrm{cm^2/s}$ (CHERNOV 1997). Therefore, the characteristic growth length of a crystal, $l_{cr} = D/V_{gr} \approx 0.1\mathrm{cm}$, which is controlled mainly by incorporation of species at the interface rather than by bulk diffusion.

In our model, we have practically $V_{gr} \approx s\, v_i$ (cf. Eq. (2)), where V_{gr}, s and v_i are defined as above, and using Eqs. (10) and (11) from Eq. (9) one obtains

$$v_i = \frac{\mathrm{L}_B}{t_\mathrm{D}} \times \exp\left(-2k r_P - \frac{E_A}{k_B\ T} \right), \tag{22}$$

where t_D is the elementary diffusion jump time from one of the minima (the deepest minimum is the best for ultimate landing) to another one; E_A is the activation energy for the diffusion, whereas $k_B T$ stands for the thermal energy. Our characteristic length for the growing crystal reads $l_{cr} = (1/3p)\, s^{-1} \left(L_D^2 / \mathrm{L}_B \right) e^{y_{\min}}$, where $y_{\min} = 2k r_P$, and where $y_{\min} \le 1$. Therefore

$$l_{cr} \approx \frac{1}{3ps} \frac{L_D^2}{\mathrm{L}_B}, \tag{23}$$

because again $e^{y_{\min}} \cong 1 + y_{\min}$, and for water one has $\mathrm{L}_B \approx 10^{-9}\,\mathrm{m}$. One may find that for a sphere $L_D^2 \approx 4p \left[r_P^{(n)} \right]^2 \approx 10^{-15}\,\mathrm{m^2}$, so that for $s \approx 10^{-4}$ one gets $l_{cr} \approx 10^{-3}\,\mathrm{m} = 10^{-1}\,\mathrm{cm}$. Here we assumed that $r_P^{(n)} \equiv r_P^{(10)} = 10 \times r_P$ i.e. the crystal consists of the order of $n = 10^3$ biomolecules. As far as the spherical approximation is concerned and for the definition of the supersaturation s given above, this agrees well with the typical characteristic crystal length reported in the literature (CHERNOV 1997; DRENTH, HAAS 1998). Note that we do not need the value of D, cf. Eq. (23).

4. Concluding remarks

In this paper we have proposed a kinetic model based on the electrical double-layer, as in the case of electrolytes, where the type and nature of layer (e.g. Stern or Chapman) taking part in growth is not known. Our model can straightforwardly be applied because all the physical quantities are measurable. Moreover, the problem deserves attention because there are some statements and data in the basic literature in the field of crystal growth, offering some rather contradictory elucidations, like (quoted): The "trial and error" mechanism controlling the selection of species during inorganic crystallization seems not to be effective in proteins (CHERNOV 1997), while in another seminal paper one reads just in the beginning an almost opposite expression in its abstract (ATAKA 1995).

Finally, it should be emphasized that the growing process studied is a curvature-dependent process, or in other words, that the surface tension effect, somehow damping the

growth, may be decisive. The non-equilibrium concentration to be specified at the crystal surface is just some concentration c_s, related with the equilibrium concentration c_0 by the Gibbs-Thomson condition:

$$c_s = c_0 \times (1 + \Gamma K), \tag{24}$$

where K is the curvature (i.e. $K = 2/R$), cf. Fig.1; and Γ is a surface tension-dependent quantity (see above). Note that Eq. (24) has been employed to derive our final expression (Eq. (1)) for the crystal growth rate. Moreover, note that when K tends to zero (i.e. in practice, for a very large object radius), c_s approaches the equilibrium concentration c_0.

Our kinetic model is an alternative proposition to some well-known ones (CHERNOV 1997) in which the role of a plasma-type electrolytic solution in the double-layer has been emphasized. In the range of validity of weakly nonideal classical plasma, one may easily arrive at the thermodynamic limit (BALESCU 1975), not kinetic one (Eqs. (12)-(13)), for our modeling:

$$c_{pl} << s^{-1}, \tag{25}$$

where $c_{pl} = Q_P^3 c_0^{1/2} b^{3/2}$ is a characteristic plasma parameter (here $c_{pl} << 1$ and $b = 1/k_B T$). However, the above condition can be well fulfilled because $s^{-1} >> 1$ as mentioned above.

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