(Bio)Polymer Crystallization in Water-Containing Environments under Complex Conditions

Adam Gadomski, Jacek Siódmia
Institute of Mathematics and Physics, University of Technology and Agriculture
al. S. Kaliskiego 7, PL-85796 Bydgoszcz, Poland

ABSTRACT

We present two statistical–mechanical aggregation models, leading to (poly)crystallization in complex electrolytic environments. The first kind of modeling assumes some aggregation events taking place on many nuclei distributed over the available solution space, whereas the second readily elaborates an ordered agglomeration phenomenon on a single seed by applying the mass–conservation law. Both of them can be applied to crystallization of proteins and/or colloids, and are suitable enough to be considered for proper description of (poly)crystallization in electrorheological (complex) fluids. They also allow to control structural properties of the complex fluid in which the aggregation takes place. This, in turn, may be of importance, for example, in designing quality procedures for food. An effective comparison of the two above mentioned models is given too.

1. INTRODUCTION

Complex fluids such as (bio)polymer-based solutions, blends, polyelectrolytes, microemulsions and micelles undergo a variety of structural phase changes, and typically manifest such a behavior like tendency toward aggregation, anomalous viscoelastic properties, thermal history-dependent properties, “unexpected” response to a yield, diffusion–relaxation peculiarities, etc. [1]. Among a few basic properties mentioned above aggregation of a dispersed matter (e.g. proteins, lipids, surfactants) in some dispersing liquid medium (water, for instance) may stand for a fingerprint of complexity [1]. It appears to be a standard observation, for example in food science [2], that one may investigate rheological characteristics of a specimen by means of exploring systematically its aggregation features in course of some control parameter(s), asking for example whether the aggregation in question is ordered or not, and how does it change the overall structure of a complex fluid of interest [3]. In this paper, we wish to propose a strategy that leads to control a model complex fluid, undergoing aggregation of dispersed matter, by means of its characteristical growth rule [4]. The growth rule we propose is based on the conservation laws, where either the conservation of mass or that of volume is encountered. We start with an observation that the solution properties are under control when the aggregation, no matter whether ordered or not, takes place on a single nucleus (mononuclear or one-nucleus aggregation), or can occur on possibly many nucleation centers, irrespective of the physical nature of the centers, however. (Sometimes, one may term it: homo– and heterogeneous nucleation [5]). The latter will be consequently called throughout the paper the many-nuclei or polynuclear aggregation; this kind of aggregation, if present in a complex system, is capable of changing substantially the viscosity of complex rheofluid, whereas its one-nucleus counterpart, depending on the stage of the growth, however, causes some local (controllable) structure changes, which would very likely mean that the quality of a liquid food, for example, cannot be changed much under such circumstances cf. Fig.1. In section 2, we present the representative growth rule, including some information on basic growing phenomena emerging in such systems. In sections 3 and 4, respectively, we tackle the problem of how to control the aggregation process, and how to be out of the control. We finish the study by some conclusion and comparison of the two basic phenomena mentioned.

2. GENERAL GROWTH RULE

From a representative number of studies on growing phenomena in complex environments [1, 4, 3] follows that a kind of growth overrule that one can propose reads

$$\frac{dR}{dt} = M(v_1, ..., v_M; p_1, ..., p_N; t)$$

where $R \equiv R(t)$ is an (average) radius of the growing object, $M$ represents a function reflecting the growing mechanism, being dependent upon a set of $M$ variables $v_i \ (i = 1, 2, ..., M)$ as well as an equally important set of $N$ (control) parameters, $p_j$, where $j = 1, 2, ..., N$, and finally upon the time $t$ (a continuous variable). As was often noticed [4, 3], such a rule is firmly based on
the mass-conservation law, and subjected to some initial condition, presumably to be of deterministic nature, $R(t = 0) = R_0 > 0$, an output is yielded which reflects the nature of the prevailing mechanism by which the growing phenomenon occurs. If $M$ in (1) contains no variables ($v_i$) or contains only some information about a single variable, $v_1$ ($M = 1$), i.e., $v_1 = f(R)$, the equation is closed ($f$ - a continuous function of $R$), and one may be lucky in solving it. If the number of dependent variables, $v_1$-$s$, of the autonomous ODE (ordinary differential equation) is greater than one, the system is not closed, and some additional conditions for the variables $v_2, v_3, \ldots, v_M$ have to be specified carefully, according to the physical mechanism(s) of the process under consideration. (The mechanism can be complex, for example, when the process goes under mixed control, like in diffusion-reaction phenomena, see the far-from-equilibrium concept of coupled fluxes, or even the flux-force relations, first analyzed by Onsager in its linear forms, cf. [5], and applications to complex nucleation phenomena considered therein.) In a paper [6], we have analyzed the kinetics of protein crystal growth in a complex water-containing environment. For describing those kinetics we have proposed the equation, like (1), containing no $v_1$-$s$ but including complex parameters $p_1$ and $p_2$, where $p_1$ stands for a dimensionless supersaturation parameter, and $p_2$ is fully identified with a Frenkel-like macrorion velocity term. Under the set of physicochemical conditions given the growing system a loss of control can happen here when one will be unable to control the latter parameter. Therefore, we have additionally proposed there a ‘noisy’ perturbation of that term [6] but other authors have even shown that a most efficient control will be either if the perturbation is uncorrelated (Gaussian noise) or exponentially-correlated [7] because a power law can then be expected. Such a complex system driven by linear $R(t)$ vs $t$ kinetics we have called the mass-convection model crystallization process [6]. In another paper [8], in turn, we have drawn a plausible scenario for either matter diffusion- or mass-convection driven crystal growth from solution (again), envisaged mostly for colloids or surfactants, in which cluster-cluster phenomena stand most probably for a kinetic limitation of the growing process. Referring to Eq. (1) again, we have, roughly speaking, arrived at a specific system for the diffusion-driven growth (short molecules) when $v_1 = 1/R$, $p_1 = D$ ($D$ - diffusion coefficient), and $p_2$ is denoted the supersaturation as above. If, however, $R \rightarrow R_{\text{char}} = \text{const} > 0$, the system is given no dependent variable on its right-hand side (r.h.s.), and then the process does not go via diffusion rather but goes vigorously in a mass-convective way. A key point, however, was to mention that the quantity $D$ can be of more complicated character that one can expect. Namely, its determination may be done on a microscopic level (Brownian motion!), and therefore a cluster-cluster merging (or more generally, attachment-detachment) mechanism has to be taken into account, see [8], and refs therein. The merging process can be realized via an immediate sticking of two entities or, a more complicated situation, via ‘delayed’ sticking (a chemical reaction), what substantially changes the kinetics of the crystal growth. The described physicochemical situation, mostly the last (reaction) case, leads somebody to a conclusion that not only a single crystal may be formed but the emerging clusters, being hardly movable (they catch other clusters while walking) are potential seeds of crystallization to occur, so that a multinuclear process is expected, see Fig. 1. again.

![Figure 1: Aggregation models, leading to (poly)crystallization in complex polyelectrolytic environments: (A) agglomeration on a single seed in a diluted solution, (B) agglomeration on many nuclei in a more condensed solution.](image)

If there is no chance to keep the crystallization process as taking place on a single seed, we may allow the system to evolve via that polynuclear path. But if so indeed, we do propose to accomplish that by an ordered procedure. Namely, to control the system behavior let us propose to keep the system under constant total volume condition which is a standard case when producing polycrystals: in physical metallurgy such a process is named normal grain growth, and is recognized to be a final (stationary) state of the recrystallization of a specimen. One may also think of soap froths or bubbles: they experience also a quite morphologically apparent similarity when compared with polycrystals [9]. The growth rule, which expresses the crystallization of a single averaged grain in a “society” of the remaining ones, will in principle be of the form of (1), but the system will be closed when an additional PDE (partial differential equation), describing the evolution of the grainy system along the grain-size axis will be specified [10]. Such a proposal for
describing polycrystalline growth may be compared with a dropwise (binary) coalescence model by Binder and Stauffer [11] where the grains do coalesce ending up with a final polycrystalline structure. Such a scenario is drawn in Fig. 2., where the two models have been compared in a picturesque way.

Figure 2: Two models of polycrystalline evolution: (A) via the action of grains’ merging, to a small number of crystallites constituting the polycrystal, (B) the action goes by absorbing a small grain by its bigger neighbor; the dashed lines mean the grain boundaries to be removed in next time step.

Moreover, the kinetics they express are really of the same ‘quality’ what can for example be seen when looking at the characteristic kinetic exponents they yield. In addition, it is worth mentioning that the ‘soft’ polycrystals we may observe in such a scenario do grow randomly, that means on randomly distributed seeds, and when a close-packing effect (a popular notion in physics of amorphous bodies) can clearly be observed [12], see Fig. 3.

Figure 3: Schematic of the random close-packing $d+1$-conception applicable to grainy systems, see Text (Eq.6) for details. To confuse the reader let us state clearly that the drawing is presented to sketch the main idea, rather, than to compare effectively balls (spheres) with the grains or bubbles.

3. CONTROLLING ONE-NUCLEUS GROWTH PROCESS

As we mentioned before, the growth process, for the specific conditions (i.e. in diluted solution), can take place on a single seed. In this case, we can distinguish two control parameters. The first of them is a single macromolecule speed $V_{ion}$. This parameter plays an important role in the local realm close to the surface of the growing object, where the system undergoes a Debye-Hückel scenario, and the realm can likely be interpreted in terms of the double-layer of Stern type. In this case, the r.h.s. of the Eq (1) will be proportional to $\sigma_s V_{ion}$ [6], where formally $p_1 = \sigma_s$, which above is termed a dimensionless supersaturation parameter, formally $p_2 = V_{ion}$ here. For mature growth stage (large $t$) a simple asymptotic solution of Eq.(1) can be given, namely: $R \propto t$, what suggests that the growth rate goes to a constant value. The control of this parameter can be realized by controlling the noise added to $V_{ion}$, namely:

$$V_{ion} = \langle V_{ion} \rangle + \xi$$

(2)

where $\xi$ is a fluctuating part, and $\langle \ldots \rangle$ means an average value [6]. For high values of the fluctuation strength it is possible that we will loose the control of $V_{ion}$, what will lead to nonlinear growth in time. The matter depends, however, upon whether we add correlated or uncorrelated noise, and which is the type of it [7].

The second control parameter, a parameter which stands for a bulk parameter, is a diffusion coefficient $D$. Now the r.h.s. of Eq.(1) will be proportional to $p_1 \cdot D / R_{char}$, where $D$ stands for the diffusion coefficient and $R_{char}$ is a characteristic distance on which the gradient takes a constant value [8]. In this case control takes place by mass changing of the diffusing cluster and by interaction of this cluster with solution (possible chemical reactions). The diffusion coefficient reads now [6]:

$$D \sim [M_0(1+t)]^{-1/D_f}$$

(3)

where $M_0$ is the initial mass of the walking and growing cluster, $D_f \equiv d_f / \kappa$, where $\kappa$ is a Flory-Huggins parameter ($\kappa \in [0, 1]$ and $\kappa = 1$ implies that cluster–aggregation process is purely diffusion-controlled, good solvent regime), $d_f$ is a fractal dimension of the diffusing cluster ($0 < d_f < d$, see below for $d$), which can presumably change but slightly. An asymptotic solution of the Eq.(1) takes the same form like in previous case, namely $R \propto t$, but for chemical reaction regime (bad solvent limit), and can visibly depart from that asymptotics in a diffusional case [8].
4. CONTROLLING MANY-NUCLEI GROWTH PROCESS

A procedure presented in [13] for describing the kinetics of a grainy system looks more or less like a standard as well as well-established way of dealing with the problems of nucleation and growth in many-nuclei systems, cf. [3, 5, 4]. This is, however, less expected that one can somehow reasonably invert the problem, and will deal with a many-nuclei growing system as if it were a certain one but average crystallite evolving in a “bath” of the others, constituting always its environment. (Such a procedure is, however, absolutely not new when invoking standard approaches to growth on a single nucleus so intensively explored in the theory of crystal growth, for example in [14].) The main reason of such an inversion can be, however, to get at least some novel insight into that traditional matter description, hoping also for some important new looks into the problem under consideration. Accepting the above, we propose thus the following algorithm: (i) Write down the growth rule of the system under study based on the relations between two first statistical moments, and by utilising, without loosing generality [15], the mean-field assumption; realize that the growth rule is a rule for an average grain, and that by differentiating both sides of the growth rule you will get a rule of type (1) you will be able to analyze by simple means; (ii) Notice that the r.h.s. of the above rule contains and needs a sufficient statistical information about the growing system that can be taken exclusively by solving it, see [13, 15]; (iii) Because the interest is mostly in the asymptotic (large times) behavior of the growing object, you may resort now to other useful approximations and insert exclusively asymptotic temporal characteristics into r.h.s. of the ODE you have to arrive at after performing the differentiation mentioned above. If we utilize relations (51)–(54) from [15] in a sense that we will perform differentiation with respect to time t over both sides of the volume conservation relation (51) therein, apply a mean-field argumentation offered there (Eqs. (52) and (54)), then we should immediately arrive at

\[
\frac{dR}{dt} \propto \frac{1}{R^{d-1}} v_{\text{spec}}(t),
\]

where formally \(v_1 = v_{\text{spec}}(t)\) is the time derivative (denoted here by prime) of the specific volume of the polycrystalline system (an average quantity), where for a system of constant volume \(V = \text{const} > 0\), and \(v_{\text{spec}}\) is just inversely proportional to an average number of crystallites, \(N(t)\), constituting it, see formulae (49)-(50) in [15]; also formally, \(v_2 = 1/R^{d-1}\), and for the values of \(v_1\)-s consult [15, 13] (d is specified below). It implies that the only quantity we need to resolve Eq. (4) is just \(N(t)\) but this is clearly the zeroth statistical moment of the diffusion-type process we examine as a model evolution of the grains-containing system we have in mind [3, 13, 15]. Such a model is acceptable for condensed-matter systems, like metallic alloys or ceramics, mostly in nanometer scale. A modification, striving for accounting subtle time effects, is needed, however, for applying it for soft–matter systems. A rationale presented, e.g. in [16] ensures that it preferentially relies on a suitable time-rescaling. Such a rescaling like \(t \rightarrow t^\nu\), where the exponent \(\nu\) contains necessary information about physics of the problem (adsorption and mass-ordering effects) [16], in most physically significant cases leads to an asymptotic time behavior like

\[
R \propto t^\sigma,
\]

where \(\sigma = 1/(d+1)\). \(d = 1,2,3,...\) \((0 < \sigma < 1)\), which is more expected in slowly evolving metallurgic systems than in some ordered (bio)polymeric ones [16, 4], in which evolution may be vigorous (but ordered, like for spherulites or cylinders), and realized in a mass-convective way. Interestingly, we see some analogies between the model of polycrystalline evolution represented by Eq (4) and a Smoluchowski–type model invented by Binder and Stauffer (BS) for describing the droplet coarsening in a pairwise manner, cf. Fig.2A. Our crystallites’ growth model leads also, via the action of grains’ merging, to a small number of crystallites constituting the polycrystal (in practice, however, no single grain will be formed). The action goes by absorbing a small grain by its bigger neighbor, so that it proceeds pairwise at least in a model sense, look at Fig.2B. The asymptotic result obtained for BS-model reads

\[
R \propto t^\chi,
\]

where \(\chi = 1/(2+x)\), so that their \(\chi\) equals our \(\sigma\) iff \(x\) (a hydrodynamic interaction parameter they introduced) obeys \(x = d - 1\), what in turn, emphasizes a crucial role of the surface \(R^{d-1}\) of an individual crystallite in our dimension \(d\)-dependent model [15, 13]. It seems, therefore, that the model under consideration suits very well for modeling colloid systems because its main entities have usually well-developed surfaces [17] though polymers cannot be excluded too [18]. (By the way, the same type of time rescaling [16] in BS-model leads to the linear asymptotics as in Eq. (5).) Let us also note that in another diffusion-type model (but with negligible surface tension or capillary effect) in which the total volume remains naturally unconserved [19] the asymptotics looks like in (6), and the following...
reasoning may apply too.

5. CONCLUSIONS AND COMPARISON

The conclusion can be drawn in the following way: (1) We have developed an on–growth–rule (Sec.2) based strategy that may be helpful, for instance, in improving food quality by controlling internal aggregation phenomena, and their kinetics, in a "model food" being generally a structured electro rheological fluid. (2) The strategy relies on controlling the aggregation phenomena by means of a localization-and-order conception: (i) If the aggregation takes place on a single seed, everything is going to be all right, especially when the occupied volume remains very focused (small); realize that the system of interest becomes locally inhomogeneous now; (ii) If one loses control in the framework of the on–one–nucleus established strategy (Sec.3), one has to accept that it will take place on many nuclei (Sec.4), and if so, one usually wished to control it by having the volume conserved (possibly small as well, what can be done by the close–packing substrategy with random mixing, see Fig.3, as a reminder) and by growing an ordered structure (order means often control!); realize that the system of interest becomes globally inhomogeneous, in turn. Certainly, the best way is to avoid inhomogeneities but it is generally not possible (temperature decrease; light illumination; storing and transporting conditions; vibrations; impurities; undesirable chemical reactions; pH; influence of bacteria; mechanical damages - these are usual causes for producing an inhomogeneous system, that means, food of worst quality). (3) Our strategy explores, at least in an implicit way, a concept of the phase separation [11, 4, 3] for which the above mentioned BS-model is a useful tool, embodied also quite unambiguously in our modeling of many–nuclei–based evolution. (4) It seems reasonable to strive for keeping the growth rule (5) as the most desirable one, since a constant growth rate (sic!), at least in an asymptotic time limit, sets properly the pace. (5) The models invented in [6, 8, 15] as well as in [19] may univocally arrive at the same linear–in–time average radius asymptotics, so that we are able to control over a large class of mostly mass-convective as well as possibly surface-driven processes [3, 4] realized with a constant, that means, easily predictable tempo, cf. relation (5).

ACKNOWLEDGMENTS

1 As an example, one can recall here that after a certain pH fall protein molecules in the milk become denatured. This means that they unfold from their normal structure, become disordered and begin to stick to each other. This is what causes the yogurt to become partially solid and gelatinous [20, 17, 10].

We thank Dr. Marco Dressler for his interest in our scientific activity. A hospitality of one of us (AG) at the Queen’s University of Belfast by the Atomistic Simulation Group, where a part of this work was thought of, is acknowledged.

References