



On the two principal curvatures as potential barriers in a model of complex matter agglomeration

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Abstract

We show that matter agglomeration mesoscopic phenomena of irreversible type are well described by nonequilibrium thermodynamics formalism. The description assumes that the thermodynamic (internal) state variables are in local equilibrium, and uses the well-known flux–force relations, with the Onsager coefficients involved, ending eventually up at a local conservation law of the Fokker–Planck type. Within the framework of the formalism offered the first two curvatures, characterizing the structure of the agglomerates, are associated with a suitable choice of a physical potential governing the system. It turns out that a certain choice of the potential of power-law type leads to emphasizing the role of the Gaussian curvature while another choice in logarithmic form results in a pronounced role of the mean curvature. The offered modeling has been related successfully with a statistical-mechanical polycrystalline matter evolution introduced for physical–metallurgical purposes, and modified for a use in biophysical soft-matter agglomerations.

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1. Introduction

In this work, we wish to focus on a matter agglomeration process involving the size of a constituting entity (grain; cluster) between micrometer (physical metallurgical specimen or colloidal flock)

and nanometer (biophysical agglomerate viz. biomembrane) scales. The systems that we are going to address possess the following characteristic basic properties [1]:

- They are diffusion–migration systems, which means that they are well-characterized by a diffusion process along the axis of their internal variable (volume, size), and they undergo a kind of migration being recognized as a drift by capillary forces, provided that they are vitally present in the system [2].

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- The growing processes are of irreversible nature, so that a thermodynamic formalism is possible to apply [3].
- The diffusion coefficient is proportional to the surface magnitude of a basic entity constituting the agglomerate under evolution, a physical scenario well-known mostly in colloidal agglomerations [4].
- The drift term is always proportional to the curvature: It turns out that it is either very related with the mean curvature, what is supposed to be true in physical–metallurgical systems being of micrometer size of its basic entity, or it appears to be identified with the Gaussian curvature, which can reasonably be judged as being characteristic of nanometer scale rather, in which (bio)polymeric agglomerations are supposed to be in favor (see Fig. 1).
- The systems we examine always obey the local conservation law.
- They are constrained systems, mostly due to: (i) boundary conditions applied: they can be either of normal (0-Dirichlet) or of abnormal types [5]; (ii) their total (hyper)volumes can be preserved

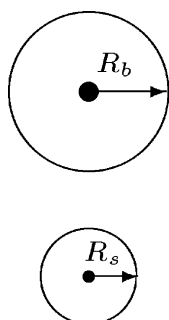


Fig. 1. Two idealized circular grains ($d = 2$). The upper grain of radius R_b has both the mean and the local curvatures equal to $1/R_b$, and represents a microagglomerate's grain, whereas the lower grain (exaggerated to be big enough for visualization purposes), of radius R_s (and the curvatures of $1/R_s$), is a nanograin. The radii R_b and R_s are drawn in a vector representation for indicating a direction of possible local advancement of matter. It becomes clear that the Gaussian curvature of that smaller one, $1/R_s^2$, has to be distinctly bigger than the same quantity for the micro-grain because $R_s \sim 10^{-9}$ m is three orders of magnitude smaller than normally $R_b \sim 10^{-6}$ m can be. Such a size-effect, and a physical scenario associated with it, have to be taken into account while modeling agglomerates of different sizes of their basic constituting entities.

(when surface tension or elasticity effects are pronounced) or not (when no special role of surface tension is assumed) [6]. Their evolutions, however, do not depend essentially upon the initial condition chosen.

Here, we wish to focus on a physical–metallurgical process called normal grain growth whose main characteristics can briefly be presented in the following way (see [7] and references therein): (i) The polycrystalline evolution takes place under a certain constraint concerning the constancy of the total system volume. (ii) It relies on evolution of grains constituting a specimen in such a way that the mean radius of the grains has to increase (the curvature has to diminish) while their total number has to decrease. (iii) An observed physical tendency while going over sufficient number of time spans of the process is a slowing down of the grain surface free energy in such a way that a possibly low surface free energy matter agglomerate is eventually obtained.

As argued in [8], and recently re-examined in [5,7], the normal grain growth results from a certain subtle interplay between topological (space-filling) but random requirements as well as those of thermodynamic nature. The latter, in turn, is preferentially due to surface tension agitation as well as elasticity-to-rigidity (bending) effects on the grain boundaries, mostly when the system “fights” to attain a local thermodynamic equilibrium state under a set complex physico-chemical circumstances it meets on its way [5,7].

Therefore, the role of curvature, and its influence on the system behavior revealed by statistical thermodynamics, seems to be absolutely essential [9]. Because, however, of differences in the size of the main constituting entity (grain; cluster) within the classes of mesoscopic systems we want to examine, we see that for some bigger and less elastic micrometer-scale systems, as those metallurgical, the conception of the mean curvature would likely suffice to describe the system satisfactorily whereas for description of fine-grained assemblies, more elastic and less brittle nanosystems, the role of the so-called Gaussian curvature must be underscored [10]. The ideas we have just developed above are supported by some thermodynamic results first reported by Tolman [11], who noticed that in

certain fluid-like systems of suitable (appreciably small) size a size-dependent correction to surface tension improves its description. This led then to extensive studies of surface tension size-dependent effects in van der Waals-like as well as other systems [11,12].

The kinetic description of the grain growth of normal type (being a Fokker–Planck–Kolmogorov (FPK)-type description), or with uniform grain boundaries [5] can be found elsewhere [13–15]. An important thing to mention here is that the corresponding matter flux has been constructed in a phenomenological way [14], and that in it a standard diffusion term has been completed by a drift curvature term, just for reflecting properly the essential mechanism governing the agglomeration realized on a polynuclear path [4,5,7].

Very recently, another more improved way of constructing the matter flux has been proposed. It is based on dealing with a system undergoing normal grain growth as an open thermodynamic system, and on applying the principles of nonequilibrium thermodynamics in the space of the grain sizes. It immediately leads to express the entropy production in terms of the aforementioned flux and its conjugate thermodynamic forces. The chemical potential contains, in turn, the physical potential, designated by Φ , that can be selected in a suitable form, conforming to physical circumstances we want to address, cf. micro- or nanometer-scale evolutions. The procedure just outlined can be found elsewhere [16–18].

The article is structured as follows. In Section 2, we present a derivation of the flux of matter, J , based on the nonequilibrium thermodynamics formalism, introduced very recently [14,15,19]. This section is intended both as a summary of the theory and as its application to the case (a logarithmic potential, referred to micro-evolutions) that we have treated previously [19]. In the next section, Section 3, we discuss another important physical case, leading to application of a power-law potential to nano-world evolutions within the agglomerating system under study [10] which constitutes, in our opinion, a significant improvement of the models proposed up to now [19]. A final address and perspective (Section 4) complete our study of irreversible matter agglomeration.

2. Mesoscopic nonequilibrium thermodynamics derivation of a normal grain growth model: emergence of a logarithmic potential

A procedure followed before [10,14,15] relied on proposing the flux of mass in a phenomenological form [19]:

$$J(v, t) = -\sigma v^{\alpha-1} f(v, t) - D v^{\alpha} \frac{\partial}{\partial v} f(v, t). \quad (1)$$

Here v is the volume of a grain, t is the time, and $f(v, t)$ is the distribution function of the grains at time t , with $f(v, t) dv$ the number of grains of size in the volume interval $[v, v + dv]$. The parameters σ and D are surface tension and a reference diffusion coefficient,¹ respectively, and $\alpha = d - 1/d$, with d the dimensionality of the system [14]. That exponent can be interpreted as a surface-to-volume exponent; for further discussion, see [19]. The first part of the right-hand side of Eq. (1) is a drift term, whereas the second stands for a diffusion term. The former is a capillary term, proportional to the grain curvature, involved in the Laplace–Kelvin–Young law [5,10]. The latter is simply the first Fick’s law, and it underscores a proportionality of the matter flux to the grain surface magnitude. Bear in mind here that via a relation $v \propto R^d$ (R , a grain radius) in the drift term, one obtains $v^{\alpha-1} \propto R^{-1}$ (see the exponent α), which means, that a curvature term $1/R$ can easily be revealed this way. In the diffusion term, in turn, one clearly gets a surface term R^{d-1} since $v^{\alpha} \propto R^{d-1}$, when $v \propto R^d$ is applied again; for example, for $d = 3$ the surface term is proportional to R^2 .

After defining explicitly the flux, we have to apply it to the local continuity equation

$$\frac{\partial}{\partial t} f(v, t) + \frac{\partial}{\partial v} J(v, t) = 0, \quad (2)$$

and complete it by suitable initial and boundary conditions. A general observation is, however, that the process in question does not depend upon any prescribed initial condition, cf. [13], and refs. therein. After a sufficient time interval being

¹ σ being a positive constant, corresponds to the surface tension of a flat interface, whereas D is the diffusion constant when $\alpha = 0$ ($d = 1$).

overcome it completely forgets its initial state [7]. This is not the case of the boundary conditions (BCs), however. The process visibly depends upon the BCs prescribed. A choice that probably remains as most explored is the choice of zero Dirichlet BCs, namely $f(v=0, t) = f(v=\infty, t) = 0$. Realize that the BCs-proposal may not work in a semi-infinite phase space, $v \in [0, \infty]$, since the volume of a single grain may exceed the total system volume which is proved to be constant here, cf. discussion in [10,13,19].

There is some physics staying behind the BCs: The grains of zero as well as of infinite sizes have zero account for the grain growth. This physical constraint is sometimes called a normality condition, and the process is said to be normal when the above is true. Otherwise, one may name the agglomeration abnormal [5].

To derive the expression of the current, we will concisely recap the main points of derivation contained in [19]. Note that another way has been shown in [20], and via some Random Walk (RW)-analogy [13], can serve as an argumentation line of what has been derived in the following section.

Let us start with the Gibbs equation that represents the entropy variations, namely [16,18,20]

$$\delta S = -\frac{1}{T} \int \mu(v, t) \delta f dv, \quad (3)$$

where T is the temperature, and $\mu(v, t)$ is the chemical potential in v -space. The latter is given by

$$\mu = k_B T \ln(af), \quad (4)$$

where k_B is the Boltzmann constant and $a \equiv a(v)$ is an activity coefficient, reflecting the fact that the system is not ideal; for $a = 1$ it would become ideal. It is given in terms of the potential Φ acting on the grain as [16,17]

$$a = e^{\Phi/k_B T}. \quad (5)$$

Proceeding exactly in the same way as in [19], for the entropy production, σ_E , one gets

$$\sigma_E = -\frac{1}{T} J \frac{\partial \mu}{\partial v} \quad (6)$$

from which we may easily infer the expression for the flux of matter

$$J = -\frac{1}{T} L(v) \frac{\partial \mu}{\partial v}. \quad (7)$$

Here, we have assumed that the process is local in v ; one would also consider non-local effects through the extension

$$J(v) = -\frac{1}{T} \int dv' L(v, v') \frac{\partial \mu}{\partial v'},$$

cf. [16,17], where $L(v, v')$ is a memory kernel in v -space [21,22]. Combining Eqs. (4), (5), and (7) one gets

$$J = -\frac{1}{Tf} L(v) \left[k_B T \frac{\partial f}{\partial v} + f \frac{\partial \Phi}{\partial v} \right]. \quad (8)$$

Defining the mobility as $b(v) = \frac{1}{Tf} L(v) = \frac{D}{k_B T} v^\alpha$, one finally obtains the expression for the current

$$J = -Dv^\alpha \frac{\partial f}{\partial v} - b(v) f \frac{\partial \Phi}{\partial v}, \quad (9)$$

which clearly depends on the potential associated to the agglomeration mechanism.

A logarithmic form of the potential,

$$\Phi = \Phi_0 \ln(v/v_0), \quad (10)$$

where $v_0 > 0$ stands for the initial grain volume, motivated by Tolman correction in curvature performed for the surface tension of a “droplet” of radius R , namely $\sigma \simeq 1 - (\delta_T/R)$, where δ_T stands for the Tolman length, was discussed in [19]. Such a correction procedure predicts a decrease of the surface (line) tension for sufficiently small objects.

Another issue that can be addressed seems more fundamental. It concerns the analogy between the RW in a position space and the walk along the grain size axis [10,15]. There are some experimental evidences [23] as well as theoretical predictions [7,10] that the walk in grain-size space would belong to a broad class of geometric Brownian motion (a Wiener process), the probability distribution of which is a logarithmic Gaussian [10]. Thus, instead of v in the mathematical form of the Gaussian distribution a $\ln(v)$ must appear as argument. Further examples with a corresponding logarithmic form of the potential can be found in [24] and in [25].

The diffusion coefficient, in its full form denoted by $D(v, t)$, is generally assumed to be defined by the Green–Kubo correlation formula, taken from

the fluctuation–dissipation theorem, in which random parts, $J^r(v, t)$, of the flux (9) are involved. It is given by $D(v, t) = \frac{k_B}{f} L(v) = Dv^\alpha$, which means that algebraic correlations are assumed in the correlator based on the $J^r(v, t)$ [16,18]. Some correlation in time domain are plausible too, mostly for describing agglomerations in soft-matter reactive systems viz biomembranes here [26].

3. Matter agglomerations in nanometer-world

Our proposal on how to deal with a model agglomeration at the nanoscale is to assume that the physical potential is a sum of power-law terms in v , namely

$$\Phi = \frac{\Phi_1}{v^{\epsilon_1}} + \frac{\Phi_2}{v^{\epsilon_2}}, \quad (11)$$

where Φ_i ($i = 1, 2$) may depend upon temperature, and as the construction of the LJ-potential suggests, they must be of opposite signs so that we choose here $\Phi_1 < 0$; ϵ_i ($i = 1, 2$) are positive exponents.

We have now to perform partial differentiation, $\frac{\partial}{\partial v}\Phi$, and put the resulting expression into Eq. (9), which gives

$$J = -Dv^\alpha \frac{\partial}{\partial v} f - \sigma_1 v^{\chi_1} f - \sigma_2 v^{\chi_2} f, \quad (12)$$

where: $\chi_1 = \alpha - \epsilon_1 - 1$, $\sigma_1 = -\Phi_1 \epsilon_1 \eta^{-1}$; $\chi_2 = \alpha - \epsilon_2 - 1$ and $\sigma_2 = -\Phi_2 \epsilon_2 \eta^{-1}$; here $\eta^{-1} = \frac{D}{k_B T}$, is the inverse of a viscosity. A direct comparison with (1) implies $\epsilon_i \rightarrow 0$ ($\chi_i \rightarrow \alpha - 1$) which yields $\Phi \rightarrow \text{const.}$ (as occurs in the van der Waals forces). Consequently, σ_i ($i = 1, 2$) tend to zero, and the drift term is completely removed.

Let us try, however, another way to put things forward. Assume that both χ -s are of the form

$$\chi_i = (\alpha - 1) - \epsilon_i, \quad i = 1, 2, \quad (13)$$

which implies the linear relation

$$\chi_2 = q_\chi \chi_1, \quad (14)$$

where $q_\chi \neq 1$, and clearly $q_\chi \neq 0$. After simple algebra, by making use of the equality (14) and applying (13), one gets

$$\epsilon_1 = (\epsilon_2/q_\chi) + (1 - q_\chi^{-1})(\alpha - 1) \quad (15)$$

or, equivalently, $\epsilon_2 = \epsilon_1 q_\chi + (1 - q_\chi)(\alpha - 1)$.

By letting $\epsilon_2 \rightarrow 0$ we wash out completely the term with σ_2 in Eq. (12), but we still have a non-zero ϵ_1 that reads in such a limiting case as follows:

$$\epsilon_1 = (1 - q_\chi^{-1})(\alpha - 1). \quad (16)$$

This exponent for a possible choice of $q_\chi = 1/2$ gives in Eq. (12) a term which looks like $v^{2(\alpha-1)}$, what again via $v^{2(\alpha-1)} \propto R^{-2}$ results in appearance of a second curvature (Gaussian) term, being proportional to $1/R^2$ [2,11,12]. This term must clearly be of importance for sufficiently small grains-containing systems, and we argue that it may happen in the nanometer scale [4].

In a nanoscale, the form of Φ is then the following:

$$\Phi(v) = \Phi_2 + \frac{\Phi_1}{v^{-(\alpha-1)}}, \quad (17)$$

what in terms of the distance (or, linear size) R results in

$$\Phi(R) = \Phi_2 + \frac{\Phi_{11}}{R}, \quad \Phi_{11} < 0, \quad \Phi_2 > 0, \quad (18)$$

with Φ_{11} being a constant.

For a microscale description [27], but given in terms of R , one provides the potential $\Phi(R)$ as

$$\Phi(R) = \Phi_{00} \ln(R/R_0), \quad (19)$$

where Φ_{00} is a constant and R_0 is an initial grain radius.

Of utmost importance appears to be to understand how the grain boundary curve, and under which physical circumstances does it? There are two possible thermodynamic routes proposed in such a situation, namely [28]:

- (i) the one, based on how does an equilibrium interface curve due to a chemical gradient change realized at the grain boundary interface,
- (ii) another one, that undergoes nonequilibrium thermal fluctuations.

Both the routes mentioned above are plausible, though the scenario drawn must always depend solely upon concrete physical mechanism applied [1,4,5]. The route (i) looks more safely applicable to microagglomeration driven by non-LJ potentials and forces as in some metallic as well as thin-film ceramic [29] systems, e.g., in relaxor multicomponent materials [30]. The route (ii), in turn, is readily supported by the LJ force-and-

potential context as is typically met in soft-matter systems, e.g., in micellar droplets and biomembranes. For them both theoretical (Kirkwood–Buff approach) [31] as well accurate numerical [32] evaluations of the rigidity constant, associated with the Gaussian curvature effects on a membrane surface, predict its value to be negative. The interactions have been assumed to be of LJ-form [28], so that according to our scenario just drawn, we have to be placed within the nanoagglomeration framework. This is, thus, another evidence that the Gaussian curvature is related with a LJ-context, and vice versa. The route (ii) suits very well the highly fluctuating ordered agglomerations in biopolymeric complex soft-polycrystals [33], for which the surfaces of the grain boundaries, denoted by $s_{d=3}$, fluctuate with the time t as $s_{d=3} \propto t^2$ for $t \gg 1$ again, cf. [33] and the discussion between formulae (14) and (15) therein.

It is worth mentioning that both the forms derived above in terms of R , Eqs. (18) and (19) respectively, are physical-potential forms well-known, e.g., in electrostatics: The former represents a far-distance electrostatic potential, emerging from an electric point charge, whereas the latter is expected for extremely long cylindrical, presumably, torus-like, capacitors in which internal cylinder is charged oppositely to its external cylindrical counterpart. A qualitative observation can be offered, namely, that here a tube-like structure of the capacitor recalls somehow the capillarity effect, which prevails in the microworld but would not be a decisive phenomenon in its nano-counterpart.

Further arguments about the interpretation of the curvatures as potential barriers in agglomeration processes follow from the RW -analogy [13,14] and the procedure proposed in [20], establishing kinetic equations in the presence of potential barriers.

The procedure mentioned provides the general expression for the current

$$J = -D \frac{\partial}{\partial v} f - \frac{D}{k_B T} \frac{\partial}{\partial v} \Delta w f,$$

where Δw is the maximum useful work that can be extracted from the system, or the available system energy [20]. In our case, an elementary available

energy change dw over the elementary grain size change, dR , results in a similarity condition, namely $dw/dR \sim \sigma_g$, where σ_g is the surface tension of an individual grain surface; for simplicity, let us restrict ourselves to a three-dimensional case of $d = 3$. Because we are mostly interested in matter drift effects, we have to calculate the term $b(v) \frac{\partial}{\partial v} w$ which nearly equals $v^\alpha \times 1/R^2 \times \sigma_g$. But since for $d = 3$, $v^\alpha \sim R^2$, and after performing a Tolman-like [11,12] expansion in $1/R$ of $\sigma_g = \sigma_g(1/R)$, up to the second term, one is capable of getting the discussed potential form $\Phi(R) \simeq \Phi_{00} \ln R + \Phi_2 + \Phi_{11}/R$, which follows from the expression $\Phi = \int \sigma_g(R) dR + \text{const}$. To obtain this expression, we have neglected the contribution to the potential coming from the first term in the development of the surface tension. That contribution is proportional to R and therefore, negligible for small grains. This result clearly shows that the drift is due to surface tension effects, and their curvature subtleties.

4. Final address and perspective

The final address and a perspective can be split up in the following:

- To sum up: We have applied mesoscopic nonequilibrium thermodynamics [19] in order to improve a phenomenological d -dependent construction [14,15] of the matter flux given finally by Eq. (9), and proposed to describe an ordered agglomeration, termed the normal grain growth [5].

- When offering such an improvement we have realized that we have either to calculate explicitly the form of the correlations of the random part of the flux [17,18] by relying on a physical mechanism proposed for such a purpose, or to assume a geometrical constraint by keeping the surface-to-volume exponent effective. It enables then to realize that the curvature has to be a principal geometrical constraint, cf. Eqs. (1) and (9).

- It has remained to note that in “hard” condensed-matter systems [5,7], mostly, the curvature would sufficiently support the description of the evolving system. In soft condensed-matter agglomerates, in turn, operating most effectively in nanoscale (see, Fig. 1), the Gaussian curvature,

being a reciprocal of R squared, as well as the Tolman correction to surface (line) tension, emphasized above, are just the case [1,9].

- The forms of the proposed physical potentials Φ are then offered twofold: Either in a logarithmic form (10) or as a sum of two power-like forms (11). Though a choice of the potentials known in physics is pretty vast [34], we have exactly picked up those two forms because they not only follow well the relatively simple mathematics staying behind the model [13,19] but above all they suit extremely well to the offered physical scenarios of agglomeration. In this moment, let us state clearly that outside the range of very small inverse Debye length values (high temperature limit or small co- and counter-ion concentrations), we see now no direct chances for applying here readily the *DLVO* physical potential (screened Coulomb) so well applicable to most of colloid as well as surfactants-containing systems [34,35]. This is likely therefore, that it describes mostly repulsion effects but for preserving agglomeration we need just attraction to prevail [35].

- The normal grain growth model [5,7,22] is a model in which agglomeration is being realized in a random fashion and under space-filling constraints [15]. It is well-known [13,14] that for it the kinetic dependence of a mean grain radius is given by $R \sim t^v$ ($t \gg 1$), where $v = 1/(d+1)$, i.e., the exponent is given by a reciprocal of the superdimension $d+1$. Interestingly, the model with a surface-to-volume exponent α assumed, which clearly invokes dense (colloidal) agglomerations [36], yields an asymptotic kinetic law constituted by the superdimension $d+1$. But it seems natural: the $d+1$ -account is just a proper description of nearest neighborhood for a grain in d -dimensions [15]; the whole matter agglomeration strategy is sometimes termed in textbooks the random close-packing. Therefore, such a kinetic law seems legitimate as well [13,14].

- The above is going to be a bit changed for the nanoworld for which a kinetic law may change, presumably as $R \sim t^\omega$ ($t \gg 1$), where $\omega = 1/(d+2)$ could be predicted here. Thus, the evolution can go slower. There is an evidence that such a slowing down of the grain-growth rate may emerge, for instance in some specially fabricated (cryomilled;

then kept in about 2/3-regime of melting temperature) nanopowders, and mostly due to pinning effects, accompanied by precipitation sub-effects at grain boundaries, presumably giving room for Gaussian-curvature assisting (or, bending) phenomena to enter [37]. Moreover, both the models, with the mean as well as the Gaussian curvatures, are quite reminiscent of a “hydrodynamic” pairwise coalescence (ripening) model proposed in the early 1970s by Binder and Stauffer, in which however, the diffusion process is really done in a position space, being as in our model, composed of two different parts: a translational as well as some rotational, cf. [38], and refs. therein. The kinetic radius vs time law was obtained the same [38], and the cluster-interaction parameter inferred from Binder and Stauffer’s formulae, say ι , obeys: $\iota = d - 1$ (the subdimension) for the microworld evolution, whereas $\iota = d$ (the Euclidean dimension) for nanoagglomeration, both of them being exhaustively described in the present article in terms of a nonequilibrium thermodynamics model with geometric constraints. Note that the exponent α introduced above combines again both ι -s just mentioned.

- A general observation appears that anticipates the agglomeration process as being accelerated (mean curvature mechanism) or decelerated (Gaussian curvature mechanism) by presence of such barriers; moreover, presence of the drift term in Eq. (1), or equivalently in Eq. (9), makes the agglomeration more directional viz ordered. In all the cases mentioned the role of surface tension is to be emphasized, but its possible neglect, characteristic of loosely agglomerating systems [39] (ripening; cluster–cluster aggregation [4,5,36]), leads also to the same $d+1$ -account in the growth law because in late time regimes the role of capillarity, according to the frequently addressed Laplace–Kelvin–Young law, is not very much underlined, and therefore, the asymptotics of both the systems, with and without pronounced capillarity influence, look roughly the same [13,22,39].

- Possible future task would remain to solve formally the LJ-potential influenced system with the Gaussian curvature mechanism, including $v^{2(\alpha-1)}$ -term

$$\frac{\partial}{\partial t} f(v, t) + \frac{\partial}{\partial v} J_G(v, t) = 0,$$

where

$$J_G(v, t) = -\sigma v^{2(\alpha-1)} f(v, t) - Dv^\alpha \frac{\partial}{\partial v} f(v, t),$$

with appropriate initial as well as boundary conditions as was already done for its ln-potential influenced counterpart [13–15,19,39]. But it is left for another study, preferentially for $d = 3$, i.e., $\alpha = 2/3$, which is physically more transparent as well as quite a common case [2,4]. Moreover, it is possible to consider other, higher order (above 2nd order) accounts to curvature, what has already been done for single-crystal growth [10,40]. For example, for $q_\chi = 1/3$ a third curvature correction, like $1/R^3$, responsible for asymmetric growth [40], may emerge. Higher curvature “modes” of the growing process,² like $q_\chi^{(n)} = 1/n$, where $n > 3$ here, would also be responsible for some other nonlinear, and quite numerous effects, arising possibly during growth in complex materials [1,4,9,18,40]. Some of the effects predicted, may advocate for superplastic behavior of the model agglomerates considered. It turns even out that effect of superplasticity can more likely be attributed to nanomaterials because they, compared to micromaterials, are composed of smaller, and by definition more curvilinear grains for which cohesion effects are rather more pronounced [10,41].

• It is also worth examining the proposed evolution equations in terms of a fractional FPK-dynamics [42] because of its better sensitivity to different short, intermediate and long timescale events [26] in nucleation-and-growth phenomena, leading quite often to formation of model biomaterials and/or biomembranes; till now it was proposed to be solved phenomenologically by postulating the corresponding but full space- and time correlations in $D(v, t)$, being of a power form, cf. [26]. Then, some attempts of applying standard derivatives, not the fractional ones, but for a finite agglomerating system, and with fractional statisti-

cal moments of the examined growing process, have recently been started as well [10].

• Last but not the least, it is clear that the offered theory of matter agglomeration is thought of to be an extension of the (normal) grain growth theory, unquestionably suitable for pure single phase systems, in which the kinetic parabolic law is mostly expected to occur [43], whereas in our approach it looks like an exception [37], being realized exclusively for $d = 1$ ($\alpha = 0$), i.e., for the one-dimensional (surface-less) reference state [14], see Section 2.

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² In general, the distance-dependent potential $\Phi(R)$ would consequently obey: $\Phi(R) \propto \text{const.} + R^{-(n-1)}$ for $n > 1$ and natural, where n -s are going to enumerate the subsequent curvature modes.

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