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STATISTICAL THEORY OF NORMAL GRAIN GROWTH REVISITED*

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In this paper, we discuss three physically relevant problems concerning the normal grain growth process. These are: Infinite *vs* finite size of the system under study (a step towards more realistic modeling); conditions of fine-grained structure formation, with possible applications to thin films and biomembranes, and interesting relations to superplasticity of materials; approach to log-normality, an ubiquitous natural phenomenon, frequently reported in literature. It turns out that all three important points mentioned are possible to be included in a Mulheran–Harding type behavior of evolving grains-containing systems that we have studied previously.

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1. Introduction

Normal grain growth (NGG) is often considered as a final stage of the recrystallization process [1], and both the processes belong, according to some physical metallurgy classification scheme due to Christian, to the so-called nucleation-and-growth phase transformations. Speaking more specifically, they represent a class of the heterogeneous phase transformations, *i.e.* they are thermally activated, in contrast with some other ones which are not, *e.g.* the spinodal decomposition; they are termed, in turn, the homogeneous phase transformations [2, 3].

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By performing this study we wish to embark upon three particular tasks that arose while modeling the grain growth mostly of a normal type. Before revealing, however, what we have in mind, let us state explicitly what do we mean by the normal grain growth. For this purpose we may rewrite accordingly a definition proposed by Weaire and McMurry in a review paper [4]. That somewhat verbal definition looks now like [4]:

- the NGG is said to be a steady state of the recrystallization process [5] in which a cellular system emerges;
- grain boundaries (GBs) do accumulate a positive surface energy;
- GBs perform a kind of motion towards lowering their energy;
- the overall grain structure evolves self-similarly with time as to augment grain size.

Notice by the way that from the above definition it immediately follows that grain growth as well as other related processes, like soap froth formation or evolution of bubbles-containing systems (foams), can be modeled by the same means. (There exists, in fact, a long-living analogy between polycrystals and soap froths, which has been invoked in various contexts, *cf.* [3].)

Inspecting more closely the mechanism of normal grain growth one notices its basic signatures. They can be summarized as follows: The GBs try to perform a deterministic motion towards their centers of curvature, caused by a pressure difference (capillarity), but the motion is somehow perturbed by presence of internal topological constraints imposed on the material as a grains-containing system. Thus it is also assumed to be of stochastic character, *i.e.* it is subjected to internal noise. This is at least a certain picture emerging from pretty complex but, no doubts, readily experimentally supported scenarios of the grain growth, in particular of a normal type [6]. Such a stochastic picture is strongly advocated by several authors [7, 8]. Another almost equally popular picture can be named a statistical picture of the process. It uses (sometimes overuses) a well-established concept called log-normality, which appears to be a quite ubiquitous feature of a good number of stochastic processes met in nature [9, 10]. It takes into account a law of proportionate effects which tells us that any relative change of physical quantities, as for example in the grain diameter, is proportional to a random fraction (number), *cf.* [11] and references therein, or can be readily thought of as a stochastic (Wiener) memoryless process [12].

As it was already mentioned, in this paper we are going to refer to three quite particular subjects, being in our opinion, of prior importance while studying the NGG phenomenon. The first topic we would like to consider is

going to be a step towards reality in our modeling which is simply a discussion on possibility of treating our system as composed exclusively of grains of finite volume. In this way we hope to remove a certain dichotomy that appeared while studying the normal grain growth based on the Mulheran–Harding model (M–H) [13], see Section 4. This model will be outlined in the next section (Section 2), and its extension will also be presented (Section 3).

Next, we will try to convince the reader that some other extension of the modeling of M–H type is worth doing. It is based on the assumption, that for certain obvious reasons (robustness) and/or because of some physically justified circumstances expected (stresses, crystallographic misfits between contiguous grains, impurities, defects) there could firmly appear a situation during the material growth in which a fine-grained structure formed will not disappear, but rather will attain a long period of living circumstances. (In a technological process it can in principle also be kept in such a stage of long duration, just for obtaining a refined material structure.) Therefore, we have to solve first a simple deterministic model with a correction due to curvature towards incorporating the so-called Tolman length [14, 15]. It seems reasonable because, as was said above, the NGG process is a kind of steady state, so that appearance of the thermodynamical quantity taken from the equilibrium thermodynamics rather cannot make someone disappointed. This is thus our address to the second topic mentioned above, with a hope on possible future applications to biomembranes, interfaces and thin films which are usually exposed to various strain-stress fields as well as other internal perturbations (for instance, pinning) causing enhanced curvature effects. The above will constitute the body of Section 5. Further, we would like to address our third task. Namely, we wish to make a constructive comparison between the M–H type of modeling that we have presented quite recently [16], and the statistical models by Kurtz–Carpay and Pandè leading to log-normal behavior [9, 10], *cf.* Section 6. In this section we will also underscore the fact that the log-normal solutions are solutions characteristic for the geometric Brownian motion [12]. A concluding address (Section 7) will be the last main section of the present paper.

2. Mulheran–Harding model: A short overview

The M–H model [13] is a sort of a Random Walk (RW)-like model where the RW is to be realized with a random “jump” that is not done in a position space but rather in the space of grain sizes [16]. Thus, it describes the size- and time-dependent rearrangement of a polycrystalline system by means of the following evolution equation [16]

$$\frac{\partial}{\partial t} f(v, t) = D \frac{\partial^2}{\partial v^2} v^\alpha f(v, t) = -\frac{\partial}{\partial v} j(v, t), \quad v \in [0, \infty), \quad (1)$$

where v is the volume of a grain, D is a constant reflecting a RW behavior in grain growth, to be named a diffusion-migration reference constant, $f(v, t)$ is the distribution function of grains at time t (having the meaning of the number density), *i.e.*, $f(v, t)dv$ is a relative number of grains of size in the volume range $[v, v + dv]$ and the parameter α depends on dimension of the system, and reads [16]

$$\alpha = 1 - \frac{1}{d} \quad (2)$$

for systems of dimension d ; notice that for $d = 1$ one provides $\alpha = 0$, so that it is hoped that the approximation invented does work effectively for $d > 1$, and in this work is confined to d -s being of integer value. The parameter α reflects the fact that the net flux of the particles wandering across the grain boundaries is proportional to the area of the surface $s \propto v^{2/3}$ of grains of volume v (for three-dimensional systems), and to the length $l \propto s^{1/2}$ of the circumference of crystallites of area s [13, 16] for two-dimensional systems. Moreover, note that for $f(v, t)$ no normalization condition holds, so that it is not a probability density function which is in turn the case of the conventional RW realized in a position space. The flux $j(v, t)$ in Eq. (1), *cf.* (1), is rewritten as [16]

$$j(v, t) = -D\alpha v^{\alpha-1} f(v, t) - Dv^\alpha \frac{\partial}{\partial v} f(v, t), \quad (3)$$

which means that it is decomposed into two parts. These are respectively: The drift and the diffusion terms. Let us realize that the deterministic drift term is proportional to curvature $1/R$ of the grains, where R is the grain radius. It is so indeed because it is proportional to $v^{-1/d}$, but clearly v is proportional to R^d . Certainly, after Kelvin, Young and Laplace the curvature-driven part is proportional to the surface tension associated with a GB [3]. The diffusional term, in turn, takes the form of the phenomenological 1st Fick's law, with an appropriate modification, however, namely that the flux is proportional to the area of a grain. In other words, grains change their volume by gaining or losing atoms (molecules; simply, entities) and the rate of attachment/detachment is closely related to the grain surface magnitude and to the gradient of the density function $f(v, t)$.

As to solve Eq.(1) we have to complete (1) by suitable initial and boundary conditions (IBC). These are [13, 16]:

(A) The initial condition (IC),

$$f(v, t = 0) = f_0(v), \tag{4}$$

where $f_0(v)$ is a given initial distribution of grains.

(B) The boundary conditions (BCs),

$$f(v = 0, t) = 0 \qquad f(v = \infty, t) = 0. \tag{5}$$

The physical interpretation of the boundary conditions makes no further hesitation: The number of grains of zero volume $v = 0$ as well as of infinite volume $v = \infty$ equal zero at any time. The latter is often anticipated to be a landmark of the NGG phenomenon [5]. Some violation of the BCs in turn causes to classify a process under consideration to be anomalous or abnormal, so that for such a reason we may also speak of an anomalous grain growth (AGG), just in contrast with the NGG.

The goal of this section as well as of the subsequent sections is not to provide the reader with both the method of solution as well as the main results obtained for the evaluated physical quantities of interest. They can be found elsewhere [16, 17]. We may summarize here the main findings concerning (1)–(5):

- (i) In the long-time limit, kinetics of the process under consideration depend very weakly on the IC applied.
- (ii) The principal physical quantities (inferred from the central statistical moments of the process): The number of grains, $n(t)$, as well as the mean grain radius, $r_{mn} \equiv r_{mn}(t)$, follow a power-like time asymptotics, inverse and direct, respectively; this is also the case of the fluctuations, $\sigma_{mn}^2 \equiv \sigma_{mn}^2(t)$, around the mean grain size (direct power law time asymptotics).
- (iii) The total hypervolume $V(t)$ of the system, evaluated from the first central moment of the statistical process under study is conserved; note that it automatically imposes a question about possibility of attaining an arbitrary large value of the volume v of the individual grain whereas the total volume of the material, being just at a time instant t chosen the sum of $n(t)$ single volumes, is the same as at time $t = 0$.
- (iv) The formal solution to the problem can be recast by using the operator method, utilizing a separation *ansatz* as well as solving an ordinary differential equation of Bessel type, *cf.* [17] and refs. therein.

3. Extensions of the Mulheran–Harding model

Let us now think of a clear and physically reasonable differentiation of the terms involved in the flux $j(v, t)$. Thus, let us postulate an extension of Eq. (3), namely,

$$j(v, t) = -F(v)f(v, t) - Dv^\alpha \frac{\partial}{\partial v} f(v, t), \quad (6)$$

where $F(v)$ is a deterministic part which takes into account various mechanisms of the growth process. The simplest extension is

$$j(v, t) = -\sigma v^{\alpha-1} f(v, t) - Dv^\alpha \frac{\partial}{\partial v} f(v, t), \quad (7)$$

where now σ and D can be independent parameters. It means that the surface tension mechanism of growth is independent of the mechanism of the migration of particles through boundaries of grains.

One can take into account the curvature effect on the surface tension [18–20]. Then the next extension reads

$$j(v, t) = -[\sigma v^{\alpha-1} + \gamma v^{2(\alpha-1)}] f(v, t) - Dv^\alpha \frac{\partial}{\partial v} f(v, t), \quad (8)$$

where the term with the parameter γ describes the Tolman curvature correction $1/R^2$ [14].

Clearly, by doing so we want to tell the reader that the two above in principle concurrent processes (convectational and diffusional) ought to be realized with different dynamics. A reflection of this fact we see is just to introduce the above independence among various parameters. We are of the opinion that such an extension given by assuming explicitly that $F(v) = \sigma v^{\alpha-1} + \gamma v^{2(\alpha-1)}$ can also be anticipated as a reasonable step towards proposing a comprehensive statistical theory of the formation of superplastic materials, see Section 7. As is known, superplasticity is a physicochemical phenomenon readily promoted by a microcrystalline structure, *i.e.* up to a certain rather small grain size, and manifested truly in high temperature limit, but these are by the way basic assumptions of our modeling.

A certain quite important underlying physics which stays behind the quadratic correction in curvature due to Tolman, in spite of being valid for crystals of sufficiently small size rather, is inevitably and above all connected with sign of the parameter γ , *cf.* Eq. (8). As can be learned from [20] when $\gamma > 0$ one may solely expect some additional enhancement of the growth rate, form the one hand, but also a symmetry breaking between the interiors and exteriors of the grains enters, on the other, what can be a meaningful

elucidation of the crystallographic misfits, or different crystallographic misorientations between a grain and its very surroundings [3,5,7]. When $\gamma < 0$, in turn, one may expect that a very small solid crystal will be going to melt back, so that a problem of unstable bubble-like nucleus appears [20]. This situation will, however, discourage a formation of tough fine-grained (superplastic) polycrystals in the modeling proposed, so that will be of minor importance from practical viewpoint. From [20] it follows as well that some higher order terms, like K^3 and/or the Laplacian of K (smoothing out the surface tension effects), can be omitted since they specifically describe fingered or dendritic growth, which are by the way not the growing processes under study.

4. Volume aspects

As is seen from point (iii) of Section 2, it would be useful to consider the model of NGG in which presence of an arbitrary large volume v of the individual grain is forbidden, contrary to what we may find in [13] or in our former studies [16,17]. It is worth inventing since it could have been a quite large step towards a more realistic NGG-modeling, a type of modeling which is still of very practical importance in many technological processes [3,5–7]. It is obvious that the volume v of the individual grain cannot be larger than the total volume of the material. It means that the phase space in (1) is not the unbounded space $\Omega_\infty = \{v : v \in [0, \infty)\}$ but should be replaced by the bounded space $\Omega_{V_0} = \{v : v \in [0, V_0]\}$, where $V_0 < \infty$ is a maximal volume of the individual grain. In other words, we will be willing to replace the second BC from (5) by the following one

$$f(v = V_0, t) = 0, \tag{9}$$

where V_0 cannot exceed the value of the total volume of the material $V \equiv V(t)$ [16], $0 < V_0 \leq V(t) < \infty$. It can be inferred from the relation for the total volume of all grains, namely,

$$V(t) = \int_0^{V_0} v f(v, t) dv. \tag{10}$$

and not from the very analogous but improper integral of the same kind [17].

There is a serious difference between unbounded Ω_∞ and bounded Ω_{V_0} phase spaces of the system. As was shown in our previous studies [16], in the former case the spectrum of the corresponding eigenvalue-problem is continuous and takes positive values. In the case of the bounded phase space, the spectrum is discrete and also positive [21]. For the model (1) with (7),

the spectrum can be found explicitly and the eigenvalues are proportional to the square of the positive zeros of the Bessel function $J_\nu(x)$ [21].

In the M–H model, the total volume $V(t)$ is conserved. It can easily be shown by use of the evolution equation (1). Let us consider this problem in the case (8) calculating the time-derivative

$$\frac{dV(t)}{dt} = \int_0^{V_0} v \frac{\partial}{\partial t} f(v, t) dv. \quad (11)$$

We substitute the right-hand side of (1) with the flux (8), integrate by parts and obtain

$$\frac{dV(t)}{dt} = Dv^{\alpha+1} \frac{\partial f(v, t)}{\partial v} \Big|_0^{V_0} + (\alpha D - \sigma)F_1(t) - \gamma F_2(t), \quad (12)$$

where

$$F_1(t) = \langle v^{\alpha-1} \rangle_t = \int_0^{V_0} v^{\alpha-1} f(v, t) dv \quad (13)$$

and

$$F_2(t) = \langle v^{2(\alpha-1)} \rangle_t = \int_0^{V_0} v^{2(\alpha-1)} f(v, t) dv \quad (14)$$

are “negative fractional statistical moments” in the volume space. If the phase space is unbounded then the first term on the right-hand side of formula (12) is equal to zero. For the bounded phase space, it need not be zero.

We can change the integration variable $v \rightarrow R$ using the relation $v = BR^d$, where the constant $B > 0$ is a geometrical factor which takes into account the shape of grains. Then

$$F_1(t) \propto \int_0^{R_0} R^{d-2} \rho(R, t) dR \quad (15)$$

and

$$F_2(t) \propto \int_0^{R_0} R^{d-3} \rho(R, t) dR, \quad (16)$$

where $\rho(R, t) = f(v = BR^d, t)$ and R_0 is determined by the relation $V_0 = BR_0^d$. It is obvious that these two integrals exist for the case $d = 3$. For the case $d = 2$, the first integral exists as well. The only problem can concern the second integral for $d = 2$ because then $R^{d-3} = R^{-1}$ and the integral can diverge. However, because of the first boundary condition in (5), for small v the distribution function $f(v, t) \sim v^\varepsilon$ and $\varepsilon > 0$. Hence, $\rho(R, t) \sim R^{2\varepsilon}$ for small R and $R^{-1}\rho(R, t) \sim R^{-1+2\varepsilon}$. Such a function is integrable in the neighborhood of zero and in consequence the integral converges. Moreover, the functions $F_1(t) > 0$ and $F_2(t) > 0$ since these are integrals of non-negative functions. For the unbounded phase space and for $\gamma = 0$, the total volume of the specimen increases in time if $\alpha D > \sigma$ and decreases if $\alpha D < \sigma$. For the M-H model, $\alpha D = \sigma$ and this is why the total volume is conserved, $V(t) = V(0)$. If we add the curvature-corrected term, *i.e.* $\gamma \neq 0$, the total volume can be *non-monotonic* function of time. For the bounded phase space, Ω_{V_0} , the volume conservation problem is much more complicated because $\partial f(v, t)/\partial v|_{v=V_0}$ can be different from zero (can be negative). Nevertheless, also in this case $V(t)$ can be a non-monotonic function of time. Physically, it means that the just recognized features can be anticipated as some first signatures of a plastic (nonconservative) behavior of the model material under study.

5. Curvature corrections as a step towards superplastic behavior of material

Volumetric aspects considered thoroughly in Section 4 led to the conclusion that for the phase space Ω_{V_0} (*i*) the overall volume of the system cannot be conserved (in general); (*ii*) the total volume can also change in course of time, which means that the material can expand or shrink during the formation of a polycrystal (or a foam, see remarks in Section 1, and a discussion after Eqs (8) and (11) in Sections 3 and 4, respectively). Such a behavior can be recognized as a signature of plastic deformation of a body, too. To guarantee somehow, in the framework of our modeling, however, a superplastic end product, we have to assure a bit more: We should find a possibility for evolution of the fine-grained structure just mentioned in the preceding sections. Let us then develop our argumentation beneath in a systematic way.

A key point of our considerations here will be some exploration of the GB motion towards its center of curvature with a speed proportional to the curvature what is inherently involved in the modeling of M-H type [22, 24]. Let us then start from Eq. (7) but drop for a while the second diffusive term by requiring $D = 0$. Applying the reasoning coming after Eq. (3) (accepting formally for the moment that $\sigma = \alpha D$), and utilizing an

efficient approximation that $j(v, t) = v_{\text{gr}} \times f(v, t)$, for the velocity of the grain boundary, one gets immediately

$$v_{\text{gr}} = \frac{dR}{dt} \propto \frac{1}{R} \quad (17)$$

for an arbitrary grain radius R . Notice that the formula (17) is also presented by Mullins in his paper on two-dimensional motion of idealized GBs as well as in a stochastic modeling of grain growth by Pandè, where the so-called internal noise, designated there by T is equal to zero, that means in deterministic case (though unfortunately taken from Hillert with negative prefactor preceding the term proportional to $1/R$) [8]. If we go further and wish to compare the model by Pandè with ours we have to accept that they are well comparable in the sense that the role of Pandè's internal topological noise, T , is played in our model by the Fickian diffusive term, denoted by $j_D(v, t)$

$$j_D(v, t) = -Dv^\alpha \frac{\partial}{\partial v} f(v, t), \quad (18)$$

which suffers also a kind of topological constraints by having incorporated the prefactor Dv^α which is proportional to R^{d-1} , and which reflects somehow a surface effect, see Section 2.

Let us continue along this line and ask a question concerning the curvature-driven motion of an arbitrary GB: Is there really so that under all possible physical circumstances met (or, expected) a GB is only driven by the magnitude of its curvature, K ? In other words: Must the pressure difference, expanded in K , be wrenched off on the first linear term, presumed that the pressure difference ΔP is the main driving force for the material exchange between two contiguous crystallites (objects)? Certainly, it does not [18, 20]. We claim, for instance, that under certain more subtle circumstances (account of fluidity; softness; strain-stress suitable context; surface tension molecular weight dependence of GBs in macromolecular polycrystals [23]; pinning; specific interactions due to existence of crystallographic misfits between contiguous grains, and so on) one has to expand ΔP like that [15]

$$\Delta P = \frac{\sigma}{R} - \frac{\gamma}{R^2} + \dots, \quad (19)$$

where $\sigma = 2\sigma_0$, and $\gamma = 2\sigma_0\delta_0$, *cf.* Eq. (8), and where σ_0 and δ_0 stand for the surface tension of the planar GB surface (practically, for a very large grain) and for the Tolman length [15] (see below), respectively. We thus postulate the mechanism like

$$v_{\text{gr}} = \frac{dR}{dt} = q^{-1} \Delta P, \quad (20)$$

where q serves for adjustment of the physical units in the above equation, having, however, the meaning of the flux passing through a GB unit surface. The solution to Eq. (20) is given in an implicit form

$$\frac{1}{2} \left[R^2(t) - R^2(0) \right] + \delta_0 \left[R(t) - R(0) \right] + \delta_0^2 \ln \frac{R(t)}{R(0)} = \frac{2\sigma_0}{q} t. \quad (21)$$

Somebody would like to pose another question: Why do we insist on solving this particularly simple deterministic model with the first correction to curvature $K \sim 1/R$? We do answer this question by saying that we have solved such an auxiliary model just to get an intuition whether is this reasonable to include such a correction of K^2 in our main statistical-physical model of M-H type. So, we may now response that by looking at the Eq. (21) we see some chances mostly for the second term of the left-hand side of it just to survive, see our discussion on superplasticity above and in Section 7. Therefore, it could be worth doing, but the explicit integration of the problem meets serious technical difficulties and up to now remains unsolved.

Let us, however, comment a bit more on Eq. (21) and its relations to known models [3, 8, 9].

First, let us state explicitly that the correction of K^2 causes appearance of two additional terms in the solution, which in absence of such a correction reads

$$R^2(t) - R^2(0) \propto t. \quad (22)$$

The two additional terms are: The term expressed by $\delta_0[R(t) - R(0)]$ and the logarithmic term. Starting from the latter we wish to say only that the logarithmic term often appears to be relevant either in an early stage of growing process or in low-temperature regime. (We may consider both the regimes to be of a certain relevance for us [25], though the low-temperature behavior is of no special interest when embarking readily on superplasticity.) Second, the Tolman length δ_0 which is involved in $\delta_0[R(t) - R(0)]$, and also in the logarithmic term mentioned, is an interesting statistical-thermodynamical parameter *per se*. It reads [14, 15]

$$\delta_0 = \frac{-kC_0}{\sigma_0}, \quad (23)$$

where σ_0 , to be expected quite small for superplastic polycrystals, is defined above and k is the rigidity constant for bending (being generally of moderate value), proportional to the so-called Gaussian curvature [26], while C_0 , being either of positive or negative sign [18], and to be expected quite large for superplastic polycrystals, stands for the spontaneous curvature, respectively. Now, it is clear why we enjoy the presence of the middle term in

the left-hand side of Eq. (21). It should be also visible why we assign the context to biomembranes, interfaces as well as thin layers interacting with their solid supports [3,7,26]. (By the way, notice here that our treatment of polycrystals by such means is not in a very distinction with treating drop-wise condensation, for example [15,28]. This makes thus another possible comparison: We cannot exclusively compare polycrystals and bubbles [4] but also there should appear a comparison between the polycrystals and the droplets.)

Completing the material of this section we wish to state only that incorporation of the second term (K^2) should certainly change the overall system behavior investigated in the framework of our statistical-physical model proposed. Such a change will probably be manifested both in the initial stages of the evolution as well as for a low-temperature regime which always gives a distinct resistance to growth [3,7,17]. Generally speaking, such a behavior can be possible to rationalize when polycrystals manifest slow or very slow dynamics, comparable to that characteristic for ceramics (relaxer materials) or glasses, the dynamics of which shows up a Gaussian logarithmic behavior [29], *cf.* the next section. If we neglect, however, the just anticipated presence of possible low-temperature limit we come back to the mentioned tendency towards superplasticity of polycrystalline as well as bubbles-containing model bodies.

Finishing this section in comparative manner let us try to foresee that so as the internal noise term T introduced in Pandè's model, together with an additional factor standing on the left-hand side of kinetic equation (proportional to R^ν , *i.e.* going to mimic the surface area term) would and does change the overall kinetic but asymptotic characteristics, like r_{mn} *vs* t in a way [8]

$$r_{mn} \sim t^{1/(2+\nu)} \quad (24)$$

with some ν , where $\nu \geq 0$, so does our diffusive term which appears in the material flux (8). Moreover, notice that for $\nu = 0$ the diffusive solution (22) can be recovered, but otherwise one gets non-diffusive solutions. Note, however, that in Section 2 of [8] (*cf.* Eq. (17)) another misprint appears which is now corrected by (24) given above. Interestingly that the model proposed by Pandè [8] conforms well to ours when in Eq. (24)

$$\nu = d - 1, \quad (25)$$

i.e. ν is d -dependent [27]. For $d = 1$ one recovers again a characteristic diffusive behavior, or in other words, the M-H behavior in $d = 1$, first explained by Louat [32]. For $d > 1$ one provides other non-diffusive cases as for example the so-called Ostwald ripening mentioned in [7,8] to be obtained formally for $d = 2$ [28].

6. Log-normality

After a very thorough study by Kurtz and Carpay [9] some doubts about appearance of a log-normal distribution of the grain sizes in a polycrystalline material have probably been thrown away, but again some renewed doubts appeared about eight years later [10], and concerned with other very exact fits to experimentally got distributions of crystallites. Before, however, looking more closely into the material just signalized above, let us define the subject in question, that means the log-normality.

The origin of log-normality in grain growth, possibly of normal type, can quantitatively be explained in the following. Namely, let us take a continuous picture and assume that a grain is located in sufficiently high topological class, *i.e.* it is considered to be large enough, *cf.* [9]. This means that it is able to augment its volume and/or surface area, designated by $A(t)$, just at the expense of the contents of its neighbors. (Note that, in general, there is nothing against dealing with A as the area of a $(d - 1)$ -dimensional hypersurface of d -dimensional hypervolume.) A probably most natural way of reflecting this fact is to write down a deterministic equation responsible for the growing process, with a change $dA(t)$ proportional to the magnitude of $A(t)$, namely

$$dA(t) = \mu_a A(t) dt, \quad (26)$$

which shows an exponentially fast growth with a drift constant equal to μ_a . In language of discrete processes one has to see that a mechanism staying unavoidably behind the exponential (natural and perennially alive) growth may readily look like

$$A(t) = A(0) \left(1 + \frac{\mu_a t}{n} \right)^n \quad (27)$$

what for $n \rightarrow \infty$ yields a solution in the form

$$A(t) = A(0) \exp(\mu_a t), \quad (28)$$

which is formally a solution to Eq. (26). But life would be very simple if the above scenario happened to a real process like for example formation of polycrystals, which suffers a sufficient account of the internal topological noise, T , *cf.* [7, 8].

As to achieve a formal description much closer to experimental reality [3, 5, 6], one has to complete Eq. (26) by some additional term, possibly of noisy character [7]. It is thoroughly proposed [12] to make it by adding a kind of memoryless Markov process called the Wiener process $W(t)$ [30]

which would account for random changes of the surface area magnitude $A(t)$. Now, the suitable equation looks like

$$dA(t) = \mu_a A(t)dt + \sigma_a A(t)dW(t), \quad (29)$$

where σ_a measures the surface area fluctuations. This is a stochastic equation given in the Ito representation [12, 30], and it is equivalent to [12]

$$d \ln[A(t)] = [\mu_a - (\sigma_a^2/2)]dt + \sigma_a dW(t). \quad (30)$$

In the above equation a signature of logarithmic behavior appears for the first time, in spite of that trivial mathematical solution which comes by solving Eq. (26), see Eq. (28).

Knowing the Fokker–Planck equation, corresponding to (29), it is also possible to calculate the transition probability from a state (A', t') to (A, t) , denoted by $p(A, t | A', t')$ which reads [12]

$$\begin{aligned} p(A, t | A', t') &= [2\pi(\sigma_a A)^2(t-t')]^{-1/2} \\ &\times \exp\left\{[\ln(A/A') - (\mu_a - (\sigma_a^2/2))(t-t')]^2 / 2\sigma_a^2(t-t')\right\}. \end{aligned} \quad (31)$$

The corresponding mean value \bar{A} and the variance Σ_a^2 read [12]

$$\bar{A} = A' \exp[\mu_a(t-t')], \quad \Sigma_a^2 = (A')^2 \exp[2\mu_a(t-t')][\exp[\sigma_a^2(t-t')] - 1]. \quad (32)$$

From Eq. (32) it follows that both \bar{A} and Σ_a^2 grow nonlinearly (exponentially) with time t . This is somehow comparable with another our model [31] which is based, however, on slightly different physical foundations (no pronounced role of surface tension was assumed) [16] and in which for instance the total hypervolume is not conserved, *cf.* Eq. (32), and the quantity \bar{A} defined in there. (Because the model served to describe a recrystallization (Re) process [31], for the purpose of the present work we will call it the Re-model.) It looks also like our present case, modeled in the finite phase space, since, as is mentioned in Section 4, the total volume (or, hypervolume) cannot be readily conserved.

It could then be argued that the just discussed log-normality-based model differs from both the models before studied by us [17, 31], though it remains close, and as expected, can reproduce the main landmark of both the models mentioned, but thoroughly studied in the infinite phase space, namely whether the total hypervolume is conserved or not. Namely, for $\mu_a \rightarrow 0$ one provides that $A \rightarrow A(0) = \text{const}$ ($A \equiv A(t)$), what is very characteristic of

the NGG-model, whereas for $\mu_a \ll 1$, one expands $\exp(\mu_a z) \simeq 1 + \mu_a z$ for small z , and then one can reproduce a linear-in-time growth of the hypervolume for the Re-model but in the limit of $d \rightarrow \infty$, *i.e.* more pronounced for high-dimensional Euclidean spaces [31]. In such a limit fluctuations σ_{mn}^2 involved in the NGG [16], *cf.* Section 2, coincide well with Σ_a^2 stated in (32), but still while taking another limit $\mu_a \rightarrow 0$, as already performed above. Summing up, let us recall that there are both differences as well as quite striking similarities between the log-normality-based grain growth model [3, 10, 33] and both the invoked models studied previously [17], so that there is practically no chance to get the NGG-behavior (or, Re-behavior) outside the limits just mentioned. It may lead to a conclusion that the log-normal behavior is a typical non-steady state behavior [28], and would serve better to describe an abnormal growth (see Section 1), or perhaps a real recrystallization process [1, 2, 5–7]. Moreover, the unconserved total volume appearing in the modeling performed in the space Ω_{V_0} suits better to log-normal characteristics \bar{A} and Σ_a^2 .

7. Concluding address

In our previous studies [16, 17] we have ascertained more or less that (*i*) the influence of the initial condition may sometimes be more pronounced, *cf.* the initial state in the form of a Weibull function of v [16], $f_0(v)$, which favors some possible application of the proposed modeling, mostly towards designing a fine-grained material; (*ii*) if the total volume of the system does not remain conserved, one may expect abnormalities, and an AGG-phenomenon instead of the NGG can occur. A prophetic meaning of the latter has quite exhaustively been proved in Section 4, dealing with volume aspects. The former, in turn, has been explored in sufficient detail in Section 3 and mainly in Section 5, showing an interesting physical consequence of our modeling, which one may see as some consideration on how to form a model fine-grained (superplastic) material [34], with a certain attractive theoretical possibility of modeling superplastic behavior of ceramic nanocrystals, intermetallics, metallic alloys and polycrystals [34].

It would be instructive to offer a reader some thought experiment interconnecting the (kinetic) final result of our modeling, *i.e.* the mean grain radius [16, 27], r_{mn} , *cf.* Eqs (24)–(25), taken certainly for large enough time instants, $t \gg 1$, and the stress magnitude, designated by σ_{HP} , where some presence of an internal σ_{HP} in the material seems unquestionable [35, 36]. Namely, let us consider a Hall–Petch (H–P) relation of both direct and inverse types [34, 35]

$$\sigma_{HP} \propto (2r_{mn})^\mu, \quad (33)$$

where μ can be a measurable exponent [34, 35] of negative (direct H–P: low

temperature non-superplastic regime) or positive (inverse H-P: high temperature superplastic regime) values. We see then that for the superplastic behavior to occur we need to have small enough grain radius and not too small temperature of the process (to assure respective fluidity of the material), that means under, in some sense, extra-conditions to be achieved. For the non-superplasticity, in turn, one cannot go below a certain quite large grain radius value, not forgetting, however, that any variation in temperature towards higher values is undesirable, *cf.* Section 5. Moreover, one has to take really care about the possible variations in total volume (see, [27]) of the material under study (Section 4), and the boundary conditions as a whole [37], not avoiding if possible statistics based on counting the frequency of appearance/disappearance of grains of a certain size, and how they conform to the model log-normal pattern, see Section 6. By the way, someone should not feel embarrassed to think over the log-normal behavior as a kind of Brownian motion, called the geometric Brownian motion [12], where the surface magnitude is the major geometric constraint and/or kinetic obstacle, see Sections 2–3, because it is just in the spirit of the presented study.

In a final word, let us go back to relation (33), which after combining it with Eqs (24) and (25) reads for a sufficiently large processing time τ_p

$$\sigma_{\text{HP}} \propto \tau_p^{\mu/(2+\nu)}. \quad (34)$$

From the above it can be seen why the polycrystalline material (or a foam even) is strengthening in very mature stages of the grain growth ($\mu > 0$, σ_{HP} grows with τ_p), whereas it is going to weaken when $\mu < 0$ because σ_{HP} decreases with τ_p , which means that a brittle structure emerges, see [35]. This final conclusion should justify internal robustness of the fine-grained and non-brittle superplastic structure under examination. Moreover, this robustness depends upon the geometrical dimension d , in the sense that Eq. (25) holds. Notice that relation (34) is often recognized to be a manifestation of anomalous relaxation behavior of the system, driven by fractional dynamics, *cf.* [35, 38], and references therein, and recall Eqs (13) and (14) in Section 4. This kind of relaxation conforms also very much to a relaxation mechanism which proceeds effectively *via* the GBs as well as their junctions, being important accumulation spots for the stress field. It can be seen as a thorough manifestation of dispersive kinetics in condensed media [39].

The authors wish to dedicate this paper to the memory of Professor Andrzej Płonka, whose invaluable insight into dispersive kinetics in condensed matter systems has stimulated enormously our studies on nucleation and growth and related phenomena discussed throughout the paper.

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