

Kinetic Approach to the Nucleation-and-Growth Phase Transition in Complex Systems

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This study deals mostly with kinetic anomalies occurring in nucleation-and-growth phenomena in complex systems, e.g. polycrystals, partly ordered alloys, quasicrystalline assemblies or mesomorphs. The main kinetic phenomenological approach utilized in a versatile way is in fact an anomalous random walk approximation, though the process is not thought to be realized in a position space (a most expected case) but in the space of grains (clusters) sizes. Two effective descriptions of the processes are discussed. The first, in which a supreme role of capillary forces as the leading kinetic mechanism is proposed. The second, for which the Fick's law is fulfilled, and the effective area of the clusters, like in the diffusion-limited cluster cluster aggregation, is of prior importance. A novel contribution to the kinetic problem mentioned is offered which seems to be very suitable for revealing kinetic anomalies in such systems. It relies on assuming that the systems under study are not only statistically self-similar when looking at their distribution over the available physical space, but that the processes proceed also in a self-similar manner when carefully inspecting their time behaviour. Therefore, the basic kinetic coefficients characterizing the system's behaviour are often assumed to be inverse power law time-dependent, which is by the way the main assumption of the so-called dispersive or long-tailed kinetics frequently applied to, e.g. reactive and fluctuating soft-matter systems, like model biomembranes or polymers. The presented description, which unfortunately offers no explicit microscopic insight, is compared to the standard approaches of theoretical analysis of heterogeneous phase transformations as the Avrami-Kolmogorov (Mehl-Johnson) concept, utilized mostly in metallic polycrystals, or to some extent, the Mullins-Sekerka-like instability mechanism applied to biopolymers. The study is completed by a brief consideration of the propagation of mechanical stresses in a polycrystal along crystalline boundaries and some order-disorder effects manifested, for example, in lipid mesomorphs. A critical comparison with other available kinetic approaches has been done as well.

Key words: phase transitions; nucleation-and-growth, anomalous kinetics, complex systems, power laws

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1 Introduction

The so-called nucleation-and-growth phase transition, belonging to a transition class termed heterogeneous phase transitions, attracts widespread attention of researchers as well as technologists. Recently, a spectacular revival of interest has undoubtedly been noticed, mostly because of considering kinetics of the transition, taking place in complex physical environments, like metallic and polymeric polycrystals or alloys, model biomaterials, organic quasicrystals, gels, ceramics, etc. The theoretical challenge here appears to solve analytically and/or numerically quite cumbersome tasks of modern nonlinear science as well as nonequilibrium statistical physics, whereas from a technological, or simply practical viewpoint, one wants to control and optimize important industrial or manufacture processes, e.g. formation of thin films and membranes, production of simple devices or protectors (for instance, microsensors, interconnects, capsules, coats), or eventually, a proper design of new materials of special purposes (for airplanes or cars, for example) [1].

Throughout the whole body of this review, we will confine ourselves to discuss, according to a perennially alive metallurgical classification scheme after Christian [2], a certain class of thermally activated growing processes. We have here in mind processes which are interface- (or grain-boundary) controlled. (This automatically implies that no one can expect long range transport, at least in the position space.) In particular, we would like to draw special attention to three subclasses of the (heterogeneous) nucleation-and-growth phase transitions, namely:

- (i) grain growth and recrystallization processes;
- (ii) polymorphic transformations;

(iii) order-disorder changes.

At this point, let us state clearly that this presentation will be by no means limited to systems of physical metallurgy, like metallic polycrystals and alloys or perhaps ceramics. Careful reader will see, however, that in certain situations we will try to benefit from many experimental as well as "theoretical" data collected by materials engineers, or specifically by physical metallurgists. It is not a completely new way that we have to follow because, at least since the eighties, there is some well-established tradition, e.g. in biophysics, just to enlighten many specific phase transitions, like gel-to-liquid crystalline phase transformations, by means of classical concepts first used in traditional solid state physics and also being successfully applied to physical metallurgy systems. One may here easily invoke a quite general example which must be placed around the Avrami-Kolmogorov (or, Mehl-Johnson) phase change concept [3].

This having in mind, we would like to offer a quite comprehensive phenomenological description of the kinetics of a number of phase transformations realized in the so-called soft-matter (complex) systems, being mostly of (bio)polymeric nature. (In this work the otherwise very important step of the transition, i.e. the nucleation step of the process under study, is not dealt with, presumed that the system "is prepared" to undergo a quite commonly accepted picture of the nucleation, mostly due to Turnbull and Zeldovich, and worked out rigorously by Avrami and others; cf. foundations of *Physical Kinetics* by Lifshitz and Pitaevskii.) The systems under study can be qualitatively characterized by means of one single term, namely: molecular or macromolecular polycrystals. Another verbal quality that can be assigned to them would be: partly ordered macromolecular quasicrystalline assemblies. To be a little bit more specific we wish to list a few examples. These are:

- (i) microcrystalline domains emerging during the gel-to-liquid crystalline phase transformation in model multilamellar lipid systems [4,3],

- (ii) lipid mesomorphs occurring in model lipid membranes [5],
 - (iii) protein polycrystals in solutions [6],
 - (iv) cylindrolites and spherulites grown on many nuclei from a polymeric melt [7],
- or, to some extent
- (v) statistically self-similar and/or partly ordered colloidal aggregates grown under diffusional control and realizing a random walk across available physical space; mobile coalescence or droplet condensation phenomena can be mentioned here as well [8].

It is rather commonly accepted that the systems mentioned above may in general include many kinetic anomalies. This is due to a complex physical nature of them. It is manifested on many levels of their dynamic structural organization. Neglecting a really microscopic insight into the problem, one can start from the structural organization on the level of a single macromolecule. If so doing we have to take into account seriously the following: the number of the degrees of freedom available to the random behaviour (motion) of the chain as well as, both, its conformation (related somehow to the degrees of freedom) and configuration, *viz.* chemical nature of the chain. The next structural level is logically connected with groups of the macromolecules. If they are ordered they constitute quasicrystalline microdomains or crystallites (grains). (These are sometimes called clusters, though this term is also used for description of disordered groups of molecules.) The orientations of the chains in different microdomains may differ, even when looking into the neighbouring ones. At this stage of dynamic organization of the system of major importance appears to be the following: how do the crystallites get together, if this is the case, and which is the basic mechanism of exchange of atoms, molecules or clusters of molecules (atoms) among them? Moreover, which are, if any, the essential kinetic obstacles of the agglomeration (aggregation) process and how do they decelerate the process as a whole? On the contrary, are there any factors which accelerate the process and how big this acceleration (deceleration)

can be? Thus, at any dynamic level of the structural organization of the system one may notice certain physical factors or agents that do influence the kinetic behaviour of the system under investigation. They may easily yield the kinetic anomalies which stand for the main object of our considerations in this study [9].

According to what will be considered the principal kinetic hindrance involved in our modeling becomes the presence of grain boundaries or interfaces between the growing quasicrystal(s) and its surroundings. Going a bit into physics of the process, one can state that the adsorption of macromolecules at the above mentioned surfaces is a serious limitation of its speed. (In general, it is commonly accepted that chemi- or physisorption effects act like a *relais* mechanism for such processes [10].) The second equally important kinetic decelerator (or sometimes accelerator) appears to be a competition effect assumed to be present within most of the systems that we are going to study. This fact will be modeled by presuming that the soft-matter systems undergo very often, due to their reactivity and "noisy" character, rules of the so-called dispersive or long-tailed kinetics [11].

The modeling that we would like to propose is generally speaking based on

$$V_{ph} = F_{ph}(X_{det}; \chi_{ndet}; p_1, \dots, p_k), \quad (1)$$

where V_{ph} stands for the rate (the first time derivative of X_{det} taken with either plus or minus sign, respectively) of appearance of a new (children) phase ($V_{ph} > 0$) or disappearance of an old (parent) phase ($V_{ph} < 0$), or simply, a rate of transformation of the growing object. The right-hand side of Eq. (1) is represented by a function F_{ph} of the following general arguments:

- (i) X_{det} , a kinetic variable (e.g. the molar concentration of the transformed species; number density of microdomains; probability of finding the system in a given physical state) being typically a function of the physical state of the system, e.g. the position of a molecule; size of the individual grain, and of

time t ; X_{det} is quite often determined by integro-differential operators acting on X_{det} ; certainly the initial as well as boundary conditions for X_{det} are supposed to be known;

(ii) χ_{ndet} , an indeterministic or stochastic kinetic variable which stands for either thermal or athermal random perturbation (correlated or not) of the phase transition; it is always assumed that the probabilistic characteristics of the transition, χ_{ndet} , are given [12];

(iii) p_1, \dots, p_K (K -finite), constitute a set of control parameters, like temperature, pressure, chemical reaction rate coefficient, degree of crystallinity, dimensionality (-ies) of the system under transformation, some parameters responsible for static as well as dynamic types of disorder in the phase transition process, etc.

Some well-known examples of the prerequisites of the transitions studied here are as follows:

(i) if F_{ph} is linear in X_{det} , $X_{det} \equiv X_{det}(t)$, $\chi_{ndet} = 0$ and p_1 is a thermodynamic parameter, whereas p_2 and p_3 stand for certain geometrical parameters, one gets the well-known Avrami-Kolmogorov phase change model or the recrystallization Mehl-Johnson model [2,3]; in this case X_{det} is a measure of the fractional completion of the new evolving phase;

(ii) if F_{ph} is linear in $1/X_{det}$ (a measure of curvature in the system), $X_{det} \equiv X_{det}(t)$, $\chi_{ndet} = 0$ and p_1, p_2 are thermodynamic parameters, then one has the Hillert model which serves for describing the kinetics of normal grain growth in metallurgical systems [13] (here X_{det} stands for the grain radius); a stochastic modification of the Hillert model by adding an uncorrelated noise term to the right-hand side of the Hillert equation ($\chi_{ndet} \neq 0$), given by Pandé [14], yields the same asymptotic result, namely that $X_{det} \sim t^{1/2}$, i.e. a diffusion-controlled process (it is interesting to notice that another model, due to Kurtz and Carpay, describing the normal grain growth as a process of elimination of grains from the smallest topological class, eventually ends up with the same asymptotic result given above [13,14]);

(iii) the Glauber or the kinetic Ising models (for one-spin systems) can be obtained if F_{ph} is linear in X_{det} , $X_{det} \equiv X_{det}(t)$, $\chi_{ndet} = 0$ and p_1 is a parameter, i.e. the probability in a time unit for the spin flip from a position "up" to a position "down" or *vice versa*; X_{det} is usually defined as the probability of finding the system in a given physical state;

(iv) the Louat model [15] of a "random walker" which stands for a theoretical basis for the stochastic modeling of the normal grain growth [13,1]; it is represented by the standard diffusion equation in which the (dependent) kinetic variable X_{det} may depend not only upon the time t but also upon the grain area (the effect of the grain size is, however, not manifested for $d = 1$, but is very much pronounced in spaces with the dimensions $d > 1$ so that one may clearly state that the diffusion process is realized in the space of grain sizes rather than in the space of their positions); the parameter p_1 is the diffusion coefficient and X_{det} stands for the distribution of grain sizes which is equivalent to a relative number of grains in a given area range; here the asymptotic result *grain radius* $\sim (time)^{1/2}$ is valid as well (also for the kinetic Ising model which mimics the continuous ferromagnetic-paramagnetic phase transition).

Models listed in (i)-(iv) do not exhaust a rather large list of models applied to description of the kinetics within certain subclasses (see above) of the heterogeneous phase transitions. (As a counterpart of this kind of phase transitions one has to invoke the homogeneous, i.e. nucleationless phase transitions being represented, e.g. by the Ostwald ripening of grains during a late stage of the phase separation in a binary system.) It would be sufficient to advertise here another model taken from physical metallurgy, named the Feltham model, or some adaptation, due to Kanehisa and Tsong (also Sugar), of the kinetic Ising (Glauber) model to the description of phase transitions occurring in lipid bilayers that apparently show a cluster structure, which is an example taken directly from biophysics or biochemistry [16]. The computer simulations of

such transition processes based on the Monte Carlo technique and utilizing certain generalizations of the Glauber model, like the q -state Potts model or its biophysical counterpart called the Pink model, cannot be omitted when looking into the kinetic behaviour of the soft-matter systems [17]. The models just mentioned are also very useful in providing a kinetic description of the order-disorder phase changes [10].

2 Formulation of the problem

We have proposed two basic types of evolution equations describing the kinetics of the nucleation-and-growth phase transitions [18,19]. They represent two rather different physical situations (see, Fig. 1) and are modeled by two different types [20] of inhomogeneous diffusion equations:

$$\frac{\partial}{\partial t} f = \frac{\partial}{\partial x} \left(\frac{\partial}{\partial x} D f \right) \quad (2)$$

and

$$\frac{\partial}{\partial t} f = \frac{\partial}{\partial x} \left(D \frac{\partial}{\partial x} f \right) \quad (3)$$

where $f \equiv f(x, t)$ is the grain (cluster) distribution function, or more precisely, $f(x, t) dx$ stands for the relative number of grains of the volume within the range $[x, x + dx]$, $\frac{\partial}{\partial t} f$ means the first time derivative of f , whereas $\frac{\partial}{\partial x}$ of the right-hand side of Eqs. (2) and (3) means differentiation over x .

The independent variable $x > 0$ represents the grain volume in the d -dimensional space. In two-dimensional systems ($d = 2$) it is the area of the grain, while in three-dimensional systems ($d = 3$) one detects the volume of an individual grain. The second independent variable is the time $t \geq 0$. Eq. (3) is of the form of the 2nd Fick's law, therefore we will call the situations modeled by (3) Fickian (abbreviated by F), whereas the case represented by Eq. (2) will consequently be named as non-Fickian, abbreviated by NF . (The reader of this paper is

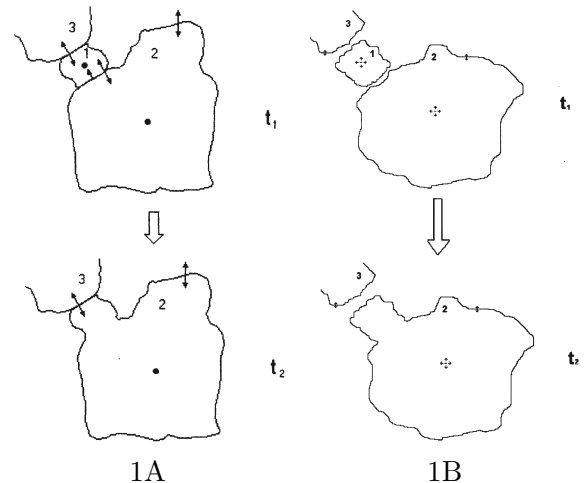


FIG. 1. Sketch of possible realizations of NF -processes (1A) as well as F -processes (1B), where $t_2 > t_1$. Notice that they differ apparently: (i) grains (clusters) 1, 2, 3 pack closely the available space only in NF -case; (ii) NF -process is therefore more efficient since for it the explicit driving force is mainly the capillary force [13]; (iii) a price for it is that the boundaries in NF -process fluctuate strongly which is seen in Fig. 1A (quite long double arrows, but rather short in Fig. 1B); (iv) no doubt that in F -process the centers of masses of the clusters perform also a random walk in a position space, which is rather not the case of NF -objects since they mostly perform a random walk in the space of their sizes (see, the crossed double arrows in Fig. 1B, and in contrast, heavy points in the middle of NF -crystallites in Fig. 1A); for possible computer realizations of F -processes one may look at pictures in [8] (cluster-cluster aggregation) or by P. Meakin in [29] (dropwise condensation).

kindly encouraged to look at Fig. 1 and its legend as a kind of starting description, serving for a more detailed microscopic insight to the phenomena under consideration, cf. references provided in the caption to Fig. 2.)

The idea of dealing with the nucleation-and-growth systems in such a way came probably first from Zeldovich who investigated transient nucleation phenomena in glass-forming liquids as a diffusion process along the size axis (under an applied force, additionally) [21]. This enabled a couple of years thereafter some useful applications as well as

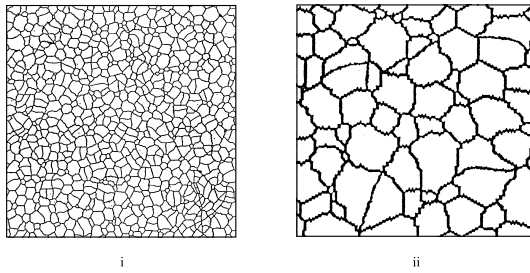


FIG. 2. Some possible computer realization of the space-filling NF -process, very similar to that presented in [28]. A polycrystalline microstructure is presented in two different regimes: (i) left view: an early time realization of the microstructure; (ii) right view: a late time realization of the microstructure. One may look at realizations of such complexes, e.g. in: V.E. Fradkov, *Philos. Mag. Lett.* 58, 271 (1988), or in: H. Flyvbjerg and C. Jeppesen, *Physica Scripta* T38, 49 (1991), provided for two-dimensional coarsening soap froths.

generalizations in the field of kinetics of the thin solid films formation as well as in surface science [22]. In the physical metallurgy this brilliant idea was probably first utilized by Louat [15] and was mathematically explained just in terms of the inhomogeneous diffusion equation concept discussed by van Kampen [20]. In general this idea relies consequently on dealing with the right-hand side of Eqs. (2) or (3) as the n -th derivative of $\frac{\partial^{(n)}}{\partial x^{(n)}}(Df)$, where $D \equiv D(x, t)$. For $n = 2$ this leads to the right-hand side of the evolution equation of the following form, namely $\frac{\partial^{(n-k)}}{\partial x^{(n-k)}} D \frac{\partial^{(k)}}{\partial x^{(k)}} f$, and for $n = 2$, $k = 0$ one gets the NF process (assumed formally that $\frac{\partial^{(0)}}{\partial x^{(0)}} f \equiv f$), whereas for $n = 1$, $k = 1$ one provides the F process, and for $n = 2$, $k = 2$ one obtains a process also mentioned by van Kampen [20], but we will consequently neglect it because we do not see the physical grounds for establishing it; notice, however, that we have finished the expansion procedure at $n = 2$, as was also done in [15,20,18-22]. (A more quantitative discussion on how to solve Eqs. (2) and (3) by means of the Laplace's transform is left for Appendix A.)

The diffusion function D introduces space-time

inhomogeneities and is thought to be an important generalization of the mechanism proposed by Zeldovich and followed by the others [21,22,15]. Assuming that the flux of molecules constituting new phase is proportional to the area of the new phase one can postulate the following mathematical (asymptotic) expression for D , namely [23-25,11]

$$D \equiv D(x, t) \sim \frac{x^\alpha}{t^h}, \quad t \gg 1 \quad (4)$$

where $\alpha = \frac{d-1}{d}$ (d - the space dimension) and h is designated to be a structure dynamics exponent which is a good measure of the structural disorder during the growing process. This measure is well-established for the NF -processes and following a certain rationale borrowed from a series of papers on the dynamics of a ligand rebinding to the protein chain, being a small energetic barrier diffusion process along a chemical reaction coordinate axis (cf., [26] and refs. therein), one can naturally define h as a competition parameter, where the competition effects are guaranteed by an interplay between the thermal (Boltzmann) energy influx which would destroy a dynamic structural order in the system and the grain-boundary free energy decrease trying to restore the structural order; cf. [23,24] for anticipating another kind of reasoning. Moreover Eq. (4) is promising since it accommodates the use of the dispersive or long-tailed kinetics concept which is very characteristic of the soft-matter polycrystalline structure formation [11,3,23-25]. Following this kind of argumentation we wish to call the case with $0 \leq h < 1$ as a classical since it is quite frequently noticed in the literature [15,27,18], whereas the case with $h \geq 1$ can be named as non-classical [28] since it is introduced rather rarely, e.g. there can be a situation with a stagnation regime in the abnormal grain growth [13] in physical metallurgy systems, or a physical scenario drawn by Srolovitz and coworkers [10] to describe some pronounced retardation effects due to chemi- or physisorption in complex systems (NF -mechanism and $h = 1$). It can also be observed in the late time very slow

evolution during the secondary recrystallization (F -mechanism and $h > 1$) [1,13]. A case with $h < 0$ will be called critical, in turn. It is mostly characteristic of the formation of cylindrolites and spherulites in readily fluctuating and reactive polymeric systems [7,23,24].

In the description of kinetics of the studied heterogeneous transformations the so-called 0-Dirichlet boundary conditions (BC) for $f(x, t)$ at $x = 0$ and $x = \infty$ have been assumed

$$f(x = 0, t) = f(x = \infty, t) = 0. \quad (5)$$

They are typical for the normal grain growth [1,13-15]. They mean that the number of crystallites of zero volume as well as of infinite volume must be always equal to zero. The necessary conditions for $f(x, t)$ have been completed by the delta Dirac initial condition (IC) [18,19,15], like $f(x, 0) = N_o \delta(x - x_o)$, where N_o stands for the initial number of crystallites of volume x_o .

Most frequently modeled processes for which Eq. (2) and the above mentioned BC's as well as IC (briefly, IBC's) have been used are: the normal grain growth, met often in metallurgical systems [1,13,15] as well as a formation of spherulitic (cylindrolitic) polycrystals in polymeric matrices [7,23,24]. As was said above the first kind of processes can be placed in a classical regime while the second can be assigned to a critical kinetic regime. Both of them, however, take place under constancy of the total volume, i.e. the total volume of the system is conserved (the grains fill perfectly the available matrix).

Processes modeled by Eq. (3) with the above listed IBC's are among many the following: the recrystallization in biophysical and metallurgical systems as well as mobile coalescence (possibly the droplet condensation [29], too) [4,13,19,22]. They take place under inconstancy of the total volume, i.e. the total volume of the system is not conserved (the grains do not perfectly fill the available matrix). They are sometimes observed to occur in the above mentioned non-classical kinetic regime

($h > 1$) and resemble to some extent a scenario drawn for phase separation processes [21,22,8].

The main quantities to be analysed after solving (2) or (3) with (4) and with the above IBC's (see Appendix for the method of solution) are the statistical moments $\langle x^n(t) \rangle$ given by

$$\langle x^n(t) \rangle = \int_0^\infty x^n f(x, t) dx, \quad n = 0, 1, 2, \dots \quad (6)$$

The moments $\langle x^n(t) \rangle$ have the following physical interpretation. When $n = 0$ $\langle x^n(t) \rangle$ stands for the number of grains in the system. When $n = 1$ $\langle x^n(t) \rangle$ is equivalent to the total area ($d = 2$) or volume ($d = 3$) of the new phase. If, in turn $n = 2$, there is a possibility of determining the fluctuations $\sigma^2(t) = \langle x^2(t) \rangle - \langle x(t) \rangle^2 = \langle x - \langle x(t) \rangle \rangle^2$ of the grain sizes represented by their areas or volumes. (We do not consider the moments with $n > 2$ since they do not have clear physical meanings.) There exists however another physical characteristics worth analysing, i.e. the average grain radius $r_{av} \equiv r_{av}(t)$ to be inferred from

$$\langle x^0(t) \rangle r_{av}^d(t) \propto \langle x^1(t) \rangle \quad (7)$$

(remember that d stands for the space dimension).

A careful analysis of asymptotic relations of the form

$$\langle q(t) \rangle \sim \Phi(t), \quad t \gg 1, \quad (8)$$

where $\langle q(t) \rangle$ can be, respectively: $\langle x^n(t) \rangle$ ($n = 0, 1$), $\sigma^2(t)$ and $r_{av}(t)$, and $\Phi(t)$ appears to be either a power function or a logarithmic function of t , or eventually approaches a constant value, depending on the competition parameter h (the physical meaning of this parameter can be sometimes, i.e. for $0 \leq h < 1$ consistent with the physical meaning of a similar quantity known from the anomalous random walk theory and strictly related to the so-called spectral or fracton dimension [30,31]).

The main goal of this presentation is some critical analysis of relations of the form given by (8) for three subclasses of the soft-matter phase transformations mentioned in the Introduction. It will

be done for both NF - as well as F - systems; some order-disorder phase changes in two-dimensional complex systems will be briefly considered as well [32]. A complementary analysis of anomalous relaxation of the stress field accompanying the mentioned phase transitions as well as some comparison of their kinetics with the kinetics of certain complex objects grown on a single nucleus and manifesting the Mullins-Sekerka-like instability effect [33] will complete the investigations. (Another comparison of the modeling offered with the Avrami-Kolmogorov [3,31] concept will shortly be sketched, too.)

3 Non-Fickian or curvature-enhanced mechanism of the nucleation-and-growth phase transition kinetics

This Section contains principal results published in [18,28,34,23,24] and a critical analysis of them.

3.1 An analytical description of the normal grain growth of materials in a d -dimensional space with some extensions to other non-metallurgical growth phenomena

The basic motivation for embarking on this difficult task was that there exist some experimentally noticed facts concerning mostly lipid systems for which the so-called main phase transition (gel-to-liquid crystalline) proceeds with anomalously small dimensionalities [3,4] and that the Avrami-Kolmogorov phase change concept does not provide a sufficient theoretical basis for understanding this anomaly. This can also be noticed in the phase transition of somewhat another type, namely in the gel-to-subgel phase transformation [35] for which the classical phase change concept appears to be rather too crude and for which another modification of the Avrami-Kolmogorov concept, utilizing effectively the fractional calculus, is believed to be

appropriate [36,31].

We recognize here the transition to be described by the NF -mechanism. Thus, there is a need of getting the solution of (2) with BC (5) and with (4) of the form $D(x, t) = D_o x^\alpha t^{-h}$ ($D_o > 0$). It is provided in the following (a Weibull function of x) [18]

$$f(x, t) = f_0 x^\beta b^{-(2+\beta)/(1+\beta)}(t) \cdot \exp[-x^{1+\beta}/(1+\beta)^2 D_o b(t)], \quad (9)$$

where $\beta = 1/d$ and $f_0 = [D_o^{-1}(1+\beta)^{-2}]^{(2+\beta)/(1+\beta)} X \Gamma^{-1}[(1+\beta)^{-1}]$, where X will be given below by Eq. (13) (Γ is the Euler gamma function).

Anticipating that the transition process is mostly placed in the classical regime of the h parameter play mentioned above, one gets for $0 \leq h < 1$ (when $t > 0$) [18]

$$b(t) = \frac{1}{1-h} t^{1-h}, \quad (10)$$

and for $h = 1$ (a non-classical regime, see above) [18]

$$b(t) = \ln(t). \quad (11)$$

The analysis of the statistical moments of the process yields [18]

$$\langle x^0(t) \rangle \sim [b(t)]^{-d/d+1}, \quad t \gg 1, \quad (12)$$

$$\langle x^1(t) \rangle = X = const, \quad \text{for } t \in (0, \infty), \quad (13)$$

and

$$\sigma^2(t) \sim [b(t)]^{2d/d+1}, \quad t \gg 1. \quad (14)$$

Utilizing (7) one obtains [18]

$$r_{av} \sim [b(t)]^{1/d+1}, \quad t \gg 1, \quad (15)$$

where $X > 0$ stands for the constant total volume in the d -dimensional space which is assumed to be known.

From the above presented asymptotic relations (12)-(15) can be seen that for $d \geq 1$ the number of crystallites (12) decreases with time t , the total volume given by (13) remains constant for all values of t and the fluctuations (14) increase linearly with t when $d \rightarrow \infty$. Eq. (15) manifests its non-diffusional character but for $d > 1$, i.e. r_{av} is not proportional to \sqrt{t} for $t \gg 1$ [15], cf. Fig. 2 for having a picturesque example of the analysed process.

Let us finish this subsection with a few examples. The first type of them can be assigned to relations (10) and (15). Thus the effective exponent appearing in (15) is now $(1-h)/(d+1)$ instead of $(d+1)^{-1}$. It is capable of showing properly small growth effects measured in zone refined metals (Al, Fe, Pb, Sn) or certain types of ceramics (MgO, ZnO, CdO), for which the exponents are around $\frac{1}{4}$ to $\frac{1}{3}$ [37] or even smaller, i.e. ca. $\frac{1}{6}$ [38]. Interestingly that such small values of the exponents are suspected to be so small not because of the existence of impurities, drag forces (due to possible pinning or thermal grooves) or strong misorientations of the neighbouring grains in the system but rather because of the retardation effect due to random topology [14,15] of the evolving network itself (this supposition comes undoubtedly from a numerical study performed by the authors of [37]). Consequently a measure of the energetic competition effect reflecting the crucial role of the random topology is represented by the h parameter. In biophysical systems in turn one may pick up equally small exponents when inspecting the domain growth in lipid multilamellar vesicles [4]. The second type of examples is represented by Eqs. (11) and (15). In this case relation (15) is logarithmic but the growth exponent remains as $(d+1)^{-1}$. The examples that one can list here are as follows. Namely, one can again start with metallic or ceramic systems manifesting a strong physio-chemisorption effects [10]. Moreover, one might loosely mention a superconducting phase transition in which the normal-superconductor phase boundary evolves according to a logarithmic law (an instability similar to that detected in solidifying systems

is present during such a phase transition) [39]. A growing process, mentioned by Huse, realized in a domain-wise way in ordered spin (Ising) glasses, exhibiting a Ginzburg-Landau kinetics can probably stand for another example, too [40].

3.2 Diffusion migration concept applied to growth and structure formation in model biomaterials

In [28,34] physical mechanisms leading to formation of ultra-thin organic layers as well as to appearance of multilamellar model quasicrystalline lipid membranes have been analysed. Instead of using the asymptotic form of D given by (4) it was decided to use the following

$$D(x, t) \sim \frac{x^\alpha}{(1+t)^h}, \quad h \geq 0, \quad (16)$$

because it enables to reveal another effect which can rather be assigned to a stagnation of the complex system under investigation. (For clarity let us note that $\alpha = 1/2$ for $d = 2$ and $\alpha = 2/3$ for $d = 3$.) This can be even understood in more general terms, namely that we are able to detect this way an effect of the cessation to growth. Also a disruption or lysis of model lipid membranes, or just a kind of freezing of the otherwise dynamic structure must be mentioned here [5,33,13]. This additional effect can be noticed for $h > 1$. Now relations (10) and (11) can be replaced by the following [28]

$$b(t) = \begin{cases} \frac{(1+t)^{1-h}-1}{1-h} & \text{for } 0 \leq h < 1, \\ \ln(1+t) & \text{for } h = 1, \\ \frac{1-1/(1+t)^{h-1}}{h-1} & \text{for } h > 1. \end{cases} \quad (17)$$

The case with $d = 2$ looks in our opinion interestingly. Especially when invoking the relation $\langle x^0(t) \rangle \sim t^{-2/3}$ ($h = 0$), which means that the number of grains in the $2d$ -system decreases algebraically; notice that for $h = 1$ a quite similar relation, i.e. $\langle x^0(t) \rangle \sim (\ln t)^{-2/3}$ arises for $t \gg 1$. The asymptotic relationship of such a type has been

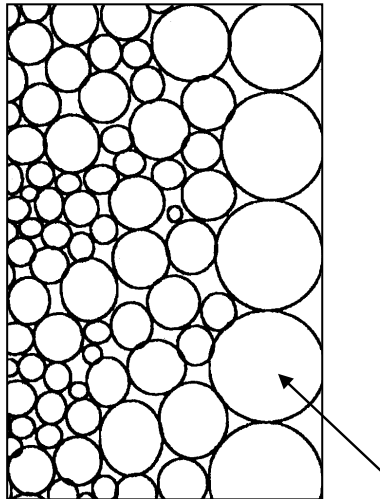


FIG. 3. Cartoon of a spheres (circles)-containing system. Notice that quite similar (topologically) but real pictures one may find in a book by Wunderlich [7] or in [46], cf. [29] for having another example. The long arrow on the picture indicates a single cylindrolite (spherulite).

noticed for the growth of a single crystal with somewhat corrugated surface. In such a situation a competition between the neighbouring pieces of the corrugations (called *doublons* sometimes), manifesting a striking analogy to the grains-containing competitive system, is possible to observe. Some analogies to the Kardar-Parisi-Zhang scenario for the dynamics of rough surfaces (the critical growth exponent equal to $2/3$) can be underscored [41].

3.3 Kinetic description of a formation of cylindrolites and spherulites in co-operative and dynamic biopolymeric agglomerates

The cylindrolites ($d = 2$) [23] as well as spherulites ($d = 3$) [24] or alike [25] (cf., Fig. 3) are systems the evolution of which is best described by a linear relation

$$r_{av} \sim t, \quad t \gg 1, \quad (18)$$

which means that the so-called superlinear dependency (compare with a 'reference' diffusional relation of the form $r_{av} \sim t^{1/2}$ for $t \gg 1$) is clearly

manifested [7,9,25]. (For the growth exponent less than $\frac{1}{2}$ one recognizes a sublinear regime frequently noticed above.)

Relationship (18) can be obtained when starting from the basic kinetic equation (2) and then making use of BC (5) and eventually utilizing the area (volume) conservation equation (7). The latter is possible to imagine, for instance, in the restricted geometry of the Apollonian gasket (a fractal construction for both two- as well as three-dimensional spaces) or in other systems for which the circle or sphere close-packing conditions are fulfilled [23].

For such systems the diffusion-migration function $D(x, t)$ reads [23,24]

$$D(x, t) \sim \frac{x^\alpha}{t^{\nu-m}}, \quad (19)$$

where for $d = 2$ one has $m \in [2, 3]$ and for $d = 3$ one provides $m \in [3, 4]$; m stands for the degree of crystallinity of the system and depends upon whether the nuclei are of athermal (a low temperature limit) or thermal (a high temperature limit) character [7]. (By the way, m is best estimated when using the Avrami phase change kinetics concept [3,31,4].) The exponent ν stands for a measure of the corrugation or even of the roughness of the crystallite's surface. If $0 \leq \nu < 1/2$, strictly, one observes a corrugated or rough surface. The closer to $1/2$ the value of ν is, the smoother the surface of the crystallite can be. For $\nu = 1/2$ one gets the ideally smooth surface. Note however some important fact here. Namely, the form of $D(x, t)$ in (19) shows up $h = \nu - m < 0$, which, according to our classification proposal given above, brings about a critical behaviour of the polycrystalline system under study. It is so indeed since there exist no well-developed boundaries placed among the neighbouring (round) crystallites, but rather crudely speaking, sets (quite possibly of 0-measure from the mathematical viewpoint) of randomly distributed common sticking points between circle-like ($d = 2$) or sphere-like ($d = 3$) contiguous objects. This is then manifested in such an unusual behaviour of h which is trapped within the domain of negative values. This makes

the competition between two main energetic (order-disorder) contributions (see Section 2) distinctly different from that characteristic of non-cylindrolitic (non-spherulitic) systems [28,37,13,15,10]. It provokes also somehow to state that the line (surface) tension of the grain boundary gets a singular behaviour due to its specific character. It will be discussed in a more detail in the final Section for all the cases studied.

4 Fickian mechanism of the nucleation-and-growth phase transition kinetics

The subsequent Section contains a critical analysis and comments on the results published mostly in [19], cf. references therein. It includes also some remarks on the heterogeneous phase transition kinetics that have much in common with the random walk processes on a continuum percolation space, where the random walk is realized by a testing particle or a "tracer" [42]. (Moreover, some useful comparisons will also be presented throughout this Section.) The motivation to bring forward the Fickian (F) mechanism, represented by Eq. (3) with the corresponding IBC's [19], is such that there are the nucleation-and-growth processes, e.g. the secondary recrystallization, droplet condensation or mobile coalescence, or even to a certain degree the cluster-cluster aggregation with local microcrystalline order, that show a set of visible differences when compared with the above studied total area- or volume conserved systems. First, they do not conserve the total volume. Second, the crystallites (clusters; droplets) are in general more mobile but this does not necessarily result in bigger mobility of the system as a whole (or, on average) since the motion of them is weaker correlated when compared with, e.g. systems that do perfectly fill the available physical space (normal grain growth [1]). It is because there exist a quite huge number of discontinuous grains (clusters) in the system, thus

it does not make sense to speak about real grain boundaries but rather about free spaces among the objects that are going to constitute a microcrystalline agglomerate [29,43,8,9]. It is also sometimes because of other physical, let us say 'dormant' effects, e.g. a presence of inhomogeneous strain fields associated with the grain boundaries and clusters of them, etc. [13,1]. (If one still wishes to keep the meaning of the grain boundary here one has to speak loosely about a "fuzzy" or extremely diffuse pseudo-boundary. This is a qualitatively different case since till now we have considered more or less well-established, quite sharp or not so diffuse, let us say "almost military", boundaries [2,13,5]. Generally one may speak of more and/or less energetic grain boundaries, respectively.) But in the approach offered we may still keep $D \sim x^\alpha$ because the x^α is a measure of the magnitude of the individual grain circumference ($d = 2$) or area ($d = 3$; see the preceding Section for realizing the values of α), and because the kinetics of the processes under consideration depend upon x^α , e.g. in colloidal or surfactants-containing milieus [44]. Unfortunately, the meaning of the competition h parameter loses its lucidity under such physical circumstances and can be safely applied at most in the limit of $h \rightarrow 0$, i.e. when very thermally activated (diffuse; disorganized) grain pseudo-boundaries are present in the system. Another possible regime of action of h can be claimed for very long times when the system will tend to cease its growth [43-45], i.e. for $h > 1$. (This regime is however not a growth regime.) To keep things possibly clear it is proposed to presume that it can be, e.g. a late time stage of the phase separation effect in which the pseudo-boundary completely loses its typical character; it will be discussed in the final Section again. The remaining physical situations, e.g. with $h < 0$ do not look convincing when the F -mechanism is proposed to work smartly.

4.1 Kinetics of microdomain formation in two dimensional complex assemblies

The first kinetic dependency that have been worked out, cf. [19] and references therein, is a sublinear relation

$$r_{av} \sim t^{1/3}, \quad t \gg 1, \quad (20)$$

which was probably first recovered many years ago by Lifshitz and Sloyozov, but for homogeneous nucleation-and-growth phenomena [2] or phase separation systems [45]. Such a relationship is also possible to get based upon the time-dependent Ginzburg-Landau equation for the order parameter (conserved or not) of the complex system [43]. It is obtained here for $d = 2$, quite similarly to the results of NF -description with $h = 0$, see Eqs. (15) and (10) again. Such a dependency may also be noticed during the dropwise condensation phenomena and can be inferred from scaling arguments [46], also confirmed by numerical simulations [29]. It can be derived as well using very simple Hillert-like phenomenological model [13] of a pairwise droplet coalescence due to Binder and Stauffer, cf. [45] and references therein.

4.2 Phase transformation kinetics in d -dimensional clusters-containing systems: diffusion-type model

The basic idea which stays behind proposing F -mechanism is twofold. Thus, it has, as the so-called Janus face, two sides. The first side is represented by a primary (practical) observation that there appear systems, e.g. those underlying the secondary recrystallization conditions [1,2] that evolve with increase of the total area or volume of the new emerging phase. This increase can at least mathematically be revealed when working just with F -mechanism, for example due to a remanent strain field present in the system. (Sometimes also the abnormal grain growth in metallic polycrystals may be modeled by the below presented formalism [47].)

The second side in turn is of purely theoretical nature. It is mostly owing to van Kampen's considerations on the inhomogeneous diffusion equation which can be either of NF - or of F -form or can take on a form in which the diffusion function D precedes the Laplace's differential operator [20]. (As was stated above we will consequently neglect this possibility in our studies. An open question however remains whether this description can also be useful, e.g. to the modeling of polycrystalline evolution.)

F -mechanism, similarly to NF -approach, works well for any dimension of space d . Let us then look at basic characteristics of F -mechanism. The solution of (3) with (4), (5) (but with $h = 0$), using the method of Laplace's transforms explained in Appendix, leads to a solution containing the modified Bessel functions $I_\omega(x)$ of x [19], where

$$\omega = \frac{1 - \alpha}{2 - \alpha} = \frac{1}{d + 1}, \quad (21)$$

($\alpha = 1 - \frac{1}{d}$, see above).

A method of finding the solutions of system (3)-(5) with $h = 0$ (see Appendix again) makes use of propagators of the distribution $f(x, t)$ denoted by $\Pi(x, t|w, 0)$. It enables to write $f(x, t)$ in terms of $\Pi(x, t|w, 0)$, namely [19]

$$f(x, t) = \int_0^\infty dw \Pi(x, t|w, 0) f(w, 0), \quad (22)$$

where

$$\Pi(x, t|w, 0) = \frac{2(xw)^{(1-\alpha)/2}}{2 - \alpha} \int_0^\infty dz z e^{-tz^2} \times J_\omega \left(\frac{2z}{2 - \alpha} x^{(2-\alpha)/2} \right) J_\omega \left(\frac{2z}{2 - \alpha} w^{(2-\alpha)/2} \right), \quad (23)$$

where J_ω are Bessel functions (but not the so-called modified [19]). It is possible to evaluate the above integral. As a result one gets [19]

$$\Pi(x, t|w, 0) = \frac{(xw)^{(1-\alpha)/2}}{(2 - \alpha)t} \exp \left[-\frac{x^{2-\alpha} + w^{2-\alpha}}{(2 - \alpha)^2 t} \right] \times I_\omega \left(\frac{2(xw)^{(2-\alpha)/2}}{(2 - \alpha)^2 t} \right), \quad (24)$$

where $I_\omega(x)$ is a modified Bessel function (see above). Let us notice that the fractional value ω

given by (21) will be permanently involved in the asymptotic kinetic relations presented below.

Assuming that in $t = 0$ our clusters-containing system has N_o clusters or microdomains of volume x_o we can write a delta-Dirac IC as follows [19]

$$f(x, 0) = N_o \delta(x - x_o). \quad (25)$$

This leads (cf. Eq. (22)) to a unique solution to the problem, namely

$$f(x, t) = N_o \Pi(x, t | x_o, 0), \quad (26)$$

where $\Pi(x, t | w, 0)$ is given above. Similarly to NF -procedure (see the preceding Section as well as [18]) it is now possible to get the statistical moments of the process in question. These are:

$$\langle x^0(t) \rangle \sim t^{-1/d+1}, \quad t \gg 1, \quad (27)$$

$$\langle x^1(t) \rangle \sim t^{d-1/d+1}, \quad t \gg 1, \quad (28)$$

and

$$\sigma^2(t) \sim t^{2d-1/d+1}, \quad t \gg 1. \quad (29)$$

From Eq. (7) one provides [19,18]

$$r_{av} \sim t^{1/d+1}, \quad t \gg 1. \quad (30)$$

Let us notice specifically that Eqs. (27) and (30) give for any d , $\langle x^0(t) \rangle r_{av} \simeq 1$ for $t \gg 1$, which is not true for the NF -mechanism except for $d = 1$, cf. relations (10), (12) and (15) for $h = 0$.

Moreover from the above relations (27)-(30) it follows that for $d \geq 1$ the number of microdomains (27) decreases with time t , the d -dimensional hypervolume (28) increases powerly with t (a visible difference between F - and NF -mechanisms) and the fluctuations (29) increase in a slightly less vigorous way than in NF -case but also linearly when $d \rightarrow \infty$. The average radius asymptotic dependency has exactly the same non-diffusional character for all $d > 1$. For $d = 1$ one gets again the diffusional behaviour introduced by Louat [15].

A comparison of the time characteristics of the above presented evolution of clusters-containing systems is of interest. Mostly which are the differences when the processes are realized in two- as well as three-dimensional spaces, cf. Ref. [25] in [19] for details. Thus the main differences are:

- (i) $\langle x^0(t) \rangle$ decreases somewhat more slowly in $3d$ - than in $2d$ -systems, cf. Eq. (27);
- (ii) conversely to point (i): $\langle x^1(t) \rangle$ increases somewhat more vigorously in $3d$ - than in $2d$ -systems but exclusively for $d > 1$, cf. Eq. (28);
- (iii) fluctuations increase somewhat more vigorously in $3d$ - than in $2d$ -systems, cf. Eq. (29);
- (iv) the average microdomain radius r_{av} increases somewhat more slowly in $3d$ - than in $2d$ -systems, cf. Eq. (30).

The possible reflections of the above offered scenario can be observed not only in the recrystallizing pieces of metallic complexes [1,47] but also in the dropwise (water) condensation (as a prerequisite the breath figures on a cold plate may be mentioned) [29] or in the mobile coalescence frequently realized in thin films systems [22,21]. In biophysics certain sub-transitions in model lipid, for instance DPPC systems, can also be carefully checked mostly because of high fluidity of the transition region [3,35].

4.3 A comparison of the heterogeneous phase transition kinetics with the random walk in a continuum percolation space

Perhaps slightly aside the mainstream of the description of the studied nucleation-and-growth phase transition an interesting theoretical problem can be recalled which is related to continuously percolating Swiss-cheese-like systems [48]. As we now know, solving both F - as well NF -scenarios (but for $h = 0$) we obtain [19,18] the asymptotic relation (30), namely $r_{av}(t) \sim t^{1/d+1}$, where $d = 1, 2, 3, \dots$, no matter whether the system is space filling (grain boundary curvature driven) or not.

A certain additional observation that appears

would be that the quantity r_{av} can be interpreted as a distance travelled by the boundary of an "averaged" cluster from its center of inertia. The process of the cluster boundary random walk can be thought of to be realized in the surroundings of other (neighboring, etc.) clusters that stand for randomly distributed obstacles perturbing the walk of the boundary. This physical situation resembles to a large extent a random walk of a tracer on the percolation Swiss cheese-like continuum space both for $d = 2$ as well as $d = 3$. For this walker however the percolation structure does not change dynamically but it gets frozen rather.

From seminal books and review papers on the percolation it follows that close to the percolation threshold, cf. [42,36] and references therein, one detects

$$r_{rw}(t) \sim t^{\kappa_p}, \quad t \gg 1 \quad (31)$$

where κ_p represents the critical overall exponent of the percolation system, when the incipient infinite cluster *IIC* is constituted for the first time. (If the cluster is finite, but really one of the largest taken from the population of finite clusters the numerator in κ_p must be slightly modified [42].) Certainly, r_{rw} is a mean distance travelled by the walker in the percolation space.

It may be anticipated as another evidence that the polycrystalline (or microdomains-containing) and percolation systems are kinetically equivalent [42]. It can be so indeed because the asymptotic relations (31) and (30) possesses the same physical meaning and the exponent $\kappa_p \approx 1/d + 1$. Thus the above stated can be gathered in the following

<i>NF/F</i> Agglomerate	Continuum Percolation <i>IIC</i>
2d : $r_{av} \sim t^{1/3}$	$r_{rw} \sim t^{0.3302}$
3d : $r_{av} \sim t^{1/4}$	$r_{rw} \sim t^{0.2414}$

where all the symbols included in the table can be found in this subsection. There exist also similar data for very large but finite clusters emerging slightly above the percolation threshold [42]. The calculated exponents differ however more markedly from $\frac{1}{3}$ as well as from $\frac{1}{4}$ than those presented in the right-hand side column of the table for *IIC* for $d = 2$ and $d = 3$, respectively.

To get the results eventually approaching κ_p -values for a finite system [42] one has to resolve *F*-problem in the limit of $h \rightarrow 0$, i.e. utilizing *D* in the form of (4) or (16). If so doing the exponent $\kappa_p \approx (1 - h)/(d + 1)$, which means that h , being slightly greater than zero, could be also proposed as a certain measure of the finiteness of the system. It seems logical since the finiteness can a bid modify the competition conditions in such a system, e.g. certain strain-stress responses due to possible clustering of the boundaries [13,47].

5 Comparison of the Non-Fickian and Fickian mechanisms with some relation to the Avrami-Kolmogorov (Mehl-Johnson) concept

This Section serves to compare both quantitatively as well as qualitatively the two main mechanisms discussed before. The comparison is offered below in a tabular form:

Process Feature	<i>NF/F Mechanism</i>	
	Equation (9)	Equation (26)+(24)
Solution	Equation (9)	Equation (26)+(24)
Number of clusters	Decreases with t : (12)	Decreases with t : (27)
Hyper-volume	Constant: (13)	Increases with t : (28)
Fluctuations	Increase with t : (14)	Increase with t : (29)
Cluster radius	Increase with t : (15)	Increase with t : (30)

The two essential common distinctions of NF - as well as F -mechanisms are:

- (i) the number of grains changes in time differently for both the mechanisms mentioned but only the asymptotic relation for NF , i.e. Eq. (12) reflects probably the fact that the microdomains gain their material (atoms or molecules, etc.) in a concurrent way [41];
- (ii) the asymptotic relations for the average radius of the microdomain in both systems appears to be the same.

Note that we omit here the evidence that NF -systems are perfectly space-filling while F -systems are not since we can accept these characteristics as their immanent (natural) features. They are simply alike but also quite different categories of kinetic processes. Moreover, the fluctuations are somewhat much pronounced for NF -process than for the Fickian one.

In the theoretical description of phase changes of many physical systems the Avrami- Kolmogorov (AK) concept is probably the most popular and worth emphasizing. It describes in a phenomenological fashion the rate of emergence of a new phase just at the expense of the old one [3,4]. The concept contains only one independent variable, i.e. the time variable t . The remaining quantities that one can notice in this rather commonly accepted description [49] are parameters, cf. point (i) listed in the Introduction. The point is that there is no spatial or alike variable involved in the description. In particular, there is no x (grain size)-dependent variable which can be anticipated as a shortage of this approach. (For NF - as well as for F -descriptions there is not the case.)

AK-equation describing the rate of a phase change reads

$$\frac{d}{dt}f_h(t) = Nk[1 - f_h(t)]\frac{dV_N(t)}{dt}, \quad (32)$$

where $f_h(t)$ stands for the fractional, e.g. molar completion of the transformed phase. N is a constant number of randomly distributed nuclei the vol-

umes of which approach a value of $V_N(t)$ in time t . Unfortunately, contrary to the possibilities offered by NF - and F -mechanisms, i.e. the possibilities of exact calculation of the individual volume, AK-description does not provide such a chance so that this quantity (-ies) must be given *a priori*, that means also the individual grain growth speed $dV_N(t)/dt$.

It was noticed [50,31] that in readily fluctuating and reactive complex agglomerates like biomembranes one may expect a modification of the transformation rate coefficient k in the following before explored way [50,51]

$$k \equiv k(t) = k_0 \left(1 + \frac{t}{\tau}\right)^{-h}, \quad h \geq 0, \quad (33)$$

(or, $k \sim t^{-h}$ [31], asymptotically) where $k_0 > 0$ is the "equilibrium" phase transformation constant and $\tau > 0$ reflects a characteristic time scale of the transformation process [49-51].

Such a modification is proved to be useful in revealing a quite complex nonexponential relaxation kinetics for barotropic as well as thermotropic (order-disorder) phase changes in model lipid membranes, cf. [51,31] and references therein. It should be emphasized that the exponent h can be directly related to the fracton dimension, d_s , of the random walk [30] since the transition process has been described as a random walk of the water molecules in their position space, e.g. pushed under a constant pressure into a domainwise and dynamically changing complex lipid structure (the so-called barotropic transformation [5,36]). The corresponding relation is known as $h = 1 - \frac{d_s}{2}$ [30].

6 Phase transition peculiarities: propagation of stresses and growth on a single nucleus

In this Section we will try to enlighten briefly the effects that accompany the evolution of the growing object(s), like strain-stress responses of the system,

temporal surface (interface) effects associated very much with instabilities resulting from the growing process.

6.1 A phenomenological model of the stress relaxation in slowly evolving three-dimensional polycrystalline materials

It was frequently noticed that complex growing as well as structure-creating processes realized in many-nuclei systems exhibit a sometimes "hidden" but clearly evidenced strain-stress dependence. In other words, in the systems of such a type exerting a certain elastic response during the growing process, some early [47] as well as late time [52,53] mechanical effects do influence the growing or stagnation (cessation to growth) conditions for the emerging new agglomerated phase. The most evident observation which is worth underscoring here appears to be the physical fact that the strain (or stress) fields accompanying the evolution of the complex system under consideration cause certain singularities within the grain boundaries. It has been noticed qualitatively at the beginning of the preceding Section, but can be now exemplified by the so-called triple junctions of adjoined crystallites involved in the grain growth process [52,53]. In particular, we have in mind the piled-up effect, due to stress accumulation, which is visibly manifested just at the branching or sticking points of the boundaries of neighbouring crystallites or clusters (droplets [29,45]).

It can also be a little bit more argumented, but for the early times zone rather, when invoking the physical scenario that clearly shows up that there is a kind of mutual repelling or at least incommensurability of recrystallized (cold-worked) regions, due to grain boundaries clustering, which results in an inhomogeneous distribution of strain fields within a metallurgical system [47,54]. There is however no doubt that it has to cause an anomalous relaxation of the stress field within the system which is as-

sumed to propagate along the main possible avenues available to the stresses, i.e. along the grain boundaries [1,47,52-54]. Some consequences of manifestation of such an anomalous phenomenon may even be extended to the late time zone behaviour, in particular when it is observed in slowly evolving systems, e.g. polymers, cf. [52] and references therein.

This important observation has been used in [52] in which some effect of the anomalous relaxation of stresses, Σ , due to a presumed dynamic Hall-Petch coupling [55], but obviously in the late time zone of a very slow evolution of the NF -polycrystal, has been described. The applied Hall-Petch coupling relation reads

$$\Sigma \sim d_g^{-1/2}, \quad (34)$$

where $d_g \sim 2r_{av}$ [52]. Since the late time growing characteristics remain, even for $t \gg 1$ linear in t (cf., Eq. (18) and discussion thereafter), which means that the average grain speed, dr_{av}/dt , is constant though expected to be small (cf., the spherulitic systems [24,52] for details), one gets a relationship

$$\Sigma \sim t^{-1/2}, \quad (35)$$

which is the well-known Nutting relaxation formula [56,52], working well under constancy of the strain field.

It is interesting to offer some retrospection of the anomalous relaxation process as a whole. It can be done when presuming that the relaxation equation is given by [52,56,57]

$$\Sigma(t) + \tau_o \frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}} \Sigma(t) = 0, \quad (36)$$

where τ_o stands for the mean relaxation time of the system, being sometimes related to the Vogel-Fulcher time [31,11] and $\frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}}$ represents the so-called fractional derivative of the order $1/2$. This can be expressed by the Weyl's integral [57,56]

$$\frac{d^{\frac{1}{2}}}{dt^{\frac{1}{2}}} \Sigma(t) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^t \Sigma(t') (t-t')^{-\frac{1}{2}} dt', \quad (37)$$

which includes a memory-feeling kernel. The general solution of the anomalous relaxation equation with the above memory-feeling (kernel) operator is known [56] to be

$$\Sigma(t) = \Sigma|_{t=0} \cdot \sum_{k=0}^{\infty} (-1)^k (t/\tau_o)^{k/2} \left[\Gamma\left(\frac{k}{2} + 1\right) \right]^{-1}, \quad (38)$$

where Γ is (again) the Euler's function. Interestingly that a particular solution of (36)-(37) is just the Nutting (nonexponential) formula (35). Another type of particular solution that one can get from (36)-(37) appears to be a stretched exponential [56,57] which clearly means that in a complex (soft-matter) polycrystal one may solely expect a non-Debye relaxation behaviour [36]. (For (36)-(37) one never gets a simple exponential Debye relaxation behaviour.)

The above presented description of the stress relaxation process is thought of to be a certain useful generalization of the well-known Maxwell model which is represented by a series connection of the elastic as well as viscous elements. (This is by the way one of the standard models of a viscoelastic body. It reads: $\Sigma(t) + \tau_o \frac{d}{dt} \Sigma(t) = 0$, for the strain $\epsilon = const$ [56,52].) Notice that the afore presented rationale can also be appropriate for systems manifesting a sufficiently small departure from $dr_{av}/dt \rightarrow const$ (asymptotically), i.e. either if $r_{av} \simeq t^{1 \pm \epsilon}$, with ϵ being negligibly small, or $dr_{av}/dt \approx const$ but mostly because of a large value of the thermodynamical prefactor certainly included in relation (18), which cannot be easily compensated by the time dependence involved, cf. [23] as well. However, because the boundaries in NF -systems (see discussion above) are mostly less diffuse and often better defined, the considerations presented in this subsection are best applicable to NF -systems, especially to the spherulitic or perhaps cylindrolitic [52,23,24].

6.2 Temporal surface effects and their influence on the asymptotic behaviour of the nucleation-and-growth phenomena in some (order-disorder) polymeric systems

The physics of growth is full of instabilities, which may be quite different in their very nature, but which result from simple diffusion-type equations [58], and where the basic physical mechanism producing instability is mostly the diffusion of matter or energy which eventually reaches either a growing interface (a single quasicrystal) or one of the grain boundaries in a polycrystal. It is therefore intriguing to compare somehow mechanisms of growing processes taking place on a one as well as on many nucleation seeds, where the number of seeds must not necessary be large. The task that we wish to introduce here relies on exploring the well-known Mullins-Sekerka (MS) instability concept and will be discussed throughout this subsection as well as in the next subsection. In both cases it will emphasize MS-method as a primer technique to be used (unfortunately insufficient in most cases applied to complex systems but enabling to get the behaviour of the system in a linear regime, by definition [59]) which gives also some information about how rapidly the system is able to evolve and upon which physical factors does the evolution depend.

In the following we wish to compare the evolution of quasicrystalline (one nucleation centre) as well as polycrystalline agglomerates, mostly in a context of the biopolymeric growth [25]. The basic point for trying to make a comparison of the two seemingly different processes is that for an object immersed, let us say, in a concentration field consisting of Brownian particles (macromolecules) the main force stabilizing or even inhibiting the growth appears to be the line ($d = 2$) or surface ($d = 3$) tension. This physical quantity is also present at any grain boundary at least of the NF -system. Since the main driving force for the polycrystalline structure formation is the capillary force (a dependence

upon the curvature of the grain) one may conclude, utilizing the Laplace's law [58,33,59], that the systems are nearly (qualitatively) similar. Therefore one can be privileged to compare the evolution of a quasicrystal grown on the single nucleus and its *alter ego* here being just the evolution of an 'averaged' grain representing the polycrystalline microstructure, grown usually on many nuclei, that means something what we have determined thus far, e.g. in Section 3.

In [25] it was already done having mostly in mind some model biopolymeric systems like proteins. The starting point was that the MS-instability formalism reveals that the objects grow according to a standard diffusional law, namely

$$r_{av} \sim t^{1/2}, \quad t \gg 1. \quad (39)$$

More than fifty years ago Ward and Tordai published a work on the time-dependence of the boundary tension of solutions [60]. They considered a diffusional transport of solute molecules to a surface and noticed a weak dependence of the surface tension upon time. By the way, this observation enabled them to determine how does the concentration of the solution depend upon time, too. They concluded that the process under study is not long-range (diffusion) transport controlled (see the Christian's table [2] as well) but is rather limited by the adsorption of the solute molecules to the surface. This conclusion was originally tested on solutions of alcohols (e.g., amyl or octyl alcohols) but presently was extended to certain macromolecular systems, also containing proteins, in which the adsorption is a rate-determining process [60]. In consequence, it led to the conclusion that a weak but explicit time-dependence of a critical quasicrystal's radius, like $R^* = R_o - \eta(\bar{D}t)^{1/2}$, where R_o jest the 'equilibrium' critical radius of the macromolecular quasicrystal, η stands for a thermodynamic parameter of the process and \bar{D} represents a diffusion constant, can be further exploited. Then performing, after Mullins and Sekerka, the linear stability analysis [25,59,58] one can only slightly modify the diffusional relation

(39) (the growth exponent is a little bit greater than 1/2, but not less than one half), since the nonlinear terms influencing the overall temporal behaviour of the system are neglected for sure. One can try augmenting the value of the growth exponents either by postulating an explicit time-dependent boundary condition for the growing crystal or by adding a noise (even Gaussian) term to the right-hand side of the original MS-dynamical system. The result is, depending on the type of IC or on the intensity of the noise, that the growth exponent may reach a value approaching one, i.e. the superlinear (or, mass convection) regime can be achieved [61,62].

Let us discuss now the situation concerning a NF -polycrystal grown under similar physical circumstances [25]. Utilizing Eqs. (2), (19), (5) and (7), for $d = 3$, i.e. for $\alpha = 2/3$ (see above) with $\nu = 1/2$, that means for rounded crystallites (with the smooth surfaces), leads to [25]

$$f(x, t) = f_0 x^{1/3} b^{-7/4}(t) \exp\left[\frac{-9x^{4/3}}{16D_0 b(t)}\right], \quad (40)$$

where f_0 oraz D_0 - see (9), which means the general solution to NF -problem, and $b(t)$ changes by a power law as

$$b(t) = \frac{1}{m - \nu + 1} t^{m - \nu + 1}. \quad (41)$$

The case with $m = 3$ (polycrystalline growth on the athermal seeds, e.g. on impurities, anesthetics, etc.) results in

$$r_{av} \sim t^{7/8}, \quad t \gg 1, \quad (42)$$

which is a case assigned to the structural order in the system and when a macromolecular adsorption is not a rate-limiting physical factor. If in turn a disorder case prevails, which means that a macromolecular adsorption to the boundary of a crystallite plays a pivotal role [25], one obtains

$$r_{av} \sim t^{1/8}, \quad t \gg 1. \quad (43)$$

Note that a case "just in between" is the diffusional relation (39). It is worth emphasizing that

relation (43) represents a markedly sublinear relation, not rarely noticed in slowly evolving systems like polycrystalline polymeric or metallic systems [38,52,25]. Such small values of the growth exponents have particularly been picked up for layered or membrane model systems or when a creeping effect in polymers is detected, cf. [63] and references therein. One may anticipate a phase transition described in this subsection as a kind of the order-disorder phase transition in a three-dimensional system [64,65].

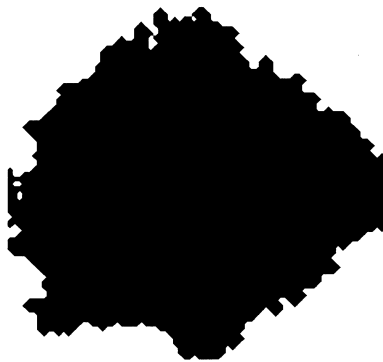


FIG. 4. A computer realization of the surface fractal. This is the Eden fractal taken from A. Gadowski, Ph.D.-Thesis, Silesian University, Katowice-Sosnowiec, Poland, 1991. The shape of the object can be described by the concept of self-avoiding path [67,63].

6.3 Towards polymorphic phase transition kinetics in two-dimensional systems

A next occasion to utilize the MS-concept but rather in more general terms, though for a two-dimensional case, will be shown in the subsequent subsection. It will be done by investigating the evolution of a cluster in a discrete (square lattice) space and eventually arriving, by assuming a standard continuity procedure, at the evolution rules of a surface fractal, like the Eden cluster (see, Fig. 4). This subsection is a little bid aside the mainstream of the kinetic description used for non-Fickian as well as Fickian systems. It differs from that because it is

not established on a set of kinetic (partial differential) equations with the corresponding IBC's, etc., see Eqs. (2)-(7) again. It is rather thought of to get a MS-like dynamical system from the first kinetic principles. This subsection will have exclusively one thing in common when compared with what has been presented up to now. Namely, the growing rules which will be derived are qualitatively of a very similar type. This is also the main reason for incorporating this subsection to Section 6.

Thus, let us think of a model system which is assumed to be represented by a self-avoiding polygon embedded in the square lattice of constant s . This may physically mean a two-dimensional vesicle which belongs to a category of model biomembranes. The boundary of the vesicle is presumed (see, Fig. 5) to be modeled by a self-avoiding trajectory. Another suitable physical example here can be two-dimensional faced crystals with dynamically stable zigzag or angular shape modulation [66].

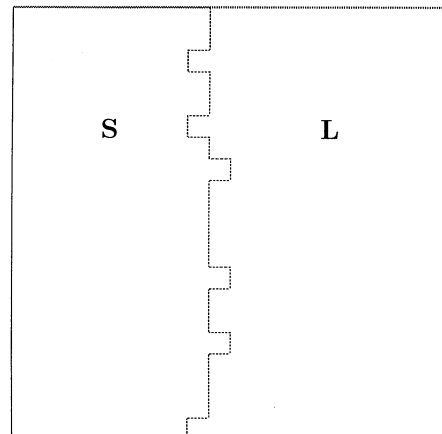


FIG. 5. A sketchy drawing of the realization of a self-avoiding trajectory, showing certain small instabilities of the *solidus* (S) vs. *liquidus* (L) line.

Fisher and coworkers utilizing Monte Carlo simulation results and scaling arguments showed that for $s \ll 1$ a scaling formula is valid for either the mean-square radius of gyration or the area (being an averaged value over many realizations) of the

polygon $\langle A \rangle$

$$\langle A \rangle = a_o p^{D_w}; \quad D_w \cong \frac{3}{2}, \quad (44)$$

where a_o is a positive constant of thermodynamic nature, $p \gg 1$ stands for the number of the perimeter sites of the polygon (cluster), and D_w represents the self-avoiding walk size exponent, where usually $D_w \in [1, 2]$ holds.

Let us notice at this stage of our considerations that there emerges a possibility towards getting a much broader behaviour than that for Eden or Eden-like aggregates. Namely, one is in principle capable of considering, by including various characteristics of the polygon's shapes and the kinetics assigned to them, a vast spectrum of the kinetic behaviour. The physical situation that we wish to discuss now can be named a polymorphic phase transition, since it assumes a theoretical possibility of understanding which cases studied may represent a certain expansion (a liquid-like behaviour) of the system and which undoubtedly may not (a compression case in which a solid-like behaviour can be observed) [65].

Let us then be interested in a more general case far exceeding the case for which $D_w = D_{SARW}$, where $D_{SARW} \approx 3/2$. Namely, we wish to consider a quite general physical situation

$$D_w = \frac{2}{d_w}, \quad (45)$$

where d_w denotes a dimension of the random Brownian path that can be either of pure Brownian nature ($d_w = 2$) or the surfaces (enveloping lines) of the aggregates are equivalent to fractional Brownian paths in superlinear viz. extremely fast ($d_w < 2$), or sublinear, i.e. anomalously slow ($d_w > 2$) regimes, respectively, cf. [65] for a more detailed information. This will however be provided at the end of this subsection. Now let us turn again to the Eden-like objects and their evolution.

Thus, using elementary planimetric knowledge we realize that a polygon with the above stated

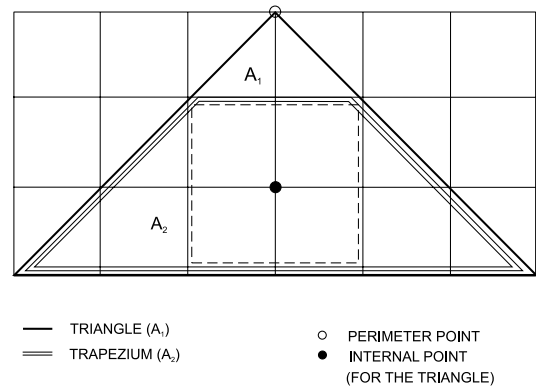


FIG. 6. Cartoon of the Steinhaus rule useful for evaluation of the polygon's area when the polygon is made of perimeter (open circles) as well as internal (dark circles) points (entities); for details, see [65]. In this study a continuous representation of the problem (see [63]) has been used to show possible relations to MS-problem [33]. One may notice that according to Steinaus rule (46) $A_1 = 9$ and $A_2 = 8$, respectively. The area of the smallest object, that means the square right in the middle (a broken line) is equal to four.

perimeter (e.g., being a SARW-perimeter; for a simple realization of a self-avoiding walk one can see, Fig. 5) is a two-dimensional (discrete) geometric object. The most simplest are for instance: triangle or trapezium, etc., see Fig. 6. Hugo Steinhaus found out that the area A of such a convex single polygon embedded in the square lattice (spanned on the lattice nodes) is found to be (cf. Fig. 6) [63,65]

$$A = i + \frac{p}{2} - 1, \quad (46)$$

where i (here: $i \gg 1$ as well) is the number of the internal points (sub-units) of the polygon (e.g., macromolecules constituting the cluster and placed in the nodes of the square lattice), and A stands for the exact value of the polygon's area. Presuming some very small statistical uncertainty in the system ("compact" lattice objects grown from a nucleus but no "extremely dispersive" aggregates), namely

$$0 < |\langle A \rangle - A| < \epsilon, \quad (47)$$

where $0 < \epsilon \ll 1$, one may conclude within the

negligible statistical error (47) that an equality, like $a_o p^{D_w} = i + \frac{p}{2} - 1$, by comparing directly (44) and (46), is possible to get. In consequence, one straightforwardly provides

$$i = a_o p^{D_w} - \frac{p}{2} + 1, \quad (48)$$

with $D_w = \frac{3}{2}$, since for a sake of clarity we assume that we continue our explanation with the self-avoiding perimeter. From (48) it crudely follows that if D_w were about 1, Eq. (48) would describe a straight-line dependence (for $i \equiv i(p)$). If in turn, D_w were around 2, a parabola-like characteristics must undoubtedly be assigned to relationship (48). Note that we are just in between since $D_w = \frac{3}{2}$, which means, that we somehow interpolate between the two types of typical $i(p)$ -behaviour mentioned; notice that $i(p)$ is nevertheless nonlinear in p .

Let from now try to perform an evolution of the cluster, i.e. our 'virtual' ensemble of i - and p -points. It is equivalent to impose a discrete time-dynamics on the system's behaviour. One can imagine that the system is willing to pass through a number of instants of stable 'dynamic' equilibria which is a kind of quasi-static approximation made since it is in agreement with the concept of interest (we are thinking about MS-instability concept [33,59]). (In general, the instants may be randomly distributed, which is the case of dispersive or fractal-like kinetics, and the probability distribution function appears to be an inverse power function of time [11].) In other words, we will be interested in knowing what is the total number of the cluster sub-units in time instant t (denoted by i_t), having known that at the preceding time instant $t - 1$ the number is i_{t-1} . We can obtain it if we simply perform discrete differentiation over the both sides of (48) which leads to

$$\Delta i = \left(a_o D_w p^{D_w-1} - \frac{1}{2} \right) \Delta p, \quad (49)$$

where $\Delta i = i_t - i_{t-1}$ and $\Delta p = p_t - p_{t-1}$. Making use of (49) one arrives at a difference equation of the form [63]

$$i_t = i_{t-1} + \gamma_d \varrho_{t,t-1}(p), \quad (50)$$

where γ_d is a constant. For example, for $a_o = 1/3$ one gets $\gamma_d = 1/2$ with $D_w = 3/2$ as above, and $\varrho_{t,t-1}(p)$ stands for a curvature change difference operator (acting on p) fully determined by p 's, i.e. by the two neighbouring total perimeter sites numbers p_t and p_{t-1} at t and $t-1$, respectively, as well as by D_w . One can see here a certain analogy between this operator and the homogeneity Laplacian operator for the difference diffusion equation, especially when an implicit difference scheme is used. Note that mathematically Laplacian is a measure of curvature of the cluster. If $p_t \neq p_{t-1}$ then $\varrho_{t,t-1}(p) \neq 0$. Otherwise, we get a stagnation (no growth) effect, which results in $i_t = i_{t-1}$, i.e. one argues that the curvature change operator has no effect when acting on p 's. The growth (or aggregation) process takes place when $\varrho_{t,t-1}(p) > 0$. Otherwise, one detects a counter-effect, namely a dissolution (or disaggregation or a kind of phase separation) process can be observed.

One can easily realize some drawback of the description proposed. First of all that it does not take into account the positions of the perimeter sites and their distances to the nucleation seed. The positions of the internal points (or entities) are not provided as well. Next, that D_w has to be additionally determined during the whole growing process so that one must achieve a saturation effect if one wants to have D_w thoroughly estimated. The first observation mentioned above is equivalent to stating that we have no explicit growth rule which stays behind the process that we just investigate. In other words, till now no growth mechanism has been offered. The only possibility of realizing with which physical mechanism one has to do relies on knowing reliably the values of D_w and a_o , but it may not suffice for being sure which is the growing process that we actually want to study. At most, we will be able to indicate a class of the growing processes. Since $D_w = 2/d_{SARW}$, where the fractal dimension of SARW-trajectory $d_{SARW} = 4/3$ ($D_w \equiv D_{SARW} = 3/2$), we may expect that we might also have to do with another type of growing

process, e.g. diffusion-controlled aggregation (polymerization) or fingered growth [33] in which not a surface fractal, but a mass fractal usually emerges. In such a case the inequality that $D_w \neq 3/2$, but $1 < D_w \leq 2$ is expected to hold. For other doubts or shortages related to the modeling proposed one is encouraged to see [63,65].

The continuity of the growing process can be physically noticed and the discreteness of the system will have no decisive meaning when something infinitesimally small describing the system, starts to change, so let us assume that $s \rightarrow 0$. Obviously, the total numbers of points, i and p , have to be large enough as well, and we have to make a formal statement that the discrete time-dynamics is to be replaced by a continuous, that means as usually, with $\Delta t \rightarrow 0$, where Δt is for simplicity taken as a deterministic time step [63]. Under such assumptions $i \equiv i(t)$ and $p \equiv p(t)$, $t \geq t_o \geq 0$ (t_o is the initial instant), and Eq. (49) can be approximated by

$$\frac{di}{dt} = \left(a_o D_w p^{D_w-1} - \frac{1}{2} \right) \frac{dp}{dt}, \quad (51)$$

where $\frac{di}{dt}$ and $\frac{dp}{dt}$ are the first order time derivatives of i and p , respectively.

At this stage of our considerations let us introduce the growth rule in a quite general way, simply by recalling a natural observation, that

$$\frac{di}{dt} = F(t; p_T) \geq 0, \quad (52)$$

where F is a non-negative and continuous function of t as well as of some thermodynamic parameter designated by p_T (In general, one wants to speak about a set of the thermodynamic parameters.) If $F = 0$ then no growth results (stagnation or "freezing" effects can likely be thought of), but if $F > 0$ the growing process is assumed to enter. There is still another requirement that we wish to assign to F . We may term it: a self-similarity requirement. This means that we expect to have F as a power function of time (either an inverse or a direct power function). Such a condition is usually expected

mostly for some complex systems, like polymers, model biomaterials, alloys, etc., and can be roughly speaking anticipated as a certain criterion of self-organization of the complex system under growth [63,65].

Let us now write explicitly Eqs. (51) and (52) as a non-autonomous dynamical system consisting of two ordinary differential equations, which are coupled by function F , namely [63]

$$\frac{di}{dt} = F(t; p_T); \quad \frac{dp}{dt} = \frac{F(t; p_T)}{a_o D_w p^{D_w-1} - \frac{1}{2}}. \quad (53)$$

Further, we see quite useful to rewrite system (53) in terms of densities of the evolving cluster. This may rigorously imply that one has to make use of the number area density ρ_i for i 's as well as the number perimeter density ρ_p for p 's. In terms of our continuous description they can be defined by the integral formulae $i = \int_0^A dA' \rho_i$ and $p = \int_0^l dl' \rho_p$, where i , p , ρ 's, A and l (the length of the circumference of the cluster) may generally be time- (t) and position- or x -dependent.

Let us again for simplicity assume that we wish to concentrate on the evolution of homogeneous clusters, i.e.

$$\rho_i(t, x) \equiv \rho_i = const; \quad \rho_p(t, x) \equiv \rho_p = const, \quad (54)$$

which is equivalent to replace (53) by

$$\rho_i \frac{dA}{dt} = F(t; p_T); \quad \rho_p \frac{dl}{dt} = \frac{F(t; p_T)}{a_o D_w (\rho_p l)^{D_w-1} - \frac{1}{2}}. \quad (55)$$

For providing some relation to MS-like (also, Taylor-Saffman, Bales-Zangwill or Grinfeld, etc. [58,59]) instability systems describing the evolution of growing objects, for example those controlled by diffusion (but with non-vanishing line or surface tension effect), we have to present system (55) in terms of a perturbed quasi-circle of radius r_{av} , which can also be thought of as an averaged radius taken in the sense of relation (47), where the circumference of the ideal circle is perturbed by a factor $\delta\chi(\phi, p_g)$,

requiring however, that $|\delta| \ll 1$, and χ is an everywhere continuous, bounded and oscillating function of ϕ (like, cosine or sine or another periodic function; here p_g is a geometrical parameter of no special importance in our further considerations so that we have to take $\chi(\phi, p_g) \equiv \chi(\phi)$ just for simplicity [63,33]). We wish to state very much here that χ does not have to be differentiable in ϕ . Conversely, it may be a nowhere differentiable function of ϕ , like the Weierstrass function or the Levy flight as well as a 'devil's staircase' as specific cases [58]. This assumption enables to have the evolution rules for a surface fractal (for instance, the Eden fractal).

Thus, making the perturbed circle approximation for (55) one gets

$$\frac{dr_{av}}{dt} = \frac{G}{2\rho_i a_1 r_{av}}; \quad \frac{dl}{dt} = \frac{2G}{\rho_p 2a_o D_w (\rho_p l)^{D_w-1} - 1}, \quad (56)$$

where for brevity $G \equiv G(t) = F(t, p_T) > 0$. Note that this term represents the driving force of the growing process, e.g. the supersaturation, undercooling, capillary force, etc., and it is always a function of thermodynamic conditions defined by p_T . Moreover, the following auxiliary relations have been assumed to be fulfilled:

$$A = a_1 r_{av}^2; \quad a_1 > 0, \quad (57)$$

which is a well-known scaling law (for the mass fractals a departure from this rule can be expected, i.e. $A \sim r_{av}^{D_f}$, $D_f \in (1, 2)$), and a clear geometrical relationship of the form

$$l = 2\pi(r_{av} \pm \chi(\phi)\delta), \quad |\delta| \ll 1. \quad (58)$$

Let us notice that we have gotten fully nonlinear system (56) with (58) which still describes our process being curvature-driven, no matter whether the driving force is specified or not. (For a discussion of the role of parameters a_o and a_1 , cf. [63,65].)

To arrive however, at a possibly simple approach but, in some sense more robust, and also to preserve its self-consistency, a linearization of (56) has to be performed, like in the original quasi-static MS-approach. It can easily be done for a sufficiently

mature stage of the growing process (here, r_{av} has to be much greater than a critical radius of the cluster), and by noticing formally that

$$|\chi(\phi)\delta/r_{av}| \ll 1, \quad (59)$$

which is very well fulfilled under such physical circumstances due to an emergence of the surface fractal. The linearized system ((56) with (58)) reads [63]

$$\frac{dr_{av}}{dt} = \frac{G}{2\rho_i a_1 r_{av}}; \quad \frac{d\delta}{dt} = \frac{-G(D_w - 1)\delta}{a_o D_w (2\pi\rho_p)^{D_w} r_{av}^2}, \quad (60)$$

(recall formally that $r_{av} \equiv r_{av}(t)$ and $\delta \equiv \delta(t)$) where the proportionality (thermodynamic) factors a_o and a_1 must be mutually dependent, namely [63]

$$\frac{a_o}{a_1} = \frac{2\rho_i}{D_w (2\pi\rho_p)^{D_w}}. \quad (61)$$

This way, a MS-like system has been recovered. It is exactly the MS-system when $G = const$ ($\nu = 0$, see below) but it is not when G depends upon time t . If we recall the growth rule (Eq. (52)) in a self-similar form, we have to expect to write explicitly (in the asymptotic regime)

$$G = G_o t^{\pm\nu}; \quad G_o > 0, \quad \nu \in [0, 1), \quad (62)$$

(G may be called: a kinetic-thermodynamic growth term, in which the prefactor G_o represents the constant driving force but some kinetic or time-dependent peculiarities of the process, due to its rheology or highly inhomogeneous character, are collected in the power law form as well as by knowing the value of ν ; G_o and ν must already be known, for example by being provided from experiment) so that as an asymptotic solution to the first of the equations of system (60), we get

$$r_{av}(t) \sim t^{(1\pm\nu)/2}. \quad (63)$$

For the mass fractals one might probably state $r_{av}(t) \sim t^{(1\pm\nu)/D_f}$. Note that result (63) does not depend essentially upon D_w though the prefactor formally does. Note also that the linearized dynamical system (60) appears to be independent of $\chi(\phi)$,

and that for $\nu = 0$ one provides $r_{av} \sim \sqrt{t}$, which is the classical diffusional power law always related to MS-approach noticed also in the preceding Section (for necessary details see [63,65,25]). Varying the scaling exponent ν in (63) we may get many power law behaviours, especially for a very slow growth (like $r_{av}(t) \sim t^{1/4}$ or slower). Assuming the inverse power law in (62), with $\nu = 1/3$, we can recover the scaling formula obtained from some extensive MC-simulations of the SARW-process (growth of small rings [67]), namely $r_{av}(t) \sim t^{1/3}$, which is also a well-known asymptotic result either for a NF - or F -system, e.g. for the two-dimensional normal grain growth, a droplet condensation or coalescence, etc. The same values of growth exponent ν and the scaling exponent (equal to $1/3$) involved in (63) are worth mentioning here.

Furthermore, a certain novel additional result can be revealed when looking at the second of equations constituting system (60). Namely, it is a stretched exponential or Kohlrausch-Williams-Watts behaviour of the small perturbation amplitude δ . Since r_{av} and δ practically grow (or shrink) in different time scales, i.e. δ being very small and extremely sensitive to the growing conditions grows (or shrinks) much more vigorously than r_{av} does, being practically kept constant for a given but small time interval. The perturbation amplitude is then provided [63] (cf., [33,58,59])

$$\delta(t) = \delta|_{t=0} \exp(-const \cdot t^{1\pm\nu}), \quad (64)$$

where the constant includes all the factors, like, e.g. $\frac{D_w-1}{D_w}$ or densities ρ 's, etc., and can even be interpreted in terms of the Vogel-Fulcher relaxation times, very characteristic of slow relaxation phenomena [63,30]. If $D_w \rightarrow 1$ (irregular shape), perturbation amplitude δ tends to a positive constant in the course of time, and practically, no perturbation effect is manifested. If in turn, $D_w \rightarrow 2$ (regular shape), the perturbation effect prevails, and Eq. (64) describes the process in a nontrivial way. Notice, by the way, that for $\nu = 0$ the classical MS-result (Debye or simple exponential

relaxation) is recovered. Let us recall that considerations on the anomalous relaxation behaviour in a NF -polycrystal led also to qualitatively similar conclusions, cf. this Section (first subsection). By the way, note that the growth exponent ν appears to be the only quantity which constitutes the relaxation exponent $1 \pm \nu$.

Finishing this subsection with a previously promised come-back to the scenario of polymorphic phase transitions in two-dimensional systems would be a useful thing [65,64]. It is quite easy to deal with when looking into the second of two equations (60) constituting the linearized system. From that it follows that the case with $D_w = 1$ is a critical case since it provides a constancy of δ in every time moment t . If $D_w < 1$ (δ grows in time t) or $D_w > 1$ (δ gets shrunken in time t) one sees two different expansion-compression behaviours thoroughly described in [65] but mostly in a discrete domain, i.e. not for $s \rightarrow 0$. (In [65] the case with $D_w = 1$ or $d_w = 2$, which means the pure Brownian path, has been discarded as a singularity point on the so-called morphological phase diagram of the system.) It is then sensible to invent such an elementary description like that presented here since there is a huge number of aggregation processes (cf., quasicrystalline domains emerging in Langmuir-Blodgett systems, Hele-Shaw fingered patterns observed in experimental set-ups of confined two-dimensional geometry or to some extent cellular networks grown in model laboratory systems [58,68]) that can be somehow approached by this means [69,33,59,8].

7 Final remarks and perspectives

The purpose of this Section is mainly to convince the reader that an extensive approach to the nucleation-and-growth phase transitions [2] in complex systems has been presented, which indicates at least two concrete types of interactions with the available basic knowledge concerning this very active area of research [2,13,8,45,68,58].

First, it fills in our opinion a gap between a large class of deterministic (analytical) growth models (for example: AK- or MS-models [2,4,33,58], or some of those mentioned in Section 1, e.g. the Hillert model [13]) and an equally numerous class of stochastic descriptions of the growing systems (see: [70,12], or recall some models mentioned in Section 1, for example due to Louat or Pandé, etc.). The presented NF - as well as F -descriptions which can be thought of as a certain alternative to the kinetic Ginzburg-Landau model [45,43] appear to be distinctly much simpler to deal with analytically, though can be placed in the same class of phenomenological models [23,52].

Second, the presented modeling, being well established within a class of cooperative (strictly speaking: competitive) diffusion-type models [41,44,65], also like those by Louat or Pandé in physical metallurgy [13], or by Sugar (and/or Kanehisa and Tsong) [16] in biophysics (a Glauber-like description of kinetics of microdomains-containing lipid systems), is capable of recovering all the relevant classes of known kinetic late time behaviours of those systems, which is presently a vivid concept under exploration just for such 'delicate' physical situations [73], mostly because of emerging possibilities of application to modeling living or biological systems [4-6]. In other words, the common kinetic description presented is able to pick up many of the kinetic anomalies which arise while studying the competitive growth phenomena in complex systems, and works in some sense in between other approaches invoked in this study, trying to complete them if a suitable chance appears.

Another important goal of this Section is to show the reader that both the presented types of approaches may work self-consistently and can reasonably be interpreted in terms of surmounting a relative energetic barrier of the kinetic process under study. In other words the role of h -parameter which has appeared frequently, mostly in NF -description, will be discussed now in detail. (Note again that for F -description two cases, namely $h \rightarrow 0$ as well

as $h > 1$ are of a certain interest, cf. Section 4 and [19].) For preparing a basis for such a discussion we have more or less borrowed an approximate expression of h from a quantitative description of a gaseous (CO , O_2) species rebinding to (heme) proteins, which is typically a process with small energetic barrier, provided in terms of the so-called dispersive kinetics [11,26,27] mentioned before, i.e. with the diffusion function being inverse powerly time-dependent (see, Eq. (4)). After [26] we wish to propose to use the following redefinition of h

$$h \simeq \frac{1}{1 + \delta_x^{-2}}, \quad (65)$$

where the relative energetic barrier reads

$$\delta_x = \frac{\sigma_x}{2k_B T}, \quad (66)$$

and where k_B stands for the Boltzmann constant whereas T represents the temperature. The quantity σ_x is a dispersion parameter, taken from a statistical distribution of changes of the individual volumes or areas, x , assumed that this distribution were Gaussian [26]. Looking at δ_x one easily sees that this relative energetic barrier is a kind of competition parameter, where the competition takes place between two main concurrent energetic contributions of the model processes under consideration.

The first contribution, represented by σ_x , is a measure of the structural order in the system. It is then straightforwardly related to the grain boundary free energy decrease, which in turn is proportional to a line (surface) tension change at the boundary, and stands also for a measure of the capillary forces acting on the polycrystalline (NF) or sometimes also on clusters-containing (F) systems.

The second contribution in turn, represented by the thermal (Boltzmann) energy term, is a measure of the structural disorder within the system. In modern concepts of the barrier surmounting it stands for the noise intensity of the delta-correlated Gaussian noise, cf. P. Reimann and P. Hänggi in [70], and references therein. Since the first energetic

contribution is related to the free energy (decrease) measured at the boundary (-ies), the second may likely be connected with a counter-effect, i.e. some entropy changes at the boundary (-ies), but due to, e.g. an increase of the average free volume per polymer segment (proportional to T) rather than with respect to the conformational changes [71]. Such a reasoning was also presented for the diffusion-controlled adsorption of macromolecules on solid supports [60,24]

In Sections 2-4 we have mentioned four regimes of action of h -parameter. They can be summarized by the following formula

$$h \in \begin{cases} [0, 1) & \text{i.e. classical growth regime,} \\ \{1\} & \text{i.e. non-classical growth regime,} \\ (1, \infty) & \text{i.e. stagnation (no growth),} \\ (-\infty, 0) & \text{i.e. critical growth regime,} \end{cases} \quad (67)$$

where three growth regimes as well as one stagnation (no growth) regime have been listed.

The first regime with $h \in [0, 1)$ represents an anomalously slow growing process in which for a long-time asymptotics a power law, with the growth exponent being less than or equal to $\frac{1}{2}$, has been recovered. One knows [59,30] that the case with the growth exponent equal to $\frac{1}{2}$, e.g. a MS-like system or alike, is a purely diffusional case and stands for a "threshold relation" between the sublinear (just mentioned) and superlinear power laws, e.g. those very characteristic of the cylindrolitic or spherulitic systems [7,23-25,60]. In this regime the relative energetic barrier δ_x is real valued, and after a straightforward analysis of (65) and (66), appears to be $0 < \delta_x < 1$; for the case with the growth exponent of $\frac{1}{2}$ one gets $0 < \delta_x \ll 1$, even. This means that the Boltzmann energy disordering term prevails when compared with the ordering term σ_x . Therefore this regime can be named as the high-temperature limit, cf. Eq. (66), though under real physical circumstances the temperature must not exceed very much the room temperature [3-6].

It is however not true in the second limit with $h = 1$. This limit provides the logarithmic growth law, and is mostly realized under the low-temperature

constrains, or quantitatively for $\sigma_x \gg 2k_B T$. In this case δ_x takes on real values as well. Also a kinetic Ginzburg-Landau [43,45] or Glauber-like [40], or Potts-like [10] or even others, i.e. of MS-type [39] descriptions show such a kinetic dependency [18,19].

According to our classification of the growth and structure formation processes the two remaining processes (cf., Eq. (67)) are well characterized by imaginary (complex) values of δ_x . They both are, again according to philosophy of our classification exceptional, since the remaining superlinear (say, spherulitic) growth regime has been frequently termed as critical while the only no growth (freezing; phase separation at the late stage of a growing process) regime is somewhat outside the scheme because it does not describe a growing but rather a stagnation process (or, when the system ceases to grow or even if the parts of a growing systems would take apart). In other words, if δ_x obeyed the requirements of our classification scheme (67), it would likely be expressed by a formula $\delta_x = i\bar{\delta}_x$, where $i^2 = -1$ (imaginary unit) and $\bar{\delta}_x$ is always of a real value. If $\bar{\delta}_x$ belonged to $(0, 1)$ we just would get the spherulitic (cylindrolitic) growth regime of high temperature rather [24], whereas for $\bar{\delta}_x$ greater than one a kind of, let us say low-temperature separation of a growing phase, could be detected [45].

Notice (look at (65) and (66) again), that for δ_x^{-2} being sufficiently small, one obtains

$$h \simeq 1 - \delta_x^{-2} \quad (68)$$

which would mean that δ_x^{-2} could be compared by $\frac{d_s}{2}$ with a fracton (spectral) dimension, d_s , of the grain-boundaries random walk [42], and because d_s is typically greater than one [31] (quite often ca. $\frac{4}{3}$ [30]), one provides that the anomalously slow (sub-linear) or vigorous (superlinear) growing processes can be characterized by (68) and (66) since they take place in sufficiently high temperatures [18,23-25]. (A judgement whether a temperature is high or not is rather subtle, so that it would sometimes be more convenient to speak of a weak or strong Gaussian noise intensity, at least if it were the case

thoroughly described in [70] due to Reimann and Hänggi.) This is mostly the case of the heterogeneous phase transitions, mentioned at the beginning of this study, in particular if the nucleation-and-growth phase transitions in complex systems are supposed to occur. (This can be the only case for which the spectral dimension concept [30] seems to be still applicable.)

Let us briefly summarize the above. It can be done by stating explicitly that:

(i) Power laws of either sublinear or superlinear (also, linear) nature survive if one assumes that the evolution of clustering or grains-containing systems take place with small relative energetic barriers to the evolution [72]; here the h -regimes are: $h \in [0, 1)$ and $h < 0$.

(ii) It is undoubtedly noticed that such evolution is facilitated by thermal activation which enables to surmount the barriers, and by the way, is very consistent with the concept of the heterogeneous phase transitions in complex systems among which the nucleation-and-growth phase transition plays a dominant role [1-4].

(iii) The only two cases which do not obey the above described scenario (cf., points (i) and (ii)) appear to be: the logarithmic case with $h = 1$ as well as the stagnation effect with $h > 1$.

(iv) the above two physical effects with hardly surmountable energetic barriers are detected under a low-temperature condition or rather well beyond the high-temperature limit; certainly, in such cases no power laws can be noticed [45,39,40].

(v) the high-temperature limit in which all the power laws (cf., the table in Section 5) appear, strongly resembles a state of the self-organized criticality driven by some extremal dynamics for which different universality classes (sublinear, linear and superlinear; cf. [65] for another outlook) have been predicted; a firm basis which stays behind that is a (physical) space-time, in our case $x - t$, scale invariance which have been presumed in (4), (19), etc., see also [73] and references therein.

Similarly to (v) a space-time invariance, but in a

real position space for a random walk of the mass (inertia) centre of a fractal cluster of dimension d_f , has been applied to get diffusional characteristics of this non-Markovian as well as non-Gaussian process [73]. The diffusion function, $D(x, t)$, for such a process (but with $\alpha = 0$, cf. Section 4 or Appendix) realized in $d = 3$, reads

$$D(x, t) \sim \frac{1}{[1 + M(t)]^{h_o}}, \quad h_o > 0, \quad (69)$$

where $M(t)$ stands for a stochastic realization of a process of the random attachment/detachment of molecules or clusters to a randomly walking as well as growing fractal cluster [74]. This processes was assumed to be modeled either by a Poissonian statistics of the attachments or detachments (here, statistically speaking the attachments strongly prevail, i.e. the mass $M(t) \propto t$) or by a linear birth-and-death process for which in turn $M(t) \propto t$ does not hold [74]. Moreover, the h -exponent, because of experimental arguments, must be substituted here by h_o [74], namely

$$h_o = \frac{1}{d_f}, \quad (70)$$

and formally the grain distribution function $f(x, t)$ by the probability density of finding a random walker (cluster) at a position x at time t (note that now x means a position not a grain size). After resolving the system, based on Eq. (3) or (2) (see [74,75] for details), one picks up three different sublinear (or, nonlinear *viz.* logarithmic) random walk regimes, very similar to those contained in Eq. (17). Despite apparent qualitative similarities between the growth of polycrystals studied in the space of the sizes of the crystallites and the process just described, but in the space of the positions of randomly walking clusters, there appears a basic difference between them, namely that h_o is unfortunately not a competition parameter since it exclusively depends upon the fractal dimension of the cluster, assumed that it is solely determined for the late stage of the random walk process. Therefore, such a process cannot be described in terms

of the relative energetic barrier concept offered in this Section. It seems to be of a certain interest however because the cluster-cluster aggregation processes in a diffusional regime take on a stationary limit that enables to draw a Wigner-Seitz cellular network (or, a Dirichlet-Voronoi mosaik) for the system, and which places the polycrystals as well as clusters-containing colloidal assemblies in similar topological classes [75,8,13]. For the last category we wish to recommend F -description which is certainly better comparable with the NF one, cf. Section 5.

Among many things two are in our opinion really worth commenting. First, a stochastically-oriented reader may notice that our modeling can be used to describe a one-dimensional diffusion process on a non-negative straight-line with the absorbing boundary in 0 (Eq. (5)); here x must play however a role of the coordinate on the straight-line. Then our system of equations (2)-(5) can be reformulated in terms of the stochastic Ito-Stratonovich equations and, depending on $\alpha = 1 - \frac{1}{d}$ the process can either be sublinear or linear, or even superlinear, cf. [20,12]. Going a little bit into detail one may realize that, e.g. Eq. (3) (with the diffusion function (4), but for simplicity with $h = 0$ and with a prefactor equal to one), being of a Fokker-Plank-Kolmogorov form, can be transformed to

$$\frac{d}{dt}x = \alpha x^{-(1-\alpha)} + x^{1-\alpha}\psi(t), \quad (71)$$

(recall: $\alpha = 1 - \frac{1}{d}$) assumed as before that ψ stands for the delta-correlated Gaussian noise (with zero mean value), cf. [62]. Note that x is proportional to r^3 for $d = 3$ and to r^2 for $d = 2$ (r - a current radius of the grain or cluster). If we take the deterministic part of Eq. (71) we get specifically the Stauffer-Binder model of coalescence [45] or, in particular the Hillert model [13], cf. Section 1. Let us realize that in this case the rate of change of the area or volume of a single grain is proportional to its local curvature $x^{-(1-\alpha)}$, cf. Eq. (71). Note that if one wishes to take the aver-

age over the both sides of (71) the noise-containing term will be cancelled out, and assuming that the clusters (grains) grow independently one gets the power law behaviour for the average radius of the cluster, mentioned frequently before, that means a manifestation of the self-organized criticality in the system [73]. (The strength of the process can be controlled if one presumes not only a control via a noise type as well intensity but also by utilizing the concept of fractal-like kinetics [50,27], which may be done "phenomenologically" by incorporating a powerly time dependent prefactor, like that involved in Eq. (32). In fact, this means has extensively been used throughout the presented study.)

Second, it seems to be quite natural because of importance of time domain [36], to think about a description of the processes mentioned in this work in terms of fractional derivatives, similarly to the description offered by subsection 6.1 for the stress relaxation. It can be done, e.g. as a modification of the Avrami-Kolmogorov approach (see, Section 5) by the following

$$f_{an}(t) + \tau_{ch} \frac{d^{\bar{\omega}}}{dt^{\bar{\omega}}} f_{an}(t) = 0, \quad (72)$$

where $f_{an}(t)$, which accounts for the old (parent) phase being transformed, can be related to $1 - f_h(t)$ from Eq. (32), and τ_{ch} is proportional to $\frac{1}{k_o}$ also from Eq. (32). The exponent $\bar{\omega}$ belongs to $(0, 1]$, and if it is equal to one, one gets the AK-limit of the process, cf. [36]. In general, $\bar{\omega}$ can be again related to the spectral dimension or its extension given in the spirit of that presented above.

Last but not the least, we would like to recall perhaps once again that by presenting the both descriptions, applied to various at least partly ordered complex soft-matter (e.g., organic) systems, like quasicrystals, polycrystals or (ordered) alloys, we wish to draw attention to a certain, we hope, relatively simple phenomenological way of getting sometimes quite interesting results available till now either by rather complicated theoretical methods (kinetic Ginzburg-Landau description [45,43]) or time-consuming computer experiments [8,29]).

Finally, one may notice that a certain additional (but not so easy) aim of this review is to try to show that some data on the growing complex systems, rather sparsely distributed all over a thick collection of papers and studies, taken for example from biophysics, chemical physics (physical chemistry) or even physical metallurgy, would appear in a form of one phenomenological but hopefully self-consistent as well as sufficiently robust kinetic description. Thus, it is believed that the presented common description assures at least a useful interaction between all the existing models mentioned, e.g. AK-model, MS-model or alike, kinetic Ginzburg-Landau or other more specific (and honestly to say, less popular), etc. aiming at some revealing of kinetic laws appearing during the evolution of microstructures (also, in the early time growth regime, what was not considered in this study) as well as systems under growth, cf. [68,8,9] or more recent literature data for trying to discover a plenty as well as variety of growing systems, and versatile theoretical methods for describing their kinetic behaviour [9,13,21,45,68].

In the last word, we wish to state clearly that we are aware that some models based on substantially different mechanisms can asymptotically yield growth exponents of exactly the same value. There is, for instance, the case of purely diffusional models, in which objects do grow just by diffusion of the matter, cf. the Mullins-Sekerka model again [33], and the models for which the growth mechanism is realized via surface tension or inward-curvature-center driven mechanism, as in a two-dimensional motion of idealized grain boundaries [76], cf. [15] for anticipating the same growth law. Both of them lead to a parabolic (say, normal diffusional) growth law, though the very basics of growth mechanisms looks so differently.

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Appendix: Method of solution of NF - as well as F -problems

A mathematically self-consistent method of resolving both NF - as well as F -problems, i.e. Eqs. (2) and (3) with the corresponding IBC's and diffusion function D , relies on the assumption that the solution to the problems can be written in the following form

$$f(x, t) = \int_0^\infty e^{-\lambda t} \mathcal{G}_\lambda(x) d\lambda, \quad (A1)$$

where \mathcal{G} is a function of x and λ stands for a non-negative parameter. The corresponding Bessel equation for NF -problem reads

$$x^\alpha \mathcal{G}_\lambda''(x) + 2\alpha x^{\alpha-1} \mathcal{G}_\lambda'(x) + [\lambda + \alpha(\alpha - 1)x^{\alpha-2}] \mathcal{G}_\lambda(x) = 0 \quad (A2)$$

while for F -problem looks like [19]

$$x^\alpha \mathcal{G}_\lambda''(x) + \alpha x^{\alpha-1} \mathcal{G}_\lambda'(x) + \lambda \mathcal{G}_\lambda(x) = 0, \quad (A3)$$

where $\alpha = 1 - \frac{1}{d}$ is known from Section 4 (subsection 4.2). Note that (A2) and (A3) take on a similar linear form if $d \rightarrow \infty$ or $\alpha \rightarrow 1$, which would mean that in higher dimensions both the equations work in a comparable way. (Notice that for $d = 1$ ($\alpha = 0$) we get exactly the same equations, which confirms again the fact that there is no difference between the two approaches proposed in one-dimensional space.)

Thus, the corresponding general solutions to both the main problems considered can be provided by

$$f(x, t) = 22x^{(1-2\alpha)/2} \int_0^\infty dz z e^{-tz^2} B_{NF}(z) \times J_{\omega_1} \left(\frac{2z}{2-\alpha} x^{(2-\alpha)/2} \right) \quad (A4)$$

and [19]

$$f(x, t) = 2x^{(1-\alpha)/2} \int_0^\infty dz z e^{-tz^2} B_F(z) \times J_{\omega_2} \left(\frac{2z}{2-\alpha} x^{(2-\alpha)/2} \right), \quad (A5)$$

where the functions B 's read

$$B_{NF}(z) = \frac{1}{2-\alpha} \int_0^\infty dx x^{1/2} f(x, 0) \times J_{\omega_1} \left(\frac{2z}{2-\alpha} x^{(2-\alpha)/2} \right), \quad (A6)$$

$$B_F(z) = \frac{1}{2-\alpha} \int_0^\infty dx x^{(1-\alpha)/2} f(x, 0) \times J_{\omega_2} \left(\frac{2z}{2-\alpha} x^{(2-\alpha)/2} \right), \quad (A7)$$

respectively. Note that J 's are the Bessel functions of fractional orders ω_1 and ω_2 , $\omega_1 = d\omega_2$, and $\omega_2 = \frac{1}{d+1}$ (d stands as before for the dimension of the space). Notice that the kinetics of NF system, i.e. the two first moments given by Eqs. (12), (13) (a constant value) as well as two next characteristics, namely the fluctuations σ and the volume of an individual grain r_{av}^d , can be expressed exclusively by exponent ω_1 . It is however not the case of a F -system which looks much complex, see Eqs. (27)-(30). The kinetics of that requires a combination of ω_1 and ω_2 when looking at the growth exponent as a measure of such a complexity, cf. Eqs. (27)-(30). (It is worth mentioning that solution (9) or its particular case (40), both given in terms of the Weibull functions of x [18], can be derived from (A4) and (A6) for the standard IBC's assumed throughout this study. By the way, the process can also be studied for versatile set of initial conditions.) For possible realizations of solutions (A4) and (A5) one can consult [25] as well as [19] (and Ref. [25] therein) for both NF - as well as F -systems, respectively.

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