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FROM A DISCRETE TO CONTINUOUS DESCRIPTION OF TWO-DIMENSIONAL CURVED AND HOMOGENEOUS CLUSTERS: SOME KINETIC APPROACH *

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Starting with a discrete picture of the self-avoiding polygon embeddable in the square lattice, and utilizing both scaling arguments as well as a Steinhaus rule for evaluating the polygon's area, we are able, by imposing a discrete time-dynamics and making use of the concept of quasi-static approximation, to arrive at some evolution rules for the surface fractal. The process is highly curvature-driven, which is very characteristic of many phenomena of biological interest, like crystallization, wetting, formation of biomembranes and interfaces. In a discrete regime, the number of subunits constituting the cluster is a nonlinear function of the number of the perimeter sites active for the growth. A change of the number of subunits in time is essentially determined by a change in the curvature in course of time, given explicitly by a difference operator. In a continuous limit, the process is assumed to proceed in time in a self-similar manner, and its description is generally offered in terms of a nonlinear dynamical system, even for the homogeneous clusters. For a sufficiently mature stage of the growing process, and when linearization of the dynamical system is realized, one may get some generalization of Mullins–Sekerka instability concept, where the function perturbing the circle is assumed to be everywhere continuous but not necessarily differentiable, like *e.g.*, the Weierstrass function. Moreover, a time-dependent prefactor appears in the simplified dynamical system.

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1. Introduction

A growing interest in kinetics as well as scaling properties of objects with randomly evolving interfaces (surfaces), being widely known in physics and chemistry as well as biology as separation boundaries, (bio)membranes, active zones, *etc.*, is of theoretical interest to materials scientists, physicists, chemists and biologists, but recently also attracts interest of technologists or materials engineers [1].

The objects in question are usually recognized as grains (or microdomains) with curved boundaries [2], systems with fluctuating interfaces, spreading or invading assemblies and/or crystals with either smooth or rough surfaces, *etc.* [3]. They may represent a behavior of such far-from-equilibrium phenomena, like *e.g.*, grain coalescence in metals and alloys, evolution of the crystallization front (*e.g.*, with a zigzag shape modulation in two-dimensional matrices), growth and volume increase of bubbles, formation of biomembranes (vesicles, micelles, *etc.*) or even expansion of natural patterns, like bacterial or algae colonies [3]. The kinetic behaviour of many of them still attracts some interest of researchers in many disciplines, and is a subject of permanent considerations. Especially, scaling or similarity properties which always assume some invariance of the system properties under a scaling rule(s), appear to be informative mostly to physicists who, most frequently under the self-similarity assumption(s), try to understand quite general static as well as dynamic properties of the system under investigation [4].

Theoretical studies on the kinetics of cluster growth are observed to split up into two main directions:

1) computer simulations: Monte Carlo (MC), cellular automata (CA) as well as molecular dynamics (MD);

2) analytical studies on dynamics or kinetics of some systems with evolving fronts, especially when utilizing the concepts of the master equation for the diffusive and/or convective front propagation; Langevin-type equations for the evolution of a fluctuating diffusion-reaction front [5]; notice that the concept of fractality of any kind is often used for description of the above mentioned phenomena; *cf.* [1, 6] for general overview; also, a scaling concept, being very useful in polymer physics, is very much advised here [4, 7].

In this study, beginning the whole story with a discrete picture of a self-avoiding polygon embedded in the square lattice (Fig. 1(a)), and applying both scaling arguments as well as a Steinhaus rule for evaluating the polygon's area (Fig. 2), we may, by imposing a discrete time-dynamics on the system in question and working within a quasi-static approximation, obtain some evolution rules for the surface fractal in $2d$ space. The surface (line)

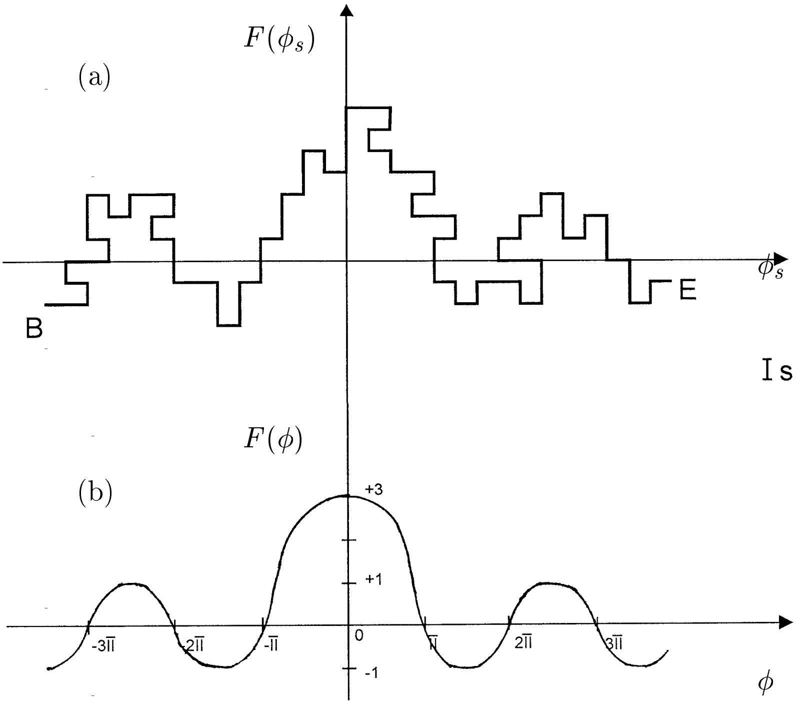

Fig. 1. Cartoon of discrete (a) and continuous (b) curves as the possible boundaries of 2*d* cluster in the discrete as well as continuous representations, respectively; note that the discrete staircase-like curve $F(\phi_s)$ (a nowhere differentiable function of its argument, starting from a beginning point B and reaching an ending point E) can also be useful for the continuous approach (a continuous periodic curve $F(\phi)$ was chosen from a standard textbook in physics; other examples applied can be found elsewhere [11, 18]; the lattice constant is designated by s, and it represents also the lower index of angular argument ϕ, which symbolizes discreteness of the upper curve).

is modelled here by the self-avoiding random walk (SARW) trajectory, *i.e.* a trajectory obtained under restriction that each of its points can never be visited or touched more than once. Such a trajectory is a fractal with the fractal dimension of 4/3 [8]. The process is highly curvature-driven, which is very characteristic of many phenomena of biological interest, like crystallization in complex (natural) media, (non)retarded wetting, formation of biomembranes (vesicles, micelles), interfaces (phase transitions from angu-

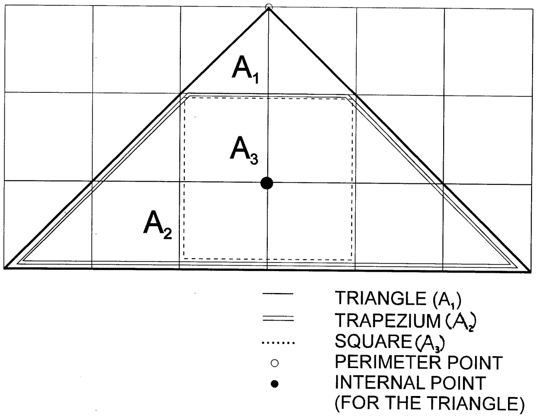

Fig. 2. Sketch of examples of Steinhaus rule (2). The areas of the triangle, trapezium and square are designated by A_1, A_2 and A_3, respectively, and are evaluated to be: 9, 8 and 4 (see, Eq. (2)); the internal as well as perimetric (periphery) points of the triangle have been drawn, too (for additional graphical symbols, see the legend of the figure).

lar to smooth shapes; *cf.* Fig. 1) or (in)commensurable layers [8,9]. In the discrete (say, microscopic) regime, the number of subunits constituting the cluster is a nonlinear function of the number of the perimeter sites. The perimeter sites can be defined as the most outer sites either of the fractal itself or the sites of its nearest neighborhood. The latter sites do not formally belong to the cluster. They can be described as the sites very active for the growth. It depends upon what kind of the growing process we wish to describe. If the process is not realized by some accretion or sticking of particles (subunits) coming from the external medium, we will have to do with a certain expansion of the cluster, like in swelling or bubble expansion; here, some increase in volume of the cluster is manifested. If, in turn, some accretion of external particles in the active zone of the cluster is allowed to take place, then the cluster tends to grow by the increase of mass than volume, rather, like *e.g.* in diffusion-controlled processes [1,6]. A change of the number of subunits in time is exclusively determined by a change in the curvature in course of time (though, a scaling prefactor and exponent do enter as the parameters), given explicitly by a difference operator. In the continuous (say, meso- or even macroscopic) regime, the process is assumed to proceed in time in a self-similar manner, and its description is generally offered in terms of a nonlinear dynamical system, even for the homogeneous clusters (of constant density). For a sufficiently mature stage of the growing process, and when a linearization of the dynamical system is performed, one can have a generalization of the Mullins–Sekerka (MS) instability concept, where the function perturbing the circle of radius R_g is assumed to be everywhere continuous but not necessarily differentiable (*cf.* Fig. 1, and compare Fig. 1(a) to Fig. 1(b)), like *e.g.*, the Weierstrass function (a special case is the Levy flight) [10], which is a kind of the SARW-trajectory; moreover, a time-dependent (kinetic-thermodynamical) prefactor may appear in the simplified dynamical system, where the radius R_g and the small perturbation amplitude δ, like in the original dynamical MS-system [11], are the so-called dependent variables (the independent variable is always time t).

2. Discrete description as a combination of Steinhaus rule and some scaling argumentation

Let us imagine a self-avoiding polygon embedded in the square lattice of constant s. This may physically represent a two-dimensional vesicle (a model biomembrane), in which the boundary of the vesicle is the perimeter of the self-avoiding trajectory (see the sketch in Fig. 1(a)). Another suitable example here can be $2d$ faced crystals with dynamically stable zigzag or angular shape modulation [2].

Fisher and co-workers (see [12–15], and Refs therein) using Monte Carlo simulation results and scaling arguments showed that for $s \ll 1$, or equivalently for $N_{\rm grid} \gg 1$ ($N_{\rm grid}$ is the number of grids of the square lattice), 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 $\langle A\rangle$, namely

$$\langle A\rangle = a_1 p^{D_1}\,; \quad D_1 \cong \frac{3}{2}\,, \tag{1}$$

where a_1 is a positive constant of thermodynamic nature, $p \gg 1$ stands for the number of the perimeter sites of the polygon (cluster), and D_1 represents the self-avoiding walk size exponent [8,12,13]; in general, $D_1 \in [1,2]$ is valid.

On the other hand, however, appealing to our elementary knowledge on planimetry, we realize that a polygon with the above stated perimeter (*i.e.*, being a SARW-perimeter) is a two-dimensional (discrete) geometric object; the most simplest are, *e.g.* : triangle, trapezium or square, or a combination of them; *cf.* Fig. 2.

Polish mathematician Hugo Steinhaus found out [16] 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. 2)

$$A = i + \frac{p}{2} - 1\,, \tag{2}$$

where i (here: $i \gg 1$, too) is the number of the internal points of the polygon (subunits composing the cluster, and placed in the nodes of the square lattice), and A stands for the exact value of the polygon's area. Postulating some very small statistical uncertainty in the system ("compact" lattice objects grown from a nucleus; no fuzzy or "extremally dispersive" aggregates or agglomerates), namely

$$| \langle A \rangle - A | < \varepsilon \,, \tag{3}$$

where $0 < \varepsilon \ll 1$, one may conclude, within the (negligible) statistical error, that an equality, like $a_1 p^{D_1} = i + \frac{p}{2} - 1$, by comparing directly (1) and (2), is possible to get; rearranging that the equality reads

$$i = a_1 p^{D_1} - \frac{p}{2} + 1 \,, \tag{4}$$

with $D_1 = 3/2$ (approximately), but with some quite high accuracy [13,15]. From (4) it crudely follows that if D_1 were about 1, Eq. (4) would describe a straigth-line dependence (for $i \equiv i(p)$). If, in turn, D_1 were around 2, a parabola-like characteristics must undoubtedly be assigned to relationship (4). Note that we are just in between since ca. $D_1 = 3/2$, which means, that we somehow interpolate between the two types of $i(p)$-behavior mentioned ($i(p)$ is nevertheless nonlinear in p).

Let from now try to evolve the system (our 'virtual' ensemble of i- and p-points) or to impose a discrete time-dynamics on it. (It will be equivalent to pass the system through a number of instants of stable 'dynamic' equilibria which is a kind of quasi-static approximation since it is in agreement with the concept of interest [11]; 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.) In other words, we will be interested in knowing what is the total number of the cluster subunits in time instant t (denoted by i_t), having known that at the preceding time moment $t-1$ the number is i_{t-1}. We can get it when we simply perform discrete differentiation over the both sides of (4), which results in

$$\Delta i = \left(a_1 D_1 p^{D_1 - 1} - \tfrac{1}{2} \right) \Delta p \,, \tag{5}$$

where $\Delta i = i_t - i_{t-1}$ and $\Delta p = p_t - p_{t-1}$. Applying (5) one arrives at a difference equation of the form

$$i_t = i_{t-1} + \gamma_d \varrho_{t,t-1}(p) \,, \tag{6}$$

where γ_d is a constant (*e.g.*, for $a_1 = 1/3$, one has $\gamma_d = 1/2$; $D_1 = 3/2$, as above), and $\varrho_{t,t-1}(p)$ is a curvature (or, a curvature like) change difference operator (acting on p) fully determined by p-s, *i.e.* by the two total perimeter sites numbers p_t and p_{t-1} at t and $t-1$, respectively, as well as by D_1 (one can see here some analogy between this operator and the homogeneity Laplacian operator for the difference diffusion equation, especially when an implicit difference scheme is applied; note that mathematically Laplacian frequently means the existence of curvature in the system [9]). If $p_t \neq p_{t-1}$ then $\varrho_{t,t-1}(p) \neq 0$. Otherwise, we get a stagnation (no growth or dissolution) effect, which results in $i_t = i_{t-1}$, *i.e.* one sees 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 has to do with a countereffect, *i.e.* a dissolution (or disaggregation) process can be observed (this effect is of no interest in our present study).

One can realize, however, some shortage of the description proposed. Mostly, that it does not take into account the positions of the perimeter sites and their distances to the aggregation center. Next, that D_1 has to be additionally determined during the whole growing process so that one must reach a staturation effect if one wishes to have D_1 solely picked up. The first remark mentioned above is equivalent to say that we have no explicit growth (aggregation or agglomeration) rule, which stays behind the whole process; 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_1 and a_1, but it may not suffice to be sure which is the growing process that we investigate; at most, being lucky, we will be able to indicate a class of the growing processes [1]. Since $D_1 = 2/D_{\mathrm{SARW}}$, where the fractal dimension of SARW-trajectory $D_{\mathrm{SARW}} = 4/3$ ($D_1 = 3/2$) [8], we can expect that we might also have to do with another type of growing process (diffusion-limited aggregation, fingered growth; polymerization, percolation, gelation, *etc.*), in which not a surface fractal, but a mass fractal emerges; in such a case the inequality that $D_1 \neq 3/2$, but $1 < D_1 \leq 2$ [17] holds. Anyway, one should state explicitly that some application of Eqs (5) or (6) makes sense if there is a precise set of growing rules that stays behind, which enables to determine D_1 (and, perhaps, a_1); we see a chance to remove this inconvenience by offering a continuous description (see below). It is worth mentioning that Steinhaus formula (2) or the evolution rules built on it, *i.e.* (5) or (6), have some information on the curvature (curvature changes) of the discrete $2d$ object contained in a natural way, just by having explicitly included the total number of the perimeter sites p or its changes Δp in course of time t.

3. Continuous limit as a generalization of Mullins–Sekerka instability concept

The continuity of the growing process [18] can be physically noticed when something infinitezimally small describing the system, starts to change, so let us assume that $s \to 0$ (or, $N_{\rm grid} \to \infty$). Obviously, the total numbers of points, i and p, have to be large enough, too, and we have to mention formally that the discrete time-dynamics is to be replaced by a continuous one, *i.e.*, as usually, with $\Delta t \to 0$, where Δt is of deterministic nature, for simplicity. Under such assumptions $i \equiv i(t)$ and $p \equiv p(t)$, $t \geq t_0 \geq 0$ (t_0 is the initial instant), and Eq. (5) can be rewritten as

$$\frac{di}{dt} = \left(a_1 D_1 p^{D_1 - 1} - \tfrac{1}{2}\right) \frac{dp}{dt} \,, \tag{7}$$

where di/dt and dp/dt are the first order time derivatives of i and p, respectively.

Now, we wish to introduce the growing rule by reminding the following natural observation, namely

$$\frac{di}{dt} = f(t; p_T) \geq 0 \,, \tag{8}$$

where f is a non negative and continuous function of t as well as of some thermodynamic parameter p_T (in general, we have to speak about a set of the thermodynamic parameters); if $f = 0$ no growth is observed (stagnation or "freezing" are realized), but if $f > 0$ the growing process is assumed to take place. There is still another requirement that we wish to assign to f; we call it: a self-similarity condition. This means that we expect to have f as a power function of time (either an inverse or a direct power function). Such a requirement is usually expected, mostly for some complex systems, like polymers, model biomaterials, alloys, *etc.* [1, 4, 7–9, 19]. By the way, it would be noticed further that this also enforces to have the behavior of the radius of giration of the cluster as a power law of time [7, 8] so that it also causes to get the problem well-posed from the mathematical point of view [20].

Now, we may explicitly write Eqs (7) and (8) as a nonautonomous dynamical system consisting of two ordinary differential equations, which are coupled by function f, namely

$$\frac{di}{dt} = f(t; p_T) \,; \qquad \frac{dp}{dt} = f(t; p_T) \left(a_1 D_1 p^{D_1 - 1} - \tfrac{1}{2}\right)^{-1} . \tag{9}$$

We see quite natural to rewrite system (9) in terms of the cluster densities. This means that one has to use the number area density ρ_i for i-s as well as the number perimeter density ρ_p for p-s. They can be defined by the integral formulae

$$i = \int_0^A dA'\rho_i \quad \text{and} \quad p = \int_0^l dl'\rho_p \, ,$$

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; notice that in the discrete description corresponding sums can be used instead of the integrals.

In this study, we wish to concentrate on the evolution of homogeneous clusters, *i.e.*

$$\rho_i(t,x) \equiv \rho_i = \text{const.}\, ; \qquad \rho_p(t,x) \equiv \rho_p = \text{const.} \tag{10}$$

which leads to a substitution of (9) by

$$\rho_i \frac{dA}{dt} = f(t;p_T)\, ; \qquad \rho_p \frac{dl}{dt} = f(t;p_T)\left(a_1 D_1 (\rho_p l)^{D_1 - 1} - \tfrac{1}{2}\right)^{-1} . \tag{11}$$

To have some relation to known systems describing the evolution of growing objects (*e.g.*, those controlled by diffusion [11, 18]), we have to present system (11) in terms of a perturbed quasi-circle of radius R_g, where the circumference of the ideal circle is perturbed by a factor $\delta F(\phi, p_g)$, requiring however, that $\mid \delta \mid \ll 1$, and F is an everywhere continuous, bounded and (usually) oscillating function of ϕ (like, cosine or sine or a combination of them — see [11,18] and Fig. 1(b); here p_g is a geometrical parameter of minor importance in our further considerations so that we take $F(\phi, p_g) \equiv F(\phi)$, for simplicity). We wish to state very much here that F does not have to be differentiable in ϕ. On the contrary, it may be a nowhere differentiable function of ϕ; *cf.* Fig. 1(a) for getting an example (some other examples can be listed, like the Weierstrass function or the Levy flight as well as a 'devil's staircase' as specific cases [10]). This assumption ensures to have the evolution rules for a surface fractal (like, *e.g.*, the Eden fractal [1]).

Rewriting (11) in terms of a perturbed quasi-circle, one gets

$$\frac{dR_g}{dt} = G(2\rho_i a_2 R_g)^{-1}\, ; \qquad \frac{dl}{dt} = 2G{\rho_p}^{-1}\left(2a_1 D_1 (\rho_p l)^{D_1 - 1} - 1\right)^{-1} , \tag{12}$$

where for brevity $G \equiv G(t) = f(t, p_T) > 0$ (note that in this term the driving force of the growing process is also included, *e.g.*, the supersaturation, undercooling, capillary force, lowering of the interfacial free energy, pressure difference, *etc.* [1, 3, 18, 21], and it is always a function of thermodynamic conditions represented by p_T). Moreover, the following relations have been assumed to hold [8]:

$$A = a_2 {R_g}^2 \, ; \quad a_2 > 0 \, , \tag{13}$$

which is a well-known scaling law [4] (for the mass fractals a departure from the rule can be expected, *i.e.* $A \sim {R_g}^{D_2}, D_2 \in (1,2)$) [1], and a clear geometrical relationship of the form [11, 18]

$$l = 2\pi(R_g \pm F(\phi)\delta) \, , \qquad | \, \delta \, | \ll 1 \, . \tag{14}$$

Notice that we have got fully nonlinear system (12) with (14), which still describes our process being curvature-driven (see, *e.g.* [9, 11, 18, 21]), no matter whether the driving force is specified or not (*cf.* Eq. (8), obviously). By the way, we also believe that a_1 and a_2 (*cf.*, Eqs (1) and (13)) survive as being independent of time, within the frame of our approximation.

The full system (12) with condition (14) is, unfortunately, not so much useful for practical reasons. We may also extend it by adding some new perturbation terms with δ^2 or higher in Eq. (14), but it increases the complexity. Nevertheless, a numerical analysis can be done in this case. To have, however, the approach simpler and, in some sense, more robust, and also to preserve its self-consistency, a linearization of it has to be done, like in the original quasi-static MS-approach [11,18]. It can easily be done for a mature growth stage (here, R_g has to be much greater than a critical radius [11]), and by noticing that

$$\left| \frac{F(\phi)\delta}{R_g} \right| \ll 1 \, , \tag{15}$$

which is very well fulfilled under such physical circumstances. Now, the simplified system ((12) with (14)) looks like

$$\frac{dR_g}{dt} = G(2\rho_i a_2 R_g)^{-1} \, ; \quad \frac{d\delta}{dt} = -G(D_1 - 1)\delta \left(a_1 D_1 (2\pi\rho_p)^{D_1} {R_g}^2 \right)^{-1} , \tag{16}$$

(note formally that $R_g \equiv R_g(t)$ and $\delta \equiv \delta(t)$) where the proportionality factors a_1 and a_2 must depend on one another, namely

$$\frac{a_1}{a_2} = \frac{2\rho_i}{D_1(2\pi\rho_p)^{D_1}} \, . \tag{17}$$

It is so indeed, because the scaling laws (1) and (13) (via Eq. (3)) are usually related to one another (see [8]).

In this way, the so-called Mullins–Sekerka (MS) Laplacian (stationary) field driven system [3,11,18] 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 (otherwise, see below again). If we recall the growing rule (Eq. (8)) in a self-similar form, we have to expect to write explicitly

$$G = G_0 t^{\pm\nu}\,; \quad G_0 > 0, \nu \in [0,1)\,, \tag{18}$$

(G may be called: a kinetic-thermodynamic growth term, in which the prefactor G_0 represents the driving force [9,18], where a certain dependence upon pH-conditions of the process should also be noticed, mostly for reactive as well as fluctuating and aggregating biosystems [11, 17, 18], but some kinetic peculiarities of the process are collected in the power law form as well as by knowing the value of ν; G_0 and ν must be known *a priori* or provided by the experiment [1, 3]) so that as an asymptotic solution to the first of the equations of system (16), we obtain

$$R_g(t) \sim t^{(1\pm\nu)/2}\,, \tag{19}$$

for the "long" times limit, certainly. For the mass fractals [17] one might probably state $R_g(t) \sim t^{(1\pm\nu)/D_2}$ (see above). Note that result (19) does not depend essentially upon D_1 (though, the prefactor formally does). Note also that dynamical system (16) does not depend upon $F(\phi)$ (recall Fig. 1), and that for $\nu = 0$ one provides $R_g \sim \sqrt{t}$, which is the classical diffusional power law, inevitably related to MS-approach [11,18]. Let us realize that, in this case, the diffusion constant used in MS-approach could be determined by $1/a_1(2\pi\rho_p)^{D_1}$, or because of (17), one can provide it by $D_1/2a_2\rho_i$ [11]. Varying the scaling exponent ν in (18) we may get many power law behaviors, especially for a very slow growth (like $R_g(t) \sim t^{1/4}$ or slower) [7, 9, 21]. Assuming the inverse power law in (18), with $\nu = 1/3$, we can recover (see (19)) the scaling formula obtained from some extensive MC-simulations of the SARW-process (growth of small rings) [8], namely

$$R_g(t) \sim t^{1/3}\,, \tag{20}$$

which is also a well-known asymptotic result for a droplet condensation or coalescence, $2d$ grain growth or for the Ostwald ripening of two-dimensional crystals at the solid–liquid interface in binary mixtures, even (with many potential practical applications to be thought of) [22]. Some 'coincidence' of growth exponent ν and the scaling exponent (equal to 1/3) involved in (20) is worth noticing here.

Another interesting result can be revealed when looking at the second of equations constituting system (16). Namely, it is a stretched exponential or Kohlrausch–Williams–Watts [10] behavior of the small perturbation amplitude δ. Since R_g and δ practically grow (or shrink) as proceeding in different time scales, for a given R_g-value (furnished or kept constant, which is also a 'physical truth' seen from the standpoint of very small perturbation amplitude δ, especially, when compared to huge R_g-value), one has to get

$$\delta(t) \propto \exp(-\text{const.} \times t^{1\pm\nu}) , \tag{21}$$

(in the "long" times limit, again) where the constant gathers all the factors, like, *e.g.* $(D_1 - 1)/D_1$, *i.e.* some competition exponent [1,5,2], or densities ρ-s (see system (16), again), and can even be interpreted in terms of the Vogel–Fulcher relaxation times, τ_{vf}, very characteristic of slow relaxation phenomena [22, 23], and to be determined by the nucleation radius, the radius of giration at a saturation limit, R_{gs}, where $R_{\text{gs}} \sim \sqrt{\tau_{vf}}$. If $D_1 \to 1$ (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, $D_1 \to 2$ (regular shape), the perturbation effect is much pronounced, and Eq. (21) describes the process in a nontrivial way. Notice, by the way, that for $\nu = 0$ the classical M-S result (Debyean or simple exponential relaxation) is recovered. (A promising generalization here would be if one will replace the ordinary first order time derivative in the second of equations of system (16) by a fractional time derivative, just to make the time scale more sensitive to changes of δ in a complex physical environment, like ferroelectric, ferromagnetic or unstable homoepitaxial thin films (deposits) or semiconductor $2d$ composites, and to get additionally a nonexponential relaxation of it; this is immediately to obtain using the results of [23]; *cf.* [22] for having a few examples.)

4. Conclusion and perspective

In this work, some preliminaries of the discrete geometrical-kinetic description of a growing process realized on a square lattice have been proposed. The key idea was to apply both the scaling argumentation as well as a planimetric (Steinhaus) rule within some level of uncertainty (Eq. (3)), and to postulate a quasi-static character of the process. The result was that a nonlinear relationship (Eq. (4)) has been found, and by imposing a (discrete) time-dynamics on the system, one may arrive at an evolution equation (difference scheme; *cf.* Eq. (6)) that includes inherently a curvature change term very characteristic of the growing phenomena, like crystallization (also, single crystalline domains in lipid monolayers [24]), solidification (faced $2d$ quasi-crystals [2]), microdomain-growth [2, 18, 21], formation of biomembranes (interfaces) [9] as well as of wetting [9, 13, 15]. It is worth stating here that the description offered is based on incorporating the self-avoiding random walk (SARW) concept, which has proved to be useful in this subject [8,19]. By the way, notice that a SARW-trajectory differs from a

Brownian path since each of its points can only be visited once by a travelling walker which is not the case of the latter [6,8].

Starting with the discrete description mentioned above (see, Section 2), we are able to perform some useful continuity procedure (Section 3), just for embarking on a certain more firm (known) landscape very much assigned to the above mentioned growing phenomena, and for arriving eventually at the effectively modified Mullins–Sekerka (MS) kinetic approach, which enables to recover many kinetic characteristics, mostly with the so-called small (fractional) dimensionalities as well as being of non-Debyean nature (*cf.*, Eqs (19) and (21); see also [2,3,21]). At this moment, we wish to state explicitly that the modification of original MS-description is due to:

(i) incorporation (use) of the nowhere differentiable functions as the boundaries of $2d$ clusters (*cf.* Fig. 1; note that a SARW-trajectory is just such a function!);

(ii) extension by including the kinetic-thermodynamical nature of the growing mechanism (rule (8) and G-term (18) in system (16)).

Also, in the continuous limit, the process remains to be curvature-driven (*cf.* system (16), and [11,18] for comparison; notice that a surface or line tension characterizes the boundary of the system, but only when assumed that the surface is sufficiently smooth) so that our continuity procedure proposed in Section 3 makes sense.

Looking at the discrete description, one might notice that some type of the physically interesting (say!) *Gedankenexperiment* have been proposed. Namely, we have straightforwardly got $i(p)$-dependence and an *a priori* discrete evolution scheme (Eq. (5)), but we did not know, which is the aggregation (growing) process that we deal with (it could be any growing process with $D_1 = 3/2$ and following scaling law (1), where the resulting clusters are not so much dispersed so that Steinhaus rule (2) may be applied; conclusion: some application of our approach to diffusion-limited or reaction-limited cluster cluster aggregation is forbidden, but to diffusion-limited aggregation is probably not, in particular, when the surface tension effect can easily be noticed [1,2]; in the latter the extension with $D_2 \approx 1.7$ or smaller included, but with $\nu = 0$, should work [24]; *cf.* discussion beneath Eq. (19).

There can be many extensions or generalizations of the approach proposed, and a few of them have been mentioned in Sections 2 and 3. Let us now mention another one, which may concern the stochastics [25] of the process. Neglecting the fact that growth term G is generally time-dependent (by enforcing $\nu = 0$, for instance), we can try to follow some natural observation (at least, for some highly fluctuating systems, like the high-temperature viscous systems, *e.g.*, polymers or some "soft-matter" systems) that G can split up into two terms: one of some deterministic nature (a "reference" growth term), say G_d, and the second of stochastic character, G_s; in this case: $G = G_d + G_s$; and $G_s \equiv G_s(t)$ stands for a noise, *e.g.* the Gausssian noise [25], for simplicity. Such kind of analyses one can find, *e.g.* in [26], and it is to be applied to the first of equations of (16) (that for R_g). Also, some other future direction of thinking can be explored when looking for common points with other concepts. Namely, because of utilizing the power law of form (18) (or having the system in a self-similar regime), and because the size of the SARW-trajectory increases powerly with the number of constitutive units (*e.g.*, points) a certain suspection of having the system as being able to be self-organized could be checked [5, 22].

To illustrate the model in a preliminary experimental way, let us recall a simple experiment done as some continuation of work [27]. This is as follows:

(i) experimental set-up:
  a) protein droplet immersed in (or placed slightly above a well of) a 1 ml precipitant solution spread on siliconized glass;
  b) crystallization is observed using *Leica* microscope of 40× (magnification factor) with observation error about $4 \div 10$ percent;
  c) temperature is maintained at 18° C.

(ii) physicochemistry of the crystallization process:
  a) the protein from which the crystallites are made of is called molecular chaperone, and belongs to heat shock proteins; it is bacterial protein expressed in *E coli*, and it is a promoting force for cellular reactions it gets from binding to ATP;
  b) the driving force is a static pressure difference between the droplet and the solution (a rheological fluid);
  c) the resulting crystallites are $2d$ hexagonal platelets of ca. $0.08 \div 0.34$ mm in size;
  d) the crystallization process is very sensitive to temperature and movement of a tray on which the experimental set-up (sealed) is placed; if one moves the tray with the crystals they start to grow twinned, from the surface starts to grow a perpendicular one or a paralell one to the old one;
  e) they are also light sensitive so that under a longer light exposure they start to "sweat", and small bubbles appear all over the surface (conclusion: one must be very careful experimenting with them; see also the preceding point);
  f) the thermodynamical equilibrium can be achieved by vapour diffusion.

(iii) kinetics:
very preliminary measurements (from a few to almost 73 hours) over some small sets of data show that the kinetics are well fitted by Eq. (18), with $\nu \approx 1/3$ or greater than $1/3$, but less than 1, though the best fitted set of data leads to the kinetics, like $R_g \sim t^{0.311}$ (very close to $1/3$) so that Eq. (19) can practically be used; this way, the dispersive kinetics given by Eq. (18), where $G \sim t^{-\nu}$, with $\nu \geq 1/3$ is manifested. Notice again a possible sensitivity of the process (with small fractional dimensionalities [10, 21, 22]) to light as well temperature, which is very characteristic of that kind of kinetics (also, as was said above, another characteristic feature is that the probability distribution of times is of a power form [10]); *cf.* [10, 23, 28].

Sometimes, there is a need to extend the approach proposed into third dimension (see [11]) so that one wants to know Steinhaus formula (2) as effectively working in $3d$ space. Such an extension is possible to be thought of, especially when some effective geometrical constructions concerning polygonal figures and their form spaces, described *e.g.* in [29], will be of use. One may easily notice here that the formula should work smartly at least when the area of the object spanned on $3d$ lattice will be, as seen from Eq. (2), a linear function of both i and p. Otherwise, one can expect some difficulties in reaching the MS-limit in such a natural way.

Finally, let us pose a question: how big (deep) is the range of action of very simple dynamical systems, like MS-system and alike (*e.g.*, Taylor–Saffman fingered growth [18]), and how do they emerge from first principles of the matter reorganization?

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