On the harmonic–mean property of model dispersive systems emerging under mononuclear, mixed and polynuclear path conditions

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Abstract. The goal of our study is to make use of the (fractally-defined) harmonic-mean criterion (HMC) as an indicator of proper/improper matter nucleation–transportation and matter-(non)densification tasks realized over certain thermodynamic-kinetic pathways in d–dimensional environments. We investigate three dynamic processes: self-avoiding random walk (SAW), cluster-cluster aggregation (CCA) and diffusion-limited aggregation (DLA). They are all considered as dispersive systems characteristic of excluded-volume effect (EVE). From our mean-field investigation it turns out that the HMC shows that SAW and CCA belong to the same kinetic (or, dispersive chemical kinetics) class, whereas DLA does not since it is realized over a mixed (non-homogeneous) thermodynamic-kinetic pathway. Our findings clearly reveal that the dimension two appears to be kinetically optimal for SAW and CCA but cast again some serious doubts on whether the so-called DLA $2D$ "paradigm" is here a well-posed problem.

1 Introduction

In this work, we are going to show that certain model dispersive systems, manifesting aggregation-desaggregation effects, underlie the same mean characteristics, whereas some other do not.

The mean characteristics we have in mind are generally related with the two-point harmonic-mean (HM), $\nu_k^{(d=2)}$, defined as

$$\frac{1}{\nu_k^{(d=2)}} = \frac{1}{2}\left(\frac{1}{\nu_k^{(d=1)}} + \frac{1}{\nu_k^{(d=3)}}\right), \tag{1}$$

where $\nu_k^{(d=2)}$, appears to play the role of the HM and is at the same time calculated as an average (logarithmically defined) speed [1] of a k-process embedded in $d = 2$. It is related by eq. (1) with its corresponding values $\nu_k^{(d=1)}$ and $\nu_k^{(d=3)}$, also calculated as the average speeds of the same type but taken in neighboring Euclidean sub- and super-spaces $d = 1$ and $d = 3$, respectively.

For a method of calculation of the average speeds, $\nu_k^{(d=j)}$, $j = 1, 2, 3$, see [1,2]. For a definition of the HM, applied to model nanoparticle formation, see [3]. A k-process realized in the d-dimensional space, here $d = 1, 2, 3$, is said to obey the harmonic-mean criterion (HMC) iff its average speeds, inserted into eq. (1), yield the average speed in $d = 2$ exactly as HM of the two other remaining

speeds, taken for $d = 1$ and $d = 3$, respectively. It ultimately means that such a (harmonic) mean quantity at $d = 2$ becomes exactly an average, evaluated by a statistical-mechanical method as the ensemble-average in the same geometric space, cf. [1–3]. By offering such a definition we automatically infer that the mean harmonicity fulfilled in the domain of the speed of the process implies a sufficient kinetic optimality of it, i.e. that the process in question goes smoothly in the Euclidean space in which it is embedded, here in $d = 2$.

Such a convergence/non-convergence of two types of the statistical measures mentioned above would implicitly resemble a type of dimension-influenced ergodic hypothesis. Its fulfillment/non-fulfillment in $d = 2$, herein specifically formulated for the model dispersive systems under consideration, demands that the HM of purely algebraic nature can/cannot equal the (fractally-defined) average. The average is taken over a certain coupled configurational-temporal space of each embedding k-process. See, especially eq. (7) and eq. (8) of sec. 2.3, and additionally [1,2] for some argumentation.

The k-processes that we analyzed throughout the present paper are [4]:

- a (topologically) linear system/polymer, i.e. the self-avoiding walk (SAW);
- a branched system/polymer, i.e. the diffusion-limited aggregation (DLA);
- a network-like/polymeric system, i.e. the cluster-cluster aggregation (CCA).

The SAW is defined as a chain of monomers that undergo an attraction-repulsion Lennard-Jones type interaction scheme measured along the chain (see, Fig. 1) [5].

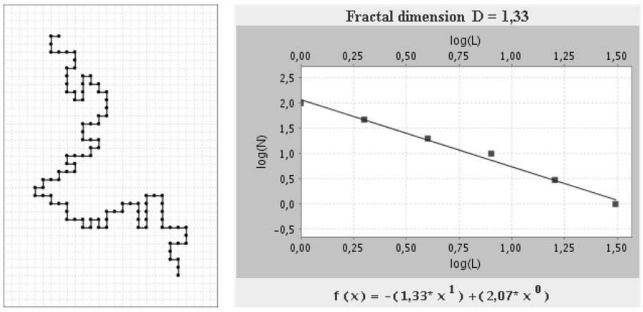

Fig. 1. Some arbitrary small-scale square-lattice realization of SAW for n=100 steps (left), and its fractal dimension depicted at the top of a log-log plot (right) [6]

The DLA is defined by a trial random walker that randomly samples an available space until it meets some accretion center at which it remains ultimately captured (see, Fig. 2) [7].

The CCA is defined by pairwise cluster-cluster interactions via the cluster's surface, where the inter-cluster space is usually recovered upon an adequate raise of the temperature as a cooperation compaction-relaxing effect between late stage growing and mechanical relaxation modes (Fig. 3) [1].

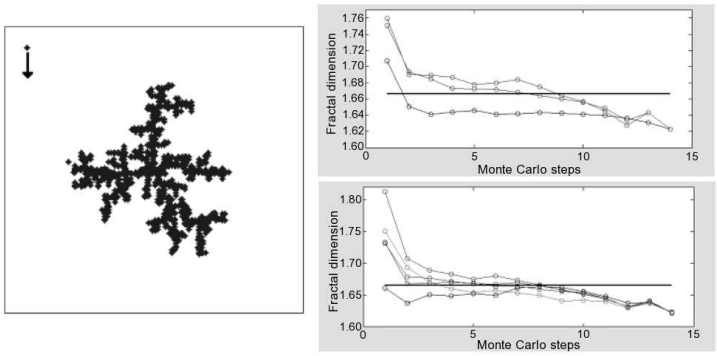

Fig. 2. Small-scale computer realization of $2D$ DLA model for the number of random walkers $N_{RW} = 9$ for thousand particles incorporated by the cluster (left) and its type of lattice, and type of accretion-seed dependent (from top to bottom) fractal characteristics. The characteristics quite fairly accommodate to the basic horizontal line which is the Meakin's estimate of DLA fractal dimension $D_{\mathrm{DLA}} \approx \frac{5}{3}$ (right) [8]

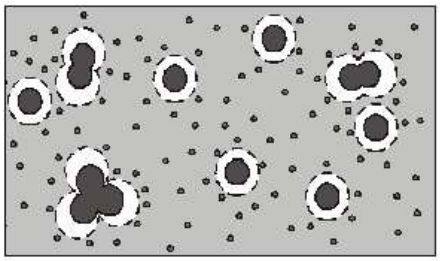

Fig. 3. Schematics of some assemblies of molecular clusters: Cluster-Cluster Aggregation (CCA) occurs. The light realms around each cluster can be considered as depletion zones, characteristic of colloid and protein aggregations, see [1,2] and refs. therein. The small dark dots are monomers

A common physics-involving feature of all above listed systems can be termed excluded-volume effect (EVE): None of them can self-overlap, and some remaining interspace is always left during its evolution in the available isotropic space. In turn, a common theoretical framework of all of them is that their dynamics undergo a Smoluchowski-type dynamics [5] while their scaling properties are quite satisfactorily described by the mean-field approach, for example, the SAW enjoys the Flory-Fisher (F-F) mean-field approach [9], with a well known d–dimensional scaling formula

$$\overline{\lambda_k}(t) \propto t^{\nu_k^{(d)}}, \tag{2}$$

where $\overline{\lambda_k}$ is an ensemble-averaged linear characteristic [9,5,2], t the time (or quite equivalently: the degree of polymerization) and $\nu_k^{(d)}$ a scaling exponent, here $\nu_{\mathrm{SAW}}^{(d)} = 3/(d+2)$. In short, the F-F approach begins with a certain Gibbs-

Boltzmann type construction of the statistical sum, Z, of the radially distributed segments (monomers) of a polymeric chain immersed in a solution. The segments are considered as a continuous cloud of homogeneous density, so that each segment "feels" the same density around it. The potential interaction of segments is a pairwise (repulsive) interaction - it enters then the statistical sum, which is included in the free energy of the chain, $F = -\beta^{-1}\ln Z$ (for β, see eq. (3) below). After minimalizing F over the chain length one notices that a scaling relation of the type of eq. (2) solves the problem with the scaling exponent $\nu^{(d)}_{\mathrm{SAW}}$ stated as above, cf. [9] (chapter 3).

Some important motivation to the present study states that the HMC is practically used in colloid (e.g., aerosol) science, here a silicon nanoparticle formation [3]. The silicon nanoparticle formation is a type of coagulation process, which is also a complicated nucleation-transportation problem. Growth of the coagulate is modeled by means of a difference scheme, which is by aerosol scientists called a standard "two-point" method. According to this method, the growth rate of the number of particles in a bin is a result of flowing in some particles from a neighboring bin as well as of flowing out a certain number of particles from the bin of interest. A kind of simple discrete master equation can be written down. It includes a quantity which is named the effective particle transfer rate between the bins. This rate, exactly as in our HMC is designed as a two-point HM, being composed of two other growth rates (precisely, as in our case), one of them coming from the free molecular motion of an aerosol particle, and the other from dealing with the aerosol as a continuum [3]. This way, an analogy between using the HM-s in our and aerosol system is completed, especially when we would compare it with CCA, which is - similarly to aerosol particle formation - a surface-involving process, see Appendix A.2 in [3] and eqs. (10) and (11) therein.

The paper is organized as follows. In Section 2, we give an overview of the common theoretical framework, finally emphasizing the fulfillment of HMC for CCA. In Section 3, we present SAW and CCA as dynamic processes that, even though being realized over two different pathways, will be shown to obey the HMC. In Section 4, we demonstrate that all known mean-field estimates of DLA speed do not obey the HMC, and attribute this shortage to the fact that DLA is realized over a mixed (non-homogeneous) kinetic pathway, or shows up a nonlinear EVE. Moreover, we draw some special attention to the fact that the proposed HMC should not be confused with the well-known harmonic-measure criterion for DLA which gives a well-established multifractal spectrum for the growth probability, properly yielding the single fractal dimension of a DLA cluster at the highest growing mode. (As a promising fact one would report here is that the numerical estimate of $\nu^{(d)}_{\mathrm{DLA}} = 6/5d$ by Meakin [10,11] obeys the HMC, which essentially means that the numerically obtained $\nu^{(d)}_{\mathrm{DLA}}$ exactly conforms to the eq. (1), cf. eq. (8) in subsection 2.3.) The last section (Section 5) includes the main results of the paper and their discussion.

2 Common theoretical framework

In this study, we deal with three essentially different nucleation–transportation and matter-compaction involving problems. In spite of their clearly different dynamical behaviors there is at least one common effect which can be assigned to all of them: The EVE, well described by the F-F as well as by Fokker-Planck and Smoluchowski (F-P&S) dynamic frameworks [5,9]. In case of SAW it is due to the repulsive part of the interactions between monomers from which the chain is made of. As concerns CCA, it can be revealed by calculating the total volume of the system for both low and high temperature matter aggregations, and then by seeing that there is a matter expansion exclusively in the case of the high temperature CCA [1]. While looking at DLA, in turn, one can immediately see that EVE is generically present in the process because the branches of the DLA microstructure do not overlap each other - they rather behave as separated SAW-s, nucleated at one nucleation seed, which always appears to be a cluster-surface (interface) process in a d-dimensional space [12].

2.1 Fokker-Planck and Smoluchowski type dynamics

For revealing the presence of the EVE as a dynamic phenomenon a standard way assumes the F-P&S type equation to be fulfilled. For most of dispersive systems it is usually based on the form of the matter current (see also Appendix for details)

$$J(x,t) = -D(x)\left(\frac{\partial f}{\partial x} + \beta \frac{dU(x)}{dx} f\right), \tag{3}$$

where $\beta = 1/k_B T$, k_B is the Boltzmann's constant (in case of dispersive soft-matter systems $dU(x) \cdot \beta \sim 1$ typically holds), T is the temperature, t - time, D - diffusion coefficient (it usually depends also upon the parameter d - the space dimension; in general: $D \equiv D(x,t;d)$ [1,5]), $U \equiv U(x)$ - potential, $f \equiv f(x,t)$ - concentration of the constituting entities characteristic of SAW, CCA and DLA, respectively. Here, the entities constituting SAW are monomers whereas for CCA one has molecular, e.g. protein clusters and for DLA there can be atoms, molecules or macromolecules sometimes [4]. As concerns the variable x, it is to be specified according to each of the three analyzed processes separately.

For SAW the "drifted" diffusion is realized along a spacial-coordinate axis, so that x stands for the current position of the monomer, for example, that of either hydrophilic or hydrophobic type [13,5,6].

For CCA model, actually based on [1], the diffusion is always realized along an axis of cluster sizes, thus, x is here typically the volume of a single cluster.

For DLA there are not so many conclusive analytic studies pointing to the F-P&S dynamics. One of the exceptions found in literature would be that of Fokker-Planck dynamics for the needles emerging during a model (1+1)-DLA. In this approach, each needle undergoes a one-dimensional random walk, starting from a horizontal line, and obeying the standard DLA rules, resulting in favoring taller needles at the cost of their non-tall neighbors. As a consequence of the

model formulated in such way a most relevant stochastic variable, x, is defined by means of an excess length of the two neighboring teeth of $(1 + 1)$–DLA microstructure [12].

In view of the above, the three processes under consideration might have another interesting dynamic feature in common: They are two-state Kramers-type processes with a weak surmountable barrier given by $U(x)$ accounting for EVE. It means that they are mesoscopic systems underlying basic rules of non-equilibrium thermodynamics [14].

2.2 Mean field approach

In order to explain the mean-field (MF) approach let us rest again on the well known F-F procedure [9]. First, the F-F as each MF approach neglects the fluctuations of the monomer concentration of a SAW. Second, it takes into account two main contributions to a SAW free energy: an entropic, due to elasticity-influenced conformational changes of the chain, as well as the enthalpic coming from repulsion between non-neighboring monomers, which inevitably leads to EVE. Third, the interactions "seen" by such a procedure are always binary interactions - it results in f^2 (Van der Waals) contribution in the free energy [5], cf. Appendix. The three above stated assumptions, after minimizing the free energy of the SAW with respect to its size, and after letting a similarity relation to be a solution of the resulting equation, lead to a straightforward derivation of the SAW exponent [9,5]

$$\nu_{\mathrm{SAW}}^{(d)} = \frac{3}{d+2}, \tag{4}$$

where d is a dimension of the Euclidean space. *Mutatis mutandis*, we can provide the CCA as well as the DLA exponents. For CCA we get [1]

$$\nu_{\mathrm{CCA}}^{(d)} = \frac{1}{d+1}, \tag{5}$$

whereas for DLA one typically[1] obtains [17]

$$\nu_{\mathrm{DLA}}^{(d)} = \frac{d+1}{d^2+1}. \tag{6}$$

2.3 HMC of the fractally-defined speed in dimension d

To compare somehow the speeds of the three processes analyzed, assumed that their descriptions are all based on the same MF Van-der-Waals (dispersive-force)

[1] There exists at least one more estimate for $\nu_{\mathrm{DLA}}^{(d)} = \frac{6+5d}{8+5d^2}$ obtained in [15] which, in turn, uses some other refined MF approach. Note that $\left[\nu_{\mathrm{DLA}}^{(d)}\right]^{-1}$ is nonlinear in d, which is the case of eq. (6) too, cf. [16], in which the number of branches of a DLA microstructure increases with d arriving, however, at a saturation effect in $d = 2$ but not for $d > 2$

type approximation, see the preceding subsection and the Appendix, let us define the speed of the process in a fractal-like manner

$$\nu_k^{(d)} = \frac{\ln\overline{\lambda_k}(t)}{\ln t}; \qquad \frac{t}{t_0^{(k)}} >> 1, \tag{7}$$

where k indicates SAW, CCA and DLA respectively, $\overline{\lambda_k}$ stands for a characteristic length of each of k-processes, $t_0^{(k)} > 0$ - the initial instant of each of k-processes, t - as above. Note that the late time condition $\frac{t}{t_0^{(k)}} >> 1$ holds.

Notice that all $\overline{\lambda_k}$–s are fully derivable from the F-P&S dynamic characteristics of each system of interest [5,1,18]. Moreover, note that formally the F-P&S dynamics define a stochastic process which is a nonequilibrium (drifted) process - its stochasticity implies that t is an "active" (kinetic) variable. The F-F type MF approach, in turn, being based on the minimization of the free energy, implies that some N (e.g., the polymerization degree of the SAW) becomes a crucial but thermodynamic variable. By postulating such a definition of the speed (cf., eq. (7)) we somehow claim that N be equivalent to (or, at least, proportional to) t which should be true in a late stage of the aggregation-compaction process when the system presumably arrives at one of its quasi-equilibrium states.

While analyzing CCA [1] we have found that the so defined speed of CCA obeys a two-point HMC, namely

$$\frac{2}{\nu_{\mathrm{CCA}}^{(2)}} = \frac{1}{\nu_{\mathrm{CCA}}^{(1)}} + \frac{1}{\nu_{\mathrm{CCA}}^{(3)}}. \tag{8}$$

From eq. (8) it is seen that the HMC unquestionably points to a special relevance of the Euclidean dimension d, here with emphasizing the role played by $d = 2$ for kinetically optimal path of any process obeying eq. (8). In the next section of the paper we are wondering whether and why it is true (or not) for SAW and DLA, which is equivalent to examining the necessary and sufficient conditions of existence of (8). (For convincing the reader that the CCA lies in the same class of pairwise-interaction driven processes, such as that of SAW and DLA, we encourage her/him to consult the Appendix.)

We find the HMC important. Firstly, because the HM inherently involves a logistic competition (Malthus-type) effect between (squared) geometric, G, matter-aggregation resources and its arithmetic, A, linear counterpart. For accepting it simply realize that based upon eq. (8) one may rewrite it as follows: $\nu_{\mathrm{CCA}}^{(2)} = [\nu_{\mathrm{CCA}}^{G}]^2/\nu_{\mathrm{CCA}}^{A}$, where ν_{CCA}^{G} and ν_{CCA}^{A} denote, respectively, the geometric and arithmetic means composed of $\nu_{\mathrm{CCA}}^{(1)}$ and $\nu_{\mathrm{CCA}}^{(3)}$. Such a presence of nonlinear (geometric) matter-aggregation resources and of their linear (arithmetic) counterparts involved in $\nu_{\mathrm{CCA}}^{(2)}$ as a ratio of them both, is reminiscent of some competition effect of mean matter-aggregation speeds, ν_{CCA}^{G} and ν_{CCA}^{A}, reflected as chemical reaction rates of second and first order (possibly of the broken order in between, Section 5, eq. (11)), respectively. Secondly, it indicates the dimension two ($d = 2$) as a relevant dimension - this is why throughout the whole paper

we have allowed ourselves to illustrate our work by some small-scale $2D$ numerical simulations [8,6] - in which some processes may go kinetically optimally but other ones, as we will see apparently of DLA-type, may not be optimal.

3 SAW & CCA as processes realized over mono- and polynuclear paths

The SAW, see Fig. 1, is clearly realized over a single kinetic pathway which we call a mononuclear path. It is because the SAW object formed may serve as a singular nucleation seed *per se*. Moreover, two or more SAW-s may form a molecular cluster, for example a dimer ($N_{SAW} = 2$). Such a formation procedure, resting upon a creation of $N_{SAW} = 2$ and $N_{SAW} > 2$ clusters, we wish to call a polynuclear path - clearly, the high-temperature polynuclear path in which any matter-compaction effect is typically relaxed [1,6].

As is mentioned in subsection 2.3 the CCA obeys the HMC. It is easy to check by inserting (4) into (8), that also SAW with its characteristic exponent, which is now according to the definition given by eq. (7) the speed of SAW process, obeys the HMC too, just in the way shown by eq. (8). We attribute this fact to the observation that both SAW and CCA go over kinetic pathways of non-mixed low-energy-barrier states: the SAW goes by addition of monomers only, and CCA goes purely by some linkage of clusters (see, Fig. 3). The addition as well as the linkage can typically be either first-order or second-order chemical reactions, see discussion in the preceding section. Therefore their speeds, assumed that each process is realized in a homogeneous (structure-less) d–dimensional space, fulfill the same (HMC) criterion.

4 DLA as a process realized over some mixed path

The HMC is hardly fulfilled in case of DLA described in terms of MF. One can easily prove by inserting (6) into (8) that here the HMC fails. It is even the case of the refined estimate of ν_{DLA} (see, footnote 1). Such a behavior may be attributed to the fact that DLA can be thought of as a dynamic process in which quite many SAW-s are nucleated on a single nucleation center (see, Figs. 1 and 2). This can be anticipated as a certain intermediate stage since this way one can only create a branched molecular cluster but neither a (topologically) linear chain nor some network-like assemblage of clusters. This difference strongly suggests that DLA is realized over an intermediate, or better said, over some mixed kinetic pathway, because we can observe therein some common signatures of both SAW and CCA. Also, the EVE must be of different type than the corresponding EVE - s characteristic of SAW and CCA. Thus, this entices us to state that the F-F type MF approach which one applied to get $\nu^{(d)}_{\mathrm{DLA}}$ is insufficient and probably must be completed by taking into account fluctuations, i.e. going visibly beyond the MF approach.

Some confirmation arises from large-scale computer simulations by Meakin and coworkers [10]. They estimated [11]

$$\nu_{\mathrm{DLA}}^{(d)} = \frac{6}{5d}, \tag{9}$$

which surprisingly obeys the HMC stated by eq. (8). Note that $[\nu_{\mathrm{DLA}}^{(d)}]^{-1}$ is a linear function of d, so is also the case of eq. (4) and eq. (5) but it is certainly not true for the reciprocal of $\nu_{\mathrm{DLA}}^{(d)}$ taken from eq. (6).

At this place, let us clearly state that the HMC proposed in the present study should not be confused with a harmonic-measure criterion so often mentioned for DLA, especially realized in $d = 2$ [18]. This criterion refers to a theoretical description of $2D$ DLA in terms of the theory of analytic functions. It extracts the growth probability distribution in such a way that inclusion of a Brownian particle at a tip of the branch of the DLA cluster is much more probable than having it landed on any fjord between two neighboring branches. Thus, it has no obvious relation to the d-dimensional HMC that we propose to use for showing here a kinetic non-optimality of $2D$ DLA, whereas the harmonic-measure criterion mostly points to the self-similarity of a DLA cluster [18,4], which we take for granted (Fig. 2).

5 Results and discussion

Let us point out that the basic common features of three model dispersions considered under F-F type scaling approximation are the following:

1. Excluded-volume effect (EVE)
   - for SAW and DLA it leads to a long-time superdiffusive behavior: $\overline{\lambda_k}(t) \propto t^{\nu_k^{(d)}}$, where $1 > \nu_k^{(d)} \geq \frac{1}{2}$ $(d = 1, 2, 3)$;
   - for CCA the total volume of the system is an unconserved quantity [1]; this way, the EVE is manifested in cluster-cluster aggregations; but the analogous scaling behavior is subdiffusive: $\overline{\lambda_k}(t) \propto t^{\nu_k^{(d)}}$, where $0 < \nu_k^{(d)} \leq \frac{1}{2}$ $(d = 1, 2, 3)$ since cluster-cluster aggregation takes more time than typically a non-cluster-cluster processes, such as SAW or DLA. It has been summarized in a picturesque way in Fig. 4.
2. The main discrimination procedure that emphasizes whether the HMC becomes eventually effective, or appears to be ineffective[2], may rest upon a fundamental observation, namely that
   - SAW and CCA are realized over uniquely defined, mononuclear (one-chain viz cluster of monomers) or polynuclear (many-cluster based) kinetic pathways [13,5,1];

[2] Thus, the HMC can also be thought of to be a measure of some (in)effectiveness of the k-process embedded in the subsequent Euclidean space

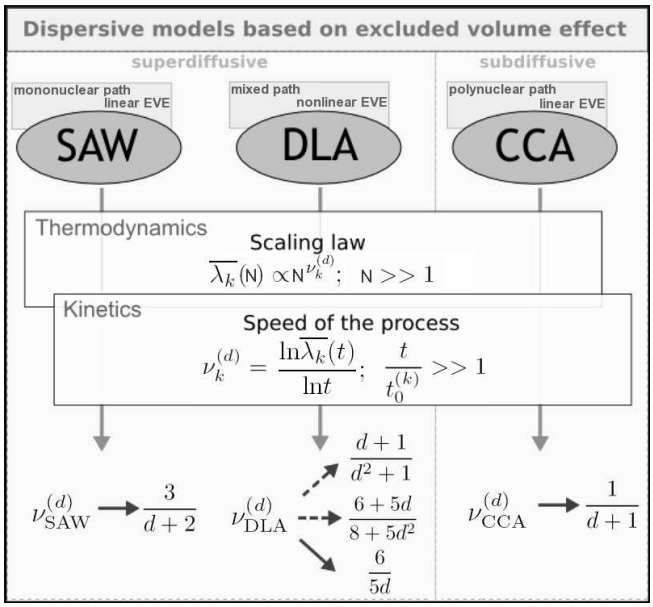

Fig. 4. Summarizing scheme for the three embedding processes, manifesting some EVE-caused dynamic disorder, with possibilities of entering the chaotic matter regime, especially when $d \to \infty$ (a need for applying then an M-point HMC might appear, where $M > 2$) [2]. It proclaims, that kinetically optimal k-processes emerge when $\left[\nu_k^{(d)}\right]^{-1}$ is linear in d, cf. eq. (10). The dashed arrows indicate kinetic non-optimality seen in terms of the MF approach

- DLA is always realized over some mixed pathway: many SAW-s are clustered on one nucleation seed, what makes a difference when formally applying the HMC [12,4,7,10]. It seems that a nonlinear branching, typically loopless topology would make some difficulties when one tried to kinetically optimize the process leading to creation of such a structure, especially in the two-dimensional embedding space.
- Notice formally, that a critical dimension for SAW, d_c, reads $d_c = 4$ [9], whereas for CCA $d_c = 1$ (surface-independent case), cf. [1]. But for DLA d_c takes on a fractional value - when evaluating it based on eq. (6), i.e. comparing it to one-half (standard-diffusion exponent), it reads $d_c \cong 2.41$, which also makes a formal difference between integer-influenced d_c of SAW and CCA and its non-integer counterpart for DLA [4,11].

Moreover, from an algebraic point of view, we have observed that for the three processes under consideration it is sufficient if the (numerical) estimate of the fractally-defined inverse speed of the process ($\frac{1}{\nu_k^{(d)}}$) is a linear function of

dimension d, such as

$$D_f^{(d)} := \frac{1}{\nu_k^{(d)}} = A \cdot d + B, \tag{10}$$

where A, B are constants. If this is not the case, like in Tokayama-Kawasaki or Hentschel [17,15] estimates, the HMC clearly favoring $d = 2$ realization space, fails. Thus, it is an unambiguously stated criterion likely favoring the EVE which is a common feature of the three processes considered, but arises naturally as interaction vs elasticity enthalpic-entropic effect in case of SAW and CCA, but rather purely diffusionally in case of DLA, i.e. when the enthalpic part is missing.

In particular, for DLA it would imply that any approach attempting for getting a final estimate of either a d–dependent fractal dimension[3] ($D_f^{(d)}$) or some d–dependent fractally-defined speed of the DLA process, should be a non mean-field approximation, enabling the influence of fluctuations in the final outcome [19,20]. It must lead to a more realistic description of the process, addressing an interaction of the DLA cluster with its surroundings, careful inspection of the sticking rules, that would make a DLA structure more mechanically compact or tenuous, as well as use of its multiparticle variants [8]. Moreover, the system has to be thermodynamically checked at least for presence of non-equilibrium steady states as well as for its consistency with the theorem of minimum entropy production [14]. It can be done by certain renormalization-group considerations [21]. Another option could be to resort to some numerical approaches that view DLA process in terms of some deterministic particle trajectories, and that the cluster is build on their realizations [22].

Bear in mind that, although DLA is widely recognized as a Laplacian growth model the two above mentioned approaches [21,22] do not need the Laplace equation to be solved for obtaining the speed of the DLA in the way shown by our paper. As is known, the $2D$ Laplacian growth is not well-formulated mathematically in $d = 2$ [23] and the problem needs logarithmic corrections [16]. It seems that in $d = 2$ the stationarity of the diffusion field is not fully guaranteed, especially under the presence of an absorbing boundary (sink) somehow violating its (external) harmonicity. As a consequence, at least certain matter fluctuations near the boundary can be suspected to occur - therefore some non mean-field DLA of turbulent type [24] looks more confident, and a suitable modification of $\nu_{\mathrm{DLA}}^{(d)}$ could emerge from such a proposal. An open question remains whether it will confirm the estimate by Meakin, eq. (9). If so, it will then formally give us the main message coming from the HMC, namely that in $d = 2$ only those processes may go thermodynamic-kinetically optimally for which the reciprocals of their speeds are linear functions of the space dimension d, eq. (10), cf. [16]. Therefore, a quite accurate numerical realization of DLA by Meakin, and even his followers [18,19], point to $D_f^{(d)} = 5d/6$ to be a reliable value [4,10].

[3] Note, however, that for CCA $D_f^{(d)} = \frac{1}{\nu_{\mathrm{CCA}}^{(d)}} = d + 1$, cf. eq (7), is not of fractal-dimension form. It is rather a superdimension, or according to ref. [9], a measure of the random close-packing [1,2] (A standard version of the approach [1] is, however, presented for non-fractal objects.)

When looking at the problem in terms of the HMC, the above results suggest an isotropic realization in space of $d = 2$ for SAW [25] and CCA [1,2] but somehow discourages the HMC for DLA-type practical experiments on a plane, i.e. as in the case of thin-films realizations of DLA patterns [4,26].

Moreover, looking at our three processes, manifesting EVE-caused dynamic disorder, cf. Fig. 4, one would interpret some of our findings in terms of dispersive (fractal-like) chemical reaction kinetics, especially when the characteristic length $\overline{\lambda_k}$ would be of order of the kinetic mean free path of the system which is often the case met in condensed phases [27] or in aerosols [3]. In such a Loschmidt-type limit [28], one would presume that a product of the (dispersive) chemical reaction rate coefficient, $\kappa \equiv \kappa(t)$, and $\overline{\lambda_k}$ will likely arrive at

$$\overline{\lambda_k} \times \kappa \sim \delta_k(d), \tag{11}$$

where a t–independent constant $\delta_k(d) \propto \nu_k^{(d)}$, where again the argumentation about (non)linearity of $\delta_k(d)^{-1}$ can be used to distinguish between the SAW/CCA and DLA different 'kinetic universality' classes, cf. eq. (10). The above, but confined to CCA only, could provide an alternative view of the time-dependent kinetics of certain more specific, e.g. nucleated-polymerization processes such as model prion growth [29,27].

To sum up, in this paper it has been shown that, within the mean-field approximation, in order to fulfill the d-dimensional HMC ($d = 1, 2, 3$), physically meaning that the system evolves toward optimal kinetic conditions in $d = 2$, a linear EVE (see, Fig. 4), to be quantitatively characterized by the dimensionless potential $\beta \times U(x)$ [5,13] from the Smoluchowski-type equation (3), has to be shown up by the system - it is just the case of SAW and CCA but, unfortunately, $2D$ DLA likely suffers a nonlinear EVE, i.e. it possesses a totally branched internal meandric and fjords-involving microstructure at all length scales (Fig. 2), hardly penetrable by, say, a testing particle that has no additional (third) dimension at its disposal to eventually escape from it, or to successfully percolate through it, once entering one of its fjords in either direction [7,4,19,16,24,18]. Therefore, eq. (10) appears to be a central HMC-oriented result of our study [10,17,18,23,2]. Thus, the Euclidean space $d = 2$ does not seem optimal from a thermodynamic-kinetic point of view for DLA and is attributed to non-fulfillment (violation of eq. (10)) of the dimension-dependent matter-aggregational ergodic hypothesis (see, sec. 1) - a case that discourages application-oriented activities, oppositely to $2D$ SAW [25] or CCA [1] colloid type applications that can be found elsewhere, e.g. in membrane science [26].

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Appendix

For the class of CCA processes [1] the local continuity equation

$$\frac{\partial}{\partial t}f(v,t)+\frac{\partial}{\partial v}J(v,t)=0, \tag{12}$$

where x is now v - the volume of a molecular cluster ($v^{(d-1)/d}$ stands for its 'reactive' surface), and $f(v,t)$ is the distribution function of the clusters at time t, is the conservation law which, after inserting $J(v,t)$ in eq. (12), leads to the F-P&S dynamic framework.

It can be found useful to transform the F-P&S equation into its possibly simple functional representation. For doing so, let us express the matter flux, eq. (3), in the following form [30]

$$J(v,t)=-(B(v)\frac{\delta F(f)}{\delta f(v,t)}+\beta D(v)\frac{\partial}{\partial v}\frac{\delta F(f)}{\delta f(v,t)}). \tag{13}$$

Here $\delta F(f)/\delta f(v,t)$ stands for the functional derivative, and the free-energy functional $F(f)$ looks as follows [31]

$$F(f)=(1/2)f(v,t)\int \mathrm{C}(v-v')f(v',t)dvdv', \tag{14}$$

where above (cf. (13)) $B(v)=b(v)dU(v)/dv$ has been used ($b(v)$ - the mobility, linearly proportional to $D(v)$). If one takes the kernel, C, $\mathrm{C}(v-v')=\delta(v-v')$, one obtains

$$F(f)=(1/2)[f(v,t)]^2, \tag{15}$$

which because of the power two in (15), unambiguously suggests the binary interactions between clusters, as is, for example, assumed in Van der Waals (real) gases between the gas molecules in the framework of a mean-field description [28]. For other details of the functional-based approach to CCA, see [31].

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