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Matter gets organized at several levels of structural rearrangements. At a mesoscopic level one can distinguish between two types of rearrangements, conforming to different close-packing or densification conditions, appearing during different evolution stages. The cluster formations appear to be temperature- and space-dimension dependent. They suffer a type of Verhulst-like saturation (frustration) when one couples the growing (instability) and mechanical stress relaxation modes together. They manifest a chaotic behavior both in space and time domains. We pretend to offer a comprehensive and realistic picture of a material or mega-cluster formation in \( d \) dimension.

I. INTRODUCTION

Matter organisations at a mesoscopic (molecular–cluster) level typically manifest a multitude of microstructural rearrangements. Cluster–cluster aggregations of proteins and/or colloids, phase separations, flocculation–coagulation phase transformations, sol-gel systems, (wet) sand or rice piles, etc., are manifestations of loosely-packed rearrangements, typically occurring under moderate or high temperature conditions. In contrast ripened polycrystals, sintered powders, soap froths and bubbles, and other cellular systems, constitute a type of rearrangement that usually emerges in a (relatively) low temperature limit and under certain ("field dependent") matter close–packing constraints. Beside such an agglomeration, fracture, desaggregation, desorption, dissolution, and alike, can be thought to be the "inverse process", finding its place in the opposite part of the relevant phase diagram [1].

In all of them spatial as well as temporal signatures of chaotic behavior, due to matter reorganisations, can be detected: They are temperature and space-dimensional dependent. In particular, one can show rigorously that in the limit of the spatial dimension going to infinity loosely-packed agglomerations become non–chaotic by suppressing totally their instability growing mode since it is related to the
nonequilibrium agglomerate’s entropy, while their closed-packed counterparts are not. When the growing mode is coupled to a mechanical stress relaxation mode as a power law via some phenomenological relation of Hall–Petch–Griffith (H-P-G) type (an Onsager-type conjecture of the present study), certain marks of Bethe–lattice frustration, related to a spatial overcrowding of the Cayley–tree branches, appear in the (mean-field) approach - a kind of frustration qualitatively of very similar type than that observed in Verhulst-type systems in an adequate time and parametric zone.

In the specific cases discussed in this review, however, by increasing the space dimension, $d$, we automatically induce some increase of the possible number of degrees of freedom in the system. Thus, when taking into account the coupling of the late-time growing and relaxation modes, say, in a fairly synchronized viz power-law way of H-P-G type, one obtains that even though the material’s relaxation goes slower than in the case when such a coupling is proposed in an unsynchronized (Debye-relaxation involving, i.e. rapid) way, one is, however, able to establish or restore an apparent dynamic microstructural order within the system the nonequilibrium (chaotic) measures of which are proposed below. There is, unfortunately, no way of establishing such an order when the coupling fails the power-law type synchronization requirement.

Thus, when an ample space amongst the clusters is recovered by the system at its mature growing stage, we consider that the system successfully tries to avoid a chaotic matter organisation in space. Note that temperature may markedly help in surmounting the activation-energy barrier of the agglomeration, especially when it is raised appropriately, whence when not “damaging’ a possibly smooth evolution of the system. Full success is, however, guaranteed when the limit of $d \to \infty$ is reached. If there is no chance for recovering the ample space, the late-time growing stage is realized in a moderately chaotic way. The mechanical stress relaxation, in turn, enters a readily chaotic regime, since the (nonequilibrium) entropy of the system diverges to plus infinity. The overall scenario resembles, in general, a formation of large (fractal) colloid aggregates that typically occurs with and without temperature and/or space-dimension dependent gravity factor domination, like as if imposing some limits to gelation of colloids.

The paper is arranged as follows. In Section 2, we define both the closely-packed as well as loosely-packed agglomerations, calling the latter the aggregation throughout. In Section 3, we list some qualitative signatures of chaos in matter-agglomerating systems, and refer briefly to different definitions
as well as meanings of chaos. In Section 4, we present quantitative measures of chaos signatures in systems of interest, whereas in Section 5 we unveil number-theoretic measures, featuring a chaotic spatio-temporal behavior of them. In Section 6, according to some suggestions given in \[6\], on which much of our report is based, in order to see which agglomerations behave orderly or non-chaotically, we explore the limit of \(d \rightarrow \infty\), and arrive at a certain interesting (perhaps, surprising) conclusion, favoring aggregation of matter, or some structural loosely-packed, and typically high-temperature, matter rearrangements – in contrast to those emerging under close-packing low-temperature conditions. We close the paper by offering a concluding address in Section 7.

II. AGGLOMERATION VS. AGGREGATION OF MATTER - A MODEL DESCRIPTION

Following \[7\], throughout the present study, we wish to distinguish between the notions of agglomeration and aggregation of matter. By the former we mean an assembly of grains or molecular clusters, kept together by relatively strong forces (e.g. ionic), so that there is no easy possibility of taking the clusters apart, or destroying them. For the latter, because of the appearance of weak bonds between clusters, such as Van der Waals or hydrogen types, the possibility of cluster separation becomes an observed tendency of the matter rearrangement due to their weak bonds. For a schematic explanation of the difference between both matter arrangements, see Fig. 1.

A. Basic system of equations describing model matter agglomeration

As in previous work \[8, 9\] we begin with a local continuity equation

\[
\frac{\partial}{\partial t} f(v, t) + \frac{\partial}{\partial v} J(v, t) = 0,
\]

preferentially supplemented by the corresponding initial (of delta-Dirac type as a first attempt) and boundary (typically, of absorbing type) conditions (IBCs).

In a few subsequent studies a thermodynamic-kinetic description \[8, 9, 10\] of model complex matter agglomeration has been worked out. For the current \[33\] in the space of cluster volumes

\[
J(v, t) = - \left[ B(v) \frac{\partial}{\partial v} \Phi \right] f(v, t) - D(v) \frac{\partial}{\partial v} f(v, t),
\]
FIG. 1: Typical cluster-merging (three-grain) scenario for closely-packed (left, denoted by A) and loosely-packed (right, denoted by B) agglomerations. Two consecutive time steps $t_1$ and $t_2$ are shown. The former usually goes by a scenario with the preservation of the total agglomerate’s volume (though in a more irregular way, when its logarithmic speed is measured, cf. Sections 3–6), whereas the latter does not$^8$. In the former, the clusters do not perform a translational motion but their boundaries may fluctuate in time and space, even though they are quite strongly confined by their neighborhood. In the latter, an almost opposite situation in the time-and-space domain is typically observed. Some void is left behind a loosely packed system

has been used$^9$, where $f(v,t)$ is the distribution of clusters of volume $v$: this means, that $f(v,t)dv$ is the (relative) number of clusters with size in the infinitesimal volume interval $[v,v+dv]$; $t$ is the time; $\Phi$ represents the physical potential, equivalent to the free energy of the system (see $^6$ for an explanation of the term). It is assumed to be one of the most relevant drivers of the agglomeration process at the mesoscopic level, assuring its nonequilibrium character. In fact, the current $^2$, in the form presented above, comes from a rigorous derivation, starting from the Gibbs equation for the entropy production $^10$. It has quite strong foundations anchored in nonequilibrium thermodynamics $^9$. It is worth mentioning that upon inserting Eq. $^2$ into the continuity equation, Eq. $^1$, one gets a second-order partial differential equation of the Fokker–Planck–Kolmogorov (F-P-K) type $^11$.

For the dynamics of such a system some routes to chaotic behavior have been sketched elsewhere by considering the (in)stability of Markov semigroups in $^12$. The mobility $B(v)$ is also defined in the configurational $v$–space and reads$^9$

$$B(v) = \frac{D}{k_BT}v^\alpha, \quad \alpha = \frac{d-1}{d},$$

(3)
where $D$ is a diffusion reference constant. Realize that the principal role of $D$ is to scale the time variable; $k_B$ represents the Boltzmann constant. Note that the mobility $B(v)$ is related to the Onsager coefficient, $L(v)$, that appears in the derivation of the matter flux equation under a set of assumptions, mostly based on the locality of the Kramers-type process, etc. $L(v)$, and hence $B(v)$, could be measured by comparing the current and the thermodynamic force. The quantity $D(v) = Dv^\alpha$ is to be inferred from the Green–Kubo (G-K) formula, so that there is some quite strong suggestion for deriving $B(v)$ both, experimentally as well as theoretically.

There is a debate about a possible violation of the G-K formula. For instance, it is proved that for a gas of charged particles subjected to an external electric field, the mean mobility of a charged particle, based on the G-K formula, is reliably well estimated for suitably small values of the external field. Moreover, at a microscopic scale one observes a nonlinear (or chaotic) behavior of the particles, which is, unfortunately, not reflected by the macroscopic (mobility) measure. In our case, we assume algebraic correlations in $v$–space, for a phenomenological formula. The assumption seems to be as natural as possible: $D(v) \propto v^\alpha$; that means that both the diffusivity $D(v)$ and the mobility $B(v)$ are proportional to the cluster hypersurface, $s^{(d)} := R^{d-1}$. It should be underlined that it is, in our opinion, the common physical case in clustering phenomena, and is working properly at the mesoscopic level considered in our approach.

Notice right here that exactly the same assumption has been used to model in a F-P-K way the formation of surface nanostructure arrays. Therein, an experimentally-observed passage between direct curvature-dependent ripening of matter nano-islands (our densely-packed agglomeration), and inverse ripening, with an elastic-field caused contraction of growing quantum dots (our sparsely-distributed agglomeration of matter), has been presented.

There are, however, matter agglomerations, for a given $T$, that do not conform usually to

$$D(v) \propto B(v) \sim v^\alpha \approx s^{(d)}.$$

To them belong both some physical-metallurgical transformations, such as martensitic, and presumably, also certain phase orderings of non-diffusive kind, emerging in model biosystems, such as those occurring in lipid biomembranes. Other than algebraic types of correlations in the hyper-space can likely be expected for these. If a power law of the type given by Eq. can be kept for
further modeling, some additional correlations in time must complete a more comprehensive correlational proposal, cf. [20]. Other types of correlations in the hyperspace, even if they allow to get a general solution to the problem, may not accommodate the boundary conditions [9], so that one would expect either to be left with an unsolved specific problem or to encounter anomalous or irregular behavior of the agglomerating system [8, 19, 20]. In such a case another type of finite, instead of infinite boundary conditions [20], can sometimes give a remedy for the problem [21]. Here, under the term \textit{infinite boundary conditions} [8] we typically understand the boundary conditions of absorbing (Dirchlet) type

\[ f(v = 0, t) = f(v = V_{\text{clust}}, t) = 0 \]

in which the single cluster volume is taken at infinity, \( V_{\text{clust}} = \infty \), whereas in case of the finite boundary conditions it assumes a finite value, \( 0 < V_{\text{clust}} < \infty \), cf. [21], and a discussion therein. Although the latter unquestionably seems more physical the former is more frequently used to reveal the evolutions in matter-agglomerating systems [22] - this resembles to some extent a situation in statistical-thermodynamical systems undergoing an equilibrium phase transition: As such they are typically considered in the so-called thermodynamic limit (here, with a number of subunits going to \( \infty \)) under the mentioned agglomeration-oriented, e.g. condensation conditions, and the analogy would presumably extend over the examined nonequilibrium evolutions too [9, 21].

\[ B. \text{ Thermodynamic potentials driving matter agglomerations} \]

In previous work [9] the analytic form of a (so-called) compaction potential was obtained, i.e.

\[ \Phi(v) = \Phi_o \ln(R/R_o), \]

where \( \Phi_o, R_o \) - constants, and \( R \) stands for some cluster radius. Because

\[ v \equiv v^{(d)} \sim R^d, \quad d = 1, 2, 3, ..., \]

one gets also \( \Phi(v) \propto \ln(v/v_o), \) where \( v_o \) is a constant.

The logarithmic potential assures the emergence of rather compact and curvature-involving structures, whence the name of "compaction potential" [22]. It should be noted that \( \Phi \) is an entropic
potential. Thus, it can be a cause of some desaggregation, or matter-influenced impingement effects, occurring within the overall aggregation space.

In a previous study on the phase transformation kinetics for loosely packed "diffusive" agglomerates we have written the matter flux of a purely diffusive nature prescribed in configurational space as follows

$$J(v, t) = -D(v) \frac{\partial}{\partial v} f(v, t). \quad (8)$$

(The diffusion function $D(v) = Dv^\alpha$ is proportional to the cluster (grain) surface.)

Both closely-packed and loosely-packed agglomerations follow from the general form (2). Indeed, the loosely-packed case is obtained when the first (drift) term in r.h.s. of (2) can be neglected. Formally, $B(v) \to 0$ when $T \to \infty$. From the physical point of view, it corresponds to sufficiently high temperatures $T \geq T_{pass} > 0$, where $T_{pass}$ can be treated as a cross-over temperature above which the agglomeration takes place exclusively by yielding loosely-packed microstructures. However, the drift term in r.h.s. of (2) depends both on $v$ and $T$. It tends uniformly, which means independently of $v$, to zero at the high temperature limit if

$$B(v) \frac{\partial \Phi(v)}{\partial v} \simeq C = const. \quad (9)$$

Then for a given system, temperature $T_{pass}$ does not depend on $v$ and looks consistently defined.

Some additional argumentation can be provided that such a constant (limit) $C$ exists and is well-defined. Namely, when applying both (3) and (7) one sees with sufficient accuracy that

$$C \propto \frac{1}{\Delta R} \times \frac{\Delta \Phi(v)}{k_B T}. \quad (10)$$

This means that $C$ is essentially determined by a product involving two contributions: a certain curvature-like term, $\kappa = 1/|\Delta R|$, and some dimensionless energetic argument, $\epsilon_E = |\Delta \Phi(v)|/k_B T$.

The above claimed high-temperature limit, with the cross-over temperature $T_{pass}$ as a reference temperature characteristic of a system of interest, would naturally demand $0 < \epsilon_E << 1$ while, because of approaching the mature growing stage any change in the cluster radius must be small, $0 < |\Delta R| << 1$, and therefore, its inverse would tend to some big value, i.e. $\kappa >> 1$. Thus, $C$ will take on a finite value. It is believed that for certain agglomerations under readily high-temperature conditions it will
eventually acquire a small value, that means, $0 < C < 1$ naturally holds. It is a case when the potential

$$\Phi(v) \propto v^{1-\alpha} \simeq v^{1/d}. \quad (11)$$

In a condition of setting the current equal to zero, $J = 0$, has been chosen to balance diffusive and non-diffusive terms in the F-P-K type description, cf. [10], aiming at getting a proper behavior of the metastable nanostructure arrays. We are of the opinion that such a proposal is legitimate in the relatively low-temperature domain. When the temperature is raised, but agglomeration is still allowed to occur, the proposal may fail. Thus, the above is a possible solution for the high-temperature limit.

A type of localization of the Gaussian distribution, characteristic of the inverse ripening (a metastable state of the nanostructure evolution) can also be obtained within the present modeling, cf. [8]. This is the case of Eq. (8) when in a (readily) mature growing stage, since the single volume $v$ of the cluster does not change much. As a matter of fact, there is no small-cluster population available for merging (Fig. 1), i.e. $D(v) \to \text{const.}$, which nearly corresponds to the high-temperature criteria of Eq. (9), or equivalently Eq. (10). In so doing, Eq. (8) represents the 1st Fick law in its standard form. Upon inserting it into Eq. (1) one immediately arrives at the 2nd Fick law (in the configurational space) with its standard Gaussian solution, the metastable case being emphasized in [16].

The above potential form, designed for loosely-packed agglomeration, seems legitimate here: Note that the 'force' $F_{c-c} \propto \partial \Phi(v)/\partial v$ behaves like

$$F_{c-c} \propto \frac{1}{v^{\alpha}} \simeq \frac{1}{s^{(d)}}, \quad (12)$$

because $v \sim R^d$. Thus, $F_{c-c}$ acts as the inverse of the area of the cluster hypersurface, $s^{(d)}$, which implies that the smaller the area is, the bigger the force acting on the cluster can be, this way impeding the formation of new clusters, which would contribute to an aggregate’s density increase. Qualitatively, a similar dependence is found for the closely-packed matter agglomeration: from [8] one gets, as above, for the 'force'

$$F_{c-c} \simeq \frac{1}{v^{(d)}.} \quad (13)$$

Here, $F_{c-c}$ acts as the inverse of the hypervolume of the cluster, $v^{(d)} := R^d$, which makes a clear
difference between closely-packed and loosely-packed agglomerations, presumably leading to a certain relaxation of the surface tension conditions for loosely-packed clusters-containing systems [22].

Referring further to (9) and using the similarity relation, Eq. (7), one gets

$$\Phi(R) \propto \Phi(R_o) \frac{R}{R_o},$$

(14)

where

$$\Phi(R_o) = \frac{k_B T}{D^\alpha} R_o, \quad T \geq T_{pass},$$

(15)

and consequently, $$\Phi(R) \propto R.$$ Moreover,

$$D^\alpha = D(1 - \alpha).$$

(16)

$R_o$ can now be specified to be the initial cluster radius. Note that $D^\alpha$ is a $d$-dependent quantity.

C. Cluster volume fluctuations as reliable characteristics of matter agglomeration

Aggregations and agglomerations emerge in a fluctuating changing medium. Therefore, any reasonable quantitative attempt on resolving the fluctuation impact on their speed is worth examining here.

In what follows, let us propose an evaluation of the reduced variance

$$\sigma^2(t) = \frac{< v^2(t) > - < v^1(t) >^2}{< v^1(t) >^2} = \frac{< v^2(t) >}{< v^1(t) >^2} - 1,$$

(17)

as a direct measure of the cluster volume fluctuations.

The notation used in Eq. (17) refers to the statistical moments

$$< v^n(t) > = \int_0^\infty v^n f(v, t) dv \quad n = 0, 1, 2, ...$$

(18)

of the stochastic process, where the matter agglomeration is usually described by the local continuity equation, Eq. (11).

The explicit solutions, $f(v, t)$–s, have been presented elsewhere [8, 9, 20], and refs. therein. The zeroth moment, $< v^0(t) >$, is related to the average number of molecular clusters in the system, and usually shows an algebraic decrease with time [8]. The first moment, $< v^1(t) >$, is related to the total volume which is a constant value for closely-packed agglomerations [22] and an increasing function...
of time for loosely-packed agglomerations \[8\], cf. Fig. 1. From the expressions of both moments, it follows that the average cluster radius, \( R_{av}(t) \), behaves as a power law in time, with a growth exponent \( 1/(d + 1) \) that apparently contains some signature of random close-packing of matter by having included the super-dimension \( d + 1 \) \[9, 23\]. \( (d + 1 \) tells us something about the minimum number of non-overlapping neighbors of a given cluster in a \( d \)-dimensional space.) These constitute the main characteristics of the model agglomeration/aggregation process in its late-stage \( (t >> 1) \) limit.

The question remains about asymptotic values of the moments \(< v^n(t) >\) that must be known when applying formula \( (17) \). For closely-packed agglomerations, the moments are found to obey a power law \[22\]

\[
<v^n(t) > \sim t^{(n-1)/(2-\alpha)} \quad (n = 0, 1, 2), \quad t >> 1,
\]

(19)

whereas for matter aggregation one finds another power law \[8\]

\[
<v^n(t) > \sim t^{[(n-1)+\alpha]/(2-\alpha)} \quad (n = 0, 1, 2), \quad t >> 1.
\]

(20)

Notice, that for \( \alpha = 0 \) \( (d = 1) \) both power laws above approach the same form, namely \( < v^n(t) > \sim t^{(n-1)/2} \). When utilizing \( (17) \) and \( (19) \) it appears that for closely-packed agglomerations, \( \sigma^2(t) \) can be fully identified with the inverse of \( < v^0(t) > \) (the average number of clusters), cf. \[22\] for details, what because of the constancy of \( < v^1(t) >\), leads to \( \sigma^2(t) \propto V_{sp}(t) \), where \( V_{sp} \equiv V_{sp}(t) \simeq < v^1(t) > / < v^0(t) >\), and can be termed the mean specific volume of the tightly-packed agglomerate, being equivalent to the inverse of its mean number density. The specific volume fluctuations read

\[
\sigma^2(t) \propto t^{d/(d+1)},
\]

(21)

and if \( d \to \infty \), \( \sigma^2(t) \simeq V_{sp} \propto t \).

When using \( (17) \) and \( (20) \), however, it turns out that for loosely-packed agglomerations \( \sigma^2(t) \) is a quantity equivalent to the average cluster radius \( R_{av}(t) \), see \[8\]. They behave in time as

\[
\sigma^2(t) \propto t^{1/(d+1)}.
\]

(22)

When \( d \to \infty \), \( \sigma^2(t) \simeq R_{av}(t) \to const \), which means, that on average the system ceases to grow. Note that the standard diffusional regime, is always characterized by the one-half exponent, is achieved
exclusively for the aggregations in $d = 1$ because the only linear characteristic is $R_{av} \equiv R_{av}(t)$: Note that $V_{sp}(t)$ is not a linear characteristic, since $V_{sp}(t) \propto [R_{av}(t)]^3$ usually holds. Here the $d = 1$–case must clearly be disqualified as standard diffusional, cf. Eq. (21).

Commenting on the last relations, (21) and (22), one might furthermore conclude that they reflect a well-known Onsager conjecture that the fluctuations in a system undergo the same type of changes as the corresponding macroscopic dynamic variables: Here one may think of the specific volume of the agglomerate and the grain radius, and their behavior in the late-time domain, respectively.

D. Coupling the instability (growing) and mechanical stress relaxation modes of matter agglomeration

Poisson was likely the first who recognized that viscoelastic properties of fluids and solids can reasonably be compared in a suitable, mostly short-time domain, though the specification of the domain must be more precise for specifying the systems of interest. Maxwell successfully followed the ideas of his famous French predecessor, arriving at his well-known, in general non–Markovian, model of relaxation. In what follows we present our Maxwell–model-based ideas on how to distinguish between the two agglomerations under study, and how to switch on a kind of coupling between the (late-stage) growing and relaxational modes in the viscoelastic $d$–dimensional matrix that we investigate. The existence of the coupling seems to be experimentally justified, see [5, 15, 16], and involves generically the viscoelastic nature of the mega-cluster late-stage formation.

Thus, the afore presented rationale toward quantifying the fluctuations of the system can be strengthened with a supporting phenomenological argumentation. The idea comes from a "coupled" diffusion-relaxation picture that appears in such a complex system. In any diffusion-migration growing process, the mechanical strain-stress fields play such a role as well. In our case, such a situation can be safely expected in the temperature domain $T \leq T_{pass}$. Another type of relaxation of the stress field, say $\sigma_m$, is expected to prevail when the closely-packed agglomeration conditions are met. A different behavior may be observed when the closely-packed agglomeration conditions are lost for the first time, that is, at $T = T_{pass}$, when the loosely-packed context appears. In both temperature regimes, the relaxation of $\sigma_m(t)$ over the course of time, is very likely to go in a way essentially described by the current. This
is expected to occur presumably under (nearly) homogeneous strain conditions, $\epsilon_m \approx const$, for $t >> 1$. For an additional motivation of coupling matter agglomeration and stress relaxation picture, related to fracture phenomena, see [1, 22].

From [22] it can be learned, that in the absence of non-Arrhenius or fractal type kinetics, seemingly modifying the diffusion coefficient $D(v)$ [20], one expects the Maxwell dashpot-and-spring model to reflect properly the relaxation behavior. We wish to set up here a phenomenological picture, showing that both agglomeration and mechanical stress relaxation, where the stress relaxation takes place under slow growth conditions, proper of a mature growing stage in a viscoelastic multiphase medium [13, 15], are coupled processes [5, 16]. To work out the problem quantitatively, we will represent one of the two contiguous and matter-exchanging clusters in the agglomerate, say cluster (grain) 1, as an expanding one, equivalent to the spring, growing at the expense of its neighbor, to be named cluster (grain) 2, i.e. the dashpot, to which, according to the Maxwell model, the contracting action should be assigned, cf., Fig. 2 for details; see [22].

For the system with non-wide gaps, the Maxwell model conditions are almost satisfied, so that the two-cluster action can be extended over all pairs of contiguous clusters until the expanding (growing) eventually survive. In a next step, the same kind of competition appears as in the well argumented Laplace-Kelvin-Young scenario suitable for cellular systems [1]. This picture holds in the closely-packed context.

In the loosely-packed context (a system with wide gaps), we may have qualitatively almost the same picture [2] but with several differences which implies that cluster expansion would not be likely so vigorous. Since the corresponding gap is wider, therefore untight, the fluid leakage might be more pronounced. Thus, the fluid response against the piston wall is weaker, and the Maxwell type stress relaxation no longer applies, cf. the caption of Fig. 2.

The stress relaxation can be described by introducing an exponent $\chi$ in the Maxwell-like quasi-fractional model presented here below. This exponent should be, in general, $d$-dependent, and points to a difference when comparing with the classical Maxwell model [2]. Here, we offer a coupled matter diffusion and stress relaxation picture, but for a random walk performed in the configurational space.
FIG. 2: Maxwell sequential spring-and-dashpot (quasi-fractional) model with narrow ($d$–independent) and wide ($d$–dependent) gaps, shown schematically in two subsequent time instants $t_1$ and $t_2$, where $t_2 > t_1 > 0$, from left to right, respectively. Grain "1" consists of the spring and the piston’s upper wall, to which the second end of the spring is attached, while its first end is mounted either on $0_1$ or $0_2$, from left to right, respectively. Grain "2" consists of the viscous medium inside the cylinder as well as the inner wall of the piston. The cylinder’s walls complete the overall model structure of the viscoelastic grains. The material exchange between "1" and "2" is assured by the existence of the gaps: narrow $CP_{1-2}$ gaps in case of closely-packed agglomeration, and some two wider (here, represented by the left-hand side gap, $LP_{1}^{(d)}$) in case of the aggregation. Therefore, the piston-and-cylinder system, containing a viscous fluid, here composed of big and small particles, is either more (densely-packed agglomeration) or less (undensely packed formation) leakproof. The overall material exchange is caused by spring expansion along $z$ axis, which results here in a longitudinal expansion of grain "1" at the expense of grain "2", cf. \url{http://www.j-npcs.org/abstracts/vol2000no4.html}. Notice formally that: $0_1E = 0_2E$, and for $t_1$ one has $z_1(t_1) = 0_1E$, $z_2(t_1) = BE$ as well as for $t_2$ one gets $z_1(t_2) = 0_2I$, $z_2(t_2) = I E$, which results in grain expansion-contraction behavior, like $0_1B < 0_2I$ and $BE > I E$, when mutually comparing the distances along the $z$ axis at $t_1$ and $t_2$, respectively.

As is known, the Maxwell stress relaxation picture leads to an exponential decay of the stress:

$$\sigma_m(t) \sim e^{\exp(-t/\tau_M)},$$

(23)

where $\tau_M$ is a reference time for the concentrated clusters to be eventually inferred from the Einstein-Stokes-like formula \[13, 22\]. This behavior holds for $T < T_{pass}$. As mentioned above, for
\( T \geq T_{\text{pass}} \) we propose
\[
\frac{d\sigma_m}{dt} + \frac{\sigma_m \chi}{\tau} = 0, \tag{24}
\]
where the above is usually true when the internal strain field, \( \epsilon_m \) is practically constant, see above.

When solving (24), one obtains
\[
\sigma_m(t) \sim \left( \frac{t}{\tau} \right)^{-1/(\chi-1)}, \quad t \gg 1, \tag{25}
\]
where \( \chi = 2d + 3; \) about \( \tau, \) see [22] or [13]. Notice that for \( \chi = 1 \) and \( \tau = \tau_M \) in Eq. (24) one gets the solution [23]; for \( \chi \neq 1 \) Eq. (26) is the only solution to the relaxational problem as stated. When comparing Eqs. (23) and (25) one sees that the relaxational response goes slower for the late-time loosely packed aggregational context than for its densely-packed agglomerational counterpart.

III. QUALITATIVE SIGNATURES OF CHAOS IN MATTER–AGGLOMERATING SYSTEM

Let us consider a few qualitative signatures of chaos in matter–agglomerating systems from the literature. Such certain signatures for systems of the type studied in the present work are summarized in Table 1.

The items stated in Table 1 do not exclude other possible forms to chaos, or its signatures, in matter-agglomerating systems. We do not pretend to describe all of them, or even their majority. For routes to chaos recommended from physical point of view one would usefully consult [27, 28]; which routes, or scenarios of chaos, are recommended by mathematicians, especially when a partial-differential-equation formalism of F-P-K type is effective, can be found in [6], and in refs. therein.

IV. SOME QUANTITATIVE MEASURES OF CHAOS SIGNATURES IN MATTER–AGGLOMERATING SYSTEM

In [22] some entropic-like nonequilibrium measures of growth
\[
\nu_{sp}^{(d)} = \left( \frac{\ln |\sigma^2(t)|}{\ln (t)} \right)_{t \gg 1}, \quad d = 1, 2, 3, \ldots \tag{26}
\]
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as well as for the mechanical stress relaxation evolution

$$\mu_{sp}^{(d)} = \left(\frac{-\ln[\sigma_m(t)]}{\ln(t)}\right)_{for~ t >> 1}, \quad d = 1, 2, 3, ...$$

have been proposed. This seems to be working most appropriately in a growth-and-relaxation synchronization metastable regime

$$\sigma_m \sim R_{av}^{-1/2} \sim \sigma^{-1},$$

which represents the H-P-G condition

$$\sigma_m \sim R_{av}^{-1/2},$$

appropriate for the fluctuational late-time regime of interest here. Bear in mind that if certain empirical modifications of the formula are applied toward obtaining a specific form, interconnecting Eq. with Eq. 27, one gets something like

$$\nu_{sp}^{(d)} = q\mu_{sp}^{(d)},$$

where typically $q > 2$. In the classical H-P-G limit $\nu_{sp}^{(d)} = 2\mu_{sp}^{(d)}$ holds. However $q$ may also strive for obtaining superplastic effects, i.e. when taking on fractional values, cf. [9] and refs. therein. This is sometimes termed in physical-metallurgical literature the inverse H-P-G effect.
Because of Eq. (22)
\[ \nu_{sp}(d) = \frac{1}{d+1}, \quad d = 1, 2, 3, \ldots \] (31)

Realize that formulae (28) and (29) might again be interpreted in terms of the Onsager conjecture [2, 4], see above. Since the overall exponent in (25) reads
\[ \frac{1}{\chi - 1} = \frac{1}{2(d + 1)}, \] (32)
which is exactly one half of the growth exponent \( \nu_{sp}(d) \) given in (22), see (31) too, one consequently provides
\[ \mu_{sp}(d) = \frac{1}{2(d + 1)}, \quad d = 1, 2, 3, \ldots \] (33)

Let us emphasize here that \( \frac{1}{\chi - 1} \) stands for the so-called Nutting exponent for relaxation, and can be interpreted in terms of the loss tangent, that means, a well-known dissipation factor in the relaxation phenomena, mostly in dielectric (e.g., macromolecular) environments [22].

V. NUMBER-THEORETIC MEASURES OF SPATIAL AND TEMPORAL IRREGULARITIES IN AGGREGATION-AGGLOMERATING SYSTEMS

It is interesting to note here that \( \chi = \chi(d) \), i.e.
\[ \chi(d) = 2(d + 1) + 1. \] (34)

A certain generator of the Bethe–lattice elements, is recovered starting from the 3-bond (initial) generator for \( d = 0 \), and continuing with \( d \), upon identifying \( d \) as the numbers of emerging bonds in a gelling system [5]. This is a very useful tool for the mean-field description of gels, and other multi bond-containing systems. This means that for loosely-packed agglomerations the harmonic-mean rule for the growth speed is exactly fulfilled. *Mutatis mutandis*, one can expect the same type of rule, Eq. (35), for \( \mu_{sp}(d) \).

In this way, an odd number Bethe–lattice generator for subsequent \( d \)-s can be offered, see Fig. 3.

Another, equally interesting observation can be offered, namely
\[ \frac{2}{\nu_{sp}(2)} = \frac{1}{\nu_{sp}(1)} + \frac{1}{\nu_{sp}(3)}, \] (35)

This means that for loosely-packed agglomerations the harmonic-mean rule for the growth speed is exactly fulfilled. *Mutatis mutandis*, one can expect the same type of rule, Eq. (35), for \( \mu_{sp}(d) \).
FIG. 3: An example of a not much developed Bethe lattice, which by itself manifests a frustration because of "having problems" with containing all of its nodes in the available $d$-dimensional space $20$, to some extent so as, for example, the population of Verhulst fellow countrymen does in the available Belgium territory $29$.

Let us recall that the fluctuations $\sigma^2(t)$ have been proposed as a reliable criterion of differentiating between aggregation and agglomeration, and that an efficiency (harmonic-rule, see $35$) additional criterion, derived from the constructed fluctuational proposal, supports the aggregation in dimension $d$ ($d = 1, 2, 3$), with an emphasis placed on $d = 2$, where 'golden-ratio-like' or harmonic-mean properties are in favor. The mean-harmonic speed implies that the center of mass of a moving body, referred consequently to as the molecular cluster, may not span the same distance, say $s$, back and forth, during a time period. This leads to a quite realistic quantification of a mean speed on the distance $2s$, and also shows that not an arithmetic mean of the back and forth speeds but a harmonic mean applies here. Such a schedule can likely be extended over the aggregation that essentially relies on random matter attachments and/or detachments of particles $8, 25$, in such a way a forward sub-process may essentially go unidimensionally, like in a ballistic motion, whereas its reverse counterpart would explore the whole three-dimensional domain. This situation typically appears in the case of matter desorption, in which detachment occurs part by part from a "reactive" surface spot.

Some other confirmation of (mean) harmonicity, its close relation to the golden rule, and to the Fibonacci sequencing (characterizing well the fractality of "diffusive" microstructures), is hidden in the (macro)ion (or, cluster $22$) diffusion coefficient $D_\alpha$, in our model, Eq. $16$, which is also included in the free energy $\Phi$. The label, or the lower index, is simply $\alpha$, which for $d = 1$ results in $\alpha = 0 \equiv 0/1$, $\alpha = 1 \equiv 1/1$. 


for $d = 2$ gives $\alpha = 1/2$, whereas for $d = 3$ offers $\alpha = 2/3$. The values of the diffusion coefficient (Eq. 10) are: $D_0 \equiv D/1$, $D_1/2 \equiv D/2$ as well as to $D_2/3 \equiv D/3$, respectively. They correspond to the first five-number Fibonacci sequence, composed of the numerators and denominators of $\alpha$-s, like 0,1,1,2,3, and obe $a_{n+2} = a_{n+1} + a_n$, for the three subsequent Fibonacci numbers $a_n$, $a_{n+1}$ and $a_{n+2}$. If so, one can provide the following two recursive formulae

$$\alpha^{(d-1)} = \frac{a_{d-1}}{a_d}, \quad d = 1,$$

and

$$\alpha^{(d-1)} = \frac{a_d}{a_{d+1}}, \quad d = 2,3,$$

where $a_0 = 0$, $a_1 = 1$, $a_2 = 1$, $a_3 = 2$, $a_4 = 3$ are the first five Fibonacci numbers. Since the analogy with gelling systems seems evident [22], this cannot be taken entirely as a surprise. The bonding in gels clearly goes as a branching process, being (as in the case of ultrametric space) quite naturally described geometrically in terms of Fibonacci numbers, thereby involving the notion of fractality [5].

When finishing this section, let us note that both the characteristic chaotic measures, cf. Eq. 11 for example, have their random close-packing account $d+1$ involved. This is a landmark of randomness but readily appears as a space-filling action of modeled matter reorganisations. Realize that our rationale may apply just in the same vein to clusters-containing assemblies, evolving in a $d$-dimensional space, where a cluster is characterized by its fractal dimension $0 < d_F < d$, cf. [9, 22].

VI. CHAOS IN AN INFINITE-DIMENSIONAL AGGLOMERATING AND/OR AGGREGATING SYSTEM

Consider the case $\lim_{d \to \infty}$. A corresponding chaotic measure for the late-stage growing event in the agglomeration of matter, very reminiscent of nonequilibrium correlational entropy measure [2], reads

$$\nu_{sp}^{(\infty)} = \lim_{d \to \infty} \left( \frac{\ln[\sigma^2(t)]}{\ln(t)} \right)_{for \quad t \gg 1},$$

whereas its counterpart for the relaxation is given by an analogous formula, namely that

$$\mu_{sp}^{(\infty)} = \lim_{d \to \infty} \left( \frac{-\ln[\sigma_m(t)]}{\ln(t)} \right)_{for \quad t \gg 1},$$
holds. They are consistent formally with the so-called correlational entropy (Kolmogorov–type) measure, defined in [28] and follow the rationale presented in [6], in which some measures of chaos in dynamical systems described by partial differential equations have been discussed. For "thermostatic" systems out of equilibrium one has to speak of the so-called generalized fractal dimension formalism, first introduced by Grassberger and Proccacia, see [28], and refs. therein.

The most attractive reason for introducing such measures arises from the fact that if one evaluates both $\nu_{sp}(\infty)$ and $\mu_{sp}(\infty)$, one unambiguously gets for the aggregation

$$\nu_{sp}(\infty) = \mu_{sp}(\infty) = 0,$$

(40)

whereas for the close-packed agglomeration one provides

$$\nu_{sp}(\infty) = 1,$$

(41)

and

$$\mu_{sp}(\infty) = \infty.$$  

(42)

Thus, for both cases, Eq. (41) and Eq. (42), one arrives at a chaotic behavior in the nonequilibrium system of a densely-packed agglomerate. This is not the case of the aggregation for which the common measure of its chaotic character is zero, cf. Eq. (40).

Thus, proceeding consistently with the approach offered in [6] we may conclude that the late-time aggregation process develops in an ordered way. The case $d = 2$ appears to be the most efficient since the harmonic-mean rule is applied; for it the nonequilibrium character of the random process should be emphasized. It is intriguing to realize that the system property called the harmonicity throughout is very much related to its nonequilibrium entropic or chaotic characteristic(s).

**VII. CONCLUDING ADDRESS**

Based on the above, we are allowed to state the following:

(i) in matter-agglomerating systems chaos is revealed as a complex spatio-temporal and temperature-dependent phenomenon;

(ii) nonequilibrium chaotic measures of any late-stage matter agglomeration modeled can be proposed.
relying upon the nonequilibrium Kolmogorov-type entropy measure, which makes a reliable (harmonic) quantification of the tempo of the process;

(iii) coupling late-stage matter agglomeration with relaxation of assisting elastic fields via an Onsager-type \cite{4}, or, in the parlance of physical metallurgy, H-P-G conjecture \cite{3}, leads to several characteristic sub-effects (Bethe-lattice generator, first-five Fibonacci-number signatures, random close-packing $d+1$-criterion \cite{23}, etc.) having their rationale in fundamental properties of the entropic or harmonic-mean character of the phenomenon \cite{36};

(iv) as for the formal point of view: The presented mesoscopic system, Section 2, serving to describe the matter aggregation can be derived rigorously based on the Gibbs entropy production equation \cite{9, 10, 22}, and

(v) its chaotic signatures can be inferred as presented in Sections 3–6, supported somehow by the ideas contained in \cite{6}; at this point, a general task remains to be done as to connect the type of chaos with the entropy-based scheme \cite{10, 22} used to derive the equations of F-P-K \cite{11}, or diffusion, types \cite{8, 9, 27}, and how far the proposed measures of chaos (also, the ones used in the present review) are reminiscent of those used conventionally in nonlinear science \cite{2, 14, 27, 28, 30}? Perhaps, the Edwards’ entropy measures for slowly moving grains, evolving (bio)polymer- or colloid-type matrices and compacted powders could also contribute to solve the problem \cite{32}.

VIII. ACKNOWLEDGEMENT

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to Ref. [16] and Prof. Miguel Rubí (Barcelona) for useful comments on the manuscript.

1999)


[33] For a method to derive diffusion currents for different types of systems one is encouraged to look into [10].

[34] Borrowing from the nomenclature of phase transitions and critical phenomena one might sometimes opt for calling it the threshold temperature

[35] Such a belief comes undoubtedly from the fact that we offer our approach for systems evolving in an overdamped regime, such as those of biopolymeric type. For them the Reynolds number is typically of the order of $10^{-3}$, i.e. very low, so that the mobility per se, even for a single biomolecule but also for a molecular cluster, must clearly be of negligible value [13], regardless of whether we measure it in the $\nu$-space or, what is usually done, in a position space

[36] As can be for example observed in clays made of an inorganic material known as laponite [31]