

Formation of soft material in terms of a coupled matter migration-and-relaxation picture: a synchronous mode

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This study is devoted to draw a mesoscopic nonequilibrium thermodynamics (mnet)-based description of the model soft material, such as that made of clusters of amphiphilic molecules or biopolymer surfactants. The description offered also enters the region of nonlinear viscoelastic behaviour of soft-matter agglomerates, both in a fluctuation-driven (quantitatively, being realized in an synchronous mode) and some flow-driven (mostly, qualitatively) regime. A special emphasis is placed on a novel concept, termed the emergent (power-law) behaviour, which tries to effectively combine data available about specific soft-matter (complex) systems that under variety of physicochemical conditions often manifest a certain interesting mesoscopic properties.

Key words: *model soft material; viscoelasticity; matter agglomeration; fluctuations; emergent behaviour*

1. Introduction

Soft matter consists of materials whose constituents have a mesoscopic size (typically, 10^3 – 10^5 nm) for which $k_B T$ is the relevant energy scale, whence the softness at ambient conditions as a main landmark. Examples of soft-matter systems include polymers, colloidal suspensions, liquid crystals, foams, gels, membranes, biological and granular matter of all types, etc. Soft matter comprises a variety of states perhaps best distinguished by being dominated by thermal energies at room temperature, with quantum aspects generally of secondary importance.

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The realization that soft matter contains innumerable examples of generalized elasticity, symmetry breaking, and many fluctuating degrees of freedom has re-opened classical fields of physics such as fluids (now frequently referred to as rheology [1], with non-Newtonian and structured-media aspects) and elasticity (membranes, filaments, and anisotropic networks are all important and common aspects) for new theoretical and experimental investigations. For both generalities and subtleties on soft matter, and the physics one may play on it, let us encourage a reader to consult Ref. [2], in which two major features of any soft-matter (complex-fluid) system have been emphasized, namely, its complexity and viscoelasticity. For a more recent review, in which weak connectivity and entropic interactions as the major features, distinguishing polyatomic (macromolecular) soft-matter systems from their non-polyatomic (small-molecule) counterparts, have been underlined, see [3].

As has been argued very recently, complexity might be a key feature of such systems, though still elusive and poorly defined, being responsible for their *emergent behaviour*, which eventually leads to a multitude of dynamic mesostructures, appearing while their parametric zone is appropriately scanned (cf. [4]) for reviewing the subject. Emergent behaviour is usually attributed to a physical system about which one may firmly say that its higher-level properties are not readily predictable from a detailed knowledge of its lower-level properties, such as those coming from the material subunits (atoms; molecules) alone. In a very real sense [4], emergence represents a democracy of physical scale: no size or time scale is more fundamental than any other. For some theoretical physicists such an assertion may imply: the renormalization-group, and in particular, self-similarity ideas are somehow hidden behind such a claim.

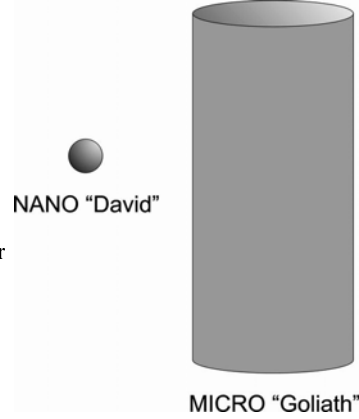
In this study, we would like to focus on one specific example of what one may, after seeing the argumentation developed in the paper, call the emergence in complex late-stage (model) matter agglomeration. The emergence discussed in our matter-agglomeration example relies on detection and exploration of power laws that, being scale-free, by definition do not distinguish any physical scale the properties of which they are pretending to describe. In the presented model, we claim that the complexity arose from a coupling of two basic modes of the slowly evolving model soft-matter system: a certain growing mode with some mechanical-relaxation one, presumed, however, that a (mechanical) stress field is generated within the material agglomerate also under its late-stage growth. Some examples of such systems, in particular biomolecular and colloidal assemblages, have been contained in [5].

The paper is structured as follows. In the next section, we have made a quick tour toward the model soft-matter agglomeration at a mesoscopic level, paying special attention to its basic notions and some landmark features (Fig. 1) which have not been reported. In Section 3, we have looked at volume fluctuations in an agglomerate under two different phase-state conditions, attributed to densely as well as loosely packed matter assemblages, abbreviated by CP and LP matter agglomerations, respectively, concentrating mainly on the so-called synchronous (coupling) mode [5], also trying to answer the question: When late-stage matter agglomeration demands its mechanical

response? In Section 4, we have elaborated the CP and LP packing states even more, and looked more carefully at the soft agglomerate in its *liquidus* and *solidus* phase-state limits. The closing address, presented in sec. 5, will summarize what we have found.

Fig. 1. How to differentiate between matter nano- (10^{-9} m) and micro-agglomerations (10^{-6} m), i.e. those occurring within the length scale of interest expressed by the present paper?

The answer, coming from mnet, would be: For instance, and amongst many things, by letting the materials-science researcher know which local curvatures [1], either only the spontaneous or twice the mean (sphere), or even that of Gaussian type (cylinder) modify the surface tension conditions of any soft-matter agglomerate (for some example, see [6], and especially, ref. [22] therein)



2. Quick tour toward model soft-matter agglomeration at a mesoscopic level

There is a consequent and unambiguous method of deriving the main kinetic equation for the overall model matter agglomeration being applicable to soft-matter agglomeration. The method is called mesoscopic nonequilibrium thermodynamics, mnet [7, 8]. It starts with the Gibbs equation which defines the variations of entropy [9, 10]

$$\delta S = -\frac{1}{T} \int \mu(v, t) \delta f dv \quad (1)$$

where $f \equiv f(v, t)$ (see below), T is the temperature, and $\mu(v, t)$ is the chemical potential in a v -space, i.e. in the (hyper)volume space of the material agglomerate. The potential $\mu(v, t)$ is given by (here, $\mu \equiv \mu(v, t)$ is taken for brevity)

$$\mu = k_B T \ln(af) \quad (2)$$

where a is the activity coefficient, k_B is the Boltzmann constant, and $k_B T$ stands for the thermal energy. Next, a is given in terms of a thermodynamic potential, denoted by $\Phi \equiv \Phi(v)$. Thus, a reads now [8, 10]

$$a = \exp(\Phi/k_B T) \quad (3)$$

Providing the temporal derivative in Eq. (1) and after partially integrating it over both sides (assuming additionally that $J \equiv J(v,t)$ vanishes at the ends of the phase space), one gets the entropy production, σ_E

$$\sigma_E = -\frac{1}{T} J \frac{\partial \mu}{\partial v} \quad (4)$$

from which we may easily get the expression for the matter flux

$$J = -\frac{1}{T} L(v) \frac{\partial \mu}{\partial v} \quad (5)$$

Here, we have assumed that the process is local in v . One could also consider, if necessary, a non-local case by [5, 8, 10]

$$J(v) = -\frac{1}{T} \int dv' L(v, v') \frac{\partial \mu}{\partial v'}$$

Combining Eqs. (5), (2) and (3) one gets

$$J = -\frac{1}{Tf} L(v) \left[k_B T \frac{\partial f}{\partial v} + f \frac{d\Phi}{dv} \right] \quad (6)$$

Now, let us define the mobility $b(v)$ as

$$b(v) = \frac{1}{Tf} L(v) = \frac{D}{k_B T} v^\alpha$$

where D is a constant [5], and α reads

$$\alpha = 1 - \frac{1}{d} \quad (7)$$

where d is the spatial dimension in which the described agglomeration occurs. The derived flux J is given by

$$J = -Dv^\alpha \frac{\partial}{\partial v} f - b(v) f \frac{d\Phi}{dv} \quad (8)$$

The obtained expression looks quite general, probably in spite of the power-law form (cluster–volume correlations) assumed in the Onsager coefficient $L(v)$ [9]. At this stage of presentation, let us anticipate this form by stating explicitly

$$D(v) = Dv^\alpha = k_B T b(v) \quad (9)$$

which also implies $b(v) \propto v^\alpha$. It means that both kinetic coefficients, namely that of diffusion as well as the one attributed to the drift term in Eq. (8), which for its own is

a kind of generalized Fick's law, are power-dependent on v . The term v^α represents the magnitude of the surface of a cluster (the contact area for an agglomeration event to take place), with the molecular cluster *per se* as the basic constituent of the agglomerate at the mesoscopic (molecular cluster-based) level of description [5].

After deriving the flux (8) in its explicit form, we have to apply it to a local continuity equation:

$$\frac{\partial}{\partial t} f(v, t) + \frac{\partial}{\partial v} J(v, t) = 0 \quad (10)$$

where v is the volume of a molecular cluster (a stochastic variable), $f(v, t)$ is the distribution function of the clusters at time t (having a meaning of the number density [11]), that means, $f(v, t)dv$ is a relative number of clusters of a size taken from the narrow volume interval $[v, v + dv]$. This way, we may arrive at a Fokker–Planck–Kolmogorov (FPK)-type equation that governs the agglomeration dynamics [5, 10, 11].

It is instructive to transform the local partial differential equation (PDE) formulation of the matter agglomeration into its possibly simple functional representation, abbreviated for further use by F -representation [12]. For doing it, let us state the matter flux, (8), in the following form

$$J(v, t) = -(B(v) \frac{\delta F(f)}{\delta f(v, t)} + \beta D(v) \frac{\partial}{\partial v} \frac{\delta F(f)}{\delta f(v, t)}) \quad (11)$$

where $B(v) = b(v)d\Phi(v)/dv$, and $\beta = 1/(k_B T)$ is the so-called inverse thermal energy. Here $\delta F(f)/\delta f(v, t)$ stands for the functional derivative, and the free-energy functional $F(f)$ is as follows:

$$F(f) = \frac{1}{2} f(v, t) \int K(v - v') f(v', t) dv dv' \quad (12)$$

If one takes the kernel K , $K(v - v') = \delta(v - v')$ (applying the delta Dirac distribution $\delta(v - v')$), i.e. when the “instantaneous” inter-cluster interaction is switched on, one provides

$$F(f) = \frac{1}{2} (f(v, t))^2 \quad (13)$$

which because of the power 2 in the equality obtained, suggests unambiguously the pairwise (binary) interactions between clusters, as is, for example, assumed in van der Waals (real) gases between the gas molecules within the framework of a mean-field description. In general, it is accepted for Lennard–Jones potential-driven systems, the class of which is quite broad. Notice, that in such a simple case just described, the energy functional $F(f)$ can be set to be zero in both ends of the phase space $v \in [0, \infty]$ because the standard and physically justified boundary conditions (bcs) to be obeyed,

are: $f(v = 0, t) = f(v = \infty, t) = 0$ [11]. They are consistent with the natural mnet bcs that require the matter flux must vanish in both ends mentioned, too. This, in turn, is very consistent with the well-known Kramers' picture of the stochastic process with a single activation barrier (see [8], and refs. therein). Such a picture is typically offered in terms of the FPK dynamics but may also be proposed in terms of the free-energy functional representation, which is actually the case presented here.

Now, the chemical potential reads

$$\mu = \frac{1}{2} \beta \ln \frac{F(f)}{F_{eq}(f)} \quad (14)$$

i.e., it is recovered in a Boltzmann-type (logarithmic) form, whereby

$$F_{eq}(f) = \frac{1}{2} f_{eq}^2 \quad (15)$$

where $f_{eq} = \exp(-\beta\Phi)$, well within the accuracy of a constant pre-factor [5]. Note that a pairwise interaction between clusters is still present when looking at Eq. (15). Moreover, note that if $K(v - v') \neq \tilde{\alpha}(v - v')$ were chosen, one would likely be able to model more complex interactions between clusters, which is usually of very interest to biological systems, such as protein aggregations under various physicochemical contexts [4]. The activity of the agglomerating system reads $a = \exp(\beta\Phi)$, this way reproducing the form of Eq. (3), where finally $f_{eq} = 1/a$ is required.

Both above kinetic-thermodynamic descriptions of the soft-matter agglomeration, the PDE-based of FPK type as well as that of F -functional representation, with the free-energy non-monotonous landscape staying behind it, enable one to proceed further toward getting its fluctuation-influenced characteristics as well as to differentiate between their principal forms, being matter-packing dependent (CP and LP), and depending mostly upon the fluctuation-influenced behaviour as well as upon a certain temperature-caused change of connectivity between clusters of which the material agglomerate is being made [5, 10]. Some d -dimensional considerations, where typically $d = 1, 2, 3$ [5], complete the overall comprehensive picture of various soft-matter clusterings.

3. Volume fluctuations under two different phase-state conditions. When late-stage matter agglomeration demands its mechanical response?

Herein, we would like to describe the matter agglomeration in a viscoelastic matrix. Our description rests on the observation that it is realized by more or less vigorous volume fluctuations of the clusters constituting the agglomerate. Though the flow of matter, in contrast to the following section, is not provided by means of the velocity gradient (Newton's law), resulting in a drift, nevertheless, the drift term is present

in the current, see Eq. (8), thus it is generically present in the system. Moreover, the driving force of the process as a whole, which is typically the free energy decrease (also, the CP agglomeration is specifically driven by capillary forces), superimposes a directional matter flow on the matter-agglomerating Potts-type system under study [11]. The direction, however, cannot be globally viewed as, say, a line in the space, but one may think of a natural course of the process; locally, one might, of course, identify some geometrical directions. The origin of more vigorous volume fluctuations, quantified by the reduced variance given below, can primarily be attributed to some thermal excitement of the soft-matter system. This is because the system is entropic, which by the way stands for the main assumption of our mnet-involving formalism. A certain inflow or outflow of thermal energy submitted to the system, may simply cause either a disconnectivity or connectivity of the clusters, thus changing the overall inter-cluster space amongst them. A second physical set-up to which the volume fluctuations can be assigned is the interaction map within the emerging agglomerate. This interaction map is related to the degrees of freedom the system exhibits, or explores, rather. They, in turn, can be estimated somehow by realizing that they are “better viewed” in higher dimensional spaces, in the sense, that a $d = 3$ space has usually more degrees of freedom than its two-dimensional counterpart can have.

As has been suggested above, the fluctuations $\sigma^2(t)$ can be different in different systems. In our case, if the LP agglomerations of loosely packed clusters emerge in the course of time t , they are evaluated to obey a power law, namely

$$\sigma_{LP}^2(t) \propto t^{1/(d+1)} \quad (16)$$

whereas the CP-counterpart is related to the above by

$$\sigma_{CP}^2(t) \propto \sigma_{LP}^2(t)^d \quad (17)$$

i.e., they proceed in a much more vigorous way, mostly because of the CP agglomerates being denser than the LP flocks [5]; note, that $\sigma^2(t)$ are defined by the reduced variance in a standard way

$$\sigma^2(t) = \frac{\langle v^2(t) \rangle - \langle v^1(t) \rangle^2}{\langle v^1(t) \rangle^2} \quad (18)$$

where, in turn, the central moments take on a standard form, namely

$$\langle v^n(t) \rangle = \int_0^\infty v^n f(v, t) dv$$

For the LP agglomeration in the long-time limit one obtains [5]

$$\langle v^n(t) \rangle \propto t^{[(n-1)+\alpha]/(2-\alpha)}, \quad n = 0, 1, 2 \quad (19)$$

whereas (under the same late-stage conditions) for CP agglomerations one appreciates another power law [5]

$$\langle v^n(t) \rangle \propto t^{(n-1)/(2-\alpha)}, \quad n = 0, 1, 2 \quad (20)$$

From the above it is then seen that our fluctuation-driven agglomeration, being a stochastic process [10], is mostly governed by power laws. Thus, and so described, it appears to be a scale-free process, since the algebraic relation such as $\omega(x) \propto x^\varepsilon$ is preserved under any arbitrary scale x change, such as $x \rightarrow \lambda x$ for any real and nonzero scaling factor λ , and for an arbitrary power-type function ω , with exponent ε , which can be, for example, σ^2 defined above. This can be viewed as a signature of the announced (see Introduction) emergent behaviour of the matter-agglomerating system.

Next, if such an eruption of power laws is naturally present in the system (see present as well as preceding section), let us proceed further along these lines. Namely, bearing in mind that we pretend to model agglomeration in a viscoelastic milieu, let us propose a coupling of the late-stage growing mode to some mechanical relaxation one [5]. If such a coupling existed, we would prefer to call it a synchronous mode of the late-stage (meaning: typically, very slow) agglomeration. This mode emerges when the LP agglomeration is switched on for the first time, typically by adequately increasing T . It can be represented by the approximate formula:

$$\sigma_{QY} \approx \sigma^{-1} \quad (21)$$

thus imposing that the quasi-yield stress σ_{QY} , emerging in the agglomerate is almost entirely due to the matter fluctuations in the system. In other words, the fluctuations in soft-matter system may also cause a small plastic effect, especially in the nanometre scale. For further argumentation accompanying the conjecture (21), one is encouraged to look into [5]. From the most general point of view, we opt for Eq. (21) since it supports very much the celebrated emergent behaviour [13], called by some researchers the middle way, i.e. the way of appreciation for mesoscopic matter organization, which is, by the way, well-described by mnet formalism proposed by the present study. A few other examples of mesoscopic systems successfully studied by mnet one can find in [14–16]. They mostly emphasize the so-called slow relaxation (ageing) effect, and possible variations of temperature with time, $T(t)$, often observed in colloidal as well as some granular, i.e. rheologically nontrivial [1] systems. It inevitably leads to an interesting temporal behaviour of the kinetic coefficients, e.g. those involved in Eq. (8). This can be of special interest for the LP agglomeration for which only one kinetic coefficient is of importance, since the drift term in Eq. (8) can be washed out. This is $D(v)$ that can be “renormalized” to some $D(v, t)$ either in a phenomenological [17] or in some more systematic, and therefore advised, way to follow. In particular, in [18] the presence of memory effects in FPK non-Markovian dynamics has been treated by means of mnet-involving formalism, where the corresponding Onsager coefficients [9] were found in terms of generalized regression laws that incorporate moments of the probability distribution higher than the second one.

The above conjecture, Eq. (21), yields slower than exponential, herein algebraic temporal behaviour

$$\sigma_{QY}(t) \propto t^{-1/(a(d+1))}, \quad t \gg 1 \quad (22)$$

It is assumed that $1/a$ is a system-dependent constant, typically close to one half, i.e. to the characteristic Hall–Petch exponent [19], see below. The constant characterizes somehow quantitatively the strengthening mechanism of the material output viz. soft-matter object. Moreover, it is worth realizing that Eq. (21) offers an inter-connecting relationship between a “macroscopic” quantity, here σ_{QY} , and its clearly microscopic *alter ego*, namely σ^2 , which is undoubtedly in the spirit of the Onsager’s regression hypothesis, though a more precise argumentation must certainly follow such an assertion [9].

Following this idea, now we will outline a quasi-phenomenological argumentation which shows that the viscoelastic milieu is responsible for memory effects similar to those shown, for example, in Eqs. (20) and (22). In this approximation, the manifestation of the viscoelastic and, in general, non-Newtonian effects (which will be analyzed in detail in the following section) can be characterized through the time dependence of the kinetic coefficient $D(v,t)$, which may, in general, be expressed through the relation

$$D(v,t) = \beta^{-1} \mu(t) b_0 v^\alpha \quad (23)$$

where $\mu(t)$, to be not confused with that of Eq. (7), has the dimension of inverse of time and b_0 accounts for the correct dimension in the resulting FPK equation

$$\frac{\partial}{\partial t} f(v,t) = \frac{\partial}{\partial v} \left[\beta^{-1} \mu(t) b_0 v^\alpha \frac{\partial}{\partial v} f \right] \quad (24)$$

which was obtained by assuming $T \gg T_{th}$, where T_{th} stands for a temperature value above which the LP agglomeration occurs [5], and by substituting Eq. (8) for (10) after using (9). Notice that $D(v,t)$ is precisely the corresponding Onsager coefficient entering the linear law (8); for a specific form of $D(v,t)$, characteristic of a biopolymer CP agglomeration of spherulitic type, taking place in some fluctuating environment, one is encouraged to see [17]. To sketch how the power-law behaviour of the moments of $f(v,t)$ arise according with this model, let us consider a simple case in which the solution of Eq. (24) can be splitted into the product $f(v,t) = g(t)h(v)$. Avoiding the details of the calculations (see, e.g., [20]), a little thought shows that, even in the simple case, the behaviour of the time dependent part $g(t)$ is determined by the properties of the viscoelastic milieu as follows

$$\frac{d}{dt} \ln g(t) = -c_0 \mu(t) \quad (25)$$

where c_0 is a constant arising from the variable separation. At the late-stage of growing, characterized by the slow relaxation of the system, the dissipation rate of the system depends, in general, on the “age” of the system and can be well described in the form of

$$\mu(t) \propto \frac{\xi}{t_0} \left(\frac{t_0}{t} \right)^{\delta+1}$$

where ξ is a constant and the exponent δ characterizes mean viscoelastic properties of the medium, and may depend, in general, on the size of the molecular clusters. Here, t_0 is the initial time measured. This dependence of $\mu(t)$ can, in principle, be calculated by analyzing the elastic properties of the background medium as a continuum; see, for example, Ref. [21], where this idea has been implemented to describe anomalous transport in an intracellular medium. Applying this relation to Eq. (25), one obtains that

$$g(t) \propto e^{\xi c_0 / \delta (t_0/t)^\delta}$$

i.e. it is here in the form of a stretched exponential. This relation, valid for a sufficiently wide range of times, can, for very long times $t \gg t_0$, be expressed in a more convenient form by expanding the exponential up to first order in its argument, thus providing

$$g(t) \propto \frac{\xi c_0}{\delta} \left(\frac{t_0}{t} \right)^\delta + O(t^{-2\delta}) \quad (26)$$

This relation is directly related with the relaxation of the moments of the distribution as, for example, the reduced variance $\sigma(t)$, see above. In particular, for this function one obtains, without taking into account constants arising from averaging over the volume space, the relation $\sigma(t) \approx g(t)^{-1} - 1$, which can finally be expressed as

$$\sigma(t) \propto \frac{\delta}{\xi c_0} \left(\frac{t}{t_0} \right)^\delta \quad (27)$$

From this point of view, it is plausible to assume that during the slow stage of the dynamics of the system, there appears a coupling between the relaxation of the elastic stresses $\sigma_{QY}(t)$ and that related with the volume fluctuations, benchmarking both the CP and LP matter agglomeration, characterized by $\sigma(t)$. This coupling takes place because the viscoelastic properties of the medium have the same characteristic time scale $\mu(t)$. Thus, in similar but slightly different form as in Ref. [5], stress relaxation can be described through the following equation [22]:

$$\frac{d\sigma_{QY}(t)}{dt} + \mu(t)\sigma_{QY} = 0$$

for another soft-matter scenario drawn, therein for describing the hydration kinetics of relaxing model lipid membranes. This equation can be obtained from the mnet-formalism by following a method similar to that followed in [14, 15]. Notice that by

integrating this equation and taking the long time approximation consistent with that to obtain Eq. (26), one arrives at the expression

$$\sigma_{QV}(t) \propto \left(\frac{t_0}{t} \right)^\delta \quad (28)$$

The last equation seems to give a solid basis for the before mentioned conjecture given in (21).

4. Soft agglomerate in its *liquidus* and *solidus* as well as intermediate phase-state limits

To get a more comprehensive picture of the soft-matter agglomeration, let us explore it further taking into account its non-Newtonian character, again well described by the Ostwald–de Waele laws of power type, interconnecting the shear stress with the shear rate [23]. From the below stated it will be seen that the agglomeration under flow, both of CP and LP type, somehow interpolates between two phase-state limits, accordingly to LP and CP agglomerations to be named: *liquidus* and *solidus* limits. Note that the mostly nonlinear viscoelastic properties of the agglomerating system are pronounced here even more.

The nonlinear flow curve of CP and LP agglomerates of deformable droplets, rigid particles, and flexible polymer chains dispersed in a viscous medium exhibit a typical power-law behaviour, i. e. the shear viscosity, $\eta = \sigma_h / \dot{\gamma}$, is a non-linear function of shear rate $\dot{\gamma}$, where σ_h is the shear stress measured in a homogeneous shear flow $\dot{\gamma}$.

The non-linear flow curve of the agglomerating system is expected to have three regimes being characterized by different shapes $\eta(\dot{\gamma})$. The low shear rate regime with a Newtonian plateau for the LP agglomerates and an infinite shear viscosity for the CP agglomerates, an intermediate regime, and a high shear rate regime. In what follows the three regimes will be explained and interpreted from a physical point of view: In the low shear rate regime the structural forces (e.g. Brownian forces) are stronger than the orienting forces due to the externally imposed flow. Consequently, we do not observe flow-induced structural changes and the shear viscosity is constant, η_0 . The infinite shear viscosity of the CP agglomerates is due to the constant yield stress, τ_0 . This means that the CP agglomerates behave as a rigid body under application of a small shear force and thus the CP agglomerates do not flow.

According to the Hall–Petch relation the yield stress τ_0 is given as

$$\tau_0 = K_2 d^{-1/2} + K_1 \quad (29)$$

where K_1 and K_2 are material-dependent constants and d , to be not confused with that of Eq. (7), is proportional to the average radius of the clusters (grains). Note that the

average radius d is taken as a scalar parameter and thus also the Hall–Petch relation does not account for anisotropic stresses. (In the same vein, the stresses arising during the late-stage matter agglomeration, when no special “macroscopic” matter flow is detected, are involved as zero-rank tensors in the description offered [5].) Moreover, note that the above equation is mostly expected to hold only for CP agglomerates which exhibit a yield behaviour. For LP agglomerates, the stress tensor is isotropic with its trace corresponding to three times the hydrostatic pressure. It would be interesting to adopt the theoretical framework used in [1] to derive a set of dynamic equations for a complex material with yield stress which takes into account anisotropic material behaviour in shear and elongational deformation.

In the intermediate shear rate regime of the non-linear flow curve, the hydrodynamic (or viscous) forces are of the same order of magnitude as the structural (e.g. Brownian) forces. Now one observes an orientation and deformation of the LP agglomerates which correlates with a decrease of the shear viscosity. For the CP agglomerates the flow stresses exceed the yield stress τ_0 and the material begins to flow. Also for the CP agglomerates one can observe a deformation and orientation of the microstructure which leads to a decrease of the shear viscosity. The reason for the decrease of the shear viscosity is that the microstructural components orient in flow thus lowering their flow resistance. This is seen as a decrease of the shear viscosity.

In the high shear rate regime, it is possible to observe a second Newtonian plateau and a shear thickening regime, i.e. a small increase of the shear viscosity for the CP as well as the LP agglomerates. The microstructural interpretation of this behaviour is the formation of aggregates in a high shear flow which increase the flow resistance and which correlates with the increase of the shear viscosity.

The qualitative behaviour described above is the most important non-Newtonian flow behaviour of CP and LP agglomerates [24]. Note that the decrease of the Newtonian viscosity in the intermediate shear rate regime can be several orders of magnitude which is very important for the processing of these fluids in chemical or food industries. However, the shear thinning behaviour displayed in a figure in [24], in general, correlates with other non-Newtonian effects such as normal stresses due to elastic material behaviour. These non-Newtonian effects are normal stresses in homogeneous shear flows. Physically this means, e.g., that in order to maintain steady shear flow in a non-Newtonian liquid one needs not only a shear stress, σ_{η} , but also normal stresses, e.g. acting perpendicular to the confining plates of the liquids. Further non-Newtonian effects can be observed in time-dependent shearing flows, e.g. in start-up or cessation of steady shearing flow. In such flows, one observes a transient behaviour of the flow stresses (i.e., shear stresses and normal stress differences).

As for some crude analogies between fluctuation-driven and flow-driven matter agglomeration, one may classify them both as activated processes, underlying to some extent the mentioned Kramers’ picture, where the energy barrier is permanently surmounted. In both cases, i.e. in the random walk theory [5, 10, 11] as well as in the Ostwald–de Waele dynamic relations for the flow [23], qualitatively the same power-

law (ultimately, also temporal) behaviour may appear: Normal diffusion (random walk) would be equivalent to Newtonian behaviour of the system, whereas the non-Newtonian behaviour would correspond to the anomalous diffusion (random walk), being either subdiffusion (slow or damped motion) or superdiffusion (vigorous or turbulent motion). This way, the analogy is completed, at least from the qualitative viewpoint.

5. Closing address

Let us start with a motto which itself characterizes well the basic motivation of our study. This motto reads: It is not enough to break up matter into its most fundamental pieces, and then to reassemble them, just to gain some, even poor, understanding about the output (matter) assemblage, see Sec. 1. According to it, we are of the opinion that the offered mnet-based description is a good tool [5, 6, 10, 14, 15, 18] for dealing with complex matter agglomerations, because for many important purposes, studying and comprehending matter organizations is sufficient just at the mesoscopic (molecular-cluster) based level of description.

For example, in protein aggregation and crystal growth ([4] and refs. therein), efforts of many researchers have been distributed over controlling really important details of the process. As a consequence, this led to (almost) full understanding of some specific (say, selected for special purpose) protein aggregations, postponing, unfortunately, to some, sometimes quite large extent, principia of matter organization, and trying to replace them by computer simulations [25]. It is a necessary way, of course, but it should be complemented by some investigations on the principia that have to go in parallel with those detailed studies. In particular, in authors' very individual (and specific) opinion there is a need to enlighten unambiguously how the speed of the crystal, being attempted to maintain by an experimenter at a constant value, which is the most stable hydrodynamic mode of the process, will influence the obtained structural output of the non-Kossel type, emerging from such an entropic environment [16].

When advocating for the mnet-based modelling, one is obliged to answer quite a basic question: What do we loose and what do we gain while doing so? Certainly, we cannot take control over most of the microscopic quantities of any agglomeration that we are dealing with – this is without question. But we may still have, just in a parametric manner, quite many of them, see [16]. Moreover, we are capable of looking into key microscopic details, thus ascertaining quite univocally, when for example the local curvatures of the end product, modifying significantly the surface-tension conditions, see Fig. 1, may really change the overall system behaviour [16]. This even enables one to first differentiate between nano- and micro-agglomerations of soft-matter (see [5, 25], and refs. therein).

What do we gain by applying mnet? Above all, a quite simple (but by no means exhaustive!) insight into the above underscored principia of matter organization [10] just in an entropic environment; also, a tractable description, preferentially in terms of

the FPK framework, or as freshly included in Sec. 2, by means of the energy-functional method. The limitations of applying mnet have been explicitly stated for the first time in [8], though many studies along these lines appeared before, giving the final address ([7], and refs. therein).

A careful reader will also notice that high appreciation is given here to almost omnipresent power laws that arise from the proposed modelling. This is, for sure, very consistent with the emergent (ageing-dependent) behaviour assigned in last years to soft-matter systems [3, 4, 13]. The question is, however: How far may such idealization go?

Concluding this section, let us mention that, in contrast with the material presented in our previous study [5], we did not include any considerations on d -dimensional as well as on chaotic behaviour of the model soft-matter system. They are really interesting per se. For example, the picture drawn under chaotic vs. regular matter-organization regime is consistently defined by the type of definition of Sinai–Kolmogorov (fractal) entropy which corresponds directly to the aggregation rate in the space of Euclidean dimension d . (Some signatures of the Farey’s three in the d -dimensional construction of the model can also be announced [26], according to the below mentioned Bethe-lattice landmarks, characteristic of model gelation.) This rate, in turn, is uniquely defined based on the volume fluctuation σ^2 derived in Sect. 3.

To sum up, and according to what has been obtained in [5], we can list even more: (i) an algebraic decay in time of the internal stresses propagating along the inter-cluster spaces (depletion zones) of lower viscosity has to be underscored as an interesting phenomenon revealed; (ii) a gelling-type effect with microstructural constraints, due to the critical relaxation exponent of the process, that bears a Flory–Stockmayer-type, though d -dependent, mean-field approximation to gelling systems, clearly of the form of the critical percolation probability, such as $p(d) = 1/(q(d) - 1)$, where $q(d) = 2(d + 1) + 1$, is possible to obtain by the present mnet model; (iii) an interesting behaviour, pertaining to a way of developing the two basic dynamic constituents of the process, i.e. late-time matter migration and mechanical relaxation [5], namely, that the rates of both of them obey the mean-harmonicity rule in dimension d , resembling partially the case of transient coagulation in aerosols and/or hydrosols [27], such as biopolymers dispersed in water solution, interpenetrating between the so-called free-molecule and continuum levels of matter microstructural organization, can be seen; the synchronous mode, because of the emergent behaviour, might resemble to some reasonable extent a *SOC* (self-organized criticality) phenomenon [28], which goes in the space d in a common mean-harmonic [5] and continuum-percolative [11] way, showing up similarity relations both in cluster-size space and time domains [29].

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