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 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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28   The realization that soft matter contains innumerable examples of generalized
29 elasticity, symmetry breaking, and many fluctuating degrees of freedom has re-opened
30 classical fields of physics such as fluids (now frequently referred to as rheology [1],
31 with non-Newtonian and structured-media aspects) and elasticity (membranes, fila-
32 ments, and anisotropic networks are all important and common aspects) for new theo-
33 retical and experimental investigations. For both generalities and subtleties on soft
34 matter, and the physics one may play on it, let us encourage a reader to consult Ref.
35 [2], in which two major features of any soft-matter (complex-fluid) system have been
36 emphasized, namely, its complexity and viscoelasticity. For a more recent review, in
37 which weak connectivity and entropic interactions as the major features, distinguish-
38 ing polyatomic (macromolecular) soft-matter systems from their non-polyatomic
39 (small-molecule) counterparts, have been underlined, see [3].
40   As has been argued very recently, complexity might be a key, though still elusive
41 and poorly defined, feature of such systems, being responsible for their *emergent be-*
42 *haviour*, which eventually leads to a multitude of dynamic mesostructures, appearing
43 while their parametric zone is appropriately scanned [4] for reviewing the subject.
44 Emergent behaviour is usually attributed to a physical system about which one may
45 firmly say that its higher-level properties are not readily predictable from a detailed
46 knowledge of its lower-level properties, such as those coming from the material sub-
47 units (atoms; molecules) alone. In a very real sense [4], emergence represents a de-
48 mocracy of physical scale: no size or time scale is more fundamental than any other.
49 For some theoretical physicists such an assertion may imply: the renormalization-
50 group, and in particular, self-similarity ideas are somehow hidden behind such
51 a claim.
52   In this study, we would like to focus on one specific example of what one may, af-
53 ter seeing the argumentation developed in the paper, call the emergence in complex
54 late-stage (model) matter agglomeration. The emergence discussed in our matter-
55 agglomeration example relies on detection and exploration of power laws that, being
56 scale-free, by definition do not distinguish any physical scale the properties of which
57 they are pretending to describe. In the presented model, we claim that the complexity
58 arose from a coupling of two basic modes of the slowly evolving model soft-matter
59 system: a certain growing mode with some mechanical-relaxation one, presumed,
60 however, that a (mechanical) stress field is generated within the material agglomerate
61 also under its late-stage growth. Some examples of such systems, in particular bio-
62 molecular and colloidal assemblages, have been contained in [5].
63   The paper is structured as follows. In the next section, we have made a quick tour
64 toward the model soft-matter agglomeration at a mesoscopic level, paying special
65 attention to its basic notions and some landmark features (Fig. 1) which have not been
66 reported. In Section 3, we have looked at volume fluctuations in an agglomerate under
67 two different phase-state conditions, attributed to densely as well as loosely packed
68 matter assemblages, abbreviated by CP and LP matter agglomerations, respectively,
69 concentrating mainly on the so-called synchronous (coupling) mode [5], also trying to
70 answer the question: When late-stage matter agglomeration demands its mechanical

71 response? In Section 4, we have elaborated the CP and LP packing states even more,
72 and looked more carefully at the soft agglomerate in its *liquidus* and *solidus* phase
73 -state limits. The closing address, presented in sec. 5, will summarize what we have
74 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)

NANO "David"

MICRO "Goliath"
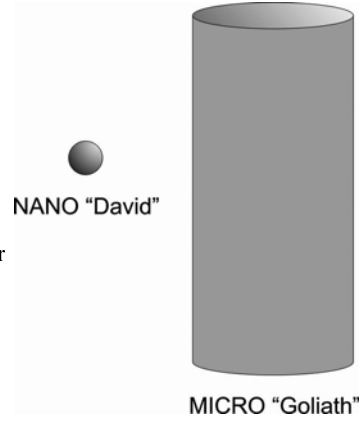
2. Quick tour toward model soft-matter
75
76 ## agglomeration at a mesoscopic level

77   There is a consequent and unambiguous method of deriving the main kinetic equa-
78 tion for the overall model matter agglomeration being applicable to soft-matter ag-
79 glomeration. The method is called mesoscopic nonequilibrium thermodynamics, mnet
80 [7, 8]. It starts with the Gibbs equation which defines the variations of entropy [9, 10]

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

81

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

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

85

86 where a is the activity coefficient, k_B is the Boltzmann constant, and $k_B T$ stands for the
87 thermal energy. Next, a is given in terms of a thermodynamic potential, denoted by
88 $\Phi \equiv \Phi(v)$. Thus, a reads now [8, 10]

$$a = \exp\left(\Phi/k_B T\right) \qquad (3)$$

89

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

93
$$\sigma_E = -\frac{1}{T} J \frac{\partial \mu}{\partial v} \tag{4}$$

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

95
$$J = -\frac{1}{T} L(v) \frac{\partial \mu}{\partial v} \tag{5}$$

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

98
$$J(v) = -\frac{1}{T} \int dv' L(v,v') \frac{\partial \mu}{\partial v'}$$

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

100
$$J = -\frac{1}{Tf} L(v) \left[k_B T \frac{\partial f}{\partial v} + f \frac{d\Phi}{dv} \right] \tag{6}$$

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

102
$$b(v) = \frac{1}{Tf} L(v) = \frac{D}{k_B T} v^{\alpha} \tag{7}$$

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

104
$$\alpha = 1 - \frac{1}{d} \tag{7}$$

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

107
$$J = -Dv^{\alpha} \frac{\partial}{\partial v} f - b(v) f \frac{d}{dv} \Phi \tag{8}$$

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

111
$$D(v) = Dv^{\alpha} = k_B T b(v) \tag{9}$$

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

114 a kind of generalized Fick's law, are power-dependent on v. The term v^{α} represents
115 the magnitude of the surface of a cluster (the contact area for an agglomeration event
116 to take place), with the molecular cluster *per se* as the basic constituent of the ag-
117 glomerate at the mesoscopic (molecular cluster-based) level of description [5].
118   After deriving the flux (8) in its explicit form, we have to apply it to a local conti-
119 nuity equation:

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

121 where v is the volume of a molecular cluster (a stochastic variable), $f(v,t)$ is the distri-
122 bution function of the clusters at time t (having a meaning of the number density
123 [11]), that means, $f(v,t)dv$ is a relative number of clusters of a size taken from the narrow
124 volume interval $[v, v + dv]$. This way, we may arrive at a Fokker–Planck–Kolmogorov
125 (FPK)-type equation that governs the agglomeration dynamics [5, 10, 11].
126   It is instructive to transform the local partial differential equation (PDE) formula-
127 tion of the matter agglomeration into its possibly simple functional representation,
128 abbreviated for further use by F-representation [12]. For doing it, let us state the mat-
129 ter flux, (8), in the following form

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

131 where $B(v) = b(v)d\Phi(v)/dv$, and $\beta = 1/(k_B T)$ is the so-called inverse thermal energy.
132 Here $\delta F(f)/\delta f(v,t)$ stands for the functional derivative, and the free-energy functional
133 $F(f)$ is as follows:

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

135 If one takes the kernel K, $K(v - v') = \delta(v - v')$ (applying the delta Dirac distribution
136 $\delta(v - v')$), i.e. when the "instantaneous" inter-cluster interaction is switched on, one
137 provides

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

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

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

153
$$\mu = \frac{1}{2}\beta \ln \frac{F(f)}{F_{eq}(f)} \tag{14}$$

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

155
$$F_{eq}(f) = \frac{1}{2}f_{eq}^2 \tag{15}$$

156   where $f_{eq} = \exp(-\beta\Phi)$, well within the accuracy of a constant pre-factor [5]. Note that
157   a pairwise interaction between clusters is still present when looking at Eq. (15). More-
158   over, note that if $K(v - v') \neq \delta(v - v')$ were chosen, one would likely be able to model
159   more complex interactions between clusters, which is usually of very interest to bio-
160   logical systems, such as protein aggregations under various physicochemical contexts
161   [4]. The activity of the agglomerating system reads $a = \exp(\beta\Phi)$, this way reproducing
162   the form of Eq. (3), where finally $f_{eq} = 1/a$ is required.
163   Both above kinetic-thermodynamic descriptions of the soft-matter agglomeration, the
164   PDE-based of FPK type as well as that of F-functional representation, with the free-energy
165   non-monotonous landscape staying behind it, enable one to proceed further toward getting
166   its fluctuation-influenced characteristics as well as to differentiate between their principal
167   forms, being matter-packing dependent (CP and LP), and depending mostly upon the fluc-
168   tuation-influenced behaviour as well as upon a certain temperature-caused change of con-
169   nectivity between clusters of which the material agglomarate is being made [5, 10]. Some
170   d-dimensional considerations, where typically $d = 1, 2, 3$ [5], complete the overall compre-
171   hensive picture of various soft-matter clusterings.

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

175   Herein, we would like to describe the matter agglomeration in a viscoelastic ma-
176   trix. Our description rests on the observation that it is realized by more or less vigor-
177   ous volume fluctuations of the clusters constituting the agglomerate. Though the flow
178   of matter, in contrast to the following section, is not provided by means of the veloc-
179   ity gradient (Newton's law), resulting in a drift, nevertheless, the drift term is present

180 in the current, see Eq. (8), thus it is generically present in the system. Moreover, the
181 driving force of the process as a whole, which is typically the free energy decrease
182 (also, the CP agglomeration is specifically driven by capillary forces), superimposes
183 a directional matter flow on the matter-agglomerating Potts-type system under study
184 [11]. The direction, however, cannot be globally viewed as, say, a line in the space,
185 but one may think of a natural course of the process; locally, one might, of course,
186 identify some geometrical directions. The origin of more vigorous volume fluctua-
187 tions, quantified by the reduced variance given below, can primarily be attributed to
188 some thermal excitement of the soft-matter system. This is because the system is en-
189 tropic, which by the way stands for the main assumption of our mnet-involving for-
190 malism. A certain inflow or outflow of thermal energy submitted to the system, may
191 simply cause either a disconnectivity or connectivity of the clusters, thus changing the
192 overall inter-cluster space amongst them. A second physical set-up to which the vol-
193 ume fluctuations can be assigned is the interaction map within the emerging agglom-
194 erate. This interaction map is related to the degrees of freedom the system exhibits, or
195 explores, rather. They, in turn, can be estimated somehow by realizing that they are
196 "better viewed" in higher dimensional spaces, in the sense, that a $d = 3$ space has usu-
197 ally more degrees of freedom than its two-dimensional counterpart can have.

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

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

202 whereas the CP-counterpart is related to the above by

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

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

$$\sigma^2(t) = \frac{<v^2(t)> - <v^1(t)>^2}{<v^1(t)>^2} \tag{18}$$

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

$$<v^n(t)> = \int_0^\infty v^n f(v,t)dv$$

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

$$<v^n(t)> \propto t^{[(n-1)+\alpha]/(2-\alpha)}, \qquad n = 0,\ 1,\ 2 \tag{19}$$

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

214
$$< v^n(t) > \propto t^{(n-1)/(2-\alpha)}, \qquad n = 0, 1, 2 \tag{20}$$

215   From the above it is then seen that our fluctuation-driven agglomeration, being a
216   stochastic process [10], is mostly governed by power laws. Thus, and so described, it
217   appears to be a scale-free process, since the algebraic relation such as $\omega(x) \propto x^\varepsilon$ is
218   preserved under any arbitrary scale x change, such as $x \to \lambda x$ for any real and nonzero
219   scaling factor λ, and for an arbitrary power-type function ω, with exponent ε, which
220   can be, for example, σ^2 defined above. This can be viewed as a signature of the an-
221   nounced (see Introduction) emergent behaviour of the matter-agglomerating system.
222   Next, if such an eruption of power laws is naturally present in the system (see pre-
223   sent as well as preceding section), let us proceed further along these lines. Namely,
224   bearing in mind that we pretend to model agglomeration in a viscoelastic milieu, let us
225   propose a coupling of the late-stage growing mode to some mechanical relaxation one
226   [5]. If such a coupling existed, we would prefer to call it a synchronous mode of the
227   late-stage (meaning: typically, very slow) agglomeration. This mode emerges when
228   the LP agglomeration is switched on for the first time, typically by adequately in-
229   creasing T. It can be represented by the approximate formula:

230
$$\sigma_{QY} \approx \sigma^{-1} \tag{21}$$

231   thus imposing that the quasi-yield stress σ_{QY}, emerging in the agglomerate is almost
232   entirely due to the matter fluctuations in the system. In other words, the fluctuations
233   in soft-matter system may also cause a small plastic effect, especially in the nano-
234   metre scale. For further argumentation accompanying the conjecture (21), one is en-
235   couraged to look into [5]. From the most general point of view, we opt for Eq. (21)
236   since it supports very much the celebrated emergent behaviour [13], called by some
237   researchers the middle may, i.e. the way of appreciation for mesoscopic matter or-
238   ganization, which is, by the way, well-described by mnet formalism proposed by the
239   present study. A few other examples of mesoscopic systems successfully studied by
240   mnet one can find in [14–16]: They mostly emphasize the so-called slow relaxation
241   (ageing) effect, and possible variations of temperature with time, $T(t)$, often observed
242   in colloidal as well as some granular, i.e. rheologically nontrivial [1] systems. It inevi-
243   tably leads to an interesting temporal behaviour of the kinetic coefficients, e.g. those
244   involved in Eq. (8). This can be of special interest for the LP agglomeration for which
245   only one kinetic coefficient is of importance, since the drift term in Eq. (8)) can be
246   washed out. This is $D(v)$ that can be "renormalized" to some $D(v,t)$ either in a phe-
247   nomenological [17] or in some more systematic, and therefore advised, way to follow.
248   In particular, in [18] the presence of memory effects in FPK non-Markovian dynamics
249   has been treated by means of mnet-involving formalism, where the corresponding
250   Onsager coefficients [9] were found in terms of generalized regression laws that in-
251   corporate moments of the probability distribution higher than the second one.
252   The above conjecture, Eq. (21), yields slower than exponential, herein algebraic
253   temporal behaviour

254
$$\sigma_{QY}(t) \propto t^{-1/(a(d+1))}, \qquad t \gg 1 \tag{22}$$

255 It is assumed that $1/a$ is a system-dependent constant, typically close to one half, i.e. to the
256 characteristic Hall–Petch exponent [19], see below. The constant characterizes somehow
257 quantitatively the strengthening mechanism of the material output viz. soft-matter object.
258 Moreover, it is worth realizing that Eq. (21) offers an inter-connecting relationship be-
259 tween a "macroscopic" quantity, here σ_{QY}, and its clearly microscopic *alter ego*, namely σ^2,
260 which is undoubtedly in the spirit of the Onsager's regression hypothesis, though a more
261 precise argumentation must certainly follow such an assertion [9].
262   Following this idea, now we will outline a quasi-phenomenological argumentation
263 which shows that the viscoelastic milieu is responsible for memory effects similar to
264 those shown, for example, in Eqs. (20) and (22). In this approximation, the manifesta-
265 tion of the viscoelastic and, in general, non-Newtonian effects (which will be ana-
266 lyzed in detail in the following section) can be characterized through the time depend-
267 ence of the kinetic coefficient $D(v,t)$, which may, in general, be expressed through the
268 relation

269
$$D(v,t) = \beta^{-1}\mu(t)b_0 v^\alpha \tag{23}$$

270 where $\mu(t)$ has the dimension of inverse of time and b_0 accounts for the correct dimen-
271 sion in the resulting FPK equation

272
$$\frac{\partial}{\partial t}f(v,t) = \frac{\partial}{\partial v}\left[\beta^{-1}\mu(t)b_0 v^\alpha \frac{\partial}{\partial v}f\right] \tag{24}$$

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

284
$$\frac{d}{dt}\ln g(t) = -c_0\mu(t) \tag{25}$$

285 where c_0 is a constant arising from the variable separation. At the late-stage of grow-
286 ing, characterized by the slow relaxation of the system, the dissipation rate of the sys-
287 tem depends, in general, on the "age" of the system and can be well described in the
288 form of

289
$$\mu(t) \propto \frac{\xi}{t_0}\left(\frac{t_0}{t}\right)^{\delta}$$

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

297
$$g(t) \propto e^{\xi c_0/\delta (t_0/t)^{\delta}}$$

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

302
$$g(t) \propto \frac{\xi c_0}{\delta}\left(\frac{t_0}{t}\right)^{\delta} + O\!\left(t^{-2\delta}\right) \qquad (26)$$

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

307
$$\sigma(t) \propto \frac{\delta}{\xi c_0}\left(\frac{t}{t_0}\right)^{\delta} \qquad (27)$$

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

315
$$\frac{d\sigma_{QY}(t)}{dt} + \mu(t)\sigma_{QY} = 0$$

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

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

321

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

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

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

324
325

326   To get a more comprehensive picture of the soft-matter agglomeration, let us ex-
327   plore it further taking into account its non-Newtonian character, again well described
328   by the Ostwald–de Waele laws of power type, interconnecting the shear stress with
329   the shear rate [23]. From the below stated it will be seen that the agglomeration under
330   flow, both of CP and LP type, somehow interpolates between two phase-state limits,
331   accordingly to LP and CP agglomerations to be named: *liquidus* and *solidus* limits.
332   Note that the mostly nonlinear viscoelastic properties of the agglomerating system are
333   pronounced here even more.
334   The nonlinear flow curve of CP and LP agglomerates of deformable droplets, rigid
335   particles, and flexible polymer chains dispersed in a viscous medium exhibit a typical
336   power-law behaviour, i. e. the shear viscosity, $\eta = \sigma_h/\dot{\gamma}$, is a non-linear function of
337   shear rate $\dot{\gamma}$, where σ_h is the shear stress measured in a homogeneous shear flow $\dot{\gamma}$.
338   The non-linear flow curve of the agglomerating system is expected to have three
339   regimes being characterized by different shapes $\eta(\dot{\gamma})$: The low shear rate regime with
340   a Newtonian plateau for the LP agglomerates and an infinite shear viscosity for the
341   CP agglomerates, an intermediate regime, and a high shear rate regime. In what fol-
342   lows the three regimes will be explained and interpreted from a physical point of
343   view: In the low shear rate regime the structural forces (e.g. Brownian forces) are
344   stronger than the orienting forces due to the externally imposed flow. Consequently,
345   we do not observe flow-induced structural changes and the shear viscosity is constant,
346   η_0. The infinite shear viscosity of the CP agglomerates is due to the constant yield
347   stress, τ_0. This means that the CP agglomerates behave as a rigid body under applica-
348   tion of a small shear force and thus the CP agglomerates do not flow.
349   According to the Hall–Petch relation the yield stress τ_0 is given as

350

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

351   where K_1 and K_2 are material-dependent constants and d is proportional to the average
352   radius of the clusters (grains). Note that the average radius d is taken as a scalar pa-

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

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

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

377   The qualitative behaviour described above is the most important non-Newtonian
378 flow behaviour of CP and LP agglomerates [24]. Note that the decrease of the Newto-
379 nian viscosity in the intermediate shear rate regime can be several orders of magnitude
380 which is very important for the processing of these fluids in chemical or food indus-
381 tries. However, the shear thinning behaviour displayed in a figure in [23], in general,
382 correlates with other non-Newtonian effects such as normal stresses due to elastic
383 material behaviour. These non-Newtonian effects are normal stresses in homogeneous
384 shear flows. Physically this means, e.g., that in order to maintain steady shear flow in
385 a non-Newtonian liquid one needs not only a shear stress, σ_h, but also normal stresses,
386 e.g. acting perpendicular to the confining plates of the liquids. Further non-Newtonian
387 effects can be observed in time-dependent shearing flows, e.g. in start-up or cessation
388 of steady shearing flow. In such flows, one observes a transient behaviour of the flow
389 stresses (i.e., shear stresses and normal stress differences).

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

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

5. Closing address

402　　　Let us start with a motto which itself characterizes well the basic motivation of our
403　study. This motto reads: It is not enough to breakeg matter into its most fundamental
404　pieces, and then to reassemble them, just to gain some, even poor, understanding
405　about the output (matter) assemblage, see Sec. 1. According to it, we are of the opin-
406　ion that the offered mnet-based description is a good tool [5, 6, 10, 14, 15, 18] for
407　dealing with complex matter agglomerations, because for many important purposes,
408　studying and comprehending matter organizations is sufficient just at the mesoscopic
409　(molecular-cluster) based level of description.
410　　　For example, in protein aggregation and crystal growth ([4] and refs. therein), efforts
411　of many researchers have been distributed over controlling really important details of
412　the process. As a consequence, this led to (almost) full understanding of some specific
413　(say, selected for special purpose) protein aggregations, postponing, unfortunately, to
414　some, sometimes quite large extent, principia of matter organization, and trying to re-
415　place them by computer simulations [25]. It is a necessary way, of course, but it should
416　be complemented by some investigations on the principia that have to go in parallel with
417　those detailed studies. In particular, in authors' very individual (and specific) opinion
418　there is a need to enlighten unambiguously how the speed of the crystal, being attempted
419　to maintain by an experimenter at a constant value, which is the most stable hydrody-
420　namic mode of the process, will influence the obtained structural output of the non-
421　Kossel type, emerging from such an entropic environment [25].
422　　　When advocating for the mnet-based modelling, one is obliged to answer quite
423　a basic question: What do we loose and what do we gain while doing so? Certainly,
424　we cannot take control over most of the microscopic quantities of any agglomeration
425　that we are dealing with – this is without question. But we may still have, just in a
426　parametric manner, quite many of them, see [25]. Moreover, we are capable of look-
427　ing into key microscopic details, thus ascertaining quite univocally, when for example
428　the local curvatures of the end product, modifying significantly the surface-tension
429　conditions, see Fig. 1, may really change the overall system behaviour [25]. This even
430　enables one to first differentiate between nano- and micro-agglomerations of soft-
431　matter (see [5, 6], and refs. therein).
432　　　What do we gain by applying mnet? Above all, a quite simple (but by no means
433　exhaustive!) insight into the above underscored principia of matter organization [10]
434　just in an entropic environment; also, a tractable description, preferentially in terms of

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

439   A careful reader will also notice that high appreciation is given here to almost om-
440   nipresent power laws that arise from the proposed modelling. This is, for sure, very
441   consistent with the emergent behaviour assigned in last years to soft-matter systems
442   [3, 4, 13]. The question is, however: How far may such idealization go?

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

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

References

[1] DRESSLER M., EDWARDS B.J., Rheol. Acta, 43 (2004), 257.

[2] DE GENNES P.G., *Nobel Prize Lecture on Soft Matter*, College de France, Paris, 1991.

[3] WITTEN T.A., Rev. Mod. Phys., 71 (1999), S367.

[4] COX D.L., PINES D., MRS Bulletin, 30 (2005), 425.

[5] GADOMSKI A., RUBÍ J.M., ŁUCZKA J., AUSLOOS M., Chem. Phys., 310 (2005), 153.

[6] GADOMSKI A., SIÓDMIAK J., SANTAMARÍA-HOLEK I., RUBÍ J.M., AUSLOOS M., Acta Phys. Pol. B, 36 (2005), 1001.

[7] REGUERA D., RUBÍ J.M., PÉREZ–MADRID A., J. Chem. Phys., 109 (1998), 5987.

[8] VILAR J.M.G Proc. Natl. Acad. Sci. USA, 98 (2001), 11081.

[9] ONSAGER L., Phys. Rev., 37 (1931), 405.

[10] RUBÍ J.M., GADOMSKI A., Physica A, 326 (2003), 333.

[11] GADOMSKI A., Physica A, 274 (1999), 325.

[12] GIACOMIN G., LEBOWITZ J.L., MARRA R., Nonlinearity, 13 (2000), 2143.

[13] LAUGHLIN R.B., PINES D., SCHMALIAN J., STOJKOVIC B.P., WOLYNES P., Proc. Natl. Acad. Sci. USA, 97 (2000), 32.

[14] SANTAMARÍA-HOLEK I., PÉREZ–MADRID A., RUBÍ J.M., J. Chem. Phys., 120 (2004), 2818.

[15] RUBÍ J.M., SANTAMARÍA-HOLEK I., PÉREZ–MADRID A., J. Phys. C: Cond. Matter., 16 (2004), S2047.

[16] FRANZ S., VIRASORO M.A., J. Phys. A: Math. Gen., 33 (2000), 861.

[17] GADOMSKI A., Chem. Phys. Lett., 258 (1996), 6.

[18] SANTAMARÍA-HOLEK I., RUBÍ J.M., Physica A, 326 (2003), 384.

[19] FRIEDMAN L.H, CHRZAN D.C., Phys. Rev. Lett., 81 (1998), 2715.

[20] NIEMIEC M., GADOMSKI A., ŁUCZKA J., Acta Phys. Pol. B, 32 (2001), 1513.

[21] LAU A.W.C. HOFFMANN B.D., DAVIES A., CROCKER J.C., LUBENSKY T.C., Phys. Rev. Lett., 91 (2003), 198101.

[22] GADOMSKI A., J. Phys. II (France), 6 (1996), 1537.

[23] PRZYGOCKI W., WŁOCHOWICZ A., *Polymer Physics*, WN PWN, Warsaw, 2001, in Polish.

[24] WEIPERT D., TSCHEUSCHNER H.-D., WINDHAB E., *Rheologie der Lebensmittel*, Behr's Verlag 1993, Hamburg, in German, p. 585.

[25] THIRUMALAI D., KLIMOV D.K., DIMA R.I., Curr. Opin. Struc. Biol., 13 (2003), 146.

[26] SCHUSTER H.-G., *Deterministic Chaos. An Introduction*, VCH, Weinheim, 1988.

[27] TALUKDAR S.S., SWIHART M.T., J. Aerosol Sci., 35 (2004), 889.

[28] BAK P., TANG C., WIESENFELD K., Phys. Rev. Lett., 59 (1987), 381.

[29] GALINA H., LECHOWICZ J.B., Macromol. Symp., 174 (2001), 307.