Rheological modelling of complex fluids.
I. The concept of effective volume fraction revisited

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Abstract. Number of complex fluids (as slurries, drilling muds, paints and coatings, many foods, cosmetics, biofluids...) can approximately be described as concentrated dispersions of Structural Units (SUs). Due to shear forces, SUs are assumed to be approximately spherical in shape and uniform in size under steady flow conditions, so that a complex fluid can be considered as a roughly monodisperse dispersion of roughly spherical SUs (with a shear-dependent mean radius), what allows to generalize hard sphere models of monodisperse suspensions to complex fluids. A rheological model of such dispersions of SUs is based on the concept of the effective volume fraction, ϕ_{eff} which depends on flow conditions. Indeed, in competition with particle interactions, hydrodynamic forces can modify (i) S, the number fraction of particles that all SUs contain, (ii) both SUs arrangements and their internal structure, especially the SU's compactness, φ. As a structural variable, S is governed by a kinetic equation. Through the shear-dependent kinetic rates involved in the latter, the general solution S depends on Γ, a dimensionless shear variable, leading to $\phi_{\mathrm{eff}}(t, \Gamma; \varphi)$. The structural modelling is achieved by introducing this expression of ϕ_{eff} into a well-established viscosity model of hard sphere suspensions. Using the steady state solution of the kinetic equation, $S_{\mathrm{eq}}(\Gamma)$, allows to model non-Newtonian behaviors of complex fluids under steady shear conditions, as pseudo-plastic, plastic, dilatant ... ones. In this model, the ratio of high shear to low shear limiting viscosities appears as a key variable. Different examples of application will be discussed.

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Introduction

Complex fluids (as drilling muds, paints and coatings, concrete, many foods, cosmetics, biofluids, *etc.*) used for industrial applications have rheological properties under steady and unsteady conditions which show strong similarities in comparison with those of concentrated dispersions. As one of the more remarkable characteristics of these fluids, such similarities are evidenced by using dimensionless variables that promotes disappearing of almost all the differences due to effects of time and space scales, so that, dimensional analysis should play a very important role. Logically, these similarities must be interpreted as resulting from some generic characteristics of these systems, in spite of their large diversity. It is widely recognized that these shared properties are due to both the existence of internal structures (very often called the microstructure, although they are observed at all length scales) and shear-induced changes of these structures.

During the two last decades, number of studies have shown that the structure of any concentrated dispersion cannot be characterized by only its microstructure: small elements (as individual particles or primary flocs) forms larger groups (as clusters, aggregates, flocs, clusters of flocs,...) up to an (eventual) sample spanning structure. These groups, herein call Structural Units (SUs), have a size which obviously depends on the applied shear through the hydrodynamic stress acting on the SUs, leading to the concept of the *shear-dependent structure*. For example, Figure 1 shows the structural interpretation of shear-thinning behavior (due to progressive rupturing of large clusters present at low shear, as the shear rate is increased), which changes into a plastic behaviour if a sample spanning network can form at very low shear, *i.e.* if the particle volume fraction is high enough.

Therefore, structural models, *i.e.* models which involve such structural changes, should be the most suitable for rheological characterization of these materials. Moreover, as complex fluids are multi-component systems, it appears irrelevant to try to take this complexity into account in rheological modelling for practical purposes. In order to obtain a correct characterization of the system,

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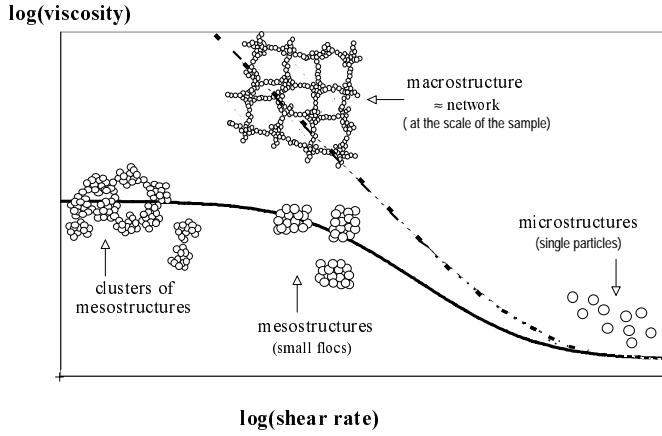
log(viscosity)

log(shear rate)

Fig. 1. Structural interpretation of shear-thinning and plastic behaviors, with a finite and an infinite viscosity at zero shear, respectively. As the shear rate in increased, large SUs break down into smaller and smaller ones, releasing an increasing amount of the suspending fluid immobilized in the inside of SUs.

the development of a structural approach thus requires:

(i) to be able to select the minimum number of parameters as a set of dimensionless, pertinent variables which should have a clear physical significance,

(ii) to start, as much as possible, from models of simple systems, already well-described, in order to be able to generalize well-established relations, what in principle will allow physical interpretations of the involved variables: in this aim, colloidal dispersions play a unique role.

Among these variables, the *effective volume fraction* (EVF) of the disperse phase has been proved to be one of the more essential for structural modelling. The aim of the present paper is to re-examine the EVF concept and, extending its definition, to enlarge its effectiveness in modelling simple non-Newtonian behavior. A second part of this work will be devoted to apply this new EVF concept of ϕ_{eff} to model more realistic non-Newtonian behaviour, as a more or less pronounced shear thinning interrupted by shear thickening occuring in an intermediate shear rate domain.

1 Some recalls (showing the essential contribution of I.M. Krieger to this field)

1.1. Dimensional Analysis was first applied by Krieger [1] to the simplest case: a suspension of small rigid monodisperse spheres (radius a, number density N), suspended in a Newtonian fluid (viscosity η_F, same specific mass than the solid material) and with only hydrodynamic interactions. He showed that the *relative viscosity* η_r should take the general form

$$\eta_r = \frac{\eta}{\eta_F} = \eta_r(\phi, \text{Pe}, \text{De}) \qquad (1.1)$$
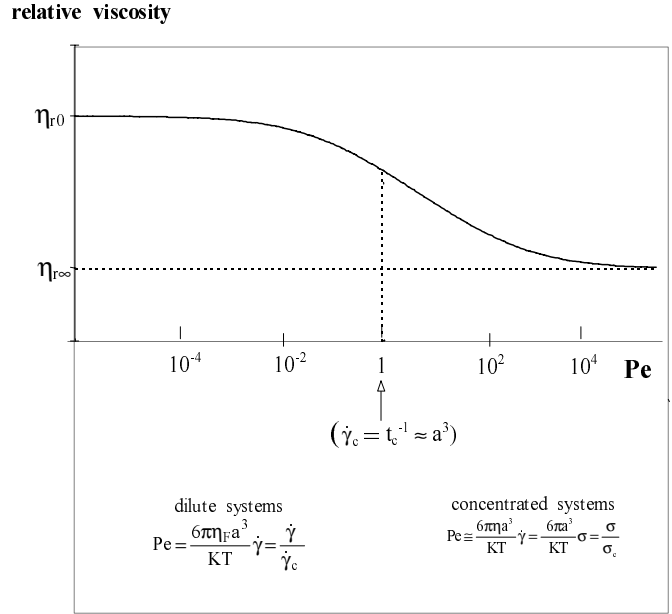
relative viscosity

Fig. 2. Master curve $\eta_r = f(\text{Pe})$, from dimensional analysis.

where $\phi = \frac{4\pi}{3}Na^3$ = volume fraction of particles, $\text{Pe} = t_{\text{Br}}\dot{\gamma}$ = Péclet number, $\text{De} = t_{\text{Br}}/t_{\text{Ex}}$ = Deborah number, these two last numbers depending on the Brownian diffusion time of particles in the suspending fluid

$$t_{\text{Br}} = \frac{a^2}{D_T} = \frac{6\pi\eta_F a^3}{KT} \qquad (1.2)$$

(with $\dot{\gamma}$ = shear rate, T = absolute temperature, K = Boltzmann constant, t_{Ex} = duration of the experiment). Under steady conditions (*i.e.* constant shear,), $\text{De} \to 0$ and equation (1.1) is reduced to $\eta_r = \eta_r(\phi, \text{Pe})$, which can be represented at $\phi = \text{cst.}$ as a master curve $\eta_r = \eta_r(\text{Pe})$, see Figure 2.

An excellent experimental model of such suspensions [2,3] is composed of monodisperse silica particles coated with a dense layer of short polymer chains grafted to the surface, suspended in a (good solvent) non-polar liquid, leading to a very strong repulsion between particles: the interaction is thus very close to that of Hard Spheres (HS).

1.2. All structural models involve at least four essential ingredients: one has to

(a) - define a set of (dimensionless) structural variables $[S]$, characterizing the structure;

(b) - choose the *kinetic equations* which governs $[S]$, describing the flow induced rupturing and restoring of the structure, in the presence of the other forces acting on particles;

(c) - determine shear-dependences of kinetic constants involved in kinetic equations, constants which should be expressed in terms of a dimensionless shear variable, Γ, either σ/σ_c or $\dot{\gamma}/\dot{\gamma}_c$, using characteristic shear stress σ_c and rate $\dot{\gamma}_c$;

(d) - select an explicit form of the viscosity-structure relation $\eta([S])$.

1.3. Based on the general frame proposed by Cheng and Evans [4] for modelling thixotropy of complex fluids, simplest models used (i) only one (scalar) variable S, governed by a kinetic equation of the form $\dot{S} = g(S, \Gamma, t)$ and (ii) a viscosity-structure relation, $\eta(S, \Gamma)$. For steady flow conditions, characterized by $\Gamma = \Gamma_{\text{st}}$, the equilibrium value, $S_{\text{eq}} = S_{\text{eq}}(\Gamma_{\text{st}})$, solution of the kinetic equation $g(S_{\text{eq}}, \Gamma_{\text{st}}, t) = 0$, leads to a non-Newtonian viscosity

$$\eta_{\text{eq}} = f(S_{\text{eq}}, \Gamma_{\text{st}}) = F(\Gamma_{\text{st}}).$$

As an example, Krieger-Dougherty model [5] describes the shear thinning behavior of suspensions of small spherical particles, forming doublets by Brownian collisions, by using:

- a structural variable S proportional to the number of doublets, the formation of which is governed by "chemical" kinetics
- a reduced shear stress $\Gamma = \sigma/\sigma_{\text{c}} \approx a^3\sigma/KT$,
- a viscosity-structure relation, assumed linear in S, such as[1]

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + \Gamma} \qquad (1.3)$$

where η_∞ and η_0 are respectively the limiting steady state viscosities, in the limits $\Gamma \to \infty$ and $\Gamma \to 0$, (in practice, $\Gamma \gg 1$ and $\Gamma \ll 1$). From equation (1.1), these limits correspond to relative viscosities which are only functions of ϕ.

For these dependences $\eta(\phi)$, Krieger et Dougherty [6] gave the correct solution of Mooney's approach [7][2]. This solution can be written in the general form

$$\eta_{\text{r}} = \left[1 - \frac{\phi}{\phi_{\text{m}}}\right]^{-q} \qquad (1.4)$$

where

$$q = [\eta]\phi_{\text{m}} \qquad (1.5)$$

is the product of ϕ_{m}, the maximum volume fraction (i.e. the maximum packing) by the intrinsic viscosity $[\eta]$, the Einstein's limit in very diluted media ($[\eta] = 2.5$ for a suspension of spheres). The condition (1.5) is required in order to recover the Einstein viscosity, $\eta_{\text{r}} = 1 + [\eta]\phi$, as $\phi \to 0$. In practice, ϕ_{m} is observed close to the Random Close Packing $\phi_{\text{RCP}} = 0.637$, not to the theoretical value $\phi_{\text{FCC}} = 0.74$ (the Face Centered Cubic packing).

An expression of the same type than (1.4), however with a fixed value, $q = 2$, was obtained [8] from a minimum principle applied to the energy dissipated by viscous effects. Obviously, the limit (1.5) at $\phi \to 0$ should not be maintained (with $[\eta] = 2.5$, it would give $\phi_{\text{m}} = 0.80$, an unacceptable value since > 0.74). Moreover, it seems rather unjustified to require the existence of a relation between, on one hand, q and ϕ_{m} –parameters which command the viscosity behavior in the vicinity of the maximun packing (hence, which mainly depend on lubrication interactions between close particles)– and, on the other hand, Einstein's coefficient $[\eta]$ –which quantifies the (long range) hydrodynamic perturbation due to the presence of an isolated particle imbedded in the suspending fluid. The only way to maintain equation (1.5) seems to argue that such a constraint would hold only at $\phi \to 0$, requiring that the relation $\eta(\phi)$ takes at low concentration (for instance, below a percolation threshold?) a form compatible with Einstein viscosity, hence different from the equation (1.4).

The relation (1.4) has been verified in several experiments carried out on colloidal suspensions of spherical particles. Early studies on latex suspensions [9] verified (1.4) with $q = 2$ by data fitting of Ree-Eyring model. Measurements on latex suspensions in non-aqueous media [10] led to the following pair values for the two limits $(\phi_{\text{m}}; q)$ at very low and very high shear: (0.57; 1.52) and (0.68; 1.82), respectively[3]. Later, the above-cited experimental models of HS systems allowed to make very precise verifications of equation (1.4): comparable quality in data fitting was obtained in two cases: by using either ϕ_{m} and q as open variables or a fixed value, $q = 2$, and only ϕ_{m} open. The former case led to the pair of values $(\phi_{\text{m}}; q) = (0.63; 1.96)$ for η_0 and $(0.71; 1.93)$ for η_∞. However, from equation (1.5) these q-values, 1.96 and 1.93, would correspond to $[\eta]$ close to 3.1 and 2.7, unacceptable for rigid spheres (theoretical value $[\eta] = 2.5$). The second case led to $\phi_{\text{m}} = 0.63$ for η_0 and $\phi_{\text{m}} = 0.72$ for η_∞ and very similar values of ϕ_{m} have been found for other suspensions of monodisperse silica spherical particles with different radii [11].

More recently, the divergent behavior of the zero shear viscosity η_0 was studied theoretically [12] from a scaling analysis of the Brownian stress: if the range of interparticle forces is comparable to the particle size, the hydrodynamic contribution to the stress scales as the Brownian stress[4], that results to η_0 following (1.4) with $q = 2$ and ϕ_{m} close to ϕ_{RCP}.

1.4. It is well-known that real (stabilized) suspensions are only approximately described as HS systems, depending on the interaction potential. However, in the case of a repulsive potential (either the abrupt steric potential or the smooth electrostatic one, often superposed to an attractive potential which reduces the interaction range), it is possible to introduce an effective radius a_{eff} which defines the equivalent HS radius: it is the *HS approximation* which permits to apply the relation (1.4) after changing ϕ into

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[1] Notice that applying (1.3) to concentrated suspensions, performed in many works, appear to contradict K−D's model assumptions, say a very dilute suspension of doublets and absence of multiplets.

[2] Which is based on calculation of the viscosity of a suspension containing ϕ_2 particles after adding an amount ϕ_1 of particles: this procedure is not equivalent to adding ϕ_2 to a suspension containing ϕ_1 as Krieger claimed, contrary to Mooney's assumption.

[3] Note that the limit (1.5) is not satisfied, giving respectively $[\eta] = 2.67$ and 2.68 instead of 2.5.

[4] In the case of very strong repulsive forces between particles, equation (1.4) remains valid, but with $q = 1$.

an *Effective Volume Fraction* (EVF)

$$\phi_{\text{eff}} = \frac{4\pi}{3} N a_{\text{eff}}^3 = (a_{\text{eff}}/a)^3 \phi \qquad (1.6)$$

equation (1.4) thus becomes

$$\eta_{\text{r}} = \left(1 - \frac{\phi_{\text{eff}}}{\phi_m}\right)^{-q}. \qquad (1.7)$$

Many works ([13–15], limiting referred papers to the more recent ones) currently used (1.7) –very often in the form of Krieger equation (*i.e.* with $q = [\eta]\phi_{\text{m}}$)– with ϕ_{eff} defined from (1.6), thus only taking the (steric or electrostatic) barrier of the stabilizing potential into account.

It is worth noting that using equation (1.6) is required every time a relation established for HS systems is taken into account, however equation (1.6) is not sufficient in the presence of a attractive potential strong enough to promote particle clustering, *i.e.* when the dispersion should be described as a suspension of clusters. Nevertheless, in concentrated systems, it appears more and more obvious that these clusters may form groups, assemblies of any scale, as shown by clay suspensions for instance. Such a structural feature leads to an important change in the above-defined EVF concept as it will be discussed in the next section.

2 Generalization of the hard sphere model and the EVF concept revisited

Some pioneer works, as those of Brinkman [16] or Roscoe [17], opened the EVF concept towards effects of polydispersity. For instance, this last author established the relation

$$\eta_{\text{r}} = (1 - \phi_{\text{eff}})^{-2.5} \qquad (2.1)$$

with $\phi_{\text{eff}} = s\phi$, the factor s only depending on the size distribution of particles. It takes the values $s = (0.74)^{-1}$ or $s = 1$ according to the system is composed of monodisperse or wholly polydisperse particles. Note that the form of equation (1.4) is unchanged if one uses ϕ_{eff} in place of the ratio ϕ/ϕ_{m}, however the limit (1.5), is satisfied for $s = 1$, not for $s = (0.74)^{-1}$, what corresponds to $[\eta] \cong 3.4$.

The needs to take the structure formation at any scale into account has been underlined in the previous section. Note that such multiscaled structures, although not included in number of even recent approaches, were early introduced by Michaels and Bolger [18] and by Firth and Hunter [19] in their studies of clay suspensions, however without considering the consequence for the EVF concept.

Extension of the HS Approximation to complex fluids directly results from including the formation of SUs in the model, what leads to a simple description of these fluids as suspensions of SUs. The size distribution of SUs, likely rather broad in the rest state, is however expected to be narrowed under flow conditions and centered on a mean size $\overline{R}(\Gamma)$ as resulting from shear forces acting on SUs. Moreover, these forces and collisions between particles promote the formation of SUs more or less spherical

in shape. Therefore, a flowing complex fluid can be considered as a roughly monodisperse dispersion of roughly spherical SUs, leading to generalize the equation (1.7) in which ϕ_{eff} is the whole volume fraction of clusters [20–22,26]. In some recent works, ϕ_{eff} was taken as the EVF of fractal aggregates in colloidal dispersions and was used in equation (1.4) with either $q = 2$ (in Ref. [23], *e.g.*) or $q = [\eta]\phi_{\text{m}}$ (in Refs. [24,25]).

Some amount of suspending fluid is immobilized inside any SU, the compactness of which is defined by the ratio φ_n of the solid volume inside the SU to its total volume. If this SU is composed of n particles of radius a, its effective radius is $R_{\text{eff}} = (na^3/\varphi_n)^{1/3}$. For the suspension of (roughly identical) SUs as a whole, one may define a mean compactness, φ, and the total EVF is thus related to true volume fraction ϕ by

$$\phi_{\text{eff}} = \phi/\varphi \qquad (2.2)$$

where $\phi_{\text{eff}} > \phi$ since $\varphi < 1$. The viscosity of the dispersion considered as a suspension of SUs should take the same form than equation (1.7)

$$\eta_{\text{r}} = \left(1 - \frac{\phi_{\text{eff}}}{\phi_{\text{m}}}\right)^{-q} \qquad (2.3)$$

where ϕ_{m} is the maximum packing fraction of SUs. It could be evaluated from the sedimentation volume if SU restructuring does not occur during settling, that is seldom the case. Particle size and shape distributions mainly contribute to cluster compactness. In many circumstances, clusters under shear forces are broadly spherical in shape that allows to use for ϕ_{m} in equation (2.3) a value close to RCP packing. On the contrary, if the cluster's shape is very different (for instance in the case of clusters composed of fibers having a very large axis ratio), the maximum packing is not known. Then, it seems better to rewrite (2.3) as a function of the true volume fraction, ϕ

$$\eta_{\text{r}} = \left(1 - \frac{\phi}{\phi_{\text{PK}}}\right)^{-q} \qquad (2.4)$$

after changing ϕ_{m} into an *effective maximum packing*

$$\phi_{\text{PK}} = \varphi\phi_{\text{m}} \qquad (2.5)$$

which involves both packing characteristics of individual particles in clusters (*i.e.* the cluster compactness) and packing characteristics of clusters in the sample. As the evaluation of ϕ_{eff} is very often difficult to carry out in complex fluids, the expression (2.4) is interesting since it contains only one unknown parameter, ϕ_{PK}. Fair data fitting of equation (2.4) have been obtained with suspensions of particles of very different kind, especially of non-spherical particles [27].

The EVF definition (2.2) may however appear rather too restrictive: the SU formation generally results from regrouping smaller elements –not necessarily the primary particles but small irreducible aggregates formed at the higher shear applied to the sample, noticely during its

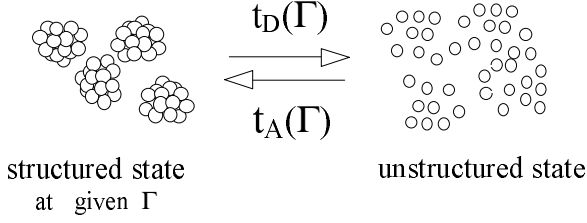**Fig. 3.** Dynamical equilibrium under steady conditions (at given Γ) between Individual Flocs and Structural Units of mean radius $R(\Gamma)$.

preparation–, elements which will be herein called Individual Flocs (IFs). Assuming that the flow makes the SUs roughly homogeneous in shape and size, it seems rather improbable that all the IFs are included in SUs, *i.e.* some of IFs have to remain free. It is therefore possible to generalize the definition (2.2) to a suspension composed of SUs and IFs in dynamical equilibrium under steady flow conditions, as illustrated on Figure 3.

Let ϕ_A and $\phi_I = \phi - \phi_A$ to be the volume fractions of particles contained in all the SUs and IFs, respectively. From equation (2.2), the EVF of SUs will be $\phi_{Aeff} = \phi_A/\varphi$, leading to define the EVF of the suspension as a whole by $\phi_{eff} = \phi_I + \phi_{Aeff}$. In terms of the structural variable, $S = \phi_A/\phi$, defined as the "aggregated" fraction (*i.e.* the total number density of primary particles contained in all the SUs), ϕ_{eff} can be written

$$\phi_{eff} = [1 + CS]\phi \qquad (2.6)$$

where

$$C = \varphi^{-1} - 1 \qquad (2.7)$$

is a "compactness factor", directly related to the mean compactness of SUs, φ.

In the case of complex fluids in which, in addition to IFs, one may identify several classes of SUs –each of them characterized by the pair (S_i, C_i)–, equation (2.6) can easily be generalized in the form

$$\phi_{eff} = \left(1 + \sum_i C_i S_i\right)\phi. \qquad (2.8)$$

Note that from equation (2.6), the alternate form (2.4) requires to use now

$$\phi_{PK} = \phi_m/[1 + CS] \qquad (2.9)$$

that led to introduce the concept of a *shear-dependent maximum packing* $\phi_{PK}(\Gamma)$ [20,29].

3 Structure kinetics and non-Newtonian behavior

Still for the sake of simplicity, the kinetic processes involved in formation and breakdown (or reduction) of SUs are supposed to be relaxation processes with mean relaxation times, t_A and t_D, respectively. In other words, the above-defined number fraction of aggregated particles, S, is governed by:

$$\frac{dS}{dt} = \kappa_A(S_0 - S) - \kappa_D(S - S_\infty) \qquad (3.1)$$

with $\kappa_A = t_A^{-1}$ and $\kappa_D = t_D^{-1}$ as shear-dependent kinetic constants of formation and rupturing of SUs, and where S_0 and S_∞ are the limits of S at very low and very high shear, $\Gamma \ll 1$ and $\Gamma \gg 1$, respectively.

The steady state $(dS/dt = 0)$ solution of equation (3.1) is given by

$$S_{eq} = \frac{S_0 + S_\infty\theta}{1 + \theta} \qquad (3.2)$$

where θ is defined by

$$\theta = \kappa_D/\kappa_A = f(\Gamma). \qquad (3.3)$$

This solution corresponds to the equilibrium structure the system reaches under constant shear, characterized by Γ.

For dilute colloidal dispersions of spherical particles of radius a, dimensional analysis allows to identify θ to the Péclet number, $Pe = t_{Br}\dot{\gamma}$, where $t_{Br} \cong \eta_F a^3/KT$ is the Brownian diffusion time[5]. For concentrated systems, considering that any Brownian particle is embedded in the whole suspension as an effective medium, the Péclet number can be generalized by replacing into the above expression of t_{Br} the viscosity of the suspending fluid, η_F, by some effective value, η_{eff}, close to the suspension viscosity, η. As a consequence, the generalized Pe number is proportional to the product $\eta\dot{\gamma}$, thus depends linearly on shear stress, what leads to $\theta \propto \sigma$. Due to the non-linear variation of σ *vs.* $\dot{\gamma}$ (very often approximated by a power law), one expects a non-linear dependence θ in $\dot{\gamma}$. Therefore, once again for the simplest modeling, it is assumed that, in concentrated systems,

$$\theta(\dot{\gamma}) = \kappa_D/\kappa_A = t_A/t_D = (t_c\dot{\gamma})^p \qquad (3.4)$$

where t_c is a characteristic time required for dimensional homogeneity. From its definition (3.4), t_c is necessarily closely related to at least one of the relaxation times t_A and t_D. Moreover, the exponent p should be < 1 in order to make equation (3.4) compatible with equation (3.2) when $\dot{\gamma} \to \infty$ and $\dot{\gamma} \to 0$. Note that the value of p has been very often found experimentally close to $1/2$, especially in colloidal dispersions [30]. In the latter case this value has some theoretical background [31]. It is worth noting that θ can be expressed as a simple function of a dimensionless shear variable, Γ, indifferently written in terms of either the shear rate, $\Gamma = (\dot{\gamma}/\dot{\gamma}_c)$, or the shear stress, $\Gamma = (\sigma/\sigma_c)$, using characteristic shear rate $\dot{\gamma}_c = t_c^{-1}$ and shear stress σ_c, respectively. In fact, the simplest modelling will be obtained by using the experimentally applied shear, either $\dot{\gamma}$ or σ, as an independent

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[5] Using relaxation times $\kappa_D^{-1} \approx \dot{\gamma}^{-1}$ and $\kappa_A^{-1} = t_{Br}$ for breaking down and building up the structure, respectively.

variable: the choice between these two forms of Γ will be dictated by the type of rheometer used in measurements.

Moreover, as Pe can also be expressed as the ratio W_{H}/KT where W_{H} is the energy dissipated by viscous flow, a further generalization of Pe to more complex systems was obtained [32,33] by changing this ratio into a new one, $W_{\mathrm{H}}/W_{\mathrm{I}}$, where W_{I} is the particle interaction energy, very large in comparison with KT in the case in stabilized dispersions. As $W_{\mathrm{H}} \approx \sigma a^3 \approx \eta_{\mathrm{eff}} a^3 \dot{\gamma}$, such a generalization leads to enlarge the physical meaning of the characteristic time involved in the reduced shear rate, $t_{\mathrm{c}}\dot{\gamma}$, by putting

$$t_{\mathrm{c}} \approx \eta_{\mathrm{eff}} a^3 / W_{\mathrm{I}}. \tag{3.5}$$

The last step in modelling, which concerns the relation between viscosity and structural variable, $\eta = f(S)$, involves the more original part in using the new EVF concept. From $\eta = \eta(\phi_{\mathrm{eff}})$ and $\phi_{\mathrm{eff}} = \phi_{\mathrm{eff}}(S)$, see equations (2.3, 2.6), a one-to-one relation is *automatically* obtained, which describes the non-Newtonian viscosity under steady conditions, $\Gamma = \mathrm{cst}$. Indeed, using the steady state solution $S_{\mathrm{eq}} = S(\Gamma)$ of the kinetic equation, obviously results into $\eta(S_{\mathrm{eq}}) = \eta(\Gamma)$. More precisely, using equation (3.2) leads to

$$\eta_{\mathrm{r}} = \left\{ 1 - \left[1 + \frac{C(S_0 + S_\infty \theta)}{1 + \theta} \right] \frac{\phi}{\phi_{\mathrm{m}}} \right\}^{-2}$$

which can easily be written in the form (with $\theta = \Gamma^p$)

$$\eta = \eta_\infty \left[\frac{1 + \Gamma^p}{\chi + \Gamma^p} \right]^2. \tag{3.6}$$

In equation (3.6) the ratio

$$\chi = \chi(\phi) = \frac{1 - \phi/\phi_0}{1 - \phi/\phi_\infty} \equiv \pm \left(\frac{\eta_\infty}{\eta_0} \right)^{1/2} \tag{3.7}$$

depends on the limiting maximum packings at $\Gamma \to \infty$ and $\Gamma \to 0$, respectively, defined by

$$\phi_\infty = \frac{\phi_{\mathrm{m}}}{1 + CS_\infty} \qquad \text{and} \qquad \phi_0 = \frac{\phi_{\mathrm{m}}}{1 + CS_0}. \tag{3.8}$$

These packings are involved in the corresponding steady state limiting viscosities η_∞ and η_0

$$\eta_\infty = \eta_{\mathrm{F}} \left(1 - \frac{\phi}{\phi_\infty} \right)^{-2} \qquad \eta_0 = \eta_{\mathrm{F}} \left(1 - \frac{\phi}{\phi_0} \right)^{-2}. \tag{3.9}$$

Alternatively, from equations (3.2, 3.4, 2.9), the shear-dependent maximum packing $\phi_{\mathrm{PK}}(S)$ should verify the following relation [20,29]

$$\phi_{\mathrm{PK}}^{-1} = \phi_\infty^{-1} + \frac{\phi_0^{-1} - \phi_\infty^{-1}}{1 + \Gamma^p}. \tag{3.10}$$

Notice that the behavior described by equation (3.6) is also obtained after putting equation (3.10) into equation (2.4), in spite of using a different formalism.

Finally, it is important to remark that although the present structural model was originally developed for concentrated dispersions, in direct association with the relation $\eta(\phi)$, such an origin can be forgotten: indeed, the model is completely defined by equation (3.6), with χ given by equation (3.7), and through these relations, it depends only on the limiting viscosities, η_∞ and η_0. Therefore, the domain of application of the model can be enlarged to complex fluids (at least those for which the above-introduced structural concepts may be accepted, as clay suspensions, for instance), although it would be very difficult, even impossible, to define (*a fortiori* to measure) a "volume fraction" in such complex fluids.

4 Prediction of simple non-Newtonian behaviors under steady conditions

The steady state viscosity (3.6) presents a monotonic variation, *i.e.* different kinds of "pure" non-Newtonian behaviors, as simple shear thinning, plastic, or shear thickening, depending on the values of the limiting viscosities, $\eta_0 > \eta_\infty$, $\eta_0 \to \infty$ and $\eta_0 < \eta_\infty$, respectively. More precisely, χ given in equation (3.7) works as a *rheological index*: indeed, its value controls the behavior of the suspension, which is *Newtonian* if $\chi = 1$, *shear-thinning* if $\chi < 1$, plastic if $\chi = 0$ –identical to the Casson behavior, for $p = 1/2$–, *shear-thickening* if $\chi > 1$ and shows a *discontinuous viscosity* if $\chi < 0$. Table 1 collects these features, in relation with corresponding values of volume fractions.

Table 1. Different rheological behaviors, associated with the value of the rheological (structural) index.

rheological index	rheological behavior	range of volume fraction
$0 < \chi < 1$	PSEUDO-PLASTIC	$\phi < \phi_0 < \phi_\infty$
$1 < \chi < \infty$	DILATANT	$\phi < \phi_\infty < \phi_0$
$\chi = 0$	PLASTIC (CASSON)	$\phi = \phi_0$
$-\infty < \chi < 0$	DISCONTINUOUS VISCOSITY	$\phi_\infty < \phi < \phi_0$
$\chi = 1$	(NEWTONIAN)	$\phi_0 = \phi_\infty$

The viscosity model (3.6) has been found to predict very well both the shear thinning behavior and the ϕ-dependences of the η_∞ and η_0 limits: very fair agreement was obtained by fitting the model to steady state viscosity data of spherical particle suspensions and some complex fluids [20,29,33–36]. An example of such data fitting is shown in Figure 4, which allows physical interpretation of model variables.

A second way to model plastic behavior. Up to now, it has been admitted that no difference can result from using the reduced shear variable, Γ, written as either $\dot{\gamma}/\dot{\gamma}_{\mathrm{c}}$ or $\sigma/\sigma_{\mathrm{c}}$. This is generally true, especially one should obtain
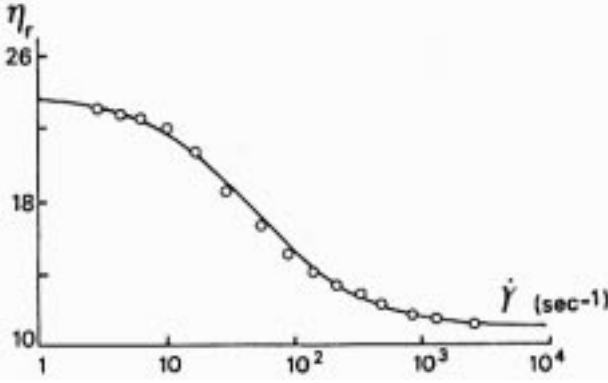
Fig. 4. Variations viscosity *vs.* shear rate in a monodisperse suspension of latex particles (diameter $= 0.155$ μm, suspending fluid viscosity $= 4.89$ mPa, particle volume fraction $= 0.50$). Data from [10]. Data fitting giving the parameter values in equation (3.6 and 3.9): $\phi_0 = 0.629$, $\phi_\infty = 0.716$, $p = 0.986$, $t_C = 11$ ms. It is worth noting that ϕ_0 and ϕ_∞ values are very close to the ones found later in dispersions of colloidal silica particles [2] and t_C, interpreted as the Brownian diffusion time, t_{Br} (*cf.* Eq. (1.2)) leads to a particle diameter $2a = 0.158$ μm, very close to the value obtained from electronic microscopy, $2a = 0.155$ μm [20,33].

same values for the limiting viscosities. However, special attention is required if $\chi = 0$ or $\chi < 0$. In particular, the present model provides two quite different ways to describe the plastic behavior, depending on the choice of the independent variable, shear rate or shear stress, as follows:

a) In the former case, $\Gamma = t_c\dot\gamma$, calculation of the square root of the shear stress from equations (3.6, 3.4) with $\chi = 0$, leads to the *Casson* equation (in the case $p = 1/2$)

$$\sigma^{1/2} = \eta^{1/2}\dot\gamma^{1/2} = \eta_\infty^{1/2}\left[1 + \Gamma^{-1/2}\right]^2 \dot\gamma^{1/2}$$
$$= \left(\frac{\eta_\infty}{t_C}\right)^{1/2} + \eta_\infty^{1/2}\dot\gamma^{1/2} \qquad \text{(for } \chi = 0) \quad (4.1)$$

in which precise expressions of both the Casson viscosity and the *yield stress* are obtained automatically

$$\eta_{Casson} = \eta_\infty \qquad \text{and} \qquad \sigma_Y = \eta_\infty/t_C. \quad (4.2)$$

However, from equation (3.7), χ takes negative values if ϕ lies in the interval between the limitings packings ϕ_∞ and ϕ_0, that gives the possibility to observe *viscosity discontinuities* if the denominator in the r.h.s. of equation (3.6) tends to zero [28]. As $\dot\gamma$ increases, the critical shear rate $\dot\gamma_{cr}$ beyond which the viscosity diverges is obtained when Γ reaches the value $(-\chi)^{1/p}$, that leads to

$$\dot\gamma_{cr}t_C^{-1}\left[\frac{1 - \phi/\phi_0}{\phi/\phi_\infty - 1}\right]^{-1/p} \qquad \text{(for } \chi < 0) \quad (4.3)$$

This agrees with the observed change of dilatancy into discontinuous viscosity if the volume fraction is high

enough. This point will be discussed in more detail in the second part of this paper.

b) Alternatively, in the second case, $\Gamma = \sigma/\sigma_c$, another definition of σ_Y can be deduced from equation (3.6) without any reference to the Casson law. Indeed, in the case of a given value $\chi < 0$, equation (3.6) can be written in the form

$$\eta = \eta_\infty\left[\frac{\sigma^p + \sigma_C^p}{\sigma^p - \sigma_Y^p}\right]^2 \quad (4.4)$$

putting $\sigma_Y = (-\chi)^{1/p}\sigma_C$. This critical stress σ_Y appears as the yield stress since the viscosity diverges at $\sigma = \sigma_Y$ and should not exist if σ is lower than σ_Y. Moreover as η is always $> \eta_\infty$ (that requires the condition $\phi < \phi_\infty$), the expression of σ_Y results as

$$\sigma_Y = \sigma_C\left[\frac{\phi/\phi_0 - 1}{1 - \phi/\phi_\infty}\right]^{1/p} \quad (4.5)$$

which exists only if $\phi > \phi_0$. Therefore, as ϕ is increased, the shear thinning behavior observed at $\phi < \phi_0$ (σ_Y does not exist there) abruptly changes at $\phi = \phi_0$ (where $\sigma_Y = 0$) then becomes a plastic behavior at $\phi > \phi_0$, with an increasing yield stress σ_Y given by equation (4.5).

Starting from the same definition (3.10) of the shear-dependent maximum packing and using the same shear stress-dependent kinetic model, the same expression of the yield stress (Eq. (4.5)) has been recently given and satisfactorily verified in several concentrated mineral suspensions [36].

5 Discussion

5.1. Almost all of the previous structural models of the literature used for S either the number of links (*e.g.*, [37]) or, as in the present model, the number of particles contained in the structured elements. The kinetic equation was chosen from reaction kinetics or from relaxation kinetics (*e.g.*, a Moore-like equation, also herein used). It is worth noting that this preliminary choice, usually made for the sake of simplicity, is more or less arbitrary. However, such a choice can be avoided since it is possible to find the form of the kinetic equation using a method based on analysing, in the frame of the present model, the characteristics of the time variation dS/dt *vs.* S deduced from viscosity data [38].

5.2. For the simplest modelling, the shear dependence of kinetic constants has been taken such as their ratio θ is a power law of the above-used dimensionless shear variable, Γ, expressed as $[\dot\gamma/\dot\gamma_C]^p$ or $[\sigma/\sigma_C]^{p'}$. Note that in the Krieger and Dougherty's model, see (1.3), θ depends linearly in σ, though this model was generally applied in the literature with an (open) non-linear dependence in σ, *e.g.*,

see [2]. Obviously, the exponents p and p' should be different. In fact, a more complicated dependence $\theta = \theta(\Gamma)$ could be introduced without limiting the improvement of the present model, for instance using the general form $\theta = \Gamma^p f(\Gamma)$, with the only requirement that the limits of equation (3.2) are satisfied, *i.e.* with $f(0) = 1$ and taking $f(\infty)$ in order to keep unchanged the power law behavior with $p > 0$. An example of such an extension of the present model is given by the shear induced flocculation described by the following form of the kinetic constant for SUs' formation,

$$\kappa_A = \kappa_0[1 + (t_F \dot{\gamma})^s], \qquad (5.1)$$

where t_F is a "flocculation" time. It will be discussed in the second part of this work.

5.3. It should be underlined that, in order to obtain the non-Newtonian viscosity (3.6) –and in spite of its very simple form–, there is nothing to assume but (i) the validity of a viscosity *vs.* volume fraction relation, (ii) a relaxation kinetics for the "aggregated" fraction. Therefore, one of the prime interests of the present structural model seems to avoid any *arbitrary* choice of the relation $\eta(S)$. On the contrary, this relation has been generally supposed linear in most of shear thinning models, an assumption which necessarily leads to a viscosity expression of the form

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty)S(\Gamma) \qquad (5.2)$$

whatever the kinetic equation may be: indeed equation (1.3) is just like this form, as well as Cross model [37]. However, from equation (5.2), the condition $0 \le S \le 1$ holds in the whole domain $\infty > \Gamma > 0$, that requires using $S_\infty = 0$ and $S_0 = 1$ in equation (3.2). In this case, the limiting packings (3.8) reduce to $\phi_\infty = \phi_m$ and $\phi_0 = \phi_m \varphi$ in agreement with equation (2.9).

5.4. Using a *reduced* structural variable

$$\hat{S}(\Gamma) = \frac{S(\Gamma) - S_\infty}{S_0 - S_\infty} \qquad (5.3)$$

which varies from 0 (for fully broken structure) to 1 (for complete structure building up) allows to express the viscosity as a simple function of $\hat{S}(\Gamma)$. Combining equations (2.3, 2.6, 5.3), leads to the viscosity equation $\eta(\Gamma)$

$$\eta(\Gamma) = \eta_\infty[1 - (1 - \chi)\hat{S}(\Gamma)]^{-2}. \qquad (5.4)$$

Expression (5.4) is interesting since

(i) it leaves open the precise dependence of $S(\Gamma)$, *i.e.* holds for any kinetic equation,

(ii) it gives the possibility to model the thixotropy without additional assumption since a time-dependent viscosity directly results from insertion into equation (5.4) of the general (time-dependent) solution of the kinetic equation, $\hat{S}[t, \Gamma(t)]$, under an unsteady shear $\Gamma(t)$,

$$\eta(t) = \eta_\infty[1 - (1 - \chi)\hat{S}(t)]^{-2}. \qquad (5.5)$$

5.5. Finally, due to the presence of large clusters in both concentrated suspensions and complex fluids, it may be argued that clustering should hide the effects of likely broad distributions of "particles" as disperse elements in complex fluids: the main difference with concentrated suspensions comes from "particle" arrangement in clusters, thus from the cluster's compactness. Therefore, with the help of ϕ_{eff}, it seems possible to apply the model to complex fluids.

Conclusive remarks and perspectives

In this work, complex fluids are considered as mixtures of Structural Units (SUs) and individual elements (as primary particles or likely irreducible flocs, called IFs), in dynamical equilibrium under steady flow conditions. As a group of IFs (or a cluster of these groups), any SU contains some amount of immobilized fluid which depends on its compactness. This approximate description leads to a new, more realistic definition of the effective volume fraction (EVF), see equation (2.6): ϕ_{eff} is defined as the whole EVF of IFs and SUs, which now depends on two variables, (i) S, the fraction of individual particles embedded in all the clusters, (ii) φ, the compactness of the clusters. A kinetic equation governs the time evolution of S under steady or unsteady shear conditions, leading to a *shear-dependent EVF*.

A model of hard sphere suspensions –a well-established relation $\eta(\phi)$ giving the viscosity *vs.* the (true) volume fraction–, is generalized to complex fluids, arguing that clustering of particles is also present in hard sphere suspensions and may mask their differences from complex fluids, mainly the broad particle distributions in size and in shape of the latter. Therefore, ϕ_{eff} is used in place of ϕ in the viscosity relation $\eta(\phi)$, leading to a one-to-one relation $\eta(S)$, what allows to discard from the present model the arbitrariness due to assuming a linear relationship $\eta(S)$, as it was done usually in classical models.

The non-Newtonian behavior is thus automatically obtained through the shear dependence of ϕ_{eff}. In fact, under steady conditions, any "pure" non-Newtonian behavior is obtained in a very simple way: the key parameter is χ which appears directly related to the ratio of the limiting viscosities at very high and very low shear rates. The domains $0 < \chi < 1$ and $1 < \chi < \infty$ correspond to shear-thinning and shear-thickening behavior, respectively, whereas plastic behavior results from taking $\chi = 0$. However, the case of negative values of χ shows interesting features, depending on what is the independent shear variable taken in the model. Using the shear stress, a ϕ-dependent plastic behavior is predicted above a threshold in volume fraction at which the yield stress vanishes, the system being shear-thinning below this threshold. On the contrary, using the shear rate, the model is able to predict viscosity discontinuities present at a ϕ-dependent critical shear rate as it has been experimentally observed in colloidal dispersions. However, these experiments do not show a pure shear-thickening behavior as $\dot{\gamma}$ is increased, but a more complex one, with shear-thinning domains on

the both sides of the shear-thickening region. As a similar complex behavior is also observed in suspensions in the presence of shear induced flocculation, a more realistic model of such behavior [39,40] will be discussed in the second part of this paper, still using the new EVF concept.

Another feature of this model is the possible generalization to rheological behavior under unsteady conditions, a very simple one since it will result from using the general, time-dependent solution $S(t)$ in the viscosity relation, $\eta(S)$, *i.e.* giving automatically a model of Thixotropy [41].

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