# Viscosity of suspensions modeled with a shear-dependent maximum packing fraction

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Abstract: A large amount of data from the literature on viscosity of concentrated suspensions of rigid spherical particles are analyzed to support the new concept that the maximum packing fraction  $(\varphi_M)$  is shear-dependent. Incorporation of this behavior in a rheological model for viscosity  $(\eta)$  as a function of particle volume fraction  $(\varphi)$  succeeds in describing virtually all non-Newtonian effects over the entire concentration range and also accounts for a yield stress. The most successful model is one proposed by Krieger and Dougherty for Newtonian viscosities,  $\eta (\varphi, \varphi_M)$ , but with  $\varphi_M$  varying from a low-shear limit  $\varphi_{M0}$  to a high-shear limit  $\varphi_{M00}$ . Microstructural interpretations of this behavior are advanced, with arguments suggesting that similar rheological models should apply to suspensions of nonspherical and irregular particles.

Key words: Suspension viscosity, maximum packing fraction, spherical particle, concentrated suspension

Symbols

- *a* particle size scale (for spheres, the diameter)
- A lumped kinetic parameter in eqs. (23) and (24)
- BS butadiene-styrene
- C coefficient in Arrhenius model, eq. (2)
- D coefficient in Mooney model, eq. (3)
- $e_i$  parameter representing one of the three electroviscous effects (i = 1, 2, or 3)
- f fraction of total particulates that exist in the dispersed phase, eq. (22)
- *h* solution factor, in Arrhenius model, eq. (2)
- k crowding factor, in Mooney model, eq. (3)

 $k_D, k_F$  kinetic rate coefficient for producing particles of dispersed or flocculated type, respectively

- K Einstein coefficient for particles of any shape, eq. (1); equal to  $[\eta]$
- KD Krieger-Dougherty model, eq. (6)
- *m* exponent to characterize shear-dependence in viscosity models of Cross, eq. (10), and eq. (23), and also in yield stress prediction eq. (24)
- N number of monodisperse components in a blend of spheres with different diameters
- PD polydispersity (in size) parameter
- S generalized shape parameter
- T temperature
- $V_c$  volume of "chamber" in figure 6, representing the entire volume of the sample
- $V_P$  total volume of particles in the sample  $V_D$ ,  $V_F$  sample volumes in which dispersed
- $V_D, V_F$  sample volumes in which dispersed particles or flocculated particles, respectively, prevail; volumes of the "dispersed phase" or "flocculated phase", containing both particles and carrier fluid

# $V_{PD}$ , $V_{PF}$ particle volume within the phase volume $V_D$ or $V_F$ , respectively

Greek

τ

- $\eta_{0}, \eta_{\infty}$  viscosity of the suspending fluid
- [ $\eta$ ] intrinsic viscosity,  $\lim (\eta \eta_s)/\varphi \eta_s$
- $\eta_r$  reduced viscosity,  $\eta/\eta_s$
- $\varkappa$  Boltzmann's constant; in  $\tau_c$ 
  - shear stress
- $\tau_c$  parameter characterizing sensitivity of viscosity to stress, in eq. (8)
- $\tau_B$  dynamic yield stress in the floc model
- $\tau_y$  yield stress
- $\varphi$  volume fraction occupied by solids in a suspension
- $\varphi_M$  maximum value of  $\varphi$  attainable by a given collection of particles under given conditions of flow
- $\varphi_{M0}, \varphi_{M\infty}$  limiting values of  $\varphi_M$  at the low- $\tau$  and high- $\tau$  conditions, respectively

#### 1. Introduction

At present there is no adequate model for describing the viscosity,  $\eta$ , of suspensions of neutrally-buoyant rigid particles over the entire range of composition (volume fraction  $\varphi$ ) and shear (rate  $\dot{\gamma}$  or stress  $\tau$ ). Most of the theoretical efforts with suspensions have been directed toward the dilute limit, where the relative viscosity  $\eta_r = \eta/\eta_s$  (with  $\eta_s$  = viscosity of the suspending liquid) is independent of particle size scale (*a*) and polydispersity (PD) of size, if electroviscous effects are absent. When particles are fully dispersed, theoretical rigor can be achieved; equations of the form

$$\eta_r = 1 + K \, \varphi + \dots \tag{1}$$

have been derived [1, 2] for particles of various uniform shapes. The coefficient  $K(S, \tau)$ , identical to the intrinsic viscosity  $[\eta] = \lim_{\varphi \to 0} (\eta - \eta_s)/\varphi \eta_s$ , is depen-

dent on the particle shape (S) and can represent non-Newtonian behavior through its dependence on  $\tau$ . For spheres, K = 2.5 and  $\tau$ -dependence is absent; for other symmetrical shapes K > 2.5 and  $\tau$  (or  $\dot{\gamma}$ ) dependence arises because of particle orientation in the flow field [3]. When particles have an electric charge [4], sizedependence enters through the first electroviscous effect that arises from distortion of the counterion cloud by the flow; for spheres, this leads to K = $2.5 (1 + e_1)$  where  $e_1$  contains information about the charge potential, dielectric constant, and a.

At higher  $\varphi$ , the interaction between particles causes both a stronger  $\varphi$ -dependence and additional mechanisms for  $\tau$ -dependence. The power-series expansion in  $\varphi$ , generalizing eq. (1), has but marginal value because only the  $\varphi^2$ -term can be evaluated [2]. Numerous empirical functions for the low-shear Newtonian limit  $\eta_0(\varphi)$  have been proposed; one review [5] cited over 250 such equations. Many other reviews are also available [6-8]. We will cite only a few pertinent theoretically-obtained results.

Arrhenius [9] proposed

$$\eta_{r0} = \exp\left[C\left(\frac{h\,\varphi}{1-h\,\varphi}\right)\right] \tag{2}$$

where the "solution factor" (h) was employed to define an *effective* volume fraction. Mooney [10] invoked a "crowding factor" (k) in deriving, from geometrical arguments,

$$\eta_{r0} = \exp\left[D\left(\frac{\varphi}{1-k\ \varphi}\right)\right] \tag{3}$$

which is functionally identical to eq. (2). In both cases, there is an implied upper bound on  $\varphi$  such that  $\varphi \to \varphi_M$  causes  $\eta \to \infty$ . This means  $h = 1/\varphi_M = k$  in eqs. (2) and (3), and also  $D = C/\varphi_M$ . Both equations can be connected with the dilute limit by setting  $D = [\eta]$ ,

$$\eta_{r0} = \exp\left[\frac{[\eta]\,\varphi}{1 - \varphi/\varphi_M}\right] \tag{4}$$

which gives the correct result as  $\varphi \to 0$ .

A totally different function was developed by Brinkman [11] and by Roscoe [12],

$$\eta_{r0} = \frac{1}{(1-\varphi)^{[\eta]}}$$
(5)

but was deficient in its lack of  $\varphi_M$ . Only in the special case of infinite polydispersity, when  $\varphi_M \rightarrow 1$ , would eq. (5) be useful at high  $\varphi$ . Krieger and Dougherty [13] introduced Mooney's concept of crowding factor into the Brinkman method to obtain

$$\eta_{r0} = \frac{1}{(1-k\,\varphi)^{[\eta]/k}} = \frac{1}{\left(1-\frac{\varphi}{\varphi_M}\right)^{[\eta]\,\varphi_M}} \tag{6}$$

where we have added the last step. Details of derivations of eqs. (3-6) and their interrelationships are provided elsewhere [14]. Still another approach, by Frankel and Acrivos [15], led in the high- $\varphi$  limit to

$$\eta_{r0}|_{\varphi \to \varphi_M} = \frac{9}{8} \frac{(\varphi/\varphi_M)^{1/3}}{1 - (\varphi/\varphi_M)^{1/3}}$$
(7)

by a purely hydrodynamics treatment of the resistance to flow of the suspending liquid in the narrow gaps separating uniform spheres. No reference to  $[\eta]$  or other dilute-solution parameters was made.

Far less effort has been directed toward shear-dependence at high  $\varphi$ . Some  $\tau$ -dependence arises, even in non-aggregated systems, from the effect of the flow field on the population ratio of temporary doublets-to-singlets [16]:

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \tau/\tau_c} \tag{8}$$

where  $\eta_{\infty}$  is the high-shear limit; and  $\tau_c = \alpha \times T/3 a^3$  where  $\varkappa$  is Boltzmann's constant, T the temperature, and  $\alpha$  is a number of order unity. Comparison of eq. (8) with data on monodisperse spheres led [17, 18] to empirical functions

$$\eta_{r\infty} = (1 - 1.47 \,\varphi)^{-1.82}, \quad \eta_{r0} = (1 - 1.75 \,\varphi)^{-1.50}$$
(9)

with a small numerical adjustment in the magnitude of  $\tau_c$ .

These results represent a minimal level of  $\tau$ -dependence, which can become exaggerated when particle aggregation exists. Then, multiparticle clusters can break up with shear into smaller clusters. A kinetics argument, with the cluster breakup rate proportional to  $\dot{\gamma}^m$ , led Cross to propose [19]

$$\eta = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \beta \dot{\gamma}^m}.$$
 (10)

Comparable concepts have been advanced for various kinds of floc models [20, 21], for which asymptotic flow curves at high shear can be extrapolated back to an intercept  $\tau_B$  ("dynamic" yield stress) with  $\tau_B \propto \varphi^2$  or  $\varphi^3$ . Other models do not predict  $\tau_B$ , and none predict a true yield stress,  $\tau_y$ .

The second electroviscous effect [4], here designated  $e_2$ , affects binary and higher particle interactions by mutual repulsion. The consequent hydrodynamic perturbations lead to higher viscosities for charged-particle systems, through the consequences for overall shear-dependence are not fully understood.

#### 2. The maximum packing fraction

#### 2.1 General

Any model for  $\eta(\varphi)$  claiming utility beyond the dilute limit must incorporate  $\varphi_M$ , and to match the dilute limit it must contain  $[\eta]$  or K. Both eqs. (4) and

(6) achieve these goals and are capable of good representations of experimental data in the low-shear limit. Our experience is that the Krieger-Dougherty (KD) model is the most successful, particularly as  $\varphi \rightarrow \varphi_M$ , and we believe its derivation to be the most general and rigorous. Most of what follows, then, will utilize the framework of the KD model, eq. (6).

It is notable that almost all physical and chemical features of a suspension are characterized through either  $[\eta]$  or  $\varphi_M$  or both. Thus,  $[\eta]$  reflects *S*,  $e_1$ , and a degree of shear-dependence consistent with *S* and  $e_1$ ; for uncharged spherical particles there is no shear-dependence in  $[\eta]$ , and in general the dependence is expected to be weak. There is no effect of size scale *a* (except through  $e_1$ ) or PD of individual particles, nor of particle surface chemistry. Appearances to the contrary are indications of particle aggregation, with  $[\eta]$  then representing the aggregate and not the dispersed particle.

However, it is through  $\varphi_M$  that most system parameters are manifested, and always more strongly than through  $[\eta]$  when  $\varphi$  achieves moderate and high values. Most obviously,  $\varphi_M = \varphi_M(S)$  because of different packing efficiencies for various shapes; the upper bound here for monodisperse particles is  $\varphi_M = 0.74$  for spheres. For any given shape, PD enters by increasing  $\varphi_M$  since the small particles can fit in the vacancies between large particles; this leads to an upper bound (for infinite PD) of  $\varphi_M = 1$ . An independent treatment [22] for predicting  $\eta_{r0}$  when N monomodal components were mixed led, in the  $N \to \infty$  limit, to  $\eta_{r0} = (1 - \varphi)^{-3}$ ; this corresponds to  $[\eta] = 3$  in eq. (6), using  $\varphi_M = 1$ . Temperature changes influence  $\eta_s(T)$  over all ranges of  $\varphi$ , but thermal expansion differences between particles and the liquid carrier cause  $\varphi$  to change and thus also  $\varphi/\varphi_M$ , which is most important at high  $\varphi$ .

Perhaps most significantly,  $\varphi_M$  reflects the state of aggregation, so it represents indirectly the particle electric charge and surface chemistry that influence the tendency to form aggregates, their microstructure, and their resistance to breakup. The microstructural variations that are possible range from chainlike to globular. In the latter case, it is clear that carrier fluid immobilization within the aggregates makes the effective  $\varphi$  larger, so even with a constant  $\varphi_M$  the enhanced  $\varphi/\varphi_M$  causes a larger  $\eta_{r0}$  (in fact [24], and also according to eq. (6)).

#### 2.2 Shear dependence

We propose to assign the principal shear-dependence of suspensions to  $\varphi_M$ . The convenience of this is obvious: established functional forms for  $\eta_0(\varphi/\varphi_M)$ , such as eq. (6), can be used directly. The physical rationale is simple and appealing: a low- $\tau$  limit  $\varphi_{M0}$  exists because of random initial orientations of particles and possible aggregated microstructure, while at very high  $\tau \ \varphi_M \rightarrow \varphi_{M\infty}$  (a higher value) because the flow permits particle orientation, particle migration (in polydisperse systems) to fit particles into voids optimally, and breakup of microstructures associated with particle aggregation. With this  $\varphi_M(\tau)$  assignment, it is suggested also that all other parameters affecting  $\varphi_M$  will influence the  $\tau$ -dependence as well. This provides a useful framework for coupling *S*, PD,  $e_1$ ,  $e_2$ , and surface chemistry with non-Newtonian behavior.

It is, of course, necessary to demonstrate that  $\varphi_M = \varphi_M(\tau)$ . This is most clearly done with data on spherical particles, for which  $[\eta]$  is independent of shear; we therefore present the non-Newtonian data of Maron and coworkers [25-27] on latex spheres. To avoid too much dependence on eq. (6), we analyze the data initially in terms of the empirical but popular Eilers model [28] that has been found highly reliable for the Newtonian viscosity of dispersed spheres:

$$\eta_r = \left[1 + \frac{1.25\,\varphi}{1 - 1.35\,\varphi}\right]^2 = \left[1 + \frac{0.5\,[\eta]\,\varphi}{1 - \varphi/\varphi_M}\right]^2 \tag{11}$$

where the second form is our generalization, using  $[\eta] = 2.5$  and  $\varphi_M = 0.74$  for spheres. (Eq. (6) becomes identical to eq. (11) if  $[\eta] \varphi_M = 2$ , a value close to those that describe a great variety of data when eq. (6) is used.) An advantage of the Eilers model is its convertability to a simple linear form for preliminary data analysis,

$$\frac{\eta_r^{1/2} - 1}{\varphi} = \frac{1}{\varphi_M} \left( \eta_r^{1/2} - 1 \right) + 0.5 \left[ \eta \right].$$
(12)

Thus, plots of  $(\eta_r^{1/2} - 1)/\varphi$  vs.  $(\eta_r^{1/2} - 1)$  should produce straight lines with slope  $1/\varphi_M$  and intercept 0.5 [ $\eta$ ], if the model is obeyed. An analogous linearization can be made from the Mooney model, eq. (3). The data [25-27] were plotted as suggested by both equations, for conditions of constant  $\tau$ . At low  $\varphi$ , both fit the data well and gave similar values of [ $\eta$ ]. However, at high  $\varphi$ the Mooney model often provided an unacceptable fit and occasionally led to  $\varphi_M > 1$ . For this reason, the parameters [ $\eta$ ] and  $\varphi_M(\tau)$  arising from the Eilers fit were selected for presentation.

Results are shown in figure 1 for neoprene spheres of diameter 0.11 µm in water [26], over a measured stress range  $0 < \tau < 50$  Pa. The excellent unification of the data demonstrates that for these particles the function  $\eta_r$  depends uniquely on  $\varphi/\varphi_M$ , with  $\varphi_M(\tau)$  incorporating virtually all shear-dependence. Values of  $\varphi_M$  ranged



Fig. 1. Non-Newtonian viscosity data [26] plotted as a function of reduced volume fraction  $\varphi/\varphi_M$ , with  $\varphi_M = \varphi_M(\tau)$ . Particles are neoprene latex spheres of uniform diameter 0.011 µm; suspending fluid is water. Values of  $(\varphi_M, \tau)$  pairs corresponding to the data symbols are:  $\Box$  (0.534, 0);  $\bullet$  (0.581, 5);  $\blacktriangle$  (0.594, 20);  $\blacksquare$  (0.598, 30);  $\lor$  (0.602, 50);  $\circ$  (0.615,  $\infty$ ), with  $\tau$  in Pascals. For all dilute cases ( $\blacklozenge$ ) at all stresses,  $\varphi_M = 0.615$  was assumed. The solid line represents eq. (6); see text

from  $\varphi_{M0} = 0.534$  to  $\varphi_{M\infty} = 0.615$ . (The solid line in figure 1 is the best fit of eq. (6) to these data; see later discussion.) A similar display is given in figure 2 for this same system together with two other latex sphere systems: both butadiene-styrene (BS, 84:16) copolymer in water, with  $a = 0.12 \,\mu\text{m}$  [27] and  $a = 0.14 \,\mu\text{m}$  [25]. Once again the superposition is very good; the solid line is the same as in figure 1 and is seen not to represent an optimum for the entire set here. Values of  $\varphi_M$  obtained from the BS data were considerably higher than those from the neoprene data, being in the range 0.68 - 0.73 [14] and having less  $\tau$ -dependence as suggested by this small  $\varphi_M$  span.

These differences in  $\varphi_M$  magnitude suggested that the neoprene latices were actually in a state of some aggregation (thus, low  $\varphi_M$ ) while the BS latices were close to being non-aggregated (high  $\varphi_M$ , approaching the ideal of spherical close packing, 0.74). Supporting evidence is provided by [ $\eta$ ], averaging about 2.8–2.9 for neoprene but only 2.5–2.6 [27] and 2.3–2.6 [25] for BS. This indicates the neoprene systems contained a significant number of doublets or higher aggregates even at high dilution, consistent with the tendency predicted by the low  $\varphi_M$  values. A very slight tendency was noted with all systems for [ $\eta$ ] values to decrease with  $\tau$ , again consistent with the low- $\varphi$  presence of



Fig. 2. Non-Newtonian viscosities for three latex systems. Values of  $(\varphi_M, \tau)$  pairs are: neoprene latex [26],  $\circ$  (0.581, 5); • (0.594, 20); • (0.598, 30); • (0.602, 50); styrene-butadiene latex [25],  $\Box$  (0.700, 10); • (0.712, 20),  $\diamond$  (0.719, 30); • (0.729, 50); styrene-butadiene latex [27];  $\triangle$  (0.682, 0.025); • (0.700, 0.60);  $\nabla$  (0.705, 1.0), with  $\tau$  in Pa

doublet aggregates and their breakup into dispersed spheres as  $\tau$  increased.

Suspensions of spherical particles having different chemical character were also analyzed [17, 18, 25-33]. Particles consisted of other polymer latices, bitumen, and glass, using as carrier fluids water, glycerol, mineral oil, lithene, and solutions involving some of these. Particle sizes ranged widely,  $0.055 < a < 65 \mu m$ . Some of the data represented Newtonian behavior, but most were non-Newtonian and some of the data reported were for the high-shear limit. All these are shown in figure 3, representing data reduction in terms of the Eilers model to obtain  $\varphi_M$ . The superposition of data is deemed excellent, considering the diversity of system parameters. The solid line represents eq. (6) with  $[\eta] \varphi_M = 2.0$ .

Similar success with a correlation for monodisperse spherical particles in terms of  $\varphi/\varphi_M$  was obtained by Chong et al. [34] for Newtonian viscosity. Their correlation function was

$$\eta_{r0} = \left[ 1 + \frac{0.75 \, \varphi/\varphi_M}{1 - \varphi/\varphi_M} \right]^2 \tag{13}$$

which has similarities to eq. (11). Eq. (13) does not contain  $[\eta]$  explicitly; it agrees with the Eilers model (and the Einstein result) in the dilute limit if  $\varphi_M = 0.60$ ,



Fig. 3. Non-Newtonian and Newtonian viscosities for a variety of systems containing spherical particles. The systems of figures 1 and 2 are represented only in the infinite-shear limit:  $\Box$  [25],  $\blacksquare$  [26],  $\blacktriangle$  [27]. Other systems are: polystyrene latex in water,  $a = 0.1-0.4 \ \mu m$  [17]  $\triangle$  and  $a = 0.1-1 \ \mu m$  [18]  $\Leftrightarrow$ ; bitumen with  $a = 4 \ \mu m$  in water and talloil [28] +; glass with  $a = 4-40 \ \mu m$  [29] in glycerol  $\diamondsuit$  and lithene  $\diamondsuit$ ; glass with  $a = 49 \ \mu m$  in ZnBr<sub>2</sub> and glycerol [30]  $\bullet$ ; glass with  $a = 65 \ \mu m$  in ZnI<sub>2</sub> and glycerol [31]  $\bigtriangledown$ ; polymethylmethacrylate latex in water,  $a = 0.055 \ \mu m$ , in the zero-shear and infinite-shear limits [32] ×; glass with  $a = 8 \ and 12 \ \mu m$  in glycerol, and  $a = 4 \ \mu m$  in ZnBr<sub>2</sub> and glycerol [33]  $\bigcirc$ 

but this causes disagreement with Eilers as  $\varphi/\varphi_M \rightarrow 1$ (when  $\varphi_M = 0.74$  is required). No attempt was made to correlate non-Newtonian data in terms of  $\varphi_M(\tau)$  as is proposed here.

Evidence for the need for a  $\tau$ -dependent  $\varphi_M$  has appeared before, but this has escaped widespread recognition. Maron and coworkers [25-27], in attempting to fit their data with an empirical model, reported that  $\varphi_M$  appeared to increase with  $\tau$ . Krieger and coworkers [16-18] fitted their  $\eta(\tau)$  data with eq. (8), but then found that  $\eta_0(\varphi)$  and  $\eta_{\infty}(\varphi)$  required two distinct values of  $\varphi_M$  - i.e.,  $\varphi_{M0}$  and  $\varphi_{M\infty}$  in our framework [see eq. (9), for which  $\varphi_{M0} = 0.57$  and  $\varphi_{M\infty} = 0.68$ ].

#### 2.3 Yield stress

The concept of  $\varphi_M(\tau)$  permits a yield stress to be predicted for  $\varphi > \varphi_{M0}$ , a concentration level that can be achieved by normal mixing procedures at high  $\tau$ . This possibility has apparently not been pointed out before.

We illustrate this with the neoprene latex data [26] from figure 2, using  $\varphi > 0.45$ . Values of  $\eta_0$  and  $\eta_{\infty}$  were

taken from Krieger and Dougherty [16], and eq. (11) was used to make predictions in the form of smoothed curves for  $\eta_r$  vs.  $\varphi$  at constant  $\tau$ . Results are displayed in figure 4, showing that  $\varphi_{M0} = 0.534$  and  $\varphi_{M\infty} = 0.615$ . Clearly, suspensions can be prepared with loadings between these limits when finite shear is applied and, when the shear is removed (or reduced), the condition  $\eta_r \to \infty$  is achieved as  $\tau \to \tau_y$ . Thus, as long as  $\varphi > \varphi_M$ , a yield stress is inescapable. This feature should arise also for nonspherical particles and for aggregating systems, though no explicit reliance on such complications is needed as long as the system can be characterized in terms of the phenomenological  $\varphi_M(\tau)$ .

#### 2.4 Derivation of stress dependence

The  $\tau_y$ -behavior described above provides a useful framework for developing a description for  $\varphi_M(\tau)$ . We envision a solid-like material structure inside a chamber volume  $V_c$  to which stress is applied with a semi-permeable piston; a figurative representation of the process is given in figure 5. The initial microstructure (figure 5a) is rather loose and chain-like, corresponding to  $\varphi_{M0}$  and  $V_{c0}$ , with the remaining space filled by the suspending fluid. Application of shear, with  $\tau > \tau_{y0}$ , causes alteration of the initial structure and a fluid-like condition develops, but pressure on the semi-permeable piston allows fluid to be squeezed out



Fig. 4. Viscosity prediction of eq. (11),  $\eta_r(\varphi)$ , when fitted to the data of figure 1 at different constant values of shear stress  $\tau$ . The viscosity becomes asymptotically infinite ( $\tau \rightarrow \tau_y$ ) when  $\varphi \rightarrow \varphi_M$ , but this condition occurs with different values of  $\varphi_M$ as  $\tau$  varies. The two limiting values  $\varphi_{M0}$  and  $\varphi_{M\infty}$  are displayed as boundaries of the  $\varphi$ -region (shaded) within which a yield stress may occur



Fig. 5. Schematic representation of material structural change as stress increases, to illustrate how  $\tau_y$  depends on  $\varphi_M$ . The solid-like material is contained in a chamber having a movable piston (cross-hatched) that is permeable only to the suspending liquid. (a) Initial condition, with floc structure occupying the entire chamber domain and  $\varphi_M = \varphi_{M0}$ . (b) Application of stress to the piston causes partial collapse of the floc structure, creating regions of densified dispersed structure and expelling some liquid through the piston; thus, at this elevated  $\tau_y$ , the value of  $\varphi_M$  has increased. (c) Even with the highest possible stress ( $\tau_y$ ), the process is limited to a complete conversion of the floc structure to the densified structure which is characterized by  $\varphi_{M\infty}$ 



Fig. 6. Schematic representation of  $\varphi_M(\tau)$ 

until another solid-like condition is achieved with  $\tau_{y1} > \tau_{y0}$ . The microstructure is viewed (figure 5b) as consisting of mixed chains and densified regions;  $V_c < V_{c0}$ , since particle volume  $V_P$  is constant and some fluid has escaped, and  $\varphi_{M1} = V_P/V_c$  is thus increased. A succession of such incremental steps ultimately achieves a limiting case (figure 5c) characterized by  $\varphi_{M\infty}$  and  $\tau_{y\infty}$  beyond which fluidization cannot occur for geometrical reasons and no more fluid can be squeezed out. A schematic depiction of the expected  $\varphi_M(\tau)$  function is given in figure 6.

For purposes of the derivation, we simplify the intermediate microstructure as a blend consisting of only two "phases": The loose flocculated phase having a particle volume  $V_{PF}$  and total volume  $V_F$ , and the dense dispersed phase with particle volume  $V_{PD}$  and total volume  $V_D$ . This provides the relationships

$$\varphi_M = \frac{V_P}{V_c} = \frac{V_P}{V_F + V_D},\tag{14}$$

$$V_F = V_{PF}/\varphi_{M0}, \qquad V_D = V_{PD}/\varphi_{M\infty}, \qquad (15)$$

$$V_P = V_{PF} + V_{PD} = \text{constant} .$$
 (16)

From eq. (14) we obtain the differential form

$$d\phi_{M} = \frac{-V_{P}}{(V_{F} + V_{D})^{2}} \left( dV_{F} + dV_{D} \right), \qquad (17)$$

and eq. (15) gives  $dV_F = dV_{PF}/\varphi_{M0}$  and  $dV_D = dV_{DF}/\varphi_{M\infty}$ . Together with  $dV_{PF} = -dV_{PD}$  from eq. (16), these allow eq. (17) to be expressed as

$$\frac{d\varphi_M}{\varphi_M^2} = \left(\frac{1}{\varphi_{M0}} - \frac{1}{\varphi_{M\infty}}\right) df \tag{18}$$

where  $df = dV_{PD}/V_P$  and f is the fraction of total particulates that exist in the dispersed phase. This can be integrated to get

$$\frac{1}{\varphi_M} = \frac{1}{\varphi_{M0}} - \left(\frac{1}{\varphi_{M0}} - \frac{1}{\varphi_{M\infty}}\right) f, \qquad (19)$$

using the condition  $\varphi_M = \varphi_{M0}$  at f = 0.

What still needs to be determined is how f depends on  $\tau$  (or on  $\dot{y}$ ). We envision that the two phases of figure 5 are in a state of dynamic exchange that depends on  $\tau$  (analogous to chemical reactions between phases at a given temperature):

$$V_{PF} \xrightarrow[k_{P}]{} V_{PD} \tag{20}$$

and that the exchange rate can be written

$$-\frac{dV_{PF}}{dt} = k_D V_{PF} - k_F V_{PD} \,. \tag{21}$$

At steady state, eq. (21) yields  $V_{PD} = (k_D/k_F) V_{PF}$  and therefore

$$f \equiv \frac{V_{PD}}{V_{PF} + V_{PD}} = \frac{1}{1 + (k_F/k_D)} \,. \tag{22}$$

The rate constant for floc recovery,  $k_F$ , is taken to depend on Brownian motion and thermal stability of the floc; thus we presume it to be independent of  $\tau$ . However, the rate constant for floc destruction (or dispersed-phase creation),  $k_D$ , should depend on the hydrodynamic forces employed to overcome interparticle attractive forces. Hence, the ratio  $k_F/k_D$  should be  $\tau$ -dependent primarily through  $k_D(\tau)$ . Since the exact mechanisms for floc breakup are not precisely known, we use  $k_D \propto \tau^m$  with m > 0. Therefore, eq. (22) becomes

$$f = \frac{1}{1 + A \tau^{-m}},$$
 (23)

with A and m to be evaluated by experiment. Behavior of  $\varphi_M(\tau)$  dictated by the combination of eqs. (19) and (23) can easily be made to resemble figure 6. No restrictions have been made concerning particle shape or polydispersity, factors that might be expected to influence A and m as well as  $\varphi_{M0}$  and  $\varphi_{M\infty}$ .

#### 3. Data analysis with eq. (6)

#### 3.1 Non-Newtonian viscosity

The KD model of eq. (6), generalized to permit  $\varphi_M = \varphi_M(\tau)$ , was used to curve-fit the data of Maron and coworkers [25-27]. A least-squares procedure was used, with input variables in pairs of  $\eta_r$  and  $\varphi$  for each value of  $\tau$ . An important constraint was that  $[\eta] =$ constant, consistent with our theoretical understanding for dispersed spheres. Results provided optimal values of  $[\eta]$  and  $\varphi_M$  at each  $\tau$ , and also optimal values of parameters in the  $\varphi_M(\tau)$  function:  $\varphi_{M0}$ ,  $\varphi_{M\infty}$ , A, m. This procedure eliminated the subjectivity associated with the graphical analysis, cited earlier in conjunction with use of the Eilers models, that led to the correlations of figures 1-3.

Agreement between the measured and predicted  $\eta_r$ was generally very good – e.g., for the neoprene latex [26] at  $\varphi = 0.559$ , the largest discrepancy over the whole  $\tau$ -range was 1.7%. The optimized parameters are given in table 1. Values of  $\varphi_M(\tau)$  agreed very well with those obtained by graphical means with the Eilers model [14], so the displays in figures 1–3 (obtained by the latter means) needed no alteration.

Earlier use of the Eilers model suggested that [n] was weakly  $\tau$ -dependent, implying slight aggregation in the dilute limit. This implication is reinforced by the magnitudes of  $[\eta]$  in table 1, all of which exceed 2.5 slightly. Thus, another data-fitting procedure was executed by allowing  $[\eta(\tau)]$ . This modest change improved the data-fit significantly throughout the whole range of  $\varphi$  and  $\tau$ . This was most noticeable for the neoprene latex data [26], for which the minimum sumof-squares for the entire collection of  $\eta_r(\varphi, \tau)$  points was reduced from 420.6 to 2.5. While this procedure also reduced the sum-of-squares for the other two data sets [25, 27], this arose primarily from improvements in predicting the high- $\varphi$  regime at the expense of the lower- $\varphi$  regime [14]. Values of the parameters emerging from these curve-fits are displayed in table 1 in parentheses.

Addressing first the parameters arising from the constant- $[\eta]$  fitting procedure, we note that the two BS latices had similar  $\varphi_M$  and  $[\eta]$ . This is not surprising, in view of their similar chemistries. The system with the higher concentration of potassium oleate emulsifier per gram [27] had the higher  $[\eta]$ , 2.75 vs. 2.59, which is consistent with the  $e_1$  effect. This higher coulombic activity would also be expected to lead to lower  $\varphi_M$ , which indeed is also seen:  $\varphi_{M0} = 0.676$  vs. 0.678 and  $\varphi_{M\infty} = 0.732$  vs. 0.758. The neoprene latex, emulsified with sodium *n*-rosinate, had  $[\eta]$  in the same range (2.61) as the BS latices but very different  $\varphi_M$ . While

Table 1. Parameters\*) for fitting eqs. (6), (9), and (23) to data on spherical latex particles

Ref.	Particle	$\tau$ range (Pa)	Largest $\varphi$	[η]	$\varphi_{M0}$	$\varphi_{M\infty}$	$A, \operatorname{Pa}^m$	m
26	neoprene	5-50	0.559	2.610 (3.284-2.659)	0.5626 (0.5785)	0.5875 (0.6006)	33.1 (47.1)	1.167 (1.131)
25	BS	5-80	0.673	2.589 (3.113-2.313)	0.6775 (0.6928)	0.7585 (0.7334)	49.3 (82.4)	1.102 (1.279)
27	BS	0.025-1	0.641	2.748 (3.059-2.771)	0.6755 (0.6876)	0.7315 (0.7082)	0.624 (0.866)	1.005 (1.008)

\*) Values in parentheses were obtained by allowing  $[\eta]$  to be  $\tau$ -dependent, with the range of  $[\eta]$  then displayed. Other values correspond to the constraint of  $[\eta]$  being independent of  $\tau$ .

the parameter  $\varphi_M$  approached the limit of 0.74 expected for hexagonal close packing of uniform dispersed spheres in BS systems, its magnitude for the neoprene system (0.578-0.601) was far short of this. We conclude that there was little tendency toward aggregation with the concentrated BS spheres, but a significant amount with the concentrated neoprene spheres.

Table 1 shows that *m* was comparable for all three systems, 1.00-1.17; this comes close to duplicating the exponent 1.0 on  $\tau$  in eq. (8), though derivation of the latter might not have been expected to be entirely valid as  $\varphi \rightarrow \varphi_M$  and the two models have different origins. A major difference among the three latex systems is seen in the low- $\tau$  non-Newtonian transition of one BS suspension [27]. This is reflected in the abnormally low value of A (0.62 Pa<sup>m</sup>, vs. 33 and 49 Pa<sup>m</sup>), but the reasons for it are not understood.

It should be recognized that data correlations of the form  $\eta_r$  vs.  $\varphi/\varphi_M(\tau) - e.g.$ , figures 1-3 - do not imply that the same curve should be followed by all systems. Even if  $\varphi_M$  were not a function of shear, the presence of the exponent  $[\eta] \varphi_M$  in eq. (6) causes particle shape factors and the state of aggregation to influence  $\eta_r(\varphi/\varphi_M)$  through the magnitude of  $[\eta]$ . Variations of PD also cause the product  $[\eta] \varphi_M$  to vary from system to system, since  $\varphi_M$  then varies. These trends are illustrated in figure 7, where the predictions of eq. (6)



Fig. 7. Viscosity predictions of eq. (6) for non-Newtonian behavior caused by  $\varphi_M(\tau)$  for various constant values of the product  $[\eta] \varphi_M$ . The highest curve corresponds to  $[\eta] \varphi_M = 2.5$ 

are given for several constant values of  $[\eta] \varphi_M$ . The upper value 2.5 was selected to represent perfectly dispersed spheres ( $[\eta] = 2.5$ ) of infinite PD ( $\varphi_M = 1$ ) but could also represent other cases. Smaller values correspond to lesser degrees of PD ( $\varphi_M < 1$ ) for dispersed spheres, or other cases.

Other modifications to the  $\eta_r(\varphi/\varphi_M)$  curve-shape occur when  $\tau$ -dependence is found in the product  $[\eta] \varphi_M$ . If  $[\eta]$  is  $\tau$ -independent (as assumed for the nonparenthetic values in table 1, for spheres), then  $\varphi_M$ provides the shear influence and  $[\eta] \varphi_M$  increases with  $\tau$ . In table 1, this case provides three illustrations, with  $[\eta] \varphi_M$  changing  $1.47 \rightarrow 1.53$  [26],  $1.75 \rightarrow 1.96$  [25],  $1.86 \rightarrow 2.01$  [27]. The latter two variations are nearly the same in range and in magnitude, explaining why they superimposed with each other so well in figure 2. The neoprene latex [26] differs considerably in its  $[\eta] \varphi_M$ values from the other two, a difference manifested in figure 2 by the curve (for neoprene) not representing the BS data equally well.

When  $[\eta]$  is also  $\tau$ -dependent, the product  $[\eta] \varphi_M$  may either increase or decrease with  $\tau$  or remain nearly constant. In the latter case, figure 7 is a suitable representation, but in general deviations from the curveshapes in figure 7 would occur. With the parenthetic values in table 1,  $[\eta] \varphi_M$  is seen to decrease with  $\tau$  as:  $1.90 \rightarrow 1.60$  [26],  $2.16 \rightarrow 1.70$  [25],  $2.10 \rightarrow 1.96$  [27]. Note that these curve-fits (all superior to the corresponding constant- $[\eta]$  cases) provide in the Newtonian limit for  $[\eta]_0 \varphi_{M0} \cong 2$ ; this corresponds to equivalence of eq. (6) with the Eilers model. The high- $\tau$  limits are also close to the expectation for close-packed spheres:  $[\eta] \varphi_{M\infty} = (2.5) (0.74) = 1.85$ . Indeed, the product  $[\eta] \varphi_M$  was found [14] to be nearly invariant with  $\tau$  over two orders of magnitude of  $\tau$ .

#### 3.2 Yield stress

A unique feature of the  $\varphi_M(\tau)$  model in eq. (19) is that it can be inverted to predict  $\tau_y$ . Since, by definition,  $\varphi_M$  is the value of  $\varphi$  above which flow is impossible, then the value of  $\tau$  prevailing at that  $\varphi$  is identified as  $\tau_y$ . Solving eqs. (19) and (23) for  $\tau$  gives

$$\tau_{y}(\varphi) = \left[ A \frac{\varphi_{M\infty}}{\varphi_{M0}} \left( \frac{\varphi - \varphi_{M0}}{\varphi_{M\infty} - \varphi} \right) \right]^{1/m}$$
(24)

where it is understood that  $\varphi_{M\infty} > \varphi > \varphi_{M0}$ . Other functions for  $f(\tau)$  in eq. (23) would lead to other predictions for  $\tau_y(\varphi)$ , but in principle such an inversion can always be made. Eq. (24) meets the requirement that  $\tau_y \to 0$  as  $\varphi \to \varphi_{M0}$  and  $\tau_y \to \infty$  as  $\varphi \to \varphi_{M\infty}$  (no flow possible). Clearly, the behavior of  $\tau_y(\varphi)$  in eq. (24) does not resemble a simple power-law dependency on  $\varphi$ ,

## 4. Other work

The rheological concepts described here were developed in the context of studying the rheology of dense coal suspensions in a variety of neutrally buoyant organic liquid carriers [14]. Because the coal particles were nonspherical, were screened to provide a variety of size distributions, and exhibited varying degrees of aggregation in the different carriers, there was a need for a simple but flexible model to accommodate all these effects. The data on coal suspensions, together with curve-fits of the present model to non-Newtonian viscosity and yield stress, will be presented in a subsequent publication [35].

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(Received December 9, 1983)

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