A structural viscosity model for magnetorheology

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A structural viscosity model is proposed, which describes the shear viscosity from the balance between build up (magnetic field-induced clustering) and breakdown (shear-induced breakup) of particle aggregates. The model accounts for typical deviations from Bingham model predictions that are extensively reported in the MR literature. More precisely, the model (i) provides a physical ground for the observed Casson-like shear flow behaviour, (ii) predicts the existence of a low shear plateau in weak MR fluids, and (iii) asymptotically recovers the typical Bingham-like behavior that is observed in (strong) conventional MR fluids at experimentally accessible times. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4734504]

Magnetorheological (MR) fluids are colloidal dispersions that exhibit a rapid increase in viscosity upon the application of an external magnetic field.[1–4] The reason for this is the formation of particle aggregates aligned in the field direction. In the absence of flow, the equilibrium structure in MR fluids is determined by only the particle volume fraction ϕ and the so-called λ parameter that is basically the ratio between the magnetic interaction energy between two particles relative to the thermal energy,

$$\lambda = \frac{\pi \mu_0 \mu_{cr} \beta^2 a^3 H^2}{2\kappa_B T}, \tag{1}$$

where $\mu_0 = 4\pi \times 10^{-7}$ Tm/A is the permeability of vacuum, μ_{cr} is the relative permeability of the continuous phase, $\beta = (\mu_{pr} - \mu_{cr})/(\mu_{pr} + 2\mu_{cr})$ is the contrast factor or coupling parameter, a is the radius of the particles, μ_{pr} is the relative permeability of the particles, H is the magnetic field strength, κ_B is the Boltzmann constant, and T is the absolute temperature. In the case of conventional (strong) MR fluids $0 < \beta < 1$, whereas for inverse ferrofluids (weak MR fluids) $-0.5 < \beta < 0$. For sufficiently small values of λ, Brownian motion dominates and field-induced aggregates are absent. However, for sufficiently large values of λ, magnetostatic particle interactions dominate over thermal motion, resulting in chain-like particle aggregates. In magnetorheology, λ is typically very large.

Another dimensionless number (so-called Mason number, Mn) is relevant when a magnetized MR fluid is subjected to flow. For steady shear flow, Mn is basically a dimensionless shear rate that can be defined as the ratio of hydrodynamic drag and magnetostatic forces acting on the particles[5]

$$Mn = \frac{8\eta_c \dot{\gamma}}{\mu_0 \mu_{cr} \beta^2 H^2}, \tag{2}$$

where η_c is the continuous phase viscosity and $\dot{\gamma}$ is the magnitude of the shear rate tensor. Interestingly, for large enough magnetic fields and in the case of negligible short range interparticle forces, any rheological property of MR fluids will depend on only ϕ, λ and Mn.[1] Importantly, Mn and λ parameters are related through Peclet number $Pe \equiv 6\pi\eta_c \dot{\gamma} a^3/\kappa_B T$ via $Mn\lambda = 2Pe/3$.

As a starting point, the flow behavior of field-responsive fluids is typically modeled by the Bingham fluid like equation where, in the case of steady shear flow, the stress is given by

$$\tau = \tau_y + \eta_\infty \dot{\gamma}. \tag{3}$$

Here τ_y ($\propto \mu_0 \mu_{cr} \beta^2 H^2$) is the Bingham yield shear stress and η_∞ is the (field strength-independent) high-shear viscosity. By using the Mason number (Eq. (2)) and the shear viscosity definition, $\eta = \tau/\dot{\gamma}$, Eq. (3) can be written in terms of the dimensionless viscosity as follows:

$$\eta/\eta_\infty = 1 + (Mn/Mn^*)^{-1}, \tag{4}$$

where Mn^* is the critical Mason number that determines the transition from magnetization to hydrodynamic control of suspension structure. Several micromechanical chain-like models exist in the literature to describe the particle volume fraction dependence of $Mn^*(\phi)$ by balancing magnetostatic and hydrodynamic forces and torques on field-induced structures.[6–9] These models give $Mn^* = C\phi\eta_c/\eta_\infty$ where different values for C are derived depending on specific assumptions and/or simplifications in the mechanical stability conditions in the problem.[1]

Although Eq. (4) captures reasonably well the general trend observed in the experiments, a closer inspection of experimental data available in the literature reveals that, Eq. (4) fails to describe the low shear regime and also predicts a too sharp solid-liquid transition;[1–5] in some cases a low shear plateau is observed while in other cases, a Casson like dependence is found. Interestingly, most of the experimental data reported so far in the MR literature are well described using the following empirical equation:[1]

$$\eta/\eta_\infty = 1 + Mn^* Mn^{\Delta} \tag{5}$$

with $-1 < \Delta < -2/3$ (e.g., Ref. 10, $-\Delta = 0.74$–0.83; Ref. 7, $-\Delta = 0.8$–0.9; and Ref. 6, $-\Delta = 0.74$–0.87). The exponents

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obtained experimentally are greater than $\Delta < -2/3$ as predicted in Ref. 11 through the minimization of the total magnetic energy of spheroidal aggregates; the experimentally determined exponents also satisfy $\Delta > -1$, consistent with the Bingham model (Eq. (4)). Unfortunately, there is not a physical explanation yet for Eq. (5).

In this letter, we aim to provide a physical ground for Eq. (5) by proposing a structural viscosity model that explains the many discrepancies observed when comparing experimental data to Bingham model predictions in MR fluids. We employ a structural model that assumes that the particle aggregation may be considered as a reversible process in which the forward (magnetic field-induced clustering) and the backward (shear-induced breakup) reactions are balanced at a given stress or shear rate. The viscosity model grounds on the following equation:

$$\frac{\eta}{\eta_c} = \left(1 - \frac{\phi}{\phi_m}\right)^{-2}, \tag{6}$$

where ϕ_m is the maximum packing fraction. Eq. (6) generalizes a relationship between the viscosity η and volume fraction ϕ for concentrated colloidal dispersions.[12,13] Introducing the concept of effective volume fraction $\phi_{eff} = \phi(1 + CS)$ and a kinetic description of the structural variable S (C is the aggregates compactness), leads to a viscosity function that describes the non-Newtonian behavior of the suspension under steady conditions,[14]

$$\frac{\eta}{\eta_\infty} = \left[\frac{1 + (\dot{\gamma}/\dot{\gamma}_C)^{1/2}}{\Re + (\dot{\gamma}/\dot{\gamma}_C)^{1/2}}\right]^2. \tag{7}$$

In this equation, $\dot{\gamma}_C$ is a characteristic shear rate (see below), and the rheological index is $\Re = (\eta_\infty/\eta_0)^{1/2}$ where η_0 is the low shear viscosity. This is so for $\phi_{eff} < \phi_0$, where the suspension is "a liquid" and a low shear plateau is expected (ϕ_0 is the maximum packing fraction for $\dot{\gamma} \to 0$). As ϕ_{eff} approaches the critical value ϕ_0, the suspension viscosity diverges and hence an apparent yield stress develops. For values ϕ_{eff} above ϕ_0 the suspension behaves virtually as "a solid," presenting elasticity and yield stress. Further details on these aspects can be found in Refs. 14 and 15. Here it is relevant to add that the model considers the balance between build-up and breakdown of microstructure under shear. The process is governed by a relaxation kinetics, which reaches a dynamical equilibrium at

$$\frac{\dot{\gamma}}{\dot{\gamma}_C} = \frac{\tau_{hy}^{-1}}{\tau_{Br}^{-1} + \tau_{in}^{-1}}. \tag{8}$$

As a first approximation, the Brownian time scale is $\tau_{Br} \approx a^2/D = 6\pi\eta_c a^3/\kappa_B T$, the characteristic time of the hydrodynamic interaction is $\tau_{hy} \approx \dot{\gamma}^{-1}$ and the relaxation time associated to the interaction potential, U, is $\tau_{in} \approx (-\partial U/\partial r)^{-1} \approx 6\pi\eta_c a^3/cU$ where c is a proportionality constant of order unity.[15] With this, Eq. (8) can be rewritten as follows:

$$\frac{\dot{\gamma}}{\dot{\gamma}_C} = \frac{Pe}{1 + cU/\kappa_B T} = \frac{Pe}{1 + c\lambda} \tag{9}$$

and thus the viscosity model obeys a rheological equation (Eq. (7)) of the form $\eta/\eta_c = f(\phi, Pe, \lambda)$, as required from the dimensionless analysis of colloidal suspensions. In this form, the model was suitably applied to different colloids.[15–17]

In the case of $\lambda \gg 1$, the relaxation kinetics of MR fluids is governed by

$$\frac{\dot{\gamma}}{\dot{\gamma}_C} = \frac{Pe}{c\lambda} = \frac{3}{2c} Mn \equiv \frac{Mn}{Mn^*}. \tag{10}$$

This result was expected because the Mason number is actually the appropriate dimensionless number group characterizing the perturbation-relaxation process under shear flows. A closed form of the viscosity equation can be obtained by simply substituting Eq. (10) in Eq. (7),

$$\frac{\eta}{\eta_\infty} = \left[\frac{1 + (Mn/Mn^*)^{1/2}}{(\eta_\infty/\eta_0)^{1/2} + (Mn/Mn^*)^{1/2}}\right]^2. \tag{11}$$

Interestingly, this equation predicts the existence of a low shear viscosity plateau value and a smooth transition from the first (low-shear) to the second (high-shear) Newtonian plateau (see Fig. 1). At this point, it is worth to stress here that similar observations are reported in the MR literature when magnetic interparticle interactions are not very strong; either under the presence of low field strengths or in the case of inverse ferrofluids (constituted by dispersion of micron-sized non-magnetic particles in a ferrofluid).[5,6,9,10,18–20] The same phenomenology has been described for electrorheological suspensions.[21]

The structural model proposed here is capable to explain deviations in the experimental data from the Bingham model predictions. A better visualization of the Mason number scaling can be achieved by reorganizing the viscosity equation (Eq. (11)) in the following form:

$$\frac{(\eta_\infty/\eta)^{1/2} - 1}{(\eta_\infty/\eta_0)^{1/2} - 1} = \frac{1}{1 + (Mn/Mn^*)^{1/2}}, \tag{12}$$

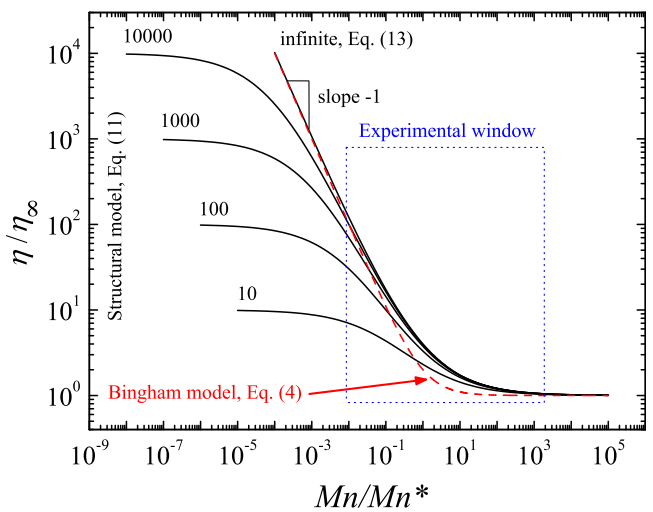

FIG. 1. Dimensionless viscosity as a function of the reduced Mason number (Mn/Mn^*). Black solid lines represent the structural model predictions for different η_0/η_∞ (Eqs. (11) and (13)). For comparison, we also include the Bingham model prediction (dashed line, Eq. (4)).

where the LHS is denoted reduced viscosity. As a way of example, Eq. (12) is compared to a set of experimental data reported in Ref. 20 for inverse ferrofluids with c.a. 800 nm diameter, in a 44 mPa s ferrofluid at a concentration of 12.6 vol. %. Results obtained using this scaling are shown in Fig. 2, where viscosity curves for different magnetic fields collapse onto the master curve predicted by Eq. (12). Small deviations in the shape of the curves are observed at high shear rates, presumably due to the fact that a certain degree of aggregation persists (ideally, all of these curves should present the same high shear plateau).

When interparticle magnetic interactions are very strong, as is the case of conventional MR fluids (constituted by dispersion of micronsized magnetizable particles in a non-magnetic medium) the low shear viscosity plateau value (if exists) is exceedingly large and hence it is hardly observed within the experimental time scales typically explored (eventually these data lay out of the experimental window shown in Fig. 1). As a consequence, an apparent yield stress and a plastic-like behavior come up. Interestingly, such a plastic constitutive equation can be easily obtained by expanding Eq. (11) for $\eta_0 \gg \eta_\infty$. With this, we get the following expression:

$$\eta/\eta_\infty = 1 + (Mn/Mn^*)^{-1} + 2(Mn/Mn^*)^{-1/2}. \qquad (13)$$

It can be demonstrated that Eq. (13) is simply a dimensionless form of the Casson plastic equation $\tau^{1/2} = \tau_y^{1/2} + (\eta_\infty \dot{\gamma})^{1/2}$.[22] Similarly to other plastic constitutive equations, it diverges at low shear with a slope of −1 (cf. Fig. 1). In fact, the first two terms in the RHS of Eq. (13) correspond to the Bingham prediction with a yield stress of $\tau_y = \frac{2c}{3}\frac{\mu_0\mu_{cr}\beta^2H^2}{8}$. The Casson equation provides a more gradual transition from the yield to the Newtonian region as is otherwise experimentally observed (cf. Fig. 2 in Ref. 23; Fig. 4 in Ref. 24). Also, Eq. (13) can be made as close as needed to the phenomenological Eq. (5) by simply taking the correct values for the fitting parameters Δ and Mn^*, in a given range of Mn numbers.

Finally, the structural model predictions are checked also with conventional MR fluids. For this purpose we use a set of experimental data reported in Ref. 25, which were obtained using carbonyl iron powder (diameter ~800 nm) in 20 mPa s silicone oil. Results are presented in Fig. 3, where viscosity curves of suspensions with different particle volume fractions, subjected to different magnetic field strengths, collapse onto the master curve predicted by Eq. (13). It is worth to mention that, for this scaling, Mn (Eq. (2)) is more appropriately written in terms of the suspension magnetization M instead of the magnetic field strength (see also Ref. 26).

In summary, in most of the experimental data reported in the MR literature the viscosity diverges with a slope of −1 at low shear rates, and thus an apparent yield stress is invoked, as predicted by plastic constitutive models. Traditionally, the Bingham model has been used because of its simplicity (Eq. (4)). Nevertheless, there are many papers reported in the literature where such a behavior is not found after closely inspecting the data (cf. Fig. 9 in Ref. 5; cf. Fig. 13 in Ref. 18; cf. Fig. 2 in Ref. 10; Fig. 13 in Ref. 19; Fig. 8 in Ref. 6; Fig. 2 in Ref. 9; Ref. 20). In most of these cases, the slope of −1 is not clearly found and the Bingham model infraestimates the experimental results. Reasons for this usually involve the presence of weak magnetostatic interactions. To cite a few, a well known example is the pioneering paper by Marshall *et al.*[5] where the deviation from the Bingham model in the transition regime in Fig. 9 of their paper was tentatively explained as a progressive degradation of the field induced structures under shear. Also, the papers by de Gans *et al.*[7] clearly show steady shear flow curves reasonably collapsing with the Mason number. However, the master curve obtained noticeably deviates from the Bingham prediction at moderate Mason numbers (cf. Fig. 11 in their paper). Authors point to several causes: the polydispersity in chain lengths, inaccurate description of interparticle magnetic interactions, over simplified description of the field induced structures. More recently, Ramos *et al.*[20] reported steady shear flow curves were an incipient low shear viscosity

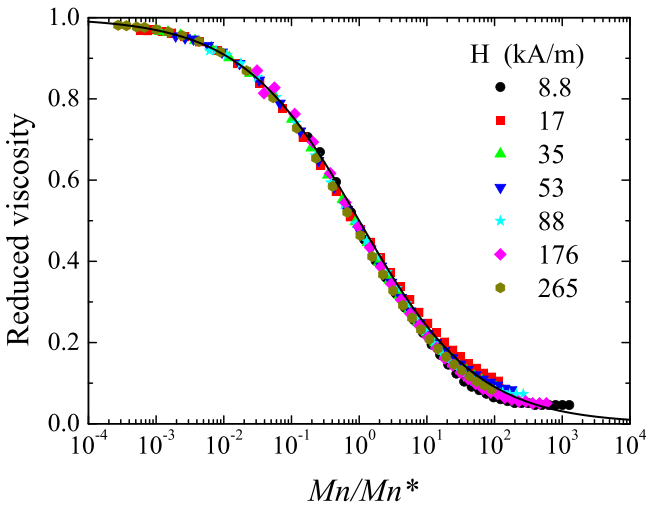

FIG. 2. Reduced viscosity (LHS of Eq. (12)) as a function of the reduced Mason number for an inverse ferrofluid (~800 nm silica particles at 12.6 vol. % in a 44 mPa s ferrofluid) subjected to different magnetic field strengths. The black solid line represents the structural model prediction (Eq. (12)).

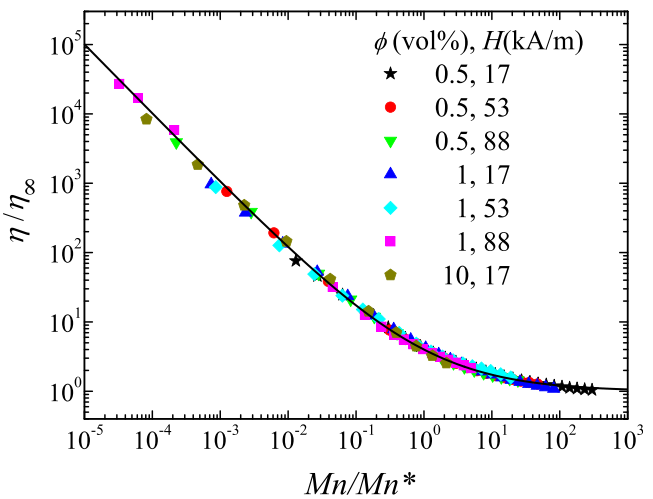

FIG. 3. Dimensionless viscosity as a function of the reduced Mason number for a conventional MR fluid (~800 nm carbonyl iron particles in 20 mPa s silicone oil), at different particle concentrations and magnetic field strengths. The black solid line represents the structural model prediction (Eq. (13)).

plateau is also envisaged. The viscosity model presented here satisfactorily describes experimental data for both weak MR fluids with a low shear viscosity plateau and strong MR fluids with a yield stress.

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[1]J. de Vicente, D. J. Klingenberg, and R. Hidalgo-Álvarez, Soft Matter **7**, 3701 (2011).
[2]J. M. Ginder, MRS Bull. **23**, 26 (1998).
[3]P. J. Rankin, J. M. Ginder, and D. J. Klingenberg, Curr. Opin. Colloid Interface Sci. **3**, 373 (1998).
[4]G. Bossis, O. Volkova, S. Lacis, and A. Meunier, "Magnetorheology: fluids, structures and rheology," in *Ferrofluids. Magnetically Controllable Fluids and Their Applications*, edited by S. Odenbach (Lecture notes in Physics, 594, Springer-Verlag 2002), pp. 202–230.
[5]L. Marshall, C. F. Zukoski, and J. Goodwin, J. Chem. Soc., Faraday Trans. **85**, 2785 (1989).
[6]O. Volkova, G. Bossis, M. Guyot, V. Bashtovoi, and A. Reks, J. Rheol. **44**, 91 (2000).
[7]B. J. de Gans, H. Hoekstra, and J. Mellema, Faraday Discuss. **112**, 209 (1999).
[8]J. E. Martin and R. A. Anderson, J. Chem. Phys. **104**(12), 4814 (1996).
[9]J. de Vicente, M. T. López-López, J. D. G. Durán, and F. González-Caballero, Rheol. Acta **44**, 94 (2004).
[10]D. W. Felt, M. Hagenbuchle, J. Liu, and J. Richard, J. Intell. Mater Syst. Struct. **7**, 589 (1996).
[11]T. C. Halsey, J. E. Martin, and D. Adolf, Phys. Rev. Lett. **68**(10), 1519 (1992).
[12]D. Quemada, Rheol. Acta **16**, 82 (1977).
[13]J. F. Brady, J. Chem. Phys. **99**, 567 (1993).
[14]D. Quemada, Eur. Phys. J. Appl. Phys. **1**, 119 (1998).
[15]D. Quemada and C. L. A. Berli, Adv. Colloid Interface Sci. **98**, 51 (2002).
[16]C. L. A. Berli and D. Quemada, Langmuir **16**, 7968 (2000).
[17]C. L. A. Berli, D. Quemada, and A. Parker, Coll. Surf. A **203**, 11 (2002).
[18]T. Y. Chen, B. J. Briscoe, and P. F. Luckham, J. Chem. Soc. Faraday Trans. **91**(12), 1787 (1995).
[19]J. W. Goodwin, G. M. Markham, and B. Vincent, J. Phys. Chem. B **101**, 1961 (1997).
[20]J. Ramos, D. J. Klingenberg, R. Hidalgo-Alvarez, and J. de Vicente, J. Rheol. **55**, 127 (2011).
[21]B. D. Chin and H. H. Winter, Rheol. Acta **41**, 265 (2002).
[22]N. Casson, *Rheology of Disperse Systems*, edited by C. C. Mill (Pergamon, London, 1959), p. 84
[23]J. C. Ulicny, M. A. Golden, C. S. Namuduri, and D. J. Klingenberg, J. Rheol. **49**(1), 87 (2005).
[24]I. G. Kim, K. H. Song, B. O. Park, B. I. Choi, and H. J. Choi, Colloid Polym. Sci. **289**, 79 (2011).
[25]J. P. Segovia-Gutiérrez, C. L. A. Berli, and J. de Vicente, "Non-linear viscoelasticity and two-step yielding in magnetorheology: A colloidal gel approach to understand the effect of particle concentration" (unpublished).
[26]D. J. Klingenberg, J. C. Ulicny, and M. A. Golden, J. Rheol. **51**(5), 883 (2007).