Nonlinear viscoelasticity and two-step yielding in magnetorheology: A colloidal gel approach to understand the effect of particle concentration

J. P. Segovia-Gutiérrez

Department of Applied Physics, Faculty of Sciences, University of Granada, C/Fuentenueva s/n, 18071 Granada, Spain

C. L. A. Berli

INTEC (Universidad Nacional del Litoral-CONICET), Güemes 3450, 3000 Santa Fe, Argentina

J. de Vicente[a)]

Department of Applied Physics, Faculty of Sciences, University of Granada, 18071 Granada, Spain

(Received 11 March 2012; final revision received 7 July 2012; published 13 August 2012)

Synopsis

The yielding behavior of conventional magnetorheological (MR) fluids is revisited for a wide range of magnetic fields and particle concentrations under a colloidal gel perspective. A two-step yielding behavior is found at intermediate magnetic fields (~10 kA/m) that can be explained as a transition from a strong-link to a weak-link (or transition) regime upon increasing the particle concentration in the MR fluid. This two-step yielding behavior is reminiscent of the classical concepts of static (frictional) and dynamic (Bingham) yield stress. By relating macroscopic elastic properties to a scaling fractal model, we could identify the prevalent gelation regime in MR fluids. © *2012 The Society of Rheology*. [http://dx.doi.org/10.1122/1.4742186]

I. INTRODUCTION

Magnetorheological (MR) fluids are field-responsive colloidal suspensions with tunable rheological properties. The presence of an external magnetic field induces string-like particulate structures in the direction of the field. This microstructure greatly affects the bulk rheology, either increasing the shear viscosity (at low volume fractions and low fields) or developing a yield stress accompanied by a viscoelastic behavior (at large field strength) [Klingenberg (2001); de Vicente *et al.* (2011); Berli and de Vicente (2012)]. Traditionally, the control over the rheology of MR fluids is essentially achieved by adjusting either the particle volume fraction or the interparticle magnetic interaction force.

[a)]Author to whom correspondence should be addressed; electronic mail: jvicente@ugr.es

With no additives, magnetic particles employed in the formulation of conventional MR fluids are rather strongly attractive (even in the absence of external fields). Hence, similarly to other aggregating suspensions, in the absence of an external magnetic field the rheological properties of MR fluids slightly increase when increasing the volume fraction at low values, and abruptly increase once the concentration is larger than a critical or threshold volume fraction (ϕ_c) corresponding to the formation of a space-filling particle network (Fig. 1). It has been reported in the literature that ϕ_c is basically independent of the external field strength and is a characteristic parameter related to the suspension itself evidencing a sort of first-order phase transition (i.e., percolation transition) [Hao *et al.* (1994)]. As a consequence, isolated clusters exist below ϕ_c while aggregated and percolated structures exist above ϕ_c, hence resulting in very different rheological behaviors when exploring the volume fractions below and above this critical concentration [Hao and Xu (1997); Chin and Winter (2002)].

Obviously, another important quantity in magnetorheology concerns the magnetic field strength. This is so because the interparticle magnetic interaction force depends on the external field [de Vicente *et al.* (2011)]. On the one hand, the effect of magnetic field strength in MR performance below ϕ_c has been described in terms of a directional gelation model [Chin and Winter (2002)]. Initially, the zero shear viscosity grows with the field strength up to a certain point when the loss factor becomes independent of the excitation frequency (the so-called gelation point). Next, at some critical value H_c, a yield stress appears and the storage modulus G' becomes higher than the loss modulus G'' (Fig. 1). On the other hand, the effect of magnetic field strength in suspensions above ϕ_c has been extensively documented mainly because most of MR fluids' applications involve volume fractions of the order of 30 vol. % and hence well above ϕ_c [Park *et al.* (2010); de Vicente *et al.* (2011)].

The physics behind the rheological behavior of MR fluids operating below or above ϕ_c and/or H_c is definitely different (cf. Fig. 1), but, surprisingly, in spite of its importance, there are very few systematic works, if any, where both magnetic field strength and particle volume fraction are varied in a wide range. On the one hand, the effect of magnetic field strength seems to be reasonably well understood. At small field strengths, the yield stress and the storage modulus are predicted to be essentially proportional to the magnetic field strength squared [Park *et al.* (2010); Ramos *et al.* (2011)]. As the applied field strength increases and the magnetization begins to saturate, the yield stress will

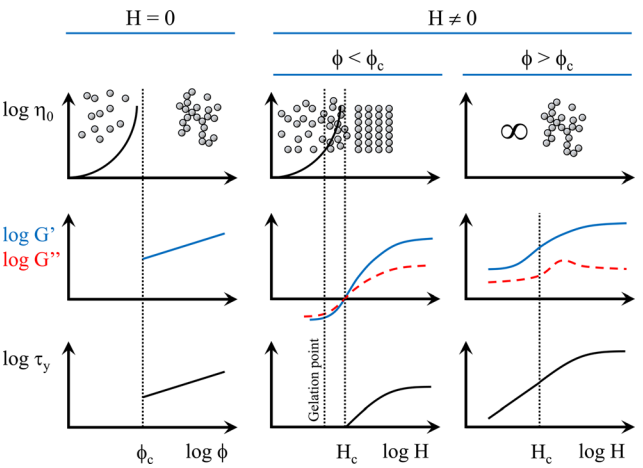

FIG. 1. Schematics of the magnetic field strength and particle concentration dependence of the low shear viscosity η_0, storage and loss moduli (G' and G''), and yield stress τ_y in magnetorheology.

increase subquadratically with the external field strength, $\tau_y = \sqrt{6}\phi\mu_0 M_s^{1/2} H_0^{3/2}$, eventually becoming field strength-independent at large field strengths, $\tau_y = 0.086\phi\mu_0 M_s^2$ [Ginder *et al.* (1996); de Vicente *et al.* (2011)]. Similarly, for intermediate magnetic field strengths, Ginder *et al.* (1996) predicted that $G' = 3\phi\mu_0 M_s H_s$. The nonquadratic dependence on the field strength arises as the particle magnetization begins to saturate near the poles in chainlike aggregates. At large field strengths where the particles' magnetization is completely saturated, the storage modulus becomes independent of field strength, and is given by $G' = 0.3\phi\mu_0 M_s^2$ [de Vicente *et al.* (2011)].

On the other hand, there is very limited number of thorough studies on the effect of particle concentration. Micromechanical models based on the fibrillation model (i.e., gap-spanning single particle-width chains) predict the yield stress and the elastic (storage) modulus that increase linearly with the number of chains, that is to say, with the volume fraction [de Vicente *et al.* (2011)]. This prediction has been experimentally confirmed in the case of diluted MR fluids at low fields where interchain interactions are ignored. Felt *et al.* (1996) claimed a linear increase of the dynamic (Bingham) yield stress with volume fraction in the range $0.014 < \phi < 0.12$. Unfortunately, these authors only investigated three volume fractions. The dynamic yield stress was also found to increase roughly linear with the particle concentration in the case of electrorheological (ER) fluids in the range $0.1 < \phi < 0.2$ [Goodwin *et al.* (1997)]. Rankin *et al.* (1999) found that the dynamic yield stress in MR greases also has an approximately linear relation with the volume fraction in the range $0.02 < \phi < 0.25$. Unfortunately, only four data were taken for the fitting. In general, more data points are needed to draw any further conclusion. In most cases, a more rapid than linear increase with volume fraction is observed for more concentrated conventional MR fluids that is thought to be associated with thick columnar structures and/or nonaffine motion of the aggregates [de Vicente *et al.* (2011)]. For example, Volkova *et al.* (2000) showed that static (frictional) and dynamic yield stresses increase faster than linear in the range $0.1 < \phi < 0.4$. Also, Chin *et al.* (2001) found that only at low volume fractions $\phi < 0.2$ a linear relation was found. As volume fraction increased, the dynamic yield stress increased faster than linear. A faster than linear increase of the dynamic yield stress has also been measured in ER fluids [Rankin and Klingenberg (1998)].

More exotic behaviors have also been reported in the literature and some of them in contradiction with each other. Using conventional MR fluids in dimethylpolysiloxane, Fujita *et al.* (2000) reported a yield stress that increases as volume fraction increases and saturates for volume fractions larger than 30 vol. %. In the case of inverse ferrofluids, Volkova *et al.* (2000) also demonstrated that after an initial increase, both static and dynamic yield stresses saturate at $\phi = 0.3$, and even decrease with the volume fraction. Linear chain models fail to predict the saturation with volume fraction; however, the yield stress dependence with volume fraction calculated with macroscopic models show an increase at low concentrations, reaches a maximum at 30 vol. % and then decreases at higher volume fractions [Volkova *et al.* (2000)].

In this work, we report a comprehensive study on the nonlinear (yielding) behavior in gelled (i.e., fully percolated, $H > H_c$) model conventional MR fluids prepared by dispersing magnetizable carbonyl iron particles in a nonmagnetic liquid medium. The yielding behavior is investigated as a function of particle volume fraction in a wide range to explore both regions below and above ϕ_c.

II. MATERIALS AND METHODS

Additive-free MR fluids were prepared by carefully mixing carbonyl iron powder (HQ grade from BASF; diameter ~800 nm) in silicone oil (20 mPa s, Sigma-Aldrich) to get

suspensions having well defined volume fractions ranging from 0.5 to 50 vol. % (metallic iron density 7.8 g/cm^3). Carbonyl iron particles (grade HQ, BASF) were chosen for this study because they are frequently used in the formulation of MR fluids [Park *et al.* (2010); de Vicente *et al.* (2011)]. It is well known that additive-free MR fluids are not kinetically stable and experience sedimentation. However, we decided not to include additives in the recipe in order to keep the fluids as simple as possible. It is also important to remark that the magnetic field employed in the rheology tests was sufficiently large for the structuration of the suspension and always applied from the beginning of the test. Under these conditions, the occurrence of sedimentation is not expected to be a problem. The preparation of suspensions consisted of the following steps: (i) Magnetic powder and silicone oil were mixed in a polyethylene container; (ii) the mixture was stirred first by hand, and then in an ultrasonic bath; and (iii) step (ii) was repeated several times to ensure the required final homogeneity.

A MCR 501 (Anton Paar) magnetorheometer was employed to investigate the rheological properties of MR fluids under shearing flows. Nonmagnetic (titanium-based) parallel plates of diameter 20mm were used. The commanded gap was set as 300 μm. An external magnetic circuit was used to generate uniaxial dc magnetic fields of the order of $\sim$100 kA/m in the gap between the plates [Wollny *et al.* (2002)]. To achieve a reasonably uniform radial magnetic flux density profile, we studied the effect of sufficiently small magnetic field strengths ($\leq$300 kA/m) [see Fig. 5 in Laun *et al.* (2008)]. As usual, magnetic field strengths reported in this manuscript refer to the maximum plateau value corresponding to radial magnetic flux density profiles provided by the manufactures of the magnetocell [Fig. 3 in Laeuger *et al.* (2005)]. Results presented below are always averages over at least three separate runs with fresh new samples. Preliminary experiments at different gap distances demonstrate that slippage effects can be discarded. All experiments were run at 25 °C.

III. LINEAR RHEOLOGICAL RESPONSE UNDER MAGNETIC FIELDS

The linear viscoelastic behavior of the MR fluids was investigated as a function of the magnetic field strength for a wide range of particle volume fractions. The strain amplitude was fixed at 0.003% and the excitation frequency was 1 Hz. Typical magnetosweep curves in the linear viscoelastic regime are shown in Fig. 2. Interestingly, two well differentiated scenarios are found depending on the particle concentration in the suspension. On the one hand, for particle volume fractions below 10 vol. %, the viscoelastic moduli are found to be negligible for magnetic field strengths below 10 kA/m. In fact, the torque at these very low moduli/field values was below the lower limit of the torque transducer and this is the reason for the scatter in the data. For larger fields, the storage modulus (G') becomes larger than the loss modulus (G'') and both moduli increase toward a final plateau at large fields close to the saturation of the dispersed particles. On the other hand, for particle concentrations larger than 10 vol. %, non-negligible moduli are measured even at low fields suggesting that for these suspensions ϕ_c is somewhere close to 10 vol. %. Actually, for concentrations larger than 20–30 vol. %, the storage modulus overpasses the loss modulus at low fields. As expected, upon increasing the magnetic field strength the storage modulus reaches a saturating value that in this case does not differ much when changing the particle concentration. Interestingly, the loss modulus reaches a local maximum and then decreases toward a final plateau value.

In summary, results presented in Fig. 2 suggest that for carbonyl iron-based conventional MR fluids the percolating transition (gelation threshold [Shih *et al.* (1990)]) appears at $\phi_c \sim$10 vol. % and that $H_c \sim$ 10 kA/m. Well below the percolating transition

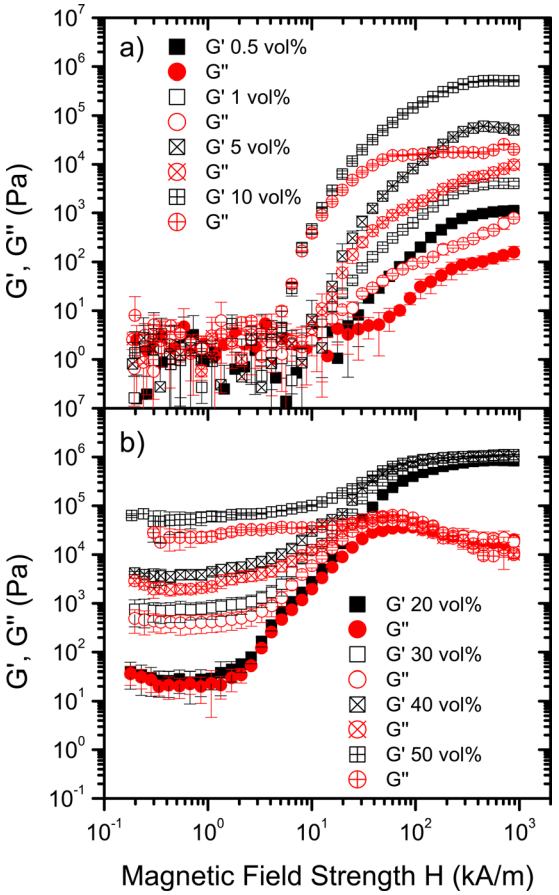

FIG. 2. Magnetic field strength dependence of storage G' and loss moduli G'' (in the linear viscoelastic region) for conventional MR fluids. (a) Particle concentrations below 10 vol. %. (b) Particle concentration above 10 vol. %. Strain amplitude $\gamma_0 = 0.003\%$ and frequency $f = 1$ Hz.

ϕ_c and for magnetic fields smaller than H_c, aggregates are expected to be short and consequently not connecting the gap. As a result, energy is completely dissipated under shear and the storage modulus is negligible. This statement is reinforced by the fact that the yield stress of the sample was found to be negligibly small. On the other hand, for magnetic fields larger than H_c percolated field-induced structures should exist for all the particle concentrations investigated (0.5–50 vol. %).

In the following, we will focus our attention to the magnetic fields above the gel point H_c, by using the criterion of the crossover of G' and G'' mentioned above. Nevertheless, it is worth noting that yield stress values from steady shear flow measurements of the same suspensions (data not shown here) indicate that the critical values H_c and ϕ_c are closely related each other, and vary inversely. In other words, the higher H_c, the lower ϕ_c, in agreement with the scenario described by Trappe *et al.* (2001) for aggregating colloids.

IV. YIELDING BEHAVIOR FROM SIMPLE SHEAR FLOW TESTS

Yield stress measurements in MR fluids are typically obtained using steady shear flow tests via extrapolation at low shear rates [Volkova *et al.* (2000); de Vicente *et al.* (2011)].

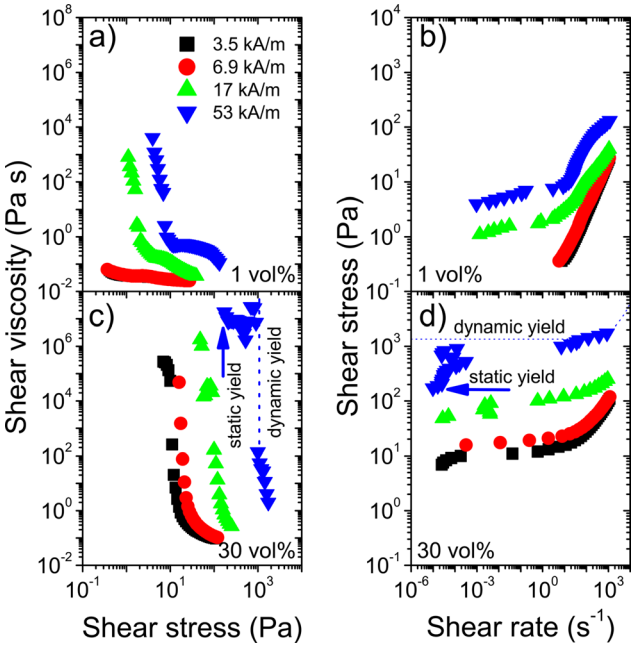

FIG. 3. Steady shear flow curves for MR fluids at two different volume fractions: (a) and (b) 1 vol. %; (c) and (d) 30 vol. %. Note the nonmonotonic behavior observed for the most concentrated MR fluid for magnetic fields larger than H_c.

In Fig. 3, we show typical results obtained for MR fluids at 1 and 30 vol. % in the presence of different magnetic fields from 3.5 to 53 kA/m. Care was taken to favor that the sheared sample had reached a steady state. Accordingly, every point in the Fig. 3 is an average during 30 s. We employ two different representations to show the onset of yielding. In the first representation [Figs. 3(a) and 3(c)], we show the shear stress dependence of the shear viscosity. Here, the yield stress is associated with the sharp drop in the viscosity when increasing the stress. On the other hand, the yield stress is given by the low shear stress plateau in shear stress versus shear rate representations [cf. Figs. 3(b) and 3(d)]. Of course, both yield stresses are the same independently of the method employed.

Magnetorheological fluids with a particle content below ϕ_c (e.g., 1 vol. % in Fig. 3) clearly show the typical behavior with a yield stress that increases with the magnetic field strength for $H > H_c$. This finding has been extensively found in the literature and in some cases a good scaling behavior with the average particle magnetization has been reported [Klingenberg *et al.* (2007)]. On the other hand, more concentrated MR fluids with particle concentration larger than ϕ_c (e.g., 30 vol. % in Fig. 3) seem to exhibit two yielding processes for intermediate fields, larger than H_c (17 and 53 kA/m). It is interesting to remark here that these results were highly reproducible both using stress and strain controlled modes, and smooth and rough surfaces. In all cases, wall slip did not occur as demonstrated by measuring at different gap thicknesses.

V. YIELDING BEHAVIOR FROM DYNAMIC OSCILLATORY SWEEPS

A more accurate determination of the yielding behavior results from unsteady dynamic oscillatory shear tests [de Vicente *et al.* (2002); Laun *et al.* (2009)]. In Fig. 4, we show the strain amplitude sweep tests for different particle volume fractions in the

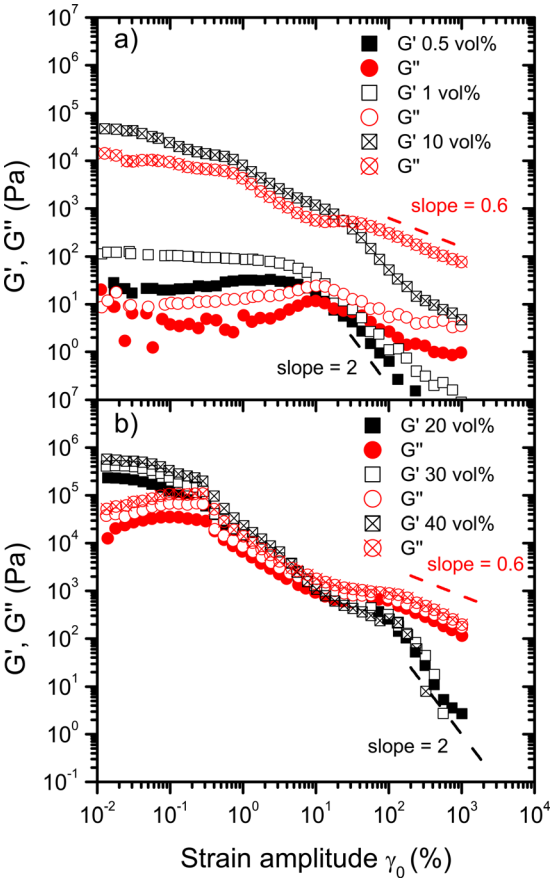

FIG. 4. Dynamic strain amplitude sweep tests with storage modulus G' (squares) and loss modulus G'' (circles) as a function of the strain amplitude at $\omega = 1$ rad/s. (a) Volume fractions below 10 vol. %, (b) volume fractions above 10 vol. %. Magnetic field strength 53 kA/m.

presence of a magnetic field strength of 53 kA/m. Experiments are grouped in two figures for better clarity. Results for volume fractions up to 10 vol. % are included in the Fig. 4(a), while those for volume fractions larger than 10 vol. % are shown in Fig. 4(b). While dilute MR fluids experience a dramatic change in the viscoelastic properties when increasing the volume fraction [see Fig. 4(a)], more concentrated MR fluids exhibit a very similar behavior very slightly dependent on the particle content [see Fig. 4(b)]. These findings are in agreement with magnetosweep tests reported in Fig. 2. As expected, MR fluids investigated clearly operate well above the gelation threshold ($H > H_c$) even for a particle volume fraction as low as 0.5 vol. %. This is so because the magnetic field strength is already very large (if compared to the thermal Brownian motion) resulting in the anisotropic connectivity of the field-induced structures and a storage modulus significantly larger than the loss modulus at low strains (cf. Fig. 2). Similar results to those reported in Fig. 4 are obtained for magnetic field strengths in the range from 17 to 265 kA/m (not shown here for brevity).

As stated in sections above, for fields larger than 10 kA/m, the storage modulus overpasses the loss modulus and this means that the samples are well above the so-called gel point [Chin and Winter (2002)]. Hence, the scaling with volume fraction is expected to be no longer of the percolation type but rather is affected mainly by the structure of the

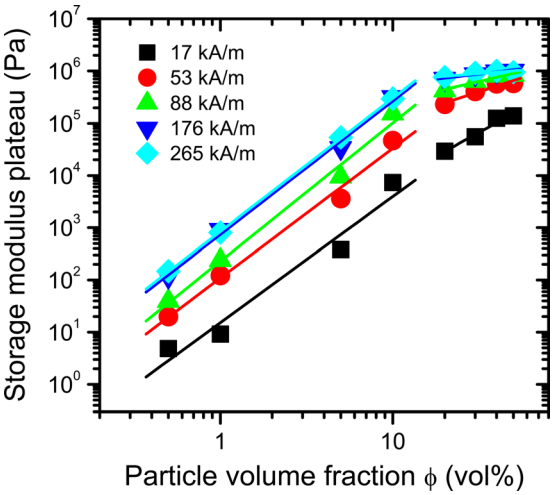

FIG. 5. Low strain storage modulus as a function of particle volume fraction (0.5–50 vol. %) for different magnetic field strengths (0–265 kA/m). The lines represent power-law fits of the data (see Table I).

individual aggregates [Brown and Ball (1985); Shih *et al.* (1990); Wu and Morbidelli (2001); Marangoni (2002)]. Accordingly, a convenient way to explore the scaling behavior is to interrogate the particle volume fraction dependence of the low strain storage modulus and the yield strain.

A. Low strain storage modulus

Let us begin reporting the low strain storage modulus dependence. The low strain G' plateau value as obtained from strain amplitude sweeps (Fig. 4) is typically used to quantify the elastic character of colloidal MR gels. In the absence of external magnetic fields, the storage modulus is negligible below 10 vol. %. This finding reinforces the idea that the percolation transition in these MR fluids is around $\phi_c = 10$ vol. %. Presumably, this limiting value of 10 vol. % should depend on the ratio between the size of the system (i.e., the gap thickness of the rheometer tools) and the typical particle size [Hao *et al.* (1997); Yanez *et al.* (1999)]. As a consequence, different formulations in the MR fluid would give a different ϕ_c. For particle contents larger than 10 vol. %, the MR fluids display a strong volume fraction dependence of the storage modulus. A power law $G' \sim \phi^n$ with exponent $n = 4.15 \pm 0.30$ is able to fit the data. Experimental values of 2.4–4.4 have been reported in the literature [Macosko (1994)]. The magnitude of the power-law exponent is believed to be related to interconnectedness and space-filling ability of the network microstructure [Tadros (1996)]. Hence, this high power in ϕ is indicative of a compact coagulated structure.

For magnetic fields larger than 10 kA/m, the storage modulus increases and tends toward a quasiplateau at large concentrations (Fig. 5). Interestingly, two well differentiated regions can be observed where G' exhibits a power-law behavior and can be fitted to the form $G' \sim \phi^n$. The best fit results for n are summarized in Table I. Below a particle concentration of 10 vol. %, n value remains approximately constant ($\sim$2.5) independently of the magnetic field applied. This value is significantly larger than the theoretical predictions under the assumption of single-width particle chains models that predict a scaling with ϕ [de Vicente *et al.* (2011)], and still larger than classical theories for strong three-dimensional particulate gels that predict a scaling with ϕ^2 [Russell *et al.* (1989);

TABLE I. Slopes corresponding to linear fits for low strain storage modulus and yield strain γ_{1L} as a function of particle volume fraction in the gel regime ($H > H_c$) from Figs. 5 and 7(a), respectively.

	Low strain storage modulus		Yield strain, γ_{1L}	
H (kA/m)	$\phi < 10$ vol. %	$\phi > 10$ vol. %	$\phi < 10$ vol. %	$\phi > 10$ vol. %
17	2.4 ± 0.3	1.8 ± 0.3	-1.35 ± 0.04	—[a]
53	2.48 ± 0.18	1.06 ± 0.18	-1.35 ± 0.04	0.4 ± 0.5
88	2.7 ± 0.2	0.76 ± 0.12	-1.35 ± 0.04	0.7 ± 0.3
176	2.55 ± 0.12	0.39 ± 0.04	-1.35 ± 0.04	1.4 ± 0.3
265	2.55 ± 0.02	0.26 ± 0.10	-1.35 ± 0.04	2.6 ± 0.2

[a]Negative slope.

Larson (1999)]. Above a particle concentration of 10 vol. %, n depends on the magnetic field strength. With increasing the field strength, the n value decreases from a value close to 2 to a value of 0.26.

B. Limiting strain/stress for linearity

Upon increasing the strain amplitude, MR fluids eventually yield exhibiting a clear decay in G' associated with the appearance of higher harmonics in the stress signal (see Fig. 4). As frequently done, we interpret the onset of nonlinearity to be the breaking of the weakest bonds in the gel-like network. Interestingly, depending on the particle content, G'' exhibits either only one or two peaks with increasing the strain amplitude, which are indicative of a maximum dissipation of energy during the period of destroying the elastic structure. Dilute MR fluids (below 10 vol. %) reveal a single yielding process associated with a single peak in G'' around a strain amplitude of $\gamma_0 = 10\%$ as commonly reported in the literature of dilute MR fluids and also predicted by macroscopic and microscopic micromechanical models with $\gamma_0 \sim 50\%$ and $\gamma_0 \sim 30\%$, respectively [de Vicente *et al.* (2011)]. Significantly, the peak in G'' occurs when G' drops below G'' meaning that local yielding coincides with macroscopic yielding. More concentrated MR fluids (above 10 vol. %) show a complex rheological response with two distinct yielding processes (two peaks in G'') similarly to attractive glasses and colloidal depletion gels with intermediate volume fraction [Laurati *et al.* (2011)]. In attractive glasses, the two yielding processes are associated with the breaking of interparticle bonds at small strains (∼4%) and with the limit of elastic cage deformations (i.e., breaking of topological constraints) at large strains (∼50%) [Pham *et al.* (2006)]. On the other hand, in depletion colloidal gels the first yield point is presumably due to the breaking of bonds between interconnected clusters (∼5%) while the second one is attributed to the breaking of clusters into smaller constituents (∼100%) [Koumakis and Petekidis (2011)].

A more convenient representation of the dynamic oscillatory strain amplitude sweep data is to plot the strain dependence of the in-phase (elastic) component of the total stress $G'\gamma_0$ [Yang *et al.* (1986)]. Interestingly, this kind of representation highlights the two key factors determining the strength of the MR fluid (i.e., the cohesive energy of the flocs $E_c \sim \frac{1}{2}G'\gamma_{1L}^2$): On the one hand, the attractive force between particles (i.e., storage modulus G') and on the other hand, the strain level at which the structure persists without losing its rigidity (i.e., the limiting strain for linearity γ_{1L}). As a way of example, in Fig. 6 we show the results for the lowest and largest fields investigated in this study (17 and 265 kA/m). The maxima or shoulders of the elastic stress provide a quantitative way of

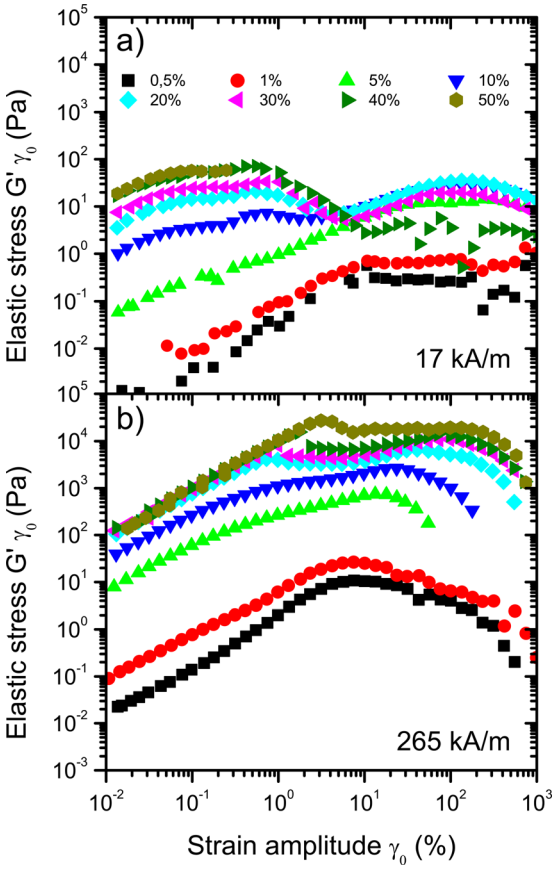

FIG. 6. Elastic stress $G'\gamma_0$ as a function of strain amplitude γ_0 for different particle concentrations from 0.5 to 50 vol. %. (a) 17 kA/m, (b) 265 kA/m.

localizing the shear yield point(s). Actually, this approach has been used in other glassy materials to illustrate the progressive structural breakdown and demonstrated the existence of two yielding processes in attractive glasses and colloidal gels [Pan and McKinley (1997); Pai and Khan (2002); Pham *et al.* (2006); Pham *et al.* (2008); Laurati *et al.* (2011); Koumakis and Petekidis (2011)]. As observed in Fig. 6, yield stresses strongly depend on magnetic field strength and particle concentration. For low and medium fields, yield strengths are of similar magnitude $(G'\gamma_0)_{\max} \sim \vartheta(10^2\text{Pa})$ as other experiments reported in literature on weakly flocculated gels, although the maxima are attained at exceedingly small strain values [Pan and McKinley (1997)]. Figure 6 reveals that a single yielding process is only present for volume fractions well below 10 vol. % independently of the magnetic field. If the particle content increases, a two-step yielding process is clearly observed. Also, the linear region is very small indeed in the case of low magnetic fields especially at the largest volume fractions investigated.

1. Yield strain

Next, we consider the dependence of the two yield points, as well as the crossing point between G' and G'' {so-called flow point [Mezger (2006)]}, on the particle volume fraction and discuss the corresponding yield strains and yield stresses (Figs. 7 and 8). The first yield strain was determined following two approaches: (i) From the point

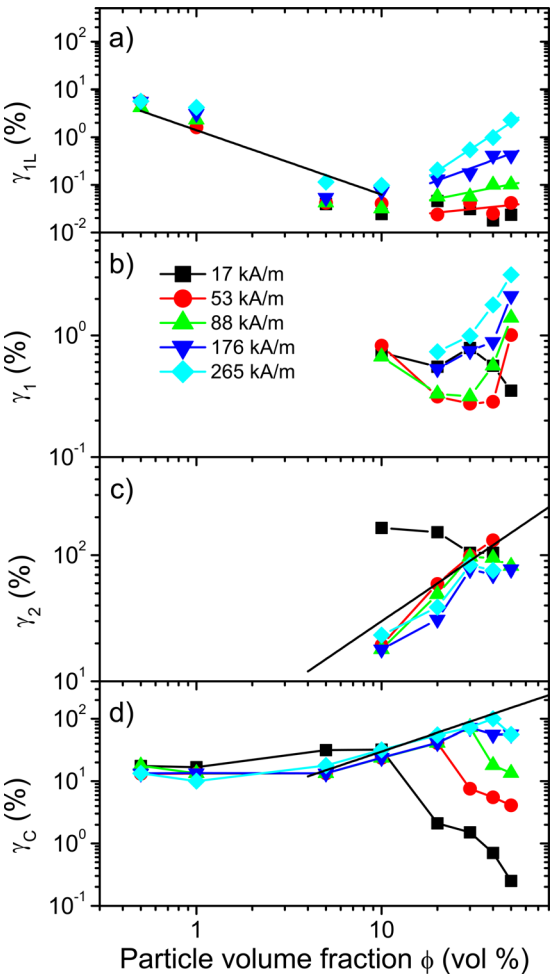

FIG. 7. Yield strains as a function of particle concentration taken from dynamic strain sweeps. (a) Limit of the linear viscoelastic region γ_{1L}, (b) first yield strain γ_1, (c) second yield strain γ_2, (d) crossover yield strain γ_c ($G' = G''$). The straight lines in (a) have power law exponents reported in Table I. Straight lines in (c) and (d) are exactly the same with a power law exponent of 1.

beyond which G' deviates more than 10% from its maximum plateau value γ_{1L} (cf. Fig. 4) and (ii) from the first maximum in elastic stress versus strain representations γ_1 (cf. Fig. 6). Their dependence with particle volume fraction and magnetic field strength is comparable. Also, the limiting strain for linearity obtained for our MR fluids (ranging from $\sim$0.01% to $\sim$1%) was about the same level as reported in the literature for MR and ER fluids [Weiss *et al.* (1994); Pan and McKinley (1997); Parthasarathy and Klingenberg (1995); Chin and Winter (2002); Claracq *et al.* (2004); de Vicente *et al.* (2005)]. As observed in Fig. 7, there are two well differentiated regions. Below 10 vol. %, the yield strain strongly decreases with a slope of -1.35 ± 0.04 (see Table I) independently of the magnetic field. This is possibly due to the lower particle densities and the higher structural and bonding flexibility that allows elongation and stretching before bonds break similarly to depletion gels [Koumakis and Petekidis (2011)]. In this region, the MR fluid becomes stiffer with increasing concentration hence showing a large modulus (cf. Fig. 5) but starts to break at smaller strain as the observable linear region shrinks with increasing particle concentration (i.e., stronger gels also are more brittle).

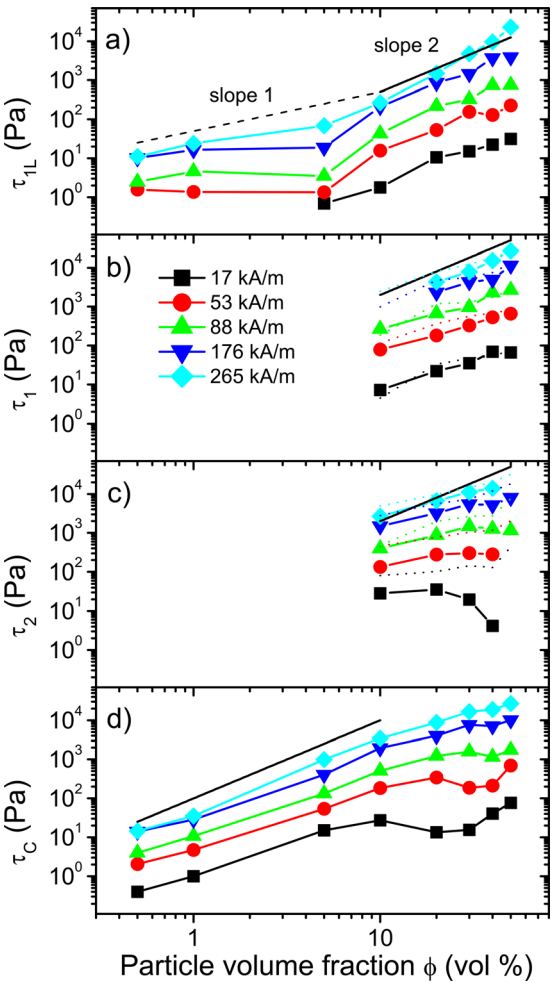

FIG. 8. Stresses corresponding to the yield strains of Fig. 7. (a) Limit of the linear viscoelastic region τ_{1L}, (b) first yield stress τ_1, (c) second yield stress τ_2, (d) crossover yield stress τ_c ($G' = G''$). The straight lines have a power law exponent of 1.0 (dashed line) and 2.0 (solid line). Dotted lines correspond to static (b) and dynamic (c) yield stress measurements under steady shear flow tests.

However, above 10 vol. % the yield strain either remains constant at a low value for small fields or increases as a power law for larger fields. We will come back to this point in Sec. VI. For the moment, it is worth to remark here that the behavior of our MR fluids at the lowest magnetic fields investigated very closely resembles the behavior of 3D depletion gels investigated by Koumakis and Petekidis (2011).

The second yield strain γ_2 is found to increase with increasing the particle concentration as expected because particle caging should reinforce as concentration increases. Only for the lowest field investigated, the second yield strain decreases. This apparently surprising result for the lowest field can be explained if cages turn into clusters due to attractions as the volume fraction decreases. Hence, the second yield strain should increase with decreasing particle content because of the enhanced flexibility of interconnected clusters [Koumakis and Petekidis (2011)]. Of course, the second yielding process disappears at particle concentrations below 10 vol. % in agreement with a critical concentration of $\phi_c = 10$ vol. %.

Magnetorheological fluids show a liquid-like behavior ($G'' > G'$) for strain amplitudes larger than the crossover strain γ_c. This crossover strain amplitude is expected to have an intermediate behavior between γ_{1L} (or γ_1) and γ_2 when increasing the particle concentration ($\gamma_{1L} \sim \gamma_1 < \gamma_c < \gamma_2$). As a consequence, for the lowest particle concentration investigated $\gamma_c \sim \gamma_{1L} \sim 10$ %, while for the largest concentrations investigated $\gamma_c \sim \gamma_2$ (see Fig. 7). Actually, for low particle concentrations, aggregates are expected to be both scarce and floppy and by simply breaking some intra-aggregate bonds the suspensions may flow. On the contrary, for more concentrated MR fluids it is necessary to break not only interaggregate bonds but also intra-aggregate links to make the suspension flow resulting in the observed power-law increase of γ_c (exponent of 1) for concentrations larger than 10 vol. %. It is interesting to observe that γ_c remains essentially constant ($\gamma_c \sim 10\%$) for particle concentrations below 10 vol. %. This suggests that in this concentration range, MR fluids are increasingly brittle but do shear melt ($G'' > G'$) at the same strain amplitude. The reason for this is unknown yet. Finally, decreasing branches in γ_c are presumably associated with flow instabilities as G' reverses to lower stresses when increasing the strain amplitude. An extreme example is the yielding behavior of MR fluids at 17 kA/m.

2. Yield stress

The yield stresses corresponding to the various yield strain points discussed above are plotted in Fig. 8. For a given particle volume fraction, these are expected to be the multiplication of the low shear storage modulus by the yield strain ($\tau = G'\gamma$). As a consequence, the stresses involved in the first yield point do linearly increase up to a particle concentration of 10 vol. %. In this region, the effect of magnetic field is manifested through the field dependence of the storage modulus as the yield strain is not sensitive to the field in this concentration range. For a particle concentration larger than 10 vol. %, the first yield stress increases with ϕ following a power-law dependence with an exponent of 2.0 that is independent of the magnetic field applied in spite of the fact that both the storage modulus and the yield strain strongly depend on the magnetic field applied (see Figs. 5 and 7, respectively). These results are in good agreement with previous experimental data reported in the literature where an intermediate slope between 1 and 2 has been claimed in a very wide volume fraction range spanning from 0.1 to 50 vol. %. Remarkably, here we show that a closer look to the volume fraction dependence reveals two well differentiated regions. It is also interesting to note that there is a good correlation between the first yield stress and the static yield stress obtained from steady shear flow tests exemplified in Fig. 3 [cf. dotted lines in Fig. 8(b)].

The second yield stress exhibits a more complex behavior. The field dependence of the second yield stress comes from the field dependence of the storage modulus. The only exception being the lowest field investigated because in this case not only the modulus but also the second yield strain depends on the field strength. As a consequence, the slopes of these curves change when changing the field. It is also interesting to note that there is a reasonably good correlation between the second yield stress and the so-called dynamic (Bingham) yield stress values extrapolated from rheograms to zero shear rate [cf. dotted lines in Fig. 8(c)]. These Bingham yield stresses were found to depend on the square of the volume fraction in many colloidal systems [Buscall *et al*. (1982); Goodwin *et al*. (1976); Larson (1999)].

The crossover yield stress represents the transition between the viscoelastic solid at low strain and the viscoelastic liquid at high strain. As observed in Fig. 8(d), a power-law exponent of 2 is obtained as a function of the volume fraction.

VI. COLLOIDAL GEL DESCRIPTION

Generally speaking, the link between the structural properties of colloidal gels and their macroscopic rheological behavior is provided by a so-called scaling theory. Basically, the structures in MR fluids are highly disordered, but similarly to other colloidal gels, there is experimental evidence that in certain length scales and at sufficiently low volume fractions they are self-similar and can be described in terms of fractal geometry [Mandelbrot (1982)]. Fractal models assume that the structure of the gels is constituted by a collection of closed packed fractal clusters of colloidal particles which during gelation aggregate with each other. Pioneering work in this field was carried out by Brown and Ball (1985). They formulated a power-law relationship of the elastic modulus to the solid volume fraction. This formulation was experimentally verified by Sonntag and Russell (1987) and Buscall *et al*. (1988) among others. Then, Shih *et al*. (1990) and Wu and Morbidelli (2001) extended the models by Brown and Ball (1985) including previous contributions by Kantor and Webman (1984) and Buscall *et al*. (1988).

In general, depending on the strength of the links between the aggregates in comparison to that of the aggregates, we can distinguish two limiting rheological regimes, namely, strong-link regime and weak-link regime reminiscent of the scaling theory for polymeric systems (Fig. 9) [Wu and Morbidelli (2001)]. The strong-link regime is achieved with very big flocs while the weak-link regime results from the formation of small flocs. At low particle concentration, well inside the strong-link regime, the links between aggregates (inter) are stronger than the intrinsic elasticity of the aggregates (intra). As a consequence, the breaking of bonds occurs within an aggregate. On the contrary, at high particle concentration, the so-called weak-link regime prevails that is dominated by the elasticity of the aggregates rather than the interlinks between aggregates. The scaling (power-law behavior) for both the storage modulus G' and the limit of linearity (i.e., yield strain) γ_{1L} with respect to the particle concentration ϕ is dictated by the fractal nature of the colloidal flocs. The forms of the equations for the strong-link regime (SLR) are

$$G'_{\mathrm{SLR}} \sim \phi^{(d+x)/(d-d_f)}, \tag{1a}$$

$$\gamma_{1L,\mathrm{SLR}} \sim \phi^{-(1+x)/(d-d_f)}, \tag{1b}$$

whereas the equations for the weak-link regime (WLR) read as follows:

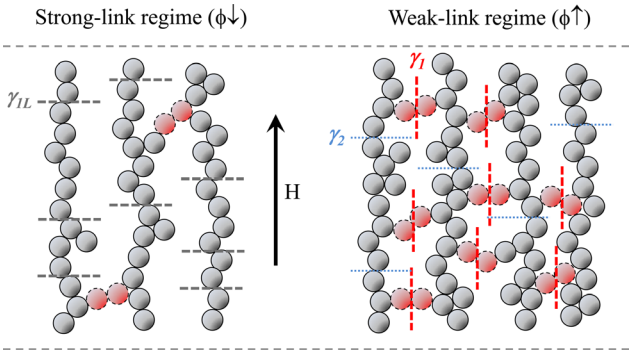

FIG. 9. Structure representation of a gelled MR fluid for $H > H_c$. Dashed lines represent the weakest bonds in the field-induced structures. Red dashed spheres represent the secondary structure reported in Pan and McKinley (1997). Left: $\phi < \phi_c$, strong-link regime. Right: $\phi > \phi_c$, weak-link regime.

$$G'_{\mathrm{WLR}} \sim \phi^{(d-2)/(d-d_f)}, \tag{2a}$$

$$\gamma_{1L,\mathrm{WLR}} \sim \phi^{1/(d-d_f)}. \tag{2b}$$

Here, d is the Euclidean dimension ($d = 3$), d_f is the fractal dimension of the flocs, and x is the backbone fractal dimension of the flocs ($1 < x < d_f$) [Shih *et al.* (1990)]. On the one hand, the fractal dimension d_f is a parameter that describes the spatial distribution of mass within the network. On the other hand, the parameter x is that fraction of the aggregate that sustains the applied load. It is difficult to estimate and is usually assumed to be in the range $x \in [1,1.3]$ [Marangoni (2002); Song *et al.* (2010)]. Both strong- and weak-link extreme situations have been verified by experiments using various gelation systems [Shih *et al.* (1990); Marangoni and Rousseau (1996); Hagiwara *et al.* (1997); Ikeda *et al.* (1999); Narine and Marangoni (1999)].

Of course, the strong- and weak-link regimes described by Shih *et al.* (1990) represent two extreme situations. In practice, intermediate situations have been reported in the literature, in the so-called transition regime (TR), where both interaggregate and intraaggregate links contribute to the gel's overall elasticity [Hagiwara *et al.* (1997); Ikeda *et al.* (1999)]. Expressions for G' and γ_{1L} in this intermediate situation were developed by Wu and Morbidelli (2001):

$$G'_{\mathrm{TR}} \sim \phi^{\beta/(d-d_f)}, \tag{3a}$$

$$\gamma_{1L,\mathrm{TR}} \sim \phi^{(d-\beta-1)/(d-d_f)}, \tag{3b}$$

where $\beta = (d-2) + (2+x)(1-\alpha)$ and α is a microscopic elastic constant in the range $\alpha \in [0,1]$. As expected, equations for the TR reproduce correctly the limiting scenarios; for the strong-link regime $\alpha = 0$, whereas for the weak-link regime $\alpha = 1$.

As shown in sections above, in the absence of magnetic fields, conventional MR fluids reported in this manuscript exhibit a power-law dependence of both the storage modulus and the yield strain on the volume fraction for $\phi > 10$ vol. %: $G' \sim \phi^{4.15\pm0.30}$ and $\gamma_{1L} \sim \phi^{-0.91\pm0.21}$, respectively. It is well known that the exponent of the volume fraction dependence of the storage modulus is related to the structure through the fractal dimension of the clusters and also related to the mechanism of particle aggregation. For example, experiments and simulations show that the exponent should be 4.5 ± 0.2 for a reaction-limited (slow) aggregation (RLA) process and 3.5 ± 0.2 for a diffusion-limited (fast) cluster-cluster aggregation (DCA) process [Buscall *et al.* (1988); Marangoni (2002)]. Using the model developed by Wu and Morbidelli (2001) and assuming a fractal dimension of backbones $x = 1.3$, we estimated a value of $\alpha = 0.527$ and a fractal dimension $d_f = 2.383$, the later being very close to the reaction-limited aggregation (RLCA) model prediction $d_f = 2.1$ suggesting that the MR fluid, in the absence of magnetic fields, behaves similarly to conventional transition gels (see Table II) [Hagiwara *et al.* (1997); Ikeda *et al.* (1999)]. Interestingly, these results suggest that other interparticle interactions apart from purely magnetostatic forces exist that are relevant in the absence of magnetic fields. As previously emphasized in Sec. I, these findings are in good agreement with microscopic observations in very similar (conventional) MR fluids reported in the MR literature. Also, similar values for the power-law exponent (4.0 ± 0.5) for the elastic modulus were obtained in silica and polystyrene latex suspensions [Buscall *et al.* (1988)] and fumed silica dispersions [Khan and Zoeller (1993)].

The behavior of MR fluids under the presence of magnetic fields is more complex. Samples below 10 vol. % do behave similarly, independently of the magnetic field

TABLE II. Evaluated microscopic parameters at $x = 1.3$ ($/x = 1.0$) using Wu–Morbidelli model (2001) for conventional MR fluids. α, microelasticity constant; d_f, fractal dimension.

		α	d_f	Gel type
>10 vol. % no field		0.527	2.383	Transition gel
<10 vol. % all fields		0	1.32	Strong-link gel
>10 vol. %	17 kA/m	0.697/0.667	1.889/1.889	Transition gel
	53 kA/m	0.863/0.849	1.63/1.63	Weak-link gel
	88 kA/m	0.988/0.986	1.63/1.63	Weak-link gel
	176 kA/m	1.171/1.188	1.883/1.883	Weak-link gel
	265 kA/m	1.248/1.273	2.301/2.301	Weak-link gel

strength. Using the corresponding equations for the strong-link regime we obtain $x = 1.269$ and $d_f = 1.319$, while using the model by Wu and Morbidelli (2001) we obtain $\alpha = 0$ and a fractal dimension $d_f = 1.32$—under the assumption of $x = 1.3$, as otherwise is frequently done in the literature [Wu and Morbidelli (2001)] (Table II). As observed, the fractal dimension estimated from the two models is very similar indeed. The similar results obtained under the application of the two fractal models indicate that the system is in the strong-link regime. Besides, the small value of the fractal dimension is in agreement with a much smaller cluster size [Marangoni (2002)], if compared to the fractal dimension obtained in the absence of magnetic fields, and also in agreement with the formation of one-dimensional elongated structures in the direction of the field [Domínguez-García and Rubio (2010)].

More concentrated suspensions (>10 vol. %) under the presence of magnetic fields do exhibit an interesting behavior. Using the corresponding relations for the weak-link regime to estimate d_f, one obtains unrealistic values as they are different when obtained from G' and γ_{1L} data. However, when using Wu–Morbidelli (2001) model remarkable results are found. Results contained in Table II show that either choosing $x = 1$ or $x = 1.3$ does not provide much difference. For the weakest field investigated, $\alpha = 0.697$ and $d_f = 1.889$ suggesting that in this case inter- and intrafloc links are comparable, and then we are in the TR. This justifies the failure of the application of the weak-link model ($\alpha = 1$). Upon increasing the field, α increases up to a value very close to $\alpha = 1$ (for fields $\gtrsim 88$ kA/m) while the fractal dimension still remains close to $d_f = 1.7$ independently of the field strength applied. Only for the largest fields investigated, d_f increases possibly due to the much larger cluster size [Marangoni (2002)].

A priori, any colloidal gel may cross over from the strong-link regime to the weak-link regime with increasing particle concentration and this seems to be the case in conventional MR fluids under the presence of an external magnetic field from the inspection of Figs. 5 and 7(a). This is manifested by the appearance of two regions. On the one hand, for low concentrations, G' increases with particle content, while γ_{1L} decreases with particle content. On the other hand, for large particle contents, G' still increases but more slowly than in the strong-link regime, and γ_{1L} increases with concentration. Accordingly, MR fluids operating in the strong-link regime (below 10 vol. %) do exhibit a single yielding process (γ_{1L}) that is associated with intracluster bond breaking. On the contrary, MR fluids operating in the weak-link regime (above 10 vol. %) do exhibit a two-step yielding process (γ_1 and γ_2). These two processes are associated with the breaking of bonds between interconnected clusters and with the breaking of clusters into smaller constituents, respectively.

The explanation above seems to be coherent with the fact that micromechanical models available in MR literature are only valid at low particle concentration [de Vicente

et al. (2011)]. This is expected because only for low particle concentrations it is feasible to assume that bond breaking first occurs inside the aggregate. Also, for large enough concentrations, the first yielding process is compatible with the existence of a secondary structure resulting from many-body interactions and comprised short chains tilted with respect to the field direction [Pan and McKinley (1997)]. This secondary structure originates a nonuniform distribution of local strain that is at the heart of the exceedingly low values of γ_{1L} and γ_1.

Finally, it is worth to remark that the application of colloidal gel scaling theories in magnetorheology has limitations. First, original fractal gel models did not take into account the field strength-dependent, long-range and anisotropic feature of the magnetic interactions between particles. As a consequence, special care has to be taken when drawing conclusions. Second, inherent to the theory is the fact that the interactions between particles are assumed to be independent of particle concentration. In general, it has been documented that clusters may swell in dilute suspensions if the interparticle interaction has a particle-concentration dependence [Shih *et al.* (1990); de Gennes (1979)]. Unfortunately, strictly speaking, this is not the case for MR fluids where interparticle magnetic forces enhance due to multipolar effects upon increasing the concentration. Consequently, this suggests that we are far from the ideal case where the volume fraction and strength of attraction could be varied independently. Third, the fractal gel models do have upper and lower concentration bounds. The lower bound is limited by the maximum size of the growing flocs and the upper bond is determined by the shrinking range of the fractal scaling region with concentration [Yanez *et al.* (1999)]. Generally speaking, fractal models can be applied only for low enough particle concentrations—even though the fractal scaling behavior has been observed at high volume fractions as well [Buscall *et al.* (1988)]. At large volume fractions, the number of particles per cluster is in fact so small that the use of fractal models can no longer be justified and more advanced theoretical models would be needed [Wu and Morbidelli (2001); Vermant and Solomon (2005)].

VII. CONCLUSIONS

We have conducted an extensive experimental research on model MR fluids having a wide range of particle concentrations and submitted to a wide range of uniaxial dc magnetic field strengths. These experiments show that most of the inconsistencies found in MR fluid literature regarding particle concentration dependences can be explained under a colloidal gel perspective well above the gelation threshold ($H > H_c$). For typical particle contents employed in the formulation of conventional MR fluids, the elastic behavior of the field-induced gels is not determined by the scaling of the percolation transition as it might be near the gelation threshold [Zimmerman *et al.* (2009)] but is instead dominated by the fractal nature of the colloidal flocs.

Considering the structure of the field-induced gel network as a collection of closed-packed fractal flocs of colloidal particles, two different scenarios are found depending on the particle concentration. On the one hand, for low enough particle volume fractions in the strong-link regime the storage modulus increases with increasing the concentration while the yield strain decreases with increasing the particle content. On the other hand, for large particle concentrations, well in the weak-link regime, both the storage modulus and the yield strain increase when increasing the particle concentration. The crossover concentration ($\phi_c \sim 10$ vol. %) from the strong-link regime to the weak-link regime does not depend on the magnetic field strength but is expected to depend on the ratio between the gap thickness and the particle size. We demonstrate that the existence of a crossover

concentration has severe consequences in the yielding behavior of MR fluids both under steady and dynamic oscillatory shearing flows. A single yielding process only appears when the concentration is below ϕ_c. For larger particle contents, a two-step yielding process comes up that reveals similarities to the rheology of attractive colloidal glasses and depletion colloidal gels, and resembles the classical static and dynamic definitions for the yield stress.

We have demonstrated that by using a colloidal gel scaling theory it is possible to extract structural information that otherwise is difficult to be obtained because MR fluids are opaque and conventional light scattering techniques are not easily applied. Surprisingly, very few papers have treated MR fluids as physical gels, in spite of that MR fluids are simple fluids amenable to be used as prototypes of the directional gel transition of colloidal gels. The rheological fractal model developed by Wu and Morbidelli (2001) is successfully employed to the case of MR fluids in the presence of magnetic fields. Its use is twofold: (i) From the rheological data, it is possible to extract structural information of the aggregates such as the fractal dimension; and (ii) assuming the backbone fractal dimension, one can compute the corresponding α value and identify the gelation regime prevailing in the system.

Results presented in this work are believed to have implications in the formulation of effective MR fluids containing the optimal amount of magnetic material according to the desired application and hence reducing costs.

ACKNOWLEDGMENTS

This work was supported by MAT-2010-15101 project (MICINN, Spain), by the European Regional Development Fund (ERDF), and by Junta de Andalucía P11-FQM-7074 and P10-RNM-6630 projects (Spain). J.P.S.-G. acknowledges financial support by the "Ministerio de Educación: Becas del Programa de Formación del Profesorado Universitario (FPU)" (AP2008-02138).

References

Berli, C. L. A., and J. de Vicente, "A structural viscosity model for magnetorheology," Appl. Phys. Lett. **101**, 021903 (2012).

Brown, W. D., and R. C. Ball, "Computer simulation of chemically limited aggregation," J. Phys. A **18**, L517–L521 (1985).

Buscall, R., J. W. Goodwin, M. W. Hawkins, and R. H. Ottewill, "Viscoelastic properties of concentrated lattices, Part 1.—Methods of examination," J. Chem. Soc., Faraday Trans. 1 **78**, 2873–2887 (1982).

Buscall, R., P. D. Mills, J. W. Goodwin, and D. W. Dawson, "Scaling behaviour of the rheology of aggregate networks formed from colloidal particles," J. Chem. Soc., Faraday Trans. **84**, 4249–4260 (1988).

Chin, B. D., and H. H. Winter, "Field-induced gelation, yield stress, and fragility of an electro-rheological suspension," Rheol. Acta **41**, 265–275 (2002).

Chin, B. D., J. H. Park, M. H. Kwon, and O. O. Park, "Rheological properties and dispersion stability of magnetorheological (MR) suspensions," Rheol. Acta **40**, 211–219 (2001).

Claracq, J., J. Sarrazin, and J. P. Montfort, "Viscoelastic properties of magnetorheological fluids," Rheol. Acta **43**, 38–49 (2004).

de Gennes, P. G., *Scaling Concepts of Polymer Physics* (Cornell University Press, Ithaca, NY, 1979).

de Vicente, J., D. J. Klingenberg, and R. Hidalgo-Álvarez, "Magnetorheological fluids: A review," Soft Matter **7**, 3701–3710 (2011).

de Vicente, J., F. González-Caballero, G. Bossis, and O. Volkova, "Normal force study in concentrated carbonyl iron magnetorheological suspensions," J. Rheol. **46(5)**, 1295–1303 (2002).

de Vicente, J., M. T. López-López, J. D. G. Durán, and G. Bossis, "A slender-body micromechanical model for viscoelasticity of magnetic colloids: Comparison with preliminary experimental data," J. Colloid Interface Sci. **282**, 193–201 (2005).

Domínguez-García, P., and M. A. Rubio, "Three-dimensional morphology of field-induced chain-like aggregates of superparamagnetic microparticles," Colloids Surf., A **358**, 21–27 (2010).

Felt, D. W., M. Hagenbuchle, J. Liu, and J. Richard, "Rheology of a magnetorheological fluid," J. Intell. Mater. Syst. Struct. **7**, 589–593 (1996).

Fujita, T., K. Yoshimura, Y. Seki, G. Dodbiba, T. Miyazaki, and S. Numakura, "Characterization of magneto-rheological suspensions for seal," J. Intell. Mater. Syst. Struct. **10**, 770–774 (2000).

Ginder, J. M., L. C. Davis, and L. D. Elie, "Rheology of magnetorheological fluids: Models and measurements," Int. J. Mod. Phys. B **10**, 3293–3303 (1996).

Goodwin, J. W., in *Colloid Science*, edited by D. H. Everett (The Chemical Society, London, 1976), Vol. II, p. 242.

Goodwin, J. W., G. M. Markham, and B. Vincent, "Studies on model electrorheological fluids," J. Phys. Chem. C **101**, 1961–1967 (1997).

Hagiwara, T., H. Kumagai, and T. Matsunaga, "Fractal analysis of the elasticity of BSA and beta-lactoglobulin gels," J. Agric. Food Chem. **45**, 3807–3812 (1997).

Hao, T., and Y. Xu, "Microstructure-confined mechanical and electric properties of the electrorheological fluids under the oscillatory mechanical field," J. Colloid Interface Sci. **185**, 324–331 (1997).

Hao, T., Y. Chen, Z. Xu, Y. Xu, and Y. Huang, "Percolation transition in electrorheological fluids," Chin. J. Polym. Sci. **12**, 97–105 (1994).

Ikeda, S., E. A. Foegeding, and T. Hagiwara, "Rheological study on the fractal nature of the protein gel structure," Langmuir **15**, 8584–8589 (1999).

Kantor, Y., and I. Webman, "Elastic properties of random percolating systems," Phys. Rev. Lett. **52**, 1891–1894 (1984).

Khan, S. A., and N. J. Zoeller, "Dynamic rheology of flocculated fumed silica suspensions," J. Rheol. **37**, 1225–1235 (1993).

Klingenberg, D. J., "Magnetorheology: Applications and challenges," AIChE J. **47**(2), 246–249 (2001).

Klingenberg, D. J., J. C. Ulicny, and M. A. Golden, "Mason numbers for magnetorheology," J. Rheol. **51**, 883–893 (2007).

Koumakis, N., and G. Petekidis, "Two step yielding in attractive colloids: Transition from gels to attractive glasses," Soft Matter **7**, 2456–2470 (2011).

Laeuger, J., K. Wollny, H. Stettin, and S. Huck, "A new device for the full rheological characterization of magneto-rheological fluids," Int. J. Mod. Phys. B **19**, 1353–1359 (2005).

Larson, R. G., *The Structure and Rheology of Complex Fluids* (Oxford University Press, New York, 1999), Chap. 7.

Laun, H. M., C. Gabriel, and Ch. Kieburg, "Magnetorheological fluid (MRF) in oscillatory shear and parameterization with regard to MR device properties," J. Phys.: Conf. Ser. **149**, 012067 (2009).

Laun, H. M., G. Schmidt, and C. Gabriel, "Reliable plate-plate MRF magnetorheometry based on validated radial magnetic flux density profile simulations," Rheol. Acta **47**, 1049–1059 (2008).

Laurati, M., S. U. Egelhaaf, and G. Petekidis, "Nonlinear rheology of colloidal gels with intermediate volume fraction," J. Rheol. **55**(3), 673–706 (2011).

Macosko, C. W., *Rheology: Principles, Measurements and Applications* (Wiley-VCH, New York, 1994), p. 457.

Mandelbrot, B., *The Fractal Geometry of Nature* (W. H. Freeman, New York, 1982).

Marangoni, A. G., "The nature of fractality in fat crystal networks," Trends Food Sci. Technol. **13**, 37–47 (2002).

Marangoni, A. G., and D. Rousseau, "Is plastic fat rheology governed by the fractal nature of the fat crystal network?," J. Am. Oil Chem. Soc. **73**, 991–994 (1996).

Mezger, T. G., *The Rheology Handbook*, 2nd ed. (Vincentz, Hannover, Germany, 2006).

Narine, S. S., and A. G. Marangoni, "Relating structure of fat crystal networks to mechanical properties: A review," Food Res. Int. **32**, 227–248 (1999).

Pai, V. B., and S. A. Khan, "Gelation and rheology of xanthan/enzyme-modified guar blends," Carbohydr. Polym. **49**, 207–216 (2002).

Pan, X.-D., and G. H. McKinley, "Structural limitation to the material strength of electrorheological fluids," Appl. Phys. Lett. **71**(3), 333–335 (1997).

Park, B. J., F. F. Fang, and H. J. Choi, "Magnetorheology: Materials and application," Soft Matter **6**, 5246–5253 (2010).

Parthasarathy, M., and D. J. Klingenberg, "A microstructural investigation of the nonlinear response of electrorheological suspensions. 1. Start-up of steady shear flow," Rheol. Acta **34**, 417–429 (1995).

Pham, K. N., G. Petekidis, D. Vlassopoulos, S. U. Egelhaaf, P. N. Pusey, and W. C. K. Poon, "Yielding of colloidal glasses," Europhys. Lett. **75**(4), 624–630 (2006).

Pham, K. N., G. Petekidis, D. Vlassopoulos, S. U. Egelhaaf, W. C. K. Poon, and P. N. Pusey, "Yielding behavior of repulsion- and attraction-dominated colloidal glasses," J. Rheol. **52**, 649–676 (2008).

Ramos, J., D. J. Klingenberg, R. Hidalgo-Álvarez, and J. de Vicente, "Steady shear magnetorheology of inverse ferrofluids," J. Rheol. **55**(1), 127–152 (2011).

Rankin, P. J., A. T. Horvath, and D. J. Klingenberg, "Magnetorheology in viscoplastic media," Rheol. Acta **38**, 471–477 (1999).

Rankin, P. J., and D. J. Klingenberg, "The electrorheology of barium titanate suspensions," J. Rheol. **42(3)**, 639–656 (1998).

Russell, W. D., D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, UK, 1989), Chap. 14.

Shih, W.-H., W. Y. Shih, S.-I. Kim, J. Liu, and I. A. Aksay, "Scaling behavior of the elastic properties of colloidal gels," Phys. Rev. A **42**(8), 4772–4779 (1990).

Song, F., L.-M. Zhang, J.-F. Shi, and N.-N. Li, "Viscoelastic and fractal characteristics of a supramolecular hydrogel hybridized with clay nanoparticles," Colloids Surf., B **81**, 486–491 (2010).

Sonntag, R. C., and W. B. Russell, "Elastic properties of flocculated networks," J. Colloid Interface Sci. **116**, 485–489 (1987).

Tadros, Th. F., "Correlation of viscoelastic properties of stable and flocculated suspensions with their interparticle interactions," Adv. Colloid Interface Sci. **68**, 97–200 (1996).

Trappe, V., V. Prasad, L. Cipelletti, P. N. Segre, and D. A. Weitz, "Jamming phase diagram for attractive particles," Nature **411**, 772–775 (2001).

Vermant, J., and M. J. Solomon, "Flow-induced structure in colloidal suspensions," J. Phys.: Condens. Matter **17**, R187–R216 (2005).

Volkova, O., G. Bossis, M. Guyot, V. Bashtovoi, and A. Reks, "Magnetorheology of magnetic holes compared to magnetic particles," J. Rheol. **44**(1), 91–104 (2000).

Weiss, K. D., J. D. Carlson, and D. A. Nixon, "Viscoelastic properties of magneto- and electrorheological fluids," J. Intell. Mater. Syst. Struct. **5**, 772–775 (1994).

Wollny, K., J. Lauger, and S. Huck, "Magneto sweep—A method for characterizing the viscoelastic properties of magneto-rheological fluids," Appl. Rheol. **12**, 25–31 (2002).

Wu, H., and M. Morbidelli, "A model relating structure of colloidal gels to their elastic properties," Langmuir **17**, 1030–1036 (2001).

Yanez, J. A., E. Laarz, and L. Bergstrom, "Viscoelastic properties of particles gels," J. Colloid Interface Sci. **209**, 162–172 (1999).

Yang, M.-C., L. E. Scriven, and C. M. Macosko, "Some rheological measurements on magnetic iron-oxide suspensions in silicone oil," J. Rheol. **30**, 1015–1029 (1986).

Zimmerman, D. T., R. C. Bell, J. A. Filer II, J. O. Karli, and N. M. Wereley, "Elastic percolation transition in nanowire-based magnetorheological fluids," Appl. Phys. Lett. **95**, 014102 (2009).