Brownian dynamic simulations and experiments of MR fluids

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Abstract. The use of computational techniques in magnetorheology is not new. In general, these approaches assume dipolar magnetic interactions, hard sphere repulsions, and no-slip conditions. In this contribution we focus on the dynamics of the equilibrium state in the presence of uniaxial DC fields. To achieve this goal we make use of Brownian Dynamic Simulations. We highlight the importance of the Brownian forces versus magnetic dipolar interaction in the range of low magnetic field strengths. We monitor the formation of columnar structures and their dynamics, in competition with the Brownian motion, until a hexatic crystal phase appears at high field strengths for monodisperse systems. The shear viscosity is computed from the Einstein relation and eventually compared with experimental data at very low-shear rates. A reasonably good agreement between both data sets is observed.

1. Introduction
The use of particle-level dynamic simulations techniques in magnetorheology is not new. Initially, these techniques were employed to interrogate the static/structural properties under no flow conditions [1]. Then, researchers moved to the investigation of MR fluids out of equilibrium under shearing [2-5] and squeezing flows [6]. Generally speaking, these approaches assume dipolar magnetic interactions, hard sphere repulsions, and no slip conditions. Most of the research efforts have assumed that Brownian motion is negligible [2-7] but there are also some reports where thermal motion is considered in spite of the large size of the constituents [8]. In this contribution we focus on the dynamics of the equilibrium state in the presence of uniaxial DC fields. To achieve this goal we make use of Brownian Dynamic Simulations [9]. We highlight the importance of the Brownian forces versus magnetic dipolar interaction in the range of low magnetic field strengths for the formation of columnar structures and its dynamics. Upon increasing the field strength, we observe the formation of columnar structures, in competition with the Brownian motion, until a hexatic crystal phase (monodisperse systems) appears at high field strengths. It is also shown that random forces introduce defects in particle aggregates along the field direction.

2. Simulations
In our simulations, we measure structure parameters to identify the formation of columnar structures and crystals. The dynamics of the system were measured with the mean square displacement and bond correlation functions. The rheology of the system was studied by means of the non-diagonal terms of the stress tensor and its correlation function. The method applied in this work presents advantages with

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respect to the classical procedure as we are capable to extract more information about the system in the equilibrium state.

Our simulation system consists in 1000 monodisperse spherical particles interacting via exponential repulsive hard-core and dipolar magnetostatic forces without bounding surfaces. Dipolar magnetic interaction between two particles is described below:

\[
\tilde{F}_{ij}^{\text{mag}} = 3U_0 \left( \frac{1}{|	ilde{r}_{ij}|} \right)^4 \left[ (2cos^2 \theta_{ij} - sin^2 \theta_{ij}) \hat{\tilde{r}} + sin2\theta_{ij} \hat{\theta} \right] \tag{1}
\]

Here, \(U_0\) controls the external magnetic field strength, \(\tilde{r}_{ij}\) denotes the relative position between two particles and \(\theta_{ij}\) is the angle that \(\tilde{r}_{ij}\) forms with the field direction. We pay special attention to the calculation of the low-shear viscosity (at zero-shear rate) following the Einstein relation \([10]\):

\[
\eta = \lim_{t \to \infty} \eta(t) = \frac{\beta}{6V} \lim_{t \to \infty} \frac{1}{t} \langle \Delta A^2(t) \rangle \tag{2}
\]

where \(\beta = 1/(k_B T)\), \(T\) is the temperature and \(k_B\) is the Boltzmann constant, \(V\) is the volume of the simulation box, \(t\) is the time and \(\langle (...) \rangle\) indicates the average over all particles. Finally, \(\Delta A(t)\) is defined as follows:

\[
\Delta A(t) = A(t+s) - A(s) = \int_s^{t+s} \sum_{\alpha<\beta} \sigma^{\alpha \beta}(t') dt'
\]

Here, \(\sigma^{\alpha \beta}(t)\) are the non-diagonal components of the stress tensor. In our case, the magnetic field is in the Z-direction, and accordingly we take the 13 and 23 components for the calculation of the viscosity. A typical calculation of the viscosity is shown in Figure 1. The shear viscosity is read from the long time plateau value.

![Figure 1. Evolution of \(\eta(t)\) in an equilibrium state. The viscosity is given by the long time plateau.](image)

3. Experiments

Conventional MR fluids were formulated by dispersing carbonyl iron spheres (HQ grade, BASF) in Newtonian silicone oils of different viscosities (20 and 500 mPa·s, Sigma-Aldrich). The particle concentration was 5 vol.%.

Low-shear viscosity data were obtained from steady simple shear flow curves using a magnetorheometer. To attain this goal, a custom-built fixture was designed to achieve sufficient torque
resolution at low magnetic field strengths (below 10 kA/m). To ensure that experimental measurements were carried out in equilibrium, prior to the test, the system was stabilized under magnetic fields during a long time period (~ $2 \times 10^3$ s). Furthermore, we took a sufficient time interval length over each measured data point to achieve a steady shear viscosity value at low-shear rates.

4. Discussion

Figure 2 shows a typical snapshot of the system for moderate field strengths (Lambda ratio is around $\lambda \approx 30$). The system is still in the fluid state as observed by the mean square displacement (see Figure 2) where we can distinguish both ballistic and diffusive regimes at very short and long times, respectively.

Thus, the columns in the snapshot are not stable over long times, but dissolve and reform, as noted in the bond correlation function (see Figure 3). This behavior is observed up to crystallization, in the case of this monodisperse system, where $\lambda \sim 50-60$.

![Figure 2](image1.png)  
**Figure 2.** (a) Microscopic structure for a monodisperse system at $U_0 = 35$. Particle columns are aligned in the field direction; (b) Mean square displacement for the three coordinate axes at the same value of $U_0$.

![Figure 3](image2.png)  
**Figure 3.** Bond correlation functions for different values of the control parameter $U_0$. 
To carry out a comparative study between experiments and simulations, the viscosity was rescaled as follows,

$$\frac{\eta - \eta_S}{\eta_{H=0} - \eta_S}$$

where $\eta_{H=0}$ corresponds to the shear viscosity at zero magnetic field and $\eta_S$ is the solvent viscosity. In this way, we correct for i) the different solvent viscosity in the simulations and experiments, and ii) the non-magnetic residual interactions in the experimental system. Importantly, using this scaling function, experimental curves collapsed for different solvent viscosities and shear rates ranging from 0.01 up to 1 s$^{-1}$ (see Figure 4).

Figure 4. Experimental normalized viscosities as a function of the magnetic field.

The comparison between experiments and simulation results is shown in Figure 5. Here, the X-axis is rescaled to collapse all curves. The reason for this rescaling is probably the remnant magnetization of the particles, or the simplification implied in the dipolar interaction. The agreement between the experimental and simulation data sets is reasonably good and deviations appear only at high magnetic fields, where the crystallization starts in the simulated monodisperse system. At this point it is worth to stress that carbonyl iron particles employed in the formulation of the MR fluids are very polydisperse and as a consequence crystallization is prevented. As expected, by introducing a slight polydispersity in the simulation system the deviation is reduced (see Figure 5).
5. Conclusions

Despite the many approximations there is a reasonably good agreement between the low shear viscosity obtained from experiments and simulation results. Polydispersity improves the behavior of the simulation system at high magnetic fields and avoids crystallization. Also, valuable information is obtained from the calculation of order parameters such as potential energy and the average number of neighbors per particle, which achieve a plateau when the system is equilibrated. The present results show that the simulation, if properly rescaled, reproduces not only qualitatively but also quantitatively. Also, we found a nondependent behavior of the rescaling with shear rate in at least two decades.

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References

[1] Tao R 1999 Rheology Series 8 659-76
[2] Klingenberg DJ, van Swol F and Zukoski CF 1989 J. Chem. Phys. 91 7888
[3] Klingenberg DJ, van Swol F and Zukoski CF 1991 J. Chem. Phys 94 6160
[4] Parthasarathy M and Klingenberg DJ 1999 J. Non-Newtonian Fluid Mech. 81 83
[5] de Vicente J, Vereda F, Segovia-Gutiérrez JP, Morales MP and Hidalgo-Álvarez R 2010 J. Rheol. 54 1337
[6] de Vicente J, Ruiz-López JA, Andablo-Reyes E, Segovia-Gutiérrez JP and Hidalgo-Álvarez R 2011 J. Rheol. 55 753
[7] Heine M, de Vicente J and Klingenberg DJ 2006 Physics of Fluids 18 023301
[8] Martin JE 2000 Phys. Rev. E 63 011406
[9] Paul W and Yoon DY 1995 Phys. Rev. E 52 2076
[10] Puertas AM, De Michele C, Sciortino F, Tartaglia P and Zacarelli E 2007 J. Chem. Phys. 127 144906