LIQUID TO SOLID TRANSITION OF INVERSE FERROFLUIDS

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Introduction. By dispersing microsized polystyrene particles in ferrofluid an ideal magneto-rheological model fluid can be created. Because polystyrene particles are available, which are practically monodisperse (sigma=0.048), this inverse fluid allows to control particle size and polydispersity, in advantage to the common ferro- and magneto-rheological fluids, which are only polydisperse. The nonmagnetic polystyrene particles create a hole in the ferrofluid, which appear to posses a magnetic moment corresponding to the amount and susceptibility of the displaced fluid. Due to the dipolar interactions of the holes, chain formation sets in and the hybrid fluid undergoes a transition from liquid to solid like behavior. We investigate this transition by recording the storage modulus G' and the loss modulus G'' versus the magnetic field for different volume fraction, particle size, and particle size distribution. Our results show that for a monodisperse fluid the liquid-to-solid transition is more pronounced than for a polydisperse one – a related effect has recently been found in MD simulations for standard ferrofluids.

1. Inverse ferrofuids. Common magnetorheological fluids (MRF) are suspensions of micron-sized, magnetizable particles like carbonyl iron, dispersed in a non-magnetic carrier liquid. They have the ability to change their rheological properties under the influence of a magnetic field. Their flow behavior is typically described as that of a classical Bingham fluid, where the yield stress is a function of the applied field strength [1].

It is known that plain ferrofluids can also be transformed in MRFs by the suspension of non-magnetic particles, like micron-size polystyrene or silica spheres. These non-magnetic particles create a hole which appears to possess a magnetic moment $m = -4\pi\beta a^3 H$, corresponding to the displaced fluid [2], where a is the radius of the spherical particles, H the magnetic field, and $\beta = (\mu_\mathrm{r} - 1)/(2\mu_\mathrm{r} + 1)$ characterizes the effective permeability of the suspension, here μ_r represents the relative permeability of the fluid.

The first studies of inverse ferrofluids were undertaken by Skjeltorp [2], who studied the structures formed in a monolayer film of polystyrene spheres of 10 μm in diameter. The structures observed are similar to those found in magnetorheological fluids consisting of ferromagnetic particles dispersed in a non-magnetic carrier.

On the other hand, oscillatory measurements were made by De Gans *et al.* [3], who investigated the dependence of the rheological properties like storage and loss modulus, yield stress and viscosity on volume fraction, magnetic field and particle size. They found a strong increase of storage modulus and viscosity with particle size and field strength. Also De Gans *et al.* [4] developed a theory for inverse ferrofluids which describes the linear viscoelasticity behavior of inverse fluids. They assume that the ferrofluid is magnetically continuous on the length scale of the radius of the non-magnetic particles, which are spherical and monodisperse, and that the stress is dominated by the contribution of the particle interactions in the chains. In addition the interchain interactions are neglected, and the deformation of the chains is affine. For the inverse ferrofluids studied at 1 Hz frequency the agreement between theory and experiments is reasonably good.

The objective of this work was to study the magnetorheological effect on inverse ferrofluids using monodisperse and polydisperse polystyrene particles of different sizes in oscillatory measurements. We compare the results with the models proposed by De Gans *et al.* for the storage modulus.

2. Experimental.

2.1. Materials. The nonmagnetic particles used in our experiments were monodisperse polystyrene particles of 3 and 10 μm and polydisperse particles with a mean diameter of 8.4 μm and density of 1.05 g (ml)$^{-1}$, supplied by Microbeads AS. They were dried in a freeze dry system and used without further treatment. The particle size distribution was measured using static light scattering (SLS). Mean diameter and standard deviation for 3 and 10 μm are $D = 2.75$ μm, $\sigma = 0.17$ and $D = 10.86$ μm, $\sigma = 0.048$, respectively. For polydisperse particles $D = 8.4$ μm, $\sigma = 0.51$. The ferrofluid used was APG 512A, Lot. N° F083094CX (Ferrotec, Co.). It contains magnetite particles dispersed in synthetic hydrocarbon with a relative viscosity of 75 mPa · s, at 27°C. The magnetization curve obtained in a SQUID magnetometer showed a saturation magnetization of M_s 27.68 kA/m.

2.2. Sample preparation. The inverse ferrofluids were prepared by taking the dried polystyrene particles (in different amounts), and dispersing them in the ferrofluid. The system was alternately stirred for 10 to 15 minutes and sonicated for the same time until a homogeneous mixture was obtained. The volume fractions of non-magnetic particles, namely, $\phi = 0.175$, 0.25 and 0.30, were determined from mass measurements. The same volume fraction was used for the three different particle sizes of polystyrene. The obtained magnetic fluids proved to be stable for several hours.

2.3. Rheological measurements. A Physica MCR300 rheometer (Anton Paar) with the commercial magnetorheological cell PP 20/MR was used to measure the magnetorheological properties of inverse ferrofluids. The field was oriented perpendicular to the plates of the rheometer, and thus, perpendicular to the direction of the shear. The distance between the plates was adjusted to 0.3 mm in order to optimize the sensitivity. Oscillatory measurements were carried out in the linear viscoelastic range checked by varying the strain amplitude on the samples in order to ensure that the structure is not destroyed. The tests were performed at a constant strain amplitude $\gamma = 0.01\%$ and a constant angular frequency $\omega = 10$ rad/s. The magnetic field strength was increased continuously from 0 to 274 kA/m. Each of the rheological measurements was performed with a freshly prepared sample.

3. Results and discussion. The storage modulus (G') and the loss modulus (G'') as a function of volume fraction, particle size and field strength are shown in Fig. 1. Here the columns of plots have a constant particle size, and the rows have constant volume fraction. It is observed that for all measurements there is an intersection of the curves for the loss modulus and the storage modulus, indicating a transition from a liquid behavior to a quasi gel like behavior. It can be understood by the variation of the micro-structure of the inverse fluid, where the non-magnetic particles form chains or columns when the magnetic field is applied.

Chain formation already sets in for rather low magnetic fields. However, here the magnetostatic forces between the particles of the chains are still unimportant if compared to the hydrodynamic forces. For this reason the storage modulus G' at low magnetic fields is smaller than the loss modulus G''.

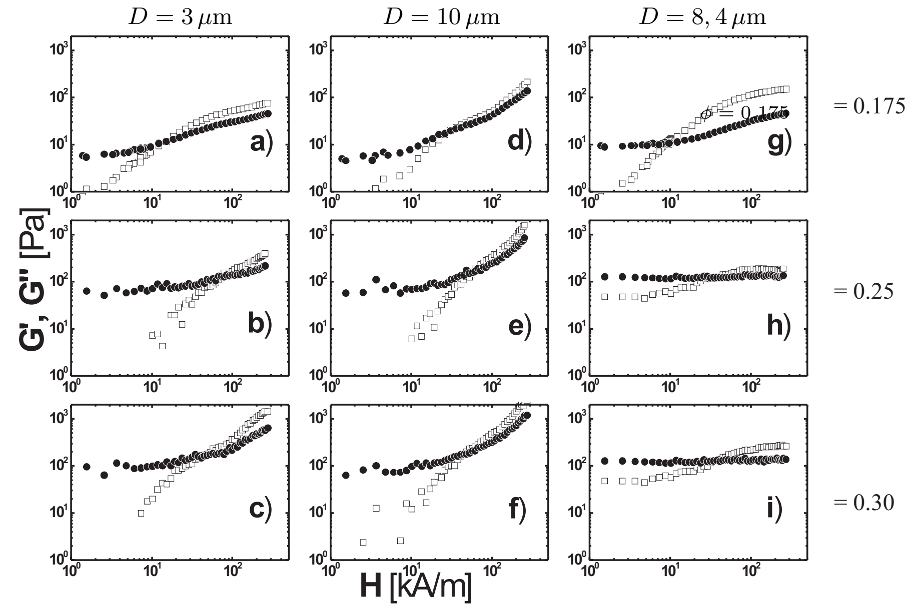

Fig. 1. Storage modulus G'(□) and loss modulus G'' (●) as a function of magnetic field strength for different volume fraction and particle sizes of non-magnetic particles in inverse ferrofluids.

With the increase of the magnetic field, the particle-particle and chain-chain interactions become stronger and a transition from a liquid to a quasi gel takes place. This transition is affected by the volume fraction of non-magnetic particles. Increasing the volume fraction ϕ from 0.175 to 0.25 (first to second row in Fig. 1), the intersection is shifted to a larger magnetic field. Increasing ϕ even further, has no remarkable effect.

The particle size has consequences for the intersection point as well, one can observe that for fluids with monodisperse particles of 3 μm (left column) the loss modulus and storage modulus aresmaller than for similar particles of 10 μm (central column). This shows that not only the particle concentration of non-magnetic particles increases the viscoelastic effects, also their particle size promotes a change.

Furthermore, also the particle size distribution has an effect on the viscoelastic response. The right column of Fig. 1 displays G' and G'' for a dispersion of polydisperse non-magnetic particles. For these particles the storage modulus G' increases more slowly with the magnetic field than for the monodisperse ones. This is valid for all the volume fractions studied. Moreover, the curves show a plateau, indicating that the viscoelastic properties are no longer affected by the influence of the magnetic field. A possible explanation is that the presence of small particles hinders the aggregation behavior. A related effect has recently been described in a molecular dynamics study of chain formation in standard ferrofluids [5]. Fig. 2 shows the storage modulus data as a function of the volume fraction, particle size and field strength made dimensionless according to the theory of De Gans *et al.* for the linear regime [4].

$$\widetilde{G}' = \frac{G'}{\frac{3}{4}\mu_0\mu_{\mathrm{r}}\beta^2\zeta(4)\phi_{\mathrm{v}}M_{\mathrm{s}}^2\left[2\left(1+\frac{\beta\zeta(3)}{2}\right)^{-2}+\left(1-\frac{\beta\zeta(3)}{4}\right)^{-2}\right]}. \tag{1}$$

Here G' represents the experimental data and M_{s} is the saturation magnetization. Moreover, also the magnetic field H_0 was scaled by M_{s}. Figs. 2*a*, *b*, and *c* give a

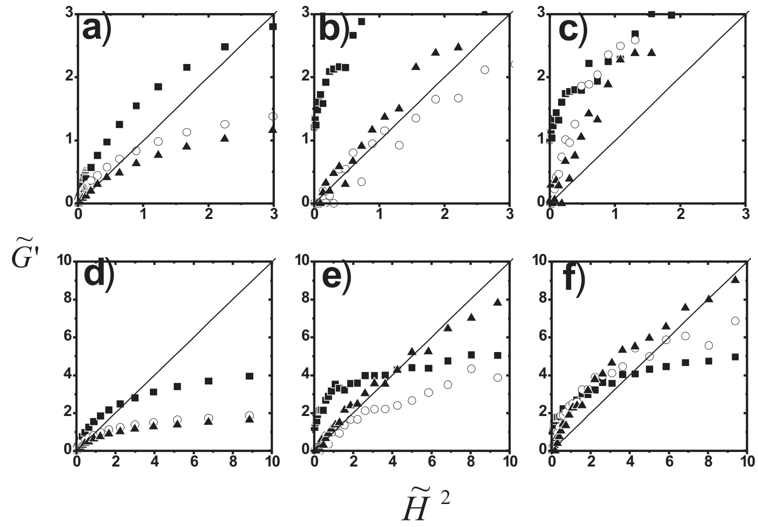

Fig. 2. Storage modulus scaled according to Eq. (1) for inverse ferrofluids with $3\,\mu$m (○), $10\,\mu$m (▲) monodisperse and $8.4\,\mu$m (■) polydisperse polystyrene particles.

comparison of experiment and theory for the volume fractions $\phi = 0.175$, 0.25 and 0.3, respectively. In the first two plots, the experimental data for monodisperse particles (denoted by circles and triangles), are found to be located in the vicinity of the diagonal. Taking into account that this model assumes that the structure of the suspension at rest is that of straight, gapspanning single chains, parallel to the field and interchain interactions are neglected, the agreement with this theory in the linear regime is relatively good. However, for the volume fraction $\phi = 0.3$ in Fig. 2*c* the experimental data exceed the predictions of the theory and the agreement is less convincing. A possible explanation is that, in this range, the formation of columns is important. It is also observed that in all three plots (*a*), (*b*), and (*c*) the results for polydisperse particles deviate considerably from the predictions. This demonstrates that the model is limited to monodisperse particles. Figs. 2*d*, *e*, and *f* show that the model is no longer valid when the linear regime is left.

4. Conclusion. We investigated the magneorheological effect of inverse ferrofluids with varying particle size and particle size distributions. These kind of fluids consist of polystyrene particles immersed in a ferrofluid which have the ability to induce a “liquid” to “solid” transition when a magnetic field is applied showed by oscillatory measurements. The storage modulus G' and loss modulus G'' do not only increase with the volume fraction, but also with the size of the monodisperse particles. For polydisperse particles the effect on G' and G'' is weaker. This supports the interpretation that the chain formation of the large particles is hindered by the presence of small ones.

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