***In situ* measurements of dispersed and continuous phase viscosities of emulsions using nanoparticles**

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Abstract

The dynamic magnetic susceptibility response of magnetic nanoparticles was used to independently determine the viscosity of the dispersed and continuous phases of oil-in-water emulsions *in situ*. Cobalt ferrite nanoparticles coated with oleic acid (OA) or poly(ethylene glycol) (PEG) were prepared and mixed with emulsions, where they partitioned to the dispersed oil phase or continuous water phase, respectively. Emulsions with a range of dispersed-phase volume fractions were prepared and characterized using the nanoparticles and conventional rheometry. Conventional rheometry showed the expected increase in emulsion viscosity with increasing volume fraction of the dispersed oil phase. In contrast, the viscosity felt by the oleic acid coated nanoparticles partitioned to the dispersed oil phase was found to be independent of the volume fraction of the discontinuous phase and quantitatively similar to the bulk phase viscosity of mineral oil. Similarly, the viscosity felt by the PEG coated nanoparticles dispersed in the continuous water phase was also found to be independent of the volume fraction of the dispersed oil phase and quantitatively similar to the bulk viscosity of water. These results demonstrate how magnetic nanoparticles can be used to directly characterize the viscosity of the dispersed and continuous phases of emulsions *in situ*.

Keywords: *magnetic nanoparticles; emulsions; macroviscosity; nanoviscosity; Dynamic Magnetic Susceptibility*

Abbreviations

DI	de-ionized
DLS	dynamic light scattering
DMS	dynamic magnetic susceptibility
OA	oleic acid
NNLS	non-linear least squares
PEG	poly(ethylene glycol)
SQUID	superconducting quantum interference device
TEM	transmission electron microscopy

Introduction

The viscous properties of the continuous and dispersed phases in emulsions are expected to contribute to the overall emulsion rheology [1-5], but have not been independently investigated *in situ* to any appreciable extent due to lack of suitable methods. Rheological properties of emulsions are commonly characterized in the bulk using conventional macro-scale instruments such as controlled-shear or controlled-stress rheometers [4, 5]. Unfortunately, macroscopic rheometry cannot provide direct measurements of the viscous properties of the individual phases in an emulsion. Additives often used to modify emulsions can significantly and disparately influence the viscosity of the individual phases. Being able to determine the effects of additives on the viscous properties of individual phases of an emulsion would be valuable in formulating emulsions with properties tailored for specific applications.

Methods for the characterization of the rheological properties of complex fluids at the microscale have been under development and use for some time. Passive and active microrheology, based on tracking or actuating the motion of beads in complex fluids, has yielded many valuable insights into the rheological properties of complex fluids at

the microscale [6, 7]. However, these techniques often require direct observation under an optical microscope and use probe particles with diameters of several micrometers. Droplet sizes in emulsions can be as small as tens of nanometers, precluding the use of micrometer diameter probe particles to characterize the internal droplet rheology.

Recently, magnetic nanoparticles have been reported to yield quantitatively accurate measurements of the viscosity of simple fluids [8], have been used to monitor gel transitions [9], and have been reported to yield estimates of nanoscale rheology of fluids [10]. These measurements are based on actively inducing magnetic nanoparticle rotation through the action of magnetic torques caused by an applied alternating magnetic field, while simultaneously measuring the alternating magnetization response of the nanoparticles dispersed in the fluid sample. The magnetization response will then lag the applied alternating magnetic field due to the hydrodynamic drag exerted on the particles, which is then related to the viscous properties of the fluid matrix the nanoparticles are suspended in through Debye's model for the dynamic magnetic susceptibility [8]. This approach has the advantages of requiring relatively small (<100 μ l) sample volumes, not requiring optic access or optically-transparent samples, and being able to probe rheological properties at the nanoscale [8, 10].

In this contribution we report experiments that demonstrate that magnetic nanoparticles can be used to directly quantify the viscosities of the dispersed and continuous phases of emulsions *in situ*. This is illustrated through experiments with oil-in-water emulsions and using cobalt ferrite nanoparticles with surface coatings that cause them to partition to either the dispersed or continuous phase upon addition to an existing emulsion. Viscosities determined using the nanoparticles are compared to those determined using conventional rheometry for the separate oil and water phases and for the emulsions. The reported technique based on magnetic nanoparticle rotation can be applied to provide understanding on the preparation of cosmetic and pharmaceutical formulations, testing of complex and biological fluids [11], estimation of viscosity in oil beds, and other situations involving multi-phase complex fluids.

Materials and Methods

Materials

Paraffin (mineral) oil, Tween 80, and Span 80 were obtained from Fisher and were used as received. Deionized water was generated using a Millipore Synergy water purification system. Cobalt chloride (II) hexahydrate (ACS reagent, 98%), iron chloride (III) hexahydrate (ACS reagent, 97%), oleic acid (technical grade, 90%), hexane (mixture of isomers, ACS reagent, $\geq 98.5\%$), chloroform (ACS reagent, $\geq 99.8\%$) and acetone (ACS reagent, $\geq 99.5\%$) were purchased in Sigma-Aldrich. Sodium oleate ($>97.0\%$) was purchased in TCI America. 1-Octadecene (90%, tech.) was purchased in ACROS Organics. All reactants were used as received and used without further purification.

Synthesis of magnetic nanoparticles

Nanoparticles coated with oleic acid (OA). Cobalt Ferrite nanoparticles were synthesized by thermal decomposition [12]. An organometallic precursor was prepared by reacting 1 mmol of cobalt chloride (II) hexahydrate, 2 mmol of iron chloride (III) hexahydrate and 8 mmol of sodium oleate in 50 mL of deionized water, 100 mL of hexane and 50 mL of ethanol at 67 °C under reflux during 4 hours. After synthesis, the metal-oleate was washed with water to remove the unreacted salts and aged in an oven at 70 °C for 15 days prior to nanoparticle synthesis, to promote predominant Brownian relaxation mechanism [12]. To obtain the nanoparticles, 25 g of the metal-oleate, 100 mL of 1-Octadecene and 2 g of oleic acid were thermally decomposed at 320 °C during 3 hours under reflux condensation. Finally, the nanoparticles were washed with a mixture 1:2 (volume ratio) chloroform/acetone, magnetically separated, and dried at room temperature to obtain the oleic acid coated cobalt ferrite nanoparticles.

Nanoparticles coated with poly(ethylene glycol) (PEG). Oleic acid coated on the surface of the cobalt ferrite nanoparticles was exchanged with PEG-silane [13] by dissolving 3 g of PEG-silane in 180 mL of toluene. 0.2 g of oleic acid coated cobalt ferrite nanoparticles were added to this solution and dispersed using a sonicator. To catalyze the hydrolysis and condensation of silane groups on the surface of the particles, 25 μ L of acetic acid were added and the solution was placed in a shaker for 72 h at room temperature. The particles were then precipitated using ethyl ether until a

turbid solution was obtained, which were then suspended in acetone and again precipitated using ethyl ether to obtain the PEG coated cobalt ferrite nanoparticles.

Dynamic Magnetic Susceptibility (DMS) Measurements

Oleic acid (OA) coated or poly(ethylene glycol) (PEG) coated nanoparticles were used to determine the viscosity of the dispersed and continuous phases of oil-in-water emulsions. A stock solution of 10 mg OA coated nanoparticles in 1 mL neat mineral oil was prepared, sonicated for 5 min at room temperature and a 100 μL aliquot was used for DMS measurements from 0 $^{\circ}\text{C}$ to 30 $^{\circ}\text{C}$ in a Quantum Design MPMS3 Superconducting Quantum Interference Device (SQUID) Magnetometer. Similar measurements were made by dispersing the nanoparticles in mineral oil mixed with a 2 % (v/v) surfactant mixture of Tween 80 and Span 80 in the ratio of 53:47 respectively, by volume. In the case of PEG coated nanoparticles, 200 μL of the original 10 mg/ml suspension in deionized water was used directly for DMS measurements at 25 $^{\circ}\text{C}$ on the Acreo DynoMag AC Susceptometer. No background subtraction was necessary as the neat emulsions had negligible signal and the particles provided a measureable signal under the conditions used.

The DMS data obtained in mineral oil at 0 $^{\circ}\text{C}$ for oleic acid coated nanoparticles and in water at 25 $^{\circ}\text{C}$ for PEG coated nanoparticles was used to obtain their hydrodynamic diameter distributions. A non-linear regression fit was made to the DMS data against the Debye model for the in-phase χ' and out-of-phase χ'' dynamic susceptibilities weighted using a volume-weighted lognormal size distribution $n_v(D_h)$ and using the known temperature of the experiment and the viscosity of neat mineral oil or of water obtained from rheometer measurements, according to the equations

$$\chi'' = \int_0^{\infty} n_v(y) \frac{\chi_{0,hv} \Omega \tau_{hv} y^3}{1 + \Omega^2 \tau_{hv}^2 y^6} dy; y = \frac{D_h}{D_{hv}}; \tau_{hv} = \frac{6\pi\eta_r D_{hv}^3}{4kT} \quad (1)$$

$$n_v(D_h) = \frac{1}{\sqrt{2\pi D_h \ln \sigma_g}} \exp\left(-\frac{\ln^2(D_h/D_{hv})}{2 \ln^2 \sigma_g}\right) \quad (2)$$

where χ_0 is the initial susceptibility, χ_∞ is the high frequency limit of the susceptibility, and τ is the relaxation time, D_{hv} the volume weighted hydrodynamic diameter, and $\ln \sigma_g$ is the geometric deviation of the distribution. In equation (1), $\mathcal{V}$ is a nondimensional diameter, and $\chi_{0,hv}$, and τ_{hv} are the volume weighted initial susceptibility and relaxation time [8].

Dynamic Light Scattering (DLS) Characterization

OA coated nanoparticles were dispersed in hexane at 10 mg/ml to characterize their hydrodynamic diameter distribution at 25 °C using a Brookhaven Instruments Zeta PALS/BI-MAS Dynamic Light Scattering instrument. The volume weighted hydrodynamic diameter distribution obtained from the instrument's software was used for comparison to estimates of hydrodynamic diameter obtained from DMS measurements. Similarly, PEG coated magnetic nanoparticles were dispersed in deionized water at 0.2 mg/ml to characterize their hydrodynamic diameter distribution at 25 °C, as above.

Transmission Electron Microscopy (TEM)

A Hitachi H-7000 operated at 110 kV acceleration voltage was used to image the nanoparticles. To prepare the samples, a drop of the nanoparticles solution was dried onto an ultra-thin carbon type A grid. Images were analyzed using the ImageJ software [14]. The mean core diameter, corresponding to the size of the inorganic core, was estimated by fitting the number weighted diameter histogram obtained using transmission electron microscopy (TEM) to a lognormal size distribution.

Emulsion Preparation

All emulsions were prepared using mineral oil with 2% (v/v) surfactant mixture of Tween 80 and Span 80 (53:47, v/v), added dropwise to de-ionized (DI) water while being homogenized using a high speed Silverson mixer (Silverson L5M-A) at 6,000 rpm for 7 mins. The emulsion samples thus obtained were then bath sonicated for 45 min at 40 °C in a secondary emulsification step. The primary emulsification step aided in

breaking apart the coarse droplets of mineral oil into smaller ones which could be further reduced to finer droplets in the secondary emulsification treatment, resulting in a relatively uniform hydrodynamic diameter distribution. Emulsions were prepared with different volume fractions (ϕ) of the dispersed mineral oil phase of 5, 10, 15, 20, and 25% (v/v).

Addition of Nanoparticles to Emulsions

OA coated nanoparticles were added to aliquots of the final emulsions. Due to the hydrophobic nature of these particles they have a greater tendency to partition to the disperse oil phase of the emulsion. The amount of nanoparticles added to each emulsion was proportional to the volume fraction of mineral oil in the emulsion in order to maintain the particle concentration in the dispersed phase at 2 mg/ml.

In the case of PEG coated nanoparticles, the particles have a hydrophilic coating which increases their tendency to partition to the continuous aqueous phase of the emulsions. Since these particles were available in aqueous suspension, direct addition to emulsion aliquots would lower the oil phase volume fraction and might cause phase separation. To circumvent this problem, the suspension was added proportionally to aliquots of higher oil phase volume fraction emulsion samples in such quantities that the resultant emulsion oil phase composition was lowered to the required composition, with negligible phase separation obtained after bath sonication for approximately 5-10 min and room temperature. A particle concentration of 4 mg/ml was maintained in the continuous phase of all emulsion samples.

Characterization of dispersed phase droplet size

Samples of each emulsion used for particle size distribution measurements were obtained by diluting the original emulsion samples 100-fold. Then, 500 μ L of the diluted sample was used for hydrodynamic diameter measurement using dynamic light scattering at 15 °C and 25 °C. The volume-weighted hydrodynamic size distribution data obtained from DLS measurements was fitted to a lognormal size distribution to obtain representative statistics of the size of the droplets constituting the dispersed oil phase in the emulsions.

Macroscopic viscosity determination

The macroscopic viscosity of oil-in-water emulsions with nanoparticles in either the dispersed or continuous phase were measured in an Anton Paar MCR 302 rheometer using a cup and bob system (double gap geometry) in a shear rate range of 0.1 – 1000 s⁻¹. A sample volume of 10 mL was used and viscosity was measured at 15°C for the emulsions oleic acid coated nanoparticles and at 27°C for the emulsions used with PEG-coated particles.

Nanoscale viscosity determination

OA coated nanoparticles were added to aliquots (1mL) of different emulsion compositions in quantities as described above and dispersed using a vortex. Further aliquots of 100 µL from these samples were used for DMS measurements on the Quantum Design MPMS3 SQUID Magnetometer at a temperature of 15°C. Similarly, PEG coated nanoparticles were added to emulsion aliquots (250 µL) in quantities as described above and dispersed using a vortex as well as a bath sonicator. An aliquot of 200µL was drawn and used for DMS measurements in an Acreo DynoMag AC Susceptometer at a temperature of 27°C. No background subtraction was necessary as the neat emulsions had negligible signal and the particles provided a measureable signal under the conditions used.

All DMS data of the nanoparticles added to oil-in-water emulsions was analyzed for the viscosity of fluid surrounding the nanoparticles using a non-linear regression fit to Debye's model weighted using the volume-weighted lognormal hydrodynamic diameter distribution, holding the volume-weighted median hydrodynamic diameter, geometric deviation, and experimental temperatures fixed during the fit.

Results and Discussion

Characterization of the Nanoparticles

The core diameter distributions for nanoparticles coated with oleic acid coated and PEG obtained by TEM were the same, with lognormal distribution parameters of 14 nm for the number weighted lognormal media diameter and 0.21 for the geometric

deviation. This result is expected because both types of nanoparticles were obtained from batches prepared using a similar synthesis protocol for cobalt ferrite. Figure 1 shows representative TEM images for both types of nanoparticles, as well the corresponding size distribution histograms.

Because they consist of thermally blocked cobalt ferrite, the nanoparticles undergo Brownian relaxation when in an alternating magnetic field. According to dynamic magnetic susceptibility measurements for the OA coated nanoparticles in neat mineral oil at 0 °C (Figure 2a), the particles display a peak in the out-of-phase susceptibility at a frequency of 1,300 rad/s. When the DMS spectra were fitted to the Debye model using a volume-weighted lognormal size distribution, a volume-weighted hydrodynamic diameter of 21.3 nm and a geometric deviation of 0.18 were obtained. Similarly, thermally blocked PEG coated nanoparticles also undergo Brownian relaxation according to dynamic magnetic susceptibility measurements in neat water at 27 °C (Figure 2b). The particles display a peak in the out-of-phase susceptibility at a frequency of 45 rad/s. When the DMS spectra were fitted to the Debye model using a volume-weighted lognormal size distribution, a volume-weighted hydrodynamic diameter of 41.0 nm and a geometric deviation of 0.27 were obtained. Note that DMS measurements for the OA coated particles had to be made in the SQUID magnetometer because the peak frequency was below the range of the Dynomag (due to the high viscosity of the mineral oil). Further, DMS measurements for the OA coated particles were made at a temperature of 0°C so as to shift the peak well into the instrument's frequency range and ensure accurate measurements. Similarly, DMS measurements for PEG-coated particles had to be made in the Dynomag as the peak frequency was well above the frequency range of the SQUID magnetometer. In that case the DMS measurements were carried out at room temperature as the Dynomag lacks capability for temperature control.

Fig. 1 Transmission Electron Microscopy (TEM) images of (a) oleic acid coated nanoparticles and (b) PEG coated nanoparticles.

Fig. 2 Dynamic magnetic susceptibility spectra of a) oleic acid coated nanoparticles in mineral oil at 0 °C and b) PEG-coated nanoparticles in water at 27 °C.

The hydrodynamic size distribution of the nanoparticles was determined by dynamic light scattering (DLS) and fitting of the autocorrelation function using a Non-Negatively constrained Least-Squares (NNLS) algorithm to produce an intensity-weighted differential size distribution, d and $G_I(d)$. The volume-weighted differential size distribution $G_V(d)$ was calculated from d and $G_I(d)$ and fitted to a lognormal size distribution to obtain the volume-weighted hydrodynamic diameter D_{hv} and geometric deviation $\ln\sigma_g$. According to DLS, the OA coated nanoparticles dispersed in hexane had a volume-weighted hydrodynamic diameter of 18.5 nm with a geometric deviation of 0.12, whereas the PEG coated nanoparticles dispersed in deionized water had a

volume-weighted hydrodynamic diameter of 31.3 nm with a geometric deviation of 0.08. For comparison purposes, the hydrodynamic diameter distributions determined from DLS and DMS measurements, and the core size distribution obtained from TEM measurements are included in Figure 3 for both nanoparticles. As expected, the hydrodynamic diameters obtained from DLS and DMS measurements are larger than the physical size observed in the TEM due to the existence of the oleic acid or PEG coating. The DLS and DMS hydrodynamic diameter distributions are similar, with the DMS distribution being slightly larger. In subsequent analyses we use the size distribution parameters obtained from the DMS measurements.

Fig. 3 Hydrodynamic and physical size distributions determined from DMS, DLS, and TEM analysis for a) oleic acid coated and b) PEG coated nanoparticles.

Characterization of emulsions with nanoparticles added to the dispersed and continuous phases

Oil-in-water emulsions with different volume fractions of dispersed phase but the same surfactant concentration and prepared using the same protocol were expected to show similar oil droplet size distributions. The droplet size distributions were obtained using DLS. It was found that unreliable correlation functions were obtained when DLS measurements were made immediately after primary emulsification. However, a secondary emulsification step with bath sonication resulted in consistent DLS measurements. The volume-weighted hydrodynamic diameters of the oil droplets in the emulsions were typically in the size range of 200–600 nm, with a geometric deviation of 0.21 (Figure 4). This method of preparation was found to be fairly robust, with various batches of emulsions prepared over a span of several months yielding essentially the same size distributions. Further, emulsions prepared in this manner were also found to be stable with respect to their size for periods of up to 4 weeks. Although there was creaming of the emulsion, gentle shaking re-dispersed the droplets, and resulted in a size distribution similar to that immediately after preparation.

Fig. 4 Representative volume-weighted hydrodynamic diameter distribution for emulsion oil droplets.

Macroscale viscosity measurements of emulsions with different compositions were made using a cup and bob system (double gap geometry) with a pre-shear of 1 s^{-1} for 5 min, followed by a shear ramp from 1 to 1000 s^{-1} at $15 \text{ }^{\circ}\text{C}$. The resulting macroscale emulsion viscosities are summarized in Table 1. In general, the viscosities of the emulsions were close in magnitude to the viscosity of deionized water (the continuous phase), but increased with increasing volume fraction of dispersed phase. Similar measurements were made at $27 \text{ }^{\circ}\text{C}$ for emulsion samples containing nanoparticles and viscosities were similar to those of the neat emulsions, which is to be expected owing to the low volume fraction of nanoparticles used for DMS measurements. The resulting macroscale emulsion viscosities are summarized in Table 2.

Table 1. Macro- ($\eta_{emulsion}$) and nanoscale ($\eta_{\chi''}$) viscosity measurements for emulsions with OA coated particles in the dispersed phase.

Oil Volume Fraction (%)	$\eta_{\chi''}$ (mPa s)	$\eta_{emulsion}$ (mPa s)	$\left \frac{\eta_{\chi''} - \eta_{oil}}{\eta_{oil}} \right \times 100\% ^*$
5	68.5	1.2	6.7
10	65.1	1.2	11
15	65.3	1.4	11
20	72.2	1.6	1.7
25	77.6	1.8	5.6

*Macro-viscosity of neat mineral oil (η_{oil}) at $15 \text{ }^{\circ}\text{C}$ measured using the cup and bob system (double gap geometry) was 73.45 mPa s .

Table 2. Macro- ($\eta_{emulsion}$) and nanoscale ($\eta_{\chi''}$) viscosity measurements for emulsions with PEG coated particles in the continuous phase.

Oil Volume Fraction (%)	$\eta_{\chi''}$ (mPa s)	$\eta_{emulsion}$ (mPa s)	$\left \frac{\eta_{\chi''} - \eta_{water}}{\eta_{water}} \right \times 100\% ^*$
5	0.7	0.9	13.6
10	0.7	1.0	17.2
15	0.7	1.0	15.9
20	0.7	1.4	13.6
25	0.7	1.4	17.2

* Macro-viscosity of water (η_{water}) at 27°C measured using the cup and bob system (double gap geometry) was 0.857 mPa s.

The DMS spectra of emulsions containing OA coated nanoparticles were obtained at 15 °C and fitted to the Debye model using the hydrodynamic diameter determined from DMS in neat mineral oil at 0 °C to estimate the viscosity of the dispersed phase of the emulsion. Figure 5a shows representative results for the DMS spectrum of an emulsion containing OA coated nanoparticles, with a peak corresponding to Brownian relaxation at a frequency of 2,800 Hz. Table 1 summarizes the results for the viscosities obtained from the DMS spectra for the emulsions with different dispersed phase volume fractions. The nanoscale viscosity determined from the Brownian relaxation of the particles was found to vary slightly with the volume fraction of the dispersed phase but was, in general, very similar to the viscosity of the neat mineral oil that made up the dispersed phase of the emulsion. Thus, as expected, for nanoparticles that are coated with OA and that partition to the dispersed oil phase the nanoscale viscosity determined from the DMS spectra corresponds to that of the dispersed phase fluid.

Fig. 5 Representative dynamic magnetic susceptibility measurements of oil-water emulsions with a) OA coated nanoparticles and b) PEG coated nanoparticles.

The DMS spectra of emulsions containing PEG coated nanoparticles were obtained at 27 °C and fitted to the Debye model using the hydrodynamic diameter determined from DMS measurements to estimate the viscosity of the continuous phase of the emulsion. Figure 5b shows representative results for the DMS spectrum of an emulsion containing PEG coated nanoparticles, with a peak corresponding to Brownian relaxation at a frequency of 55 kHz. Table 2 summarizes the results for the viscosities obtained from the DMS spectra for the emulsions with different dispersed phase volume fractions. The nanoscale viscosity determined from the Brownian relaxation of the particles was found to be lower than the viscosity of the emulsions, independent of the volume fraction of the oil phase, and similar to the viscosity of water. This indicates that the PEG coated particles are dispersed within the continuous water phase and sense the viscosity of this phase.

Figure 6a shows a comparison of the nanoscale and macroscale viscosities for the case of OA coated nanoparticles. Herein we denote by “nanoviscosity” the viscosity “felt” by the nanoparticles as they rotate, and by “macroviscosity” the viscosity determined using the rheometer. It is evident that the nanoscale viscosity determined from the rotational response of the nanoparticles is nearly constant with respect to change in the volume fraction of the dispersed phase of the emulsion and is, within experimental error, identical to the viscosity of the neat mineral oil used to form the dispersed phase. The converse is true for the case of emulsions with PEG-coated nanoparticles (Figure 6b). In that case, the nanoviscosity felt by the nanoparticles is similar to the viscosity of water, which is the continuous phase (solid black line). Interestingly, the nanoviscosity was found to be comparable to the viscosity of neat water, with the difference being about 17% of the viscosity of neat water at 27 °C. The difference in viscosities obtained for the OA and PEG coated nanoparticles is attributed to their partitioning to the dispersed mineral oil (in the case of OA coated particles) and continuous water (in the case of PEG coated particles) phases.

Interestingly, the viscosities measured by the nanoparticles are independent of the overall volume fraction of dispersed phase in the emulsion. One can argue that this is to be expected as from the point of view of dispersed nanoparticles the interfaces between the two phases are, on average, very far (many particle diameters). This is relatively

simple to see for the case of OA coated particles which partition to the dispersed mineral oil phase. In that case the average emulsion droplet diameter of ~400 nm (Fig. 3) is more than an order of magnitude larger than the hydrodynamic diameter of the OA coated nanoparticles. For the PEG coated particles which partition to the continuous phase we consider the average surface-to-surface distance between nearest neighbor droplets and the size of the voids formed between multiple emulsion droplets. We focus on the case of the highest dispersed phase volume fraction emulsion used here (25% v/v), as distances will be greater for emulsions with lower volume fractions. The average surface-to-surface distance h between emulsion droplets with diameter D_s can be estimated using the Woodcock equation [15]

$$\frac{h}{D_s} = \sqrt{\frac{1}{3\pi\phi} + \frac{5}{6}} - 1 \quad (3)$$

to be approximately 48 nm, using a droplet diameter of 400 nm as representative of the average of the size distribution shown in Fig. 4. However, nanoparticles would be expected to partition mostly to the voids formed between multiple spheres. Although theoretical expressions for the size of those voids are not available we can estimate their size based on the spherical diameter of the voids between spheres in close packing [16, 17]. For the case of a void formed between four spheres (a so-called tetrahedral void) the diameter of a sphere that fits inside the void is given by $D_v = 0.225D_s$, with D_v the spherical void diameter and D_s the diameter of the spheres. Assuming the spheres are emulsion droplets of roughly 400 nm in close packing the resulting void diameter would be 90 nm. Similarly, for the case of a void formed between six spheres (a so-called octahedral void) the diameter of a sphere that fits inside the void is given by $D_v = 0.414D_s$. In that case, assuming the spheres are emulsion droplets of roughly 400 nm in close packing the resulting void diameter would be 165 nm. Of course, the actual voids between emulsion droplets in our experiments will be larger because the volume fraction of the dispersed phase is much below that for close packing, however, these calculations serve to illustrate the smallest dimensions of the space occupied by the PEG coated nanoparticles that partition to the continuous phase. In all cases the distances between confining droplet surfaces are expected to be

much larger than the hydrodynamic diameter of the particles, hence we would expect that the rotation of the particles in response to the alternating magnetic field would reflect the viscosity of the individual dispersed and continuous phases, as confirmed by the results in Fig. 6.

Fig. 6 Comparison of nanoscale and macroscale viscosities for emulsions analyzed using a) OA coated and b) PEG coated nanoparticles.

Conclusions:

Methods for the characterization of viscous properties of the separate dispersed and continuous phases are currently lacking, particularly for emulsions with droplet sizes that impede application of particle tracking microrheology techniques [6, 7]. Here we demonstrate that a previously reported method to measure fluid viscosity through the rotational response of magnetic nanoparticles [8, 9] can be applied to measure the viscosities of dispersed and continuous phases in emulsions by choosing appropriately coated nanoparticles. Using OA and PEG coated nanoparticles, we demonstrated that DMS measurements yield viscosities that are independent of the volume fraction of the dispersed mineral oil phase and that are quantitatively similar to the viscosities of neat mineral oil (in the case of OA coated particles) and neat water (in the case of PEG coated particles). This suggests that the OA and PEG coated particles have partitioned to the dispersed and continuous phases of the emulsion, respectively, and report the viscosity of those phases in the emulsion. In contrast, conventional macroscopic rheological measurements provide information on the suspension-scale effective viscosity, which is difficult to separate into contributions due to the continuous and dispersed phases. The reported technique is suitable for small volume samples (sample volumes as small as 100 μ l) and for opaque samples, making it an attractive approach to characterization of emulsions of practical interest.

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Table of Contents Graphic:

Magnetic nanoparticles allow for *in situ* characterization of the viscosity of the dispersed and continuous phases of emulsions.