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The influence of interparticle correlations and self-assembly on the dynamic initial magnetic susceptibility spectra of ferrofluids

A.O. Ivanov[a,*], S.S. Kantorovich[a,b], E.A. Elfimova[a], V.S. Zverev[a], J.O. Sindt[c], P.J. Camp[a,c]

[a] Institute of Mathematics and Computer Sciences, Ural Federal University, Lenin Avenue 51, 620000 Ekaterinburg, Russia
[b] Faculty of Physics, University of Vienna, Sensengasse 8, 1090 Vienna, Austria
[c] School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, Scotland, UK

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ABSTRACT

Using computer simulations and a mean-field theoretical approach, we study how the growth in dipolar interparticle correlations manifests itself in the frequency-dependent initial magnetic susceptibility of a ferrofluid. Our recently developed theory gives the correct single-particle Debye-theory results in the low-concentration, non-interacting regime; and it yields the exact leading-order contributions from interparticle correlations. The susceptibility spectra are analysed in terms of the low-frequency behaviours of the real and imaginary parts, and the position of the peak in the imaginary part. By comparing the theoretical predictions to the results from Brownian dynamics simulations, it is possible to identify the conditions where correlations are important, but where self-assembly has not developed. We also provide a qualitative explanation for the behaviour of spectra beyond the mean-field limit.

1. Introduction

Magnetic AC susceptometry is a widely used technique for analysing and characterising the dynamic magnetic response in ferrofluids [1–4]. The dynamic response of magnetic-nanoparticle suspensions is fundamentally important for medical applications in general [5], and in particular for magnetic hyperthermia, usually applied alone or in combination with other treatments to eliminate tumours [6]. The efficiency of the latter methods relies on the frequencies and the characteristic relaxation times of the magnetic nanoparticle systems [7–9]. The influence of magnetic dipolar interactions on the specific absorption rate leads to a decrease or an increase in the hypothermia efficiency depending on the magnetic particle size [10–12]. This observation has been confirmed in other investigations [13,14] and it is clear that interparticle correlations should be taken into account when predicting the dynamic susceptibility spectra of magnetic nanoparticles. Until recently, though, a theoretical formalism to allow for correlations was missing. To address this, we have put forward a new theoretical approach [15] based on the analytical solution of the Fokker-Planck equation with an additional term allowing for the interparticle interactions and system polydispersity. We have tested our theory against Brownian dynamics computer simulations of a model monodisperse ferrofluid [16] and against experimental measurements for true polydisperse ferrofluids [17]. In these studies, it was shown that at low temperature and/or high magnetic phase concentration, some complex internal structure developed in the systems, leading to a dramatic increase of the characteristic relaxation times. About 30 years ago, it was suggested that at very low temperatures, the magnetic nanoparticles undergo dynamic arrest and enter a dipolar glass phase [18,19], but this does not account for typical ferrofluid behaviour.

In the present study we identify how internal structure affects the susceptibility spectrum of a monodisperse system of magnetic dipolar particles by comparing our theory to the results of Brownian dynamics simulations for a broad range of temperatures and concentrations.

2. Problem

Consider the simplest case of a weak probing AC magnetic field $\mathbf{H}(t)$ applied along the symmetry axis (Oz-direction) of a highly elongated cylindrical ferrofluid sample: $\mathbf{H}(t) = (0, 0, h\exp(i\omega t))$; h and ω are the field amplitude and oscillation frequency, respectively. The orientation of each particle's magnetic moment $\mathbf{m}$ is described its polar angle θ with respect to the external field $\mathbf{H}$. A common approach for describing the dynamic magnetic response in ferrofluids is based on the Fokker-Planck-Brown (FPB) equation [20–22] for the normalised orientational probability density $W(t, \theta_1) \equiv W(1)$ of a randomly chosen magnetic nanoparticle 1.

* Corresponding author.
E-mail address: alexey.ivanov@urfu.ru (A.O. Ivanov).

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$$2\tau_1 \frac{\partial W(1)}{\partial t} = \frac{1}{\sin\theta_1}\frac{\partial}{\partial \theta_1}\left\{\sin\theta_1\left[\frac{\partial W(1)}{\partial \theta_1} - \frac{\partial U(1)}{\partial \theta_1}W(1)\right]\right\}, \quad (1)$$

where τ_1 is the characteristic relaxation time of the ferroparticle magnetic moment, which depends on the ferroparticle size, and $U(1)$ is the interaction energy in units of the thermal energy k_BT. Traditionally, only the Zeeman particle-field interaction is considered and so $U(1) = \mu_0(\mathbf{m}_1\cdot\mathbf{H})/k_BT$, where μ_0 is the vacuum magnetic permeability. The advantage of this approach is that Eq. (1) can easily be solved analytically for each randomly chosen particle 1 with a magnetic core diameter x:

$$W_0(1) = 1 + \frac{\mu_0 m_1(x) h}{k_BT}\frac{\cos\theta_1 \exp(i\omega t)}{1 + i\omega\tau_1(x)}. \quad (2)$$

The total magnetic response of the ferroparticle system is given by averaging over the granulometric composition $p(x)$. This procedure leads to the Debye expressions for the real (χ'_D) and imaginary (χ''_D) parts of the susceptibility spectrum $\chi_D = \chi'_D - i\chi''_D$:

$$\chi_D(\omega) = \frac{\mu_0 n}{3k_BT}\int_0^\infty \frac{m^2(x)}{1+\omega^2\tau^2(x)}p(x)dx, \quad (3)$$

$$\chi_{\prime\prime D}(\omega) = \frac{\mu_0 n}{3k_BT}\int_0^\infty \frac{m^2(x)\omega\tau(x)}{1+\omega^2\tau^2(x)}p(x)dx. \quad (4)$$

Here n is the ferroparticle number concentration. These expressions are widely used for analysing experimental data, but the problem is that the zero-frequency limit ($\omega \to 0$) gives the Langevin static susceptibility $\chi(0) \equiv \chi_L = \mu_0 n\langle m^2\rangle/3k_BT$, which depends on the $p(x)$-weighted mean-squared magnetic moment. The Langevin susceptibility is linear in n, but this is only accurate for extremely dilute ferrofluids. For dense systems the susceptibility obeys a parabolic growth with concentration, which is quite close to the prediction of the first-order modified mean-field model (MMF1): $\chi(0) = \chi_L(1 + \chi_L/3)$ [23,24]. So, the Debye expressions (3) and (4) should be used only for very dilute ferrofluids.

3. Interparticle interaction correction

Recently, the Debye expressions (3) and (4) were extended by incorporating dipole-dipole interactions on the basis of the MMF1 model [15]. The single-particle energy $U(1)$ in the FPB Eq. (1) now includes an extra term representing these interactions:

$$U(1) = \frac{\mu_0(\mathbf{m}_1\cdot\mathbf{H})}{k_BT} + n\,<W_0(2)U_{dd}(1,2)\Theta(1,2)>_2. \quad (5)$$

Here, $U_{dd}(1,2)$ is the dipole-dipole interaction energy between the magnetic moments of particles 1 and 2, the step-function $\Theta(1,2)$ describes the impenetrability of the two particles, and $W_0(2)$ is the ideal orientational probability (2) for particle 2. The angled brackets denote an average over all possible orientations and positions of the second ferroparticle and a $p(x)$-weighted averaging over the granulometric composition. It is worth mentioning that this averaging can be made for particle 2 independently of particle 1. The extra term in Eq. (5) represents the interaction of moment 1 with the magnetic field produced by all other magnetic dipoles in the system in addition to the external magnetic field. Details of the solution of Eqs. (1) and (5) are given in Ref. [15]. The final result for the MMF1 susceptibility spectrum $\chi = \chi' - i\chi''$ is

$$\chi'(\omega) = \chi'_D(\omega) + \frac{1}{3}\{[\chi'_D(\omega)]^2 - [\chi''_D(\omega)]^2\}, \quad (6)$$

$$\chi''(\omega) = \chi_{\prime\prime D}(\omega)\left[1 + \frac{2}{3}\chi'_D(\omega)\right], \quad (7)$$

where both the real (χ') and imaginary (χ'') parts of the susceptibility are expressed in terms of the Debye results (3) and (4). The static susceptibility is

$$\chi(0) = \chi_L\left(1 + \frac{\chi_L}{3}\right), \quad (8)$$

which corresponds to the MMF1 result. In the latter the effective field is expressed in terms of Langevin susceptibility χ_L. Importantly, the expressions (6) and (7) are the exact results of first-order perturbation theory, and they are quadratic in the ferroparticle concentration n.

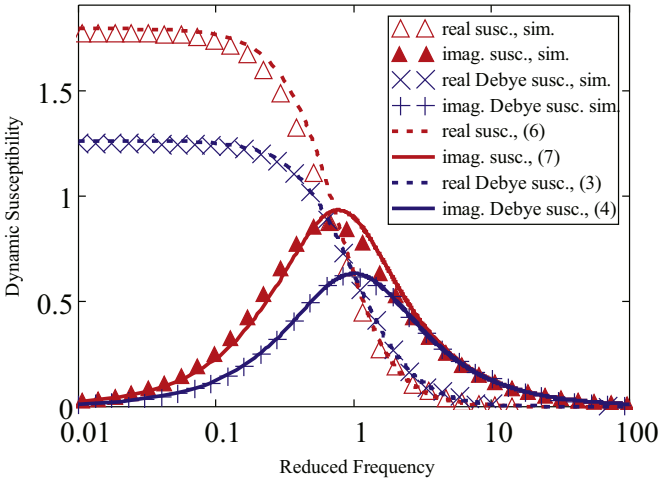

Fig. 1. The susceptibility spectra $\chi(\omega\tau)$ of systems at $\varphi = 0.158$ and $\lambda = 1$ (red), and with the dipole-dipole interactions turned off (λ=0) (blue). The points are from simulations, the blue lines are from Debye theory [Eqs. (3) and (4)], and the red lines are from the dynamic MMF1 theory [Eqs. (6) and (7)]. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

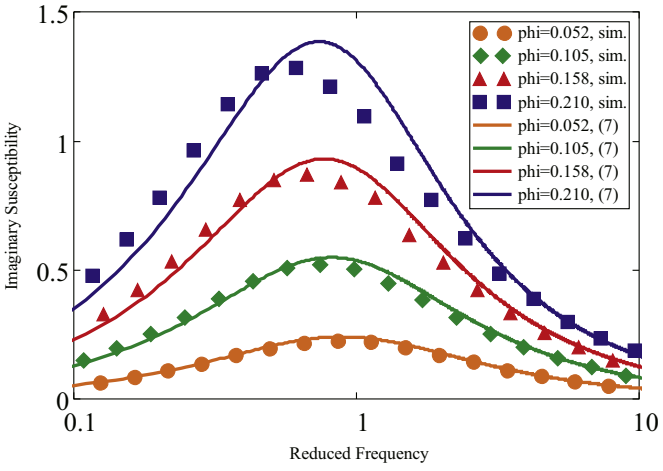

Fig. 2. The peak of the imaginary susceptibility $\chi''(\omega\tau)$ for interacting particles at $\lambda = 1$ and volume fractions $\varphi = 0.052$ (orange), 0.105 (green), 0.158 (red), and 0.210 (dark blue). The points are from simulations, and the lines are from the dynamic MMF1 theory (7). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

4. Comparision between theory and computer simulations

The difference between Debye spectra and MMF1 spectra is illustrated in Fig. 1 for a model monodisperse ferrofluid with particle volume fraction $\varphi = \pi n x^3/6 = 0.158$ and dipolar coupling constant $\lambda = \mu_0 m^2/k_BTx^3 = 1$. The latter parameter describes the strength of the interparticle dipole-dipole interaction as compared to the thermal energy. The product of the two parameters gives the Langevin susceptibility $\chi_L = 8\varphi\lambda$, which is equal to 1.26 for the system shown. Comparing a real dipolar fluid and the ideal non-interacting fluid, we discover three spectral characteristics that are especially sensitive to

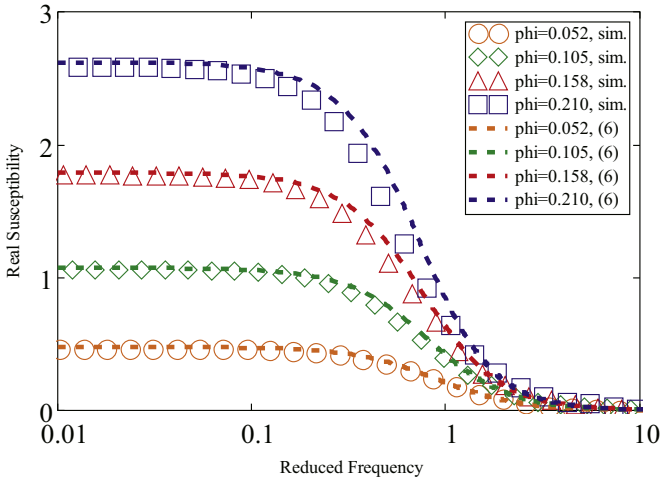

Fig. 3. The real part χ' of the susceptibility spectrum *vs* the reduced frequency $\omega\tau$ for interacting particles at $\lambda = 1$ and volume fractions $\varphi = 0.052$ (orange), 0.105 (green), 0.158 (red), and 0.210 (dark blue). The points are from simulations, and the lines are from the dynamic MMF1 theory (6). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

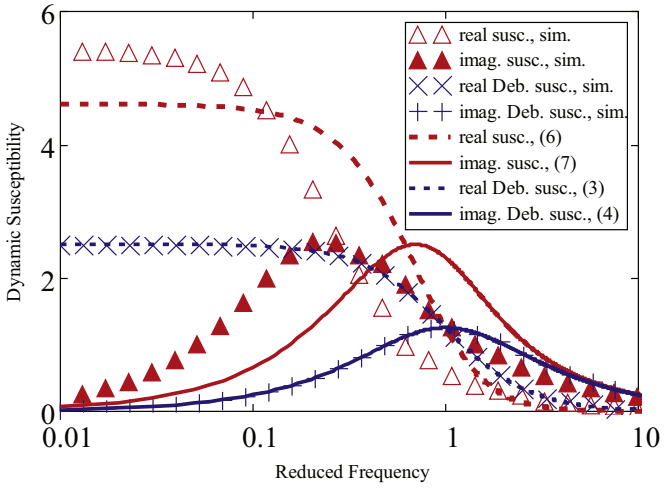

Fig. 4. The susceptibility spectra $\chi(\omega\tau)$ of the system at $\varphi = 0.105$, $\lambda = 3$, $\chi_L = 2.51$ (red), and with the dipole-dipole interactions turned off ($\lambda = 0$) (blue). The points are from simulations, the blue lines are from Debye theory [Eqs. (3) and (4)], and the red lines are from the dynamic MMF1 theory [Eqs. (6) and (7)].

the non-ideality of the system: the low-frequency behaviour of the real part; the low-frequency growth of the imaginary part; and the peak frequency of the imaginary part.

The theoretical predictions are confirmed by Brownian dynamics simulations, performed for the systems with 256 and 512 particles. The linear-response theory was used; and the susceptibility spectrum was calculated within the equilibrium (zero-field) magnetisation autocorrelation function. The simulation details are given in Ref. [16]. Note that the simulations reproduce very accurately the Debye behaviour for the ideal non-interacting fluid. Evidently, dipole-dipole interactions affect the susceptibility spectra significantly.

A prominent effect is the shift in position of the maximum of χ'' with increasing concentration; note, that for the Debye spectrum (4) the peak frequency $\omega = \tau^{-1}$ is independent of concentration. Simulation data for $\chi''(\omega\tau)$ are presented in Fig. 2 for the model monodisperse ferrofluid with weakly interacting particles ($\lambda = 1$) and different volume fractions. The shift of the maximum towards lower frequencies with increasing φ is clear. The agreement between the dynamic MMF1 theory (7) and the simulation data is very accurate at the lowest concentrations ($\varphi = 0.052$, $\chi_L = 0.42$ and $\varphi = 0.105$, $\chi_L = 0.84$). For more concentrated fluids ($\varphi = 0.158$, $\chi_L = 1.26$ and $\varphi = 0.210$, $\chi_L = 1.68$) the shift in the simulation data is more pronounced than the present theory predicts. This fact obviously indicates that the influence of interparticle interactions is stronger than is accounted for within the first-order perturbation (5) [16]. This is a well-known effect in the static susceptibility, for which the second-order modified mean-field model [23–25] contains an additional positive term as compared to Eq. (8). So, we may conclude that the region of validity of the dynamic MMF1 theory is defined by $\chi_L \lesssim 1$.

Fig. 3 shows that the real part of the MMF1 susceptibility spectrum (6) fits the simulation data very accurately; the parameters of the systems are the same as those in Fig. 2. In particular, the low-frequency behaviour is described very well. At high volume fractions, some deviations are apparent near $\omega\tau \simeq 1$, and are of the same nature as the deviations seen in the imaginary part presented in Fig. 2.

5. Influence of dipolar chains

In previous Sections we discussed the susceptibility spectra of moderately concentrated dipolar fluids ($\varphi \lesssim 0.2$) in which the dipole-dipole interactions do not exceed the thermal energy, i.e., $\lambda \lesssim 1$. In this range the dipole-dipole interactions result in slower relaxation of the instantaneous magnetisation, and thus in a small shift of the imaginary-part maximum to lower frequencies. The situation changes drastically with the increase of the dipolar coupling constant. In Fig. 4 susceptibility spectra are shown for a system at $\lambda = 3$ and low volume fraction $\varphi = 0.105$.

The simulations show that the peak frequency of χ'' decreases by several times as compared to the case of noninteracting particles. The Langevin susceptibility $\chi_L = 2.51$, and so the dynamic MMF1 theory is not expected to describe the simulation data accurately. Note that the simulations reproduce the expected Debye behaviour for the same system with the dipole-dipole interactions turned off, which shows that the simulation results are correct. For the system with strong interactions, the question arises, “What is the physical reason for a strong delay in the relaxations? ” One possible explanation is that since the system is rather diluted, and the particles are interacting quite strongly, small chain-like clusters are formed. It is well-known that chain formation begins in this range of parameters [26–28]. Evidently, the orientational relaxation of a ferroparticle chain is much slower than that of an individual particle; the relaxation time increases with the chain length. So, chain formation should influence the susceptibility spectrum by shifting the absorption peak to lower frequencies. Additionally, the presence of chains of various length imposes a wide range of characteristic relaxation times, and as a result, the absorption peak should be broader. This last effect is evident in Fig. 4 by comparing the simulation data and the prediction of the dynamic MMF theory (note that the frequency is shown on a logarithmic scale). The qualitative explanations looks reasonable, but of course, the magnetic response of highly aggregated ferrofluids is still an open problem.

6. Conclusion

In the present study we used a combination of Brownian dynamics simulations and a mean-field theoretical approach to describe the influence of the interparticle interactions on the susceptibility spectrum of monodisperse magnetic nanoparticles dispersed in the liquid carrier. By comparing the predictions of the mean-field theory to the simulation data it was possible to estimate the range of parameters where interactions influence the dynamic response, but do not yet give rise to self-assembled structures. As the dipolar coupling constant and/or magnetic particle concentration grow, the first-order perturbation theory fails to describe the significant increase in the low-frequency region of the real part of the susceptibility spectrum, and the correct shift of the imaginary part maximum to lower frequencies. Another

effect that emerges beyond the mean-field regime is the broadening of the peak in the imaginary part. This can be explained in term of chain formation: the chain length distribution broadens the spectrum of intrinsic relaxations in comparison to the system of non-clustered particles. Our study clearly reveals the necessity to thoroughly investigate the dynamic response of magnetic nanoparticles in the range of parameters where at thermodynamic equilibrium one observes extensive self-assembly.

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