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Electronic Supplementary Information for "Structure and dynamics in suspensions of magnetic platelets"

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The formation of chains of magnetic nanoparticles is a long-studied subject that dates back to the early 70s of the 20th century[1,2]. Many theoretical, experimental and computational studies reported the impact of chains on the systems' magnetic, rheological and optical response[3–10]. A rigorous derivation of the theoretical expression for the magnetisation of chain-forming dipolar hard spheres was first proposed by Mendelev and Ivanov[11]. This model is based on the iterative approximation of a n-particle chain partition function, $Q_n(H)$, for any value of an applied field, H, and the density functional theory that yields the number of such chains as an outcome of the entropy-energy interplay. Let us consider n identical particles with volume v in a chain, whose magnetic moments are denoted with $m\vec{u}_i$ and positions through $\vec{r}_i$, with index i running along the chain. For a particle with index i, its magnetic moment and position vector orientations are characterised in spherical coordinates by respectively azimuthal, ω_i and θ_i, and polar ζ_i and φ_i, angles calculated with respect to the particle indexed $i-1$. In this case, the orientation of the chain with respect to the field can be encoded via the angle between $\vec{H}$ and μ_1, ξ. Considering that only each nearest neighbour pair of particles in a chain interact with dipole-dipole potential $U_{dd}(\vec{\mu}_i, \vec{\mu}_{i-1})$ and sterically via $U_S(\vec{r}_i, \vec{r}_{i-1})$; whereas for each particle the interaction with $\vec{H}$ is denoted by $U_H(\vec{\mu}_i, \vec{H})$, one can write the partition function in the following way:

$$Q_n(\alpha) = \left(\frac{\alpha}{\sinh\alpha}\right)^n \int_0^\pi \frac{\sin\xi \, d\xi}{2} \times \quad (1)$$

$$\times \int \prod_{i=2}^n \frac{d\vec{r}_i d\vec{\Omega}_i}{v} \exp\left(-\frac{U_s + U_{dd} + U_H}{k_B T}\right),$$

$$d\vec{\Omega}_i = (4\pi)^{-1} \sin\omega_i d\omega_i d\zeta_i, \; d\vec{r}_i = |\vec{r}_i|^2 d|\vec{r}_i| \sin\theta_i d\theta_i d\varphi_i,$$

with thermal energy, $k_B T$.

When these integrals are simplified for hard spheres, a recursive form of a partition function is obtained (as detailed in the aforementioned work[11]):

$$Q_n(\alpha) = (q_\infty^s)^{n-1} D_{n-1}(\alpha) \prod_{j=1}^{n-1} C_j(\alpha), \quad (2)$$

$$D_{n-1}(\alpha) = \frac{\alpha}{\sinh\alpha} \frac{\sinh[\alpha(1+aB_{n-1})]}{\alpha(1+aB_{n-1})},$$

$$C_j(\alpha) = \frac{\alpha}{\sinh\alpha} \frac{\sinh A_j}{A_j} \exp[-a(1+\alpha B_j)],$$

$$A_j = \alpha f_j + a, \; B_j = f_j L(A_j)/A_j,$$

$$f_{j+1} = 1 + a f_j L(\alpha f_j + a)/(\alpha f_j + a), f_1 = 1$$

The expression q_∞^s – dimer partition function for an infinitely strong applied field, is asymptotically approached with growing Langevin parameter, $\alpha = |m\vec{u}_i||\vec{H}|/(k_B T)$. For dipolar hard spheres, $a = \lambda/2$, $\lambda = m\vec{u}_i^2/(k_B T)$ and the ratio between partition function in zero field, q_0^s, and q_∞^s is

$$\frac{q_0^s}{q_\infty^s} = \frac{1}{2a} = \frac{1}{\lambda}. \quad (3)$$

For platelets instead, the exact result is not known, so, in this work we assume, analogously to the correlation coefficient (main text), that in strong field two platelets get correlated as high as spheres only for high concentrations, ϕ, i.e., q_∞ for platelets can be expressed via its counterpart in zero field, calculated in our previous work[12], q_0, as

$$q_\infty = \lambda q_0 \tanh\kappa\phi, \quad (4)$$

allowing for concentration dependent orientational order parameter, $Q = \tanh\kappa\phi$.

When comparing the results for magnetisation, using expression (29) from the aforementioned work[11], we were pleased to

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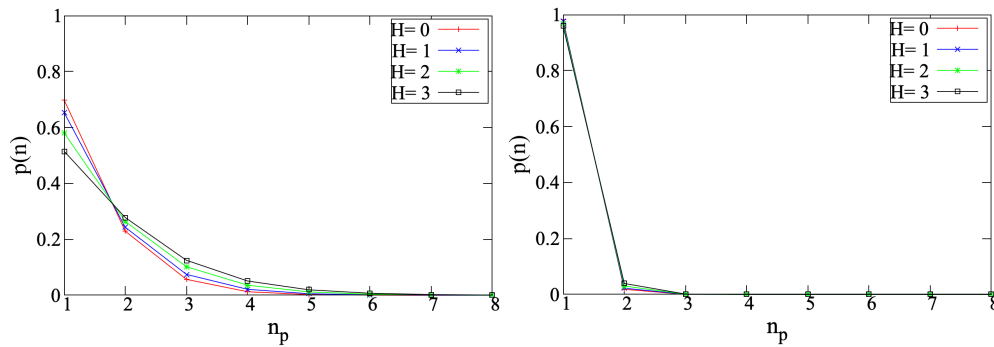[d] School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, Scotland

Fig. 1 The fractions of particles $p(n)$ calculated via DFT, using the rescaled q_∞ from Eq. (4).

find the same value $\kappa = 5.5$ as previously obtained for the susceptibility (see, Figure 5 of the main manuscript, $M^*(q_\infty)$ and compare to a non-rescaled version $M^*(q_\infty^s)$).

Even though, this scaling is not general and cannot be used for ϕ going to zero, its usage can be justified by the following observation. If we calculate the concentration of chains $g(n)$ numerically from DFT, using expression (4), the structural properties obtained for two concentrations of interest appear to be very close to those observed in simulations. Analytical results for the fraction $p(n) = ng(n)$ of particles in chains of a certain length are presented in Fig. 1.

Additional simulation data

As alluded to in the caption of Figure 7, at high values of ϕ, the data grows increasingly noisy at long t. This presents an obstacle to direct Fourier transformation of the data: an overly aggressive truncation and/or smoothing would remove any physical features present at long timescales t, while a lack of processing could introduce oscillations without a physical meaning behind them. For this reason, we chose to fit the data as described in Methods. An example of the fitted autocorrelation functions $C(t)$ is shown in Figure 2, for the "worst case" of a high ($\phi = 0.195$) density and a comparatively small ($N = 256$) system. This corresponds to Figure 7c). For this specific density, three separate simulation runs were carried out, and the fit parameters which showed the best overall agreement were chosen to represent the data.

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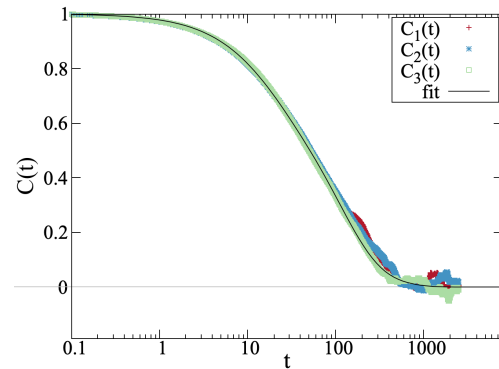
Fig. 2 The autocorrelation function $C(t)$ of the magnetic dipole moment, shown for three separate runs (arbitrarily numbered 1-3) of $\phi = 0.195$ systems, with the fit shown in black. We see that the noise increases as t grows; however, the long-t behavior is relevant for the physical relaxation of the system.

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