Effect of size distribution on ferrofluid configuration:  
A Monte Carlo simulation

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Dipole-dipole interaction plays a major role in governing the pattern formation phenomena in a ferrofluid. Usually this interaction varies as the concentration is changed. A theoretical analysis on the effect of dipole-dipole interaction on a ferrofluid configuration by varying the size distribution of the particles is being presented here. Two types of distributions viz., log normal and flat top are chosen for the study. The simulations were carried out using a simple model incorporated in the Monte Carlo simulation technique. Results of the simulations are compared with those experimentally observed.

Pre-existed small and large aggregates as well as chains impair long term stability of a magnetic fluid. Application of magnetic field may induce aggregation and/or association in the fluid, which may in turn adversely affect the performance of a device in which such a fluid is used. Further when large agglomerates are formed under the action of a weak magnetic field, it can be regarded as a kind of gas-liquid transition induced by the field. Therefore study of such phenomena is scientifically interesting and technologically important. De Gennes and Pincus have and later Jorden have discussed the condensation of the magnetic particles into linear chains at low density, high magnetic field and low temperature. Hayes observed with the help of microscope that needle-like agglomerates appear even when a weak magnetic field is applied. The agglomerates disappear when the magnetic field is switched off. This phenomenon has been studied by the measurements of magnetic birefringence, optical scattering, small angle neutron scattering, electron spin resonance and others. Sano and Doi have developed a mean field theory for such a macroscopic condensation. Kashersky has considered dipole-dipole interaction, repulsive surface interaction and hydrodynamic interactions and numerically simulated the structuring in a magnetic fluid. Recently Antonyms et al. have considered magnetic, surface and capillary interactions and used Brownian dynamics to simulate the pattern formation. In most of the above mentioned works a magnetic fluid is considered as a colloidal dispersion of ferro or ferrimagnetic particles in a passive carrier liquid like water or hydrocarbon. Size of the particle is considered to be around 10 nm and dispersion is considered as monodispersed. It is known that most of the fluids are polydispersed. Here, the effect of size distribution in the agglomeration and chaining of particles using the Monte Carlo simulation technique has been studied. The results are analysed in light of experimental investigations.

Theory

Magnetic fluids consist of magnetic particles either coated with surfactant or suitably charged and dispersed in a carrier liquid like water or hydrocarbon. Usually, average size of particles is much smaller than the magnetic domain in bulk solids. Hence the magnetization of the individual particle is saturated, but the direction of the magnetic moment ($\mu$) is subject to thermal agitation. When placed in a magnetic field ($H$), the interaction energy ($E_i$) in units of $k_B T$, where $k_B$ is the Boltzmann constant and $T$ the absolute temperature of a uniformly magnetized spherical particle $i$ in a
cloud of \( N \) magnetic particles is expressed as\textsuperscript{14},

\[ E_i = E_d + E_r + E_h \quad \text{... (1)} \]

The magnetic moment \( \mu = (\pi D^3 / 6) I_p \), and \( I_p \) is the saturation magnetization of the particle. \( R_{ij} \) is the interparticle distance between \( i \) and \( j \)\textsuperscript{th} particle, \( \psi \) is the angle between the direction of the interparticle dipole-dipole vector (\( R_{ij} \)) and the applied magnetic field (\( H \)). When \( R_{ij} > 5D \) the contribution due to \( E_d \) to the total energy \( E_i \) is negligible and may be neglected. The steric repulsion energy due to surfactant coating on the particle is given by\textsuperscript{15},

Fig. 1—Thermal equilibrium configuration for a monodispersed system in (a) Zero magnetic field, (b) 1 kG and (c) 10 kG.

Fig. 2—Equilibrium configuration for a Flat-top distribution in (a) Zero magnetic field and (b) 10 kG.

where

\[ E_d = \sum_{i \neq j} \left( \mu^2 / \left( R_{ij} \right)^3 \right) \times \left[ 2 \cos(\theta_i - \psi)\cos(\theta_j - \psi) - \sin(\theta_i - \psi)\sin(\theta_j - \psi) \right] \]
then the move was allowed and the particle was retained in the new location. On the other hand if \( \Delta E_i \) is positive the move was not allowed unless the Boltzmann factor, \( \exp(-\Delta E_i /k_B T) \), exceeds a random number whose value ranges from 0 to 1. This procedure was adopted for all the particles in turn and the iteration for the whole system was carried out until the reduced magnetization, \( I_r(=I/I_n) \) converge to a statistically steady value where \( I \) is the magnetisation of the system in a field \( H \) and is given by,

\[
I = \sum_{k=1}^{n} \left( \cos \theta_k \right) / n.
\]

where \( \theta_k \) is the value of \( \theta \) at the end of move \( k \) and \( n \) is total number of moves. While calculating total energy of the system (\( E_{tot} = \Sigma E_i \)) the number concentration of the particles having size \( D_i \) was considered according to the appropriate size distribution. The final positional parameters of the particles represent a typical configuration of the system in thermal equilibrium.

**System Details**

Magnetcite is the most commonly used material in a magnetic fluid and average spherical size of particles in such a fluid is around 8 nm, which is less than the domain size of magnetite. Its domain magnetisation is \( \approx 450 \) emu/cc. In sterically stabilized fluid oleic acid is the mostly used surfactant and size of this surfactant molecule is \( \approx 2 \) nm. Hence 10 nm was considered as the average size of the particles in the magnetic fluid. Temperature of the system was assumed to be 290 K. The number fraction of magnetic particles was assumed to be 0.21 (\( = N/\)size of matrix). The configuration was stabilized under these different values of applied magnetic field, \( H \), viz. 0 Gauss, 1 kG and 10 kG.

For the flat top distribution width of the distribution was assumed to be 2 nm, while for the log-normal distribution four different values of standard deviation, \( \sigma \), viz. 0.1, 0.2, 0.3 and 0.4 were considered.

**Results and Discussion**

**Monodisperse system**—Fig. 1 shows the thermal equilibrium configuration at zero magnetic field. It is observed that about 10% of particles formed randomly oriented dimers and a few trimers are
Fig. 4—Effect of particle size for $\sigma = 0.3$ on formation of agglomerates.
also seen. Existence of such dimers was predicted by Scholten\textsuperscript{17} and was also observed in SANS measurements\textsuperscript{7}. At 1 kG (Fig. 1b) number of dimers (\textapprox 15\%) and trimers increases while small chains having four particles are also seen, but no long chains in the direction of the field are seen. Even at 10 kG (Fig. 1c) no significant change in the configuration is observed. From these simulations one can infer that no long chains can be formed in a monodispersed system of magnetic particles even when 10 kG field is applied. It was also found that at this field $\frac{I}{I_p} = 0.99$ i.e. system tends to saturation.

**Flat Top Distribution**—In zero field certain long chains (size >4\(D\)) are seen. Moreover there is a tendency to form regions whose tendency of forming long chains is concentrated. This effect is more pronounced under the field (Figs 2a & b).

**Lognormal Distribution**—It is well known that most colloids and hence magnetic fluids follow lognormal particle size distribution. Figs 3a & b show configuration for $\sigma = 0.1$ for zero field and 10 kG. At zero field certain random chains (length >4\(D\)) are observed. At 10 kG a few clusters are found. The reduced magnetization ($\frac{I}{I_p}$) was found to be 0.90 compared to 0.99 for a monodispersed system. This reduction in the value of reduced magnetisation is either due to the existence of smaller particles which does not saturate at 10 kG or/and due to formation of closed loop structure. Figs 3a & d show the effect of size distribution on pattern configuration. Inferences drawn from these figures are—(i) in zero magnetic field the increase in $\sigma$ increases the number of aggregates as well as the compactness of agglomerates increases. These agglomerates are found to be for $D<10$nm. (Fig. 4) and (ii) application of the magnetic field induces ordering in the configuration as well as results in redistribution of aggregates. The reasons for the formation of aggregates by only small particles are not yet clear.

**References**