Microstructure of ferrofluid monolayers: theory and computer simulations

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SUMMARY

We investigate the peculiarities brought by the 2D geometry into the process of aggregate formation in ferrofluids using two different approaches: density functional theory, and Molecular Dynamics simulations. In the MD simulations long-range interactions are taken into account using a recently developed dipolar-P3M method plus a dipolar layer correction (DLC) to properly account for the 2D geometry of the problem.

DENSITY FUNCTIONAL THEORY FOR 2D FERROFLUID SYSTEMS

Our purpose is to minimize the free energy density, e.g., with respect to the chain and ring surface distribution functions, g(n), and f(n)/s respectively under the constraint of the mass balance equation, eq. 2. Surprisingly, the 2D geometry of the system complicates substantially the theoretical description.

\[ F(g(n), f(n)) = \int_0^\infty \left( \frac{\partial g(n)}{\partial n} \right) \ln g(n) + \int_0^\infty \left( \frac{\partial f(n)}{\partial n} \right) \ln f(n) \]

\[ \frac{\partial g(n)}{\partial n} = \frac{\partial f(n)}{\partial n} \]

\[ n \geq 1 \]

\[ g(n) = \text{Number chains of length } n \text{ / s} \]

\[ f(n) = \text{Number of rings of length } n \text{ / s} \]

\[ s = \text{area of the system} \]

\[ W(n) = \text{Partition function for a doublet in a ring of length } n \]

\[ W(n) = \frac{1}{n!} \sum_{n} \lambda^{n-1} \]

\[ \lambda = \text{ratio of } n \text{ to } \lambda \text{ for different types of aggregates} \]

\[ W(n) \text{ as a function of the minimization we get the following expressions for } g(n) \text{ and } f(n): \]

\[ g(n) = W(n) n! \lambda^{n-1} \]

\[ f(n) = W(n) n! \lambda^{n-1} \]

The partition function for chains can be rewritten in terms of q, i.e., the partition of a chain of length n:

\[ Q(n) = \frac{\sum q(n)}{s} = q(n) \]

\[ q(n) = g(n) / s \]

\[ g(n) = \sum q(n) = \frac{1}{n!} \sum_{n} \lambda^{n-1} \]

\[ f(n) = \sum f(n) = \frac{1}{n!} \sum_{n} \lambda^{n-1} \]

\[ \lambda = \text{ratio of } n \text{ to } \lambda \text{ for different types of aggregates} \]

A FAST COMPUTATIONAL ALGORITHM: dipolar-P3M + DLC

The use of 2D dipolar Ewald sums in systems beyond a few particles is very expensive computationally. A better alternative consist in the use of two recently developed techniques: the dipolar-P3M method (J. Cerda, C. Holm, et al., to be published) for 3D systems plus the dipolar layer correction DLC (A. Brodka, Chem Phys. Lett. 400, 62, 2004) which adapts the 3D-results obtained by P3M to a 2D-geometry. This clever combination of techniques: the dipolar-P3M method (J. Cerda, C. Holm, et al., to be published) for 3D systems plus the dipolar layer correction DLC (A. Brodka, Chem Phys. Lett. 400, 62, 2004) which adapts the 3D-results obtained by P3M to a 2D-geometry. This clever combination provides an almost linear algorithm for 2D, which drastically improves the performance of previous quadratic dipolar algorithms.

We assume our monolayer to be inside a cubic box which repeats to the infinity along the three directions in order to be able to apply the dipolar-P3M technique. In our MD simulations, particles interact through LJ to mimic steric repulsion, and long-range dipole-dipole interactions.

HOW P3M WORKS

1. Map dipolar particle positions to a lattice.
2. Compute the FFT of the lattice density.
3. Compute the Fourier space of the mesh potential, Electrostatic field, forces and torques.
4. Compute the back FFT of these mesh magnitudes.
5. Map back the mesh magnitudes to the particles.

In bidisperse systems our simulations show that for certain ratios of the size of the particles there exist a shortening effect for both chains and rings. Similar shortening effects have been also reported for experimental monolayers.

### Key Points of the theoretical model:

- Monodisperse quasi-2D system.
- Dipole-dipole + LJ to mimic steric repulsion.
- We consider as possible aggregates: chains, and rings.
- Only nearest neighbor interactions.
- No interactions among aggregates.