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Thermodynamic (in)stability of ferrofluid–polymer mixtures

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Abstract

The phase behavior of mixtures of ferrofluid and non-adsorbing polymer is studied using a combination of a perturbation theory for dipolar spheres and a mean field theory for colloid–polymer mixtures. The polymer is used to induce an effective isotropic attraction with tunable strength and range. It was found that for typical ferrofluids, dipolar interaction only weakly affects the stability of the mixture; isotropic attraction dominates the phase behavior. This conclusion is supported by measurements on a real ferrofluid–polymer mixture.
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Keywords: Phase separation; Ferrofluid; Magnetic fluid; Polymer; Depletion attraction

1. Introduction

Ferrofluids are colloidal dispersions of (roughly) spherical, monodomain magnetic particles in a non-magnetic solvent. The macroscopic properties of ferrofluids are often predicted by modeling the particles as dipolar hard spheres (DHS). One particular property is the phase behavior of ferrofluids. Due to the—on average—attractive nature of the dipolar interaction between the particles, ferrofluids can become thermodynamically unstable and separate into a dilute (''gas'') phase and a concentrated (''liquid'') phase. Moreover, the average strength of attraction can be increased by applying a magnetic field, thereby promoting phase separation.

Experimentally, phase separation in ferrofluids has been observed under several conditions [1]. In charge stabilized ferrofluids, addition of salt can induce gas–liquid phase separation. Sterically (oleic acid) stabilized ferrofluids can be destabilized in zero field by decreasing the solvent quality or adding non-adsorbing polymer [2]. Phase separation induced by a magnetic field is probably the most frequently reported instability. In at least three of these cases, the DHS description of ferrofluids is insufficient because the instability involves significant isotropic attraction. Moreover, the presence of free surfactant and irreversible aggregates [3] is often neglected, which hampers the correct interpretation of experimental results.

In this paper, we study both theoretically and experimentally the phase behavior of an aggregate-free magnetic fluid, which does not contain free oleic acid. The effect of isotropic attraction and of an external magnetic field on the thermodynamic stability are investigated independently. Isotropic attraction is induced by adding non-adsorbing polymer, which leads to the so-called ''depletion attraction''. It is found that the thermodynamic stability of the ferrofluid is only weakly affected by a magnetic field; the stability is mainly determined by the strength of isotropic attraction.

2. Theory

In a mixture of hard spheres and non-adsorbing polymer coils, the minimal distance between a sphere surface and a coil roughly equals the coil radius. Therefore, if two spheres are at a surface-to-surface distance smaller than the coil diameter, there will be a polymer-free region in between the spheres, resulting in an uncompensated osmotic polymer pressure pushing

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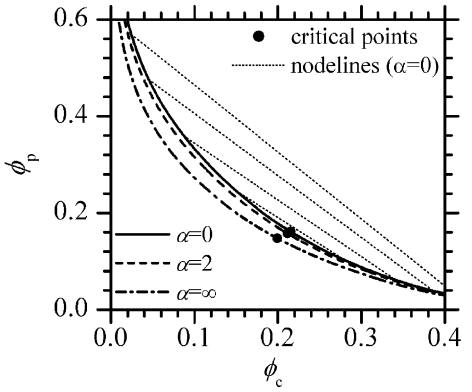

Fig. 1. Gas–liquid binodals of a ferrofluid–polymer mixture at several field strengths.

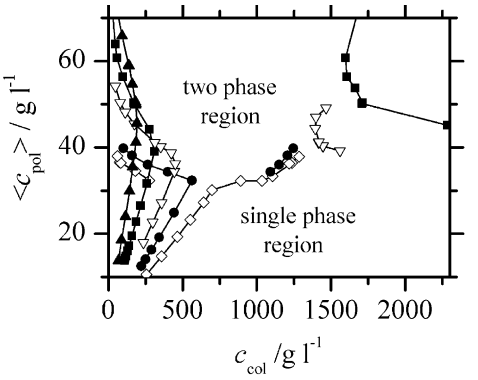

Fig. 2. Experimental zero-field phase diagram of the ferrofluid–polymer mixture. Different symbols refer to the five different samples.

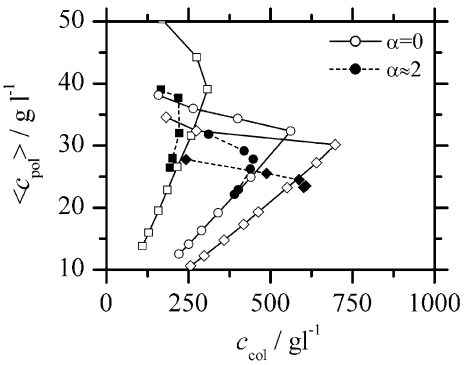

Fig. 3. Effect of a magnetic field on the phase diagram of the ferrofluid–polymer mixture.

the spheres towards each other [4]. This effect can be regarded as an effective isotropic attraction (“depletion attraction”), the range and strength of which are determined by the polymer size and concentration, respectively. When spheres and polymer coils are of similar size, depletion attraction can give rise to phase separation into a colloid-poor, polymer-rich phase and a colloid-rich, polymer-poor phase.

Phase diagrams of ferrofluid–polymer mixtures were calculated using a thermodynamic perturbation theory [5] combined with a mean field theory for colloid–polymer mixtures [4]. The free energy of the mixture reads (terms irrelevant for the phase behavior are left out) as following:

$$\beta F = \beta F_{\mathrm{HS}} - 4N_c\phi_c\lambda L^2(\alpha) - \frac{4}{3}N_c\phi_c\lambda^2 - N_p \ln\frac{\phi_p}{f(\phi_c)}. \quad (1)$$

The first three terms in Eq. (1) comprise the DHS part and the last term the depletion part: the free energy of ideal polymer coils (effective volume fraction ϕ_p) depends on the fraction f of the volume accessible to polymer, which in turn depends on the colloid volume fraction ϕ_c. For a typical ferrofluid with a dipole–dipole interaction parameter $\lambda = \mu_0 m^2/d^3kT = 0.5$, and a polymer/colloid size ratio of 0.5, binodals at three reduced field strengths $\alpha = \mu_0 mH/kT$ are shown in Fig. 1. Note that free oleic acid, as a small ‘polymer’, might also induce depletion attraction.

3. Experiments

The ferrofluid, provided by L. Vékás and D. Bica (“Polytehnica” University, Timi°oara, Romania), consisted of Fe_3O_4 particles with a physical diameter of 9.1 nm ± 26%, grafted with chemically pure oleic acid, and dispersed in cyclohexane. Free oleic acid and aggregates were removed after synthesis. Small angle X-ray scattering curves, measured at the DUBBLE beamline at ESRF (Grenoble, France) confirm the absence of aggregates [6].

For phase separation experiments, the ferrofluid was mixed with a known amount of poly(dimethylsiloxane) with MW = 41.5 kg mol^{-1}, and the total composition was changed by adding or evaporating solvent. The local ferrofluid concentration in the separate phases was measured with a magnetic sensing coil [7]. The local polymer concentration cannot be determined directly; therefore, the overall polymer concentration is plotted in the measured diagrams (Figs. 2 and 3). The theoretical diagram can be replotted in the representation of the experimental diagram [6]. This causes the ‘hillside-shaped’ coexistence curve in Fig. 1 to change into a ‘bowl-shaped’ curve as in Fig. 2.

The destabilizing effect of a magnetic field, shown in Fig. 3, is comparable in magnitude to the theoretical prediction (Fig. 1). Note that, contrary to many reports

but consistent with theory, the ferrofluid without polymer is stable at all concentrations and field strengths. This discrepancy with literature may be due to the absence of aggregates and/or free oleic acid.

4. Conclusions

Both theory and experiments show that the thermodynamic stability of ferrofluid–polymer mixtures is dominated by (polymer-induced) isotropic interaction between ferrofluid particles. Dipolar interaction only manifests itself in mixtures that are on the verge of instability.

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