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Magnetic Field Assisted Fractionation of Nonmagnetic Colloids in Ferrofluid

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Flocculation of nonmagnetic colloidal particles in ferrofluid while in the presence of an external uniform magnetic field is investigated experimentally. Magnetic nanoparticles in ferrofluid create magnetic interactions between nonmagnetic colloidal particles. It is demonstrated that nonmagnetic particles can be fractionated by size much more efficiently in the presence of these magnetic interactions.

Index Terms—Fractionation, magnetic separation, magnetic sorting.

I. INTRODUCTION

CREATING monodisperse colloidal droplets or particles is an area of substantial current interest. Monodispersity can be achieved either through controlled production or through fractionation and separation starting from a broad distribution of droplet or particle sizes. A good example of controlled production is the recently developed drop break-off method [1], [2], which relies on micronozzles. Fractionation and separation by centrifugation [3], electrophoresis [4], and magnetophoresis [5] are well known. All these methods rely on different kinetics for particles of different sizes. However, size selectivity with these methods is sensitive to different material properties such as density, magnetic moment, and surface charge. An alternative method [6], [7], which can be called depletion fractionation, relies on a higher equilibrium flocculation probability for larger particles or emulsion droplets in the presence of much smaller nanometer diameter micelles. It is the micelle depletion between the particles that creates larger osmotic pressures for larger particles, resulting in a proportionally greater probability of their flocculation. In each step of the depletion fractionation process micelle concentration is changed to floc smaller and smaller particles. The advantage of depletion fractionation is that size selectivity is insensitive to material properties in principle. However, this fractionation technique can be very slow because osmotic forces due to micelle depletion have a very short range and diffusion alone takes a long time to bring particles together. In addition, changing the micelle concentration to keep separating smaller and smaller particles can be inconvenient.

In this paper we propose and demonstrate a magnetic field assisted method of fractionation of nonmagnetic colloidal components in a magnetic fluid. The proposed method involves the addition of 10–15 nm diameter magnetic nanoparticles (ferrofluid) to a suspension of nonmagnetic emulsion droplets or particles and the application of a uniform magnetic field to this solution. On the one hand, magnetic nanoparticles perform the same function as micelles in depletion fractionation. On the other hand and more importantly, magnetic nanoparticles create magnetic interactions between the nonmagnetic components in the fluid when

a magnetic field is applied. The long-range nature of these interactions rapidly brings the nonmagnetic components together, substantially speeding-up the fractionation process. Moreover, magnetic forces are selective to particle size similarly to the micelle depletion forces, and magnetic field strength can be easily adjusted to selectively floc particles of larger size while leaving smaller particles suspended. Stepwise reduction of the magnetic field can be used instead of increases in micelle concentration to sequentially separate particles of smaller sizes. Although field gradients can be used for separation of fractionated components, the proposed fractionation method is fundamentally different from magnetophoretic methods [5], which rely only on field gradients. Using the uniform field for fractionation, rather than the field gradient, is more convenient for larger fluid volumes.

II. FRACTIONATION MODEL

Simplified models of different forces in colloidal solutions are used below to illustrate the main differences in depletion and magnetically assisted fractionations. One important force is the short-range attractive London's dispersion force that usually leads to strong aggregation when particles approach each other to a fraction of their diameter. If the particles' diameter is d and their shortest separation is s , the potential energy due to this force at small particle separations is approximately [8]

$$U_L = -\frac{A}{12} \left(\frac{d^2}{s^2 + 2sd} + \frac{d^2}{(s+d)^2} + 2 \ln \left(\frac{(s^2 + 2sd)}{(s+d)^2} \right) \right) \quad (1)$$

where $A \approx 5 \times 10^{-21} J$ is the modified Hamaker constant. In stable colloidal solutions repulsive forces are usually created between particles to oppose this aggregation. The main ideas can be illustrated using the force due to charged double-layers around the particles. The potential energy of the double-layer interaction is approximately [8]

$$U_{dl} = \pi \epsilon d \Psi^2 \ln \left(1 + e^{(-\lambda s)} \right) \quad (2)$$

where Ψ is the electrostatic potential on the particle's surface, λ is the inverse Debye length, and ϵ is the permittivity of the dispersion medium (80× the permittivity of free space). Combining the attractive London's dispersion interaction with repulsive double-layer interaction yields the so-called DLVO interaction energy [9], [10], which is: 1) strongly attractive in a very short range; 2) repulsive in the intermediate range; and 3) very

slightly attractive in the long range. This type of particle interaction is very weakly dependent on particle diameter.

The introduction of micelles (with an effective diameter of a few nanometers) changes the effective particle interaction; because when particles approach each other, some regions between the particles become inaccessible to the micelles. This leads to an osmotic force that drives the particles toward each other. Particles pushed close to each other by this force, but held apart by the double-layer repulsion are sometimes referred to as a floc, rather than an aggregate. Flocculation can be easily reversed, while aggregation is a nearly irreversible process. The interaction energy due to the micelle depletion is approximately given by (3) [11], shown at the bottom of the page, where d_m is the effective diameter of the micelles, n is the volume concentration of the micelles, k is the Boltzmann constant and T is the absolute temperature. From (3) it is clear that the force due to depletion of the micelles between the particles is strongly dependent on particle diameter. It is smaller for smaller particles and larger for larger particles. Therefore, larger particles can flocculate, while smaller particles escape flocs through Brownian motion. This is essentially the basis of depletion fractionation. It is also clear from (3) that the depletion interaction has a very short range, which is about equal to the effective micelle diameter. One typically relies on random Brownian motion to bring the particles into the depletion interaction range. This process can be very slow, particularly for larger particles. Additionally in double-layer stabilized systems, an energy barrier to flocculation may exist if the effective micelle diameter is not sufficiently larger than the Debye length.

Magnetic interactions are taken to be due to dipoles oriented along the line through their centers

$$U_{\text{mag}} = -\mu_f \frac{v^2 H^2 d^6}{2\pi(d+s)^3} \quad (4)$$

where μ_f is the magnetic permeability of the fluid, μ_0 is the permeability of free space, H is the magnetic field in the fluid, and [12]

$$v = \frac{\pi(\mu_0 - \mu_f)}{2(\mu_0 + 2\mu_f)} \quad (5)$$

is a coefficient of proportionality between the particle's magnetic moment and the field. Its typical value in the dilute ferrofluid examples given here is -0.03 , although for stock ferrofluid concentrations it is -0.2 .

As evident from (4) the magnetic interaction, just like the depletion interaction in (3), is proportional to the cube of the particle diameter. As a result, magnetic forces alone can achieve selectivity in particle sizes similar to depletion forces. However, magnetic forces decay slowly with the interparticle distance in contrast with the micelle depletion forces. This creates a much

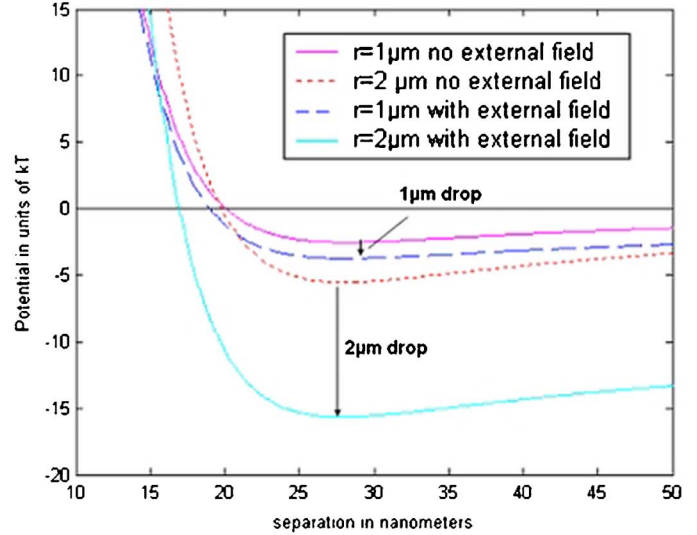


Fig. 1. Effect of a 1.8-kA/m external magnetic field on two different sizes of o/w emulsion droplets with a surface potential of 21.7 mV. The ferrofluid is modeled as a 1 : 9 dilution of stock EMG 705 giving a volume fraction of 0.43% for a μ_f of 1.0622. The Debye length is 3.6 nm, $T = 300$ K, $A = 5 \times 10^{-21}$ J, and $\epsilon = 7.08 \times 10^{-10}$ Farads/meter.

longer attractive region in the particle interaction energy, as illustrated in Fig. 1, which quickly brings particles into flocs, circumventing the diffusion limited nature of depletion fractionation. In addition, magnetic field strength can be easily adjusted in steps to floc and separate larger particles before repeating the procedure for smaller particles. These effects are qualitatively illustrated in the experiments described below.

III. EXPERIMENTAL DEMONSTRATIONS

The basic ideas described above are demonstrated using fluorescent microscopy of polystyrene microspheres (Bangs Lab, Duke Scientific) of different diameters and fluorescing at different wavelengths. Two related fractionation methods are demonstrated. In one, Sodium Dodecyl Sulfate (SDS) micelles (4 nm diameter) are used in conjunction with iron-oxide nanoparticles (10–15 nm diameter) to demonstrate fractionation. In the other, magnetic nanoparticles are employed without any additional micelles.

The fluid chamber for observation of microparticle aggregation through a fluorescent microscope (upright Leica DMLFS with a 1.3 numerical aperture 100 \times oil-immersion lens) was formed between two glass slides separated by 10- μ m spacers (10- μ m fiber spacers, EM Industries). An oil drop was used over the top slide to provide optical coupling into the oil immersion lens. For separation experiments a 64 \times water immersion lens over a cover slip and glass slide is used. A uniform magnetic

$$U_{\text{dep}} = \begin{cases} \frac{\pi n k T}{4} (d + d_m)^2 \left[s - d_m + \frac{2(d+s)^3}{3(d+d_m)^2} - \frac{2}{3}(d+d_m) \right], & s \leq d_m \\ 0, & \text{otherwise} \end{cases} \quad (3)$$

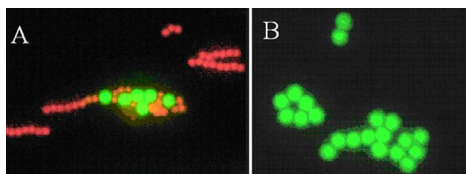


Fig. 2. The 1- μm and 2- μm polystyrene particles in 0.08 mol/L SDS and 0.34% volume fraction EMG 705 ferrofluid. In (a), a 24-kA/m magnetic field is present causing rapid floc formation. In (b), the external field is removed leaving only the larger particles in flocs after gentle rinsing. A $64\times$ water immersion lens is used.

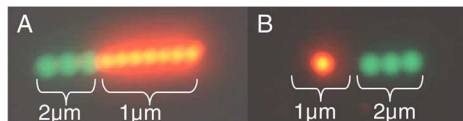


Fig. 3. Fractionating 0.033% by volume 2- and 1- μm polystyrene particles in 0.34% volume fraction EMG 705 ferrofluid. In (a), a 24-kA/m field is present causing all particles to floc. In (b), the field is reduced to 3.2kA/m, which is sufficient to keep the 2 μm particles in flocs, but not the 1- μm particles. A $100\times$ objective is employed.

field, whose direction and magnitude could be varied dynamically, was created using two Kepco bipolar operational power supplies/amplifiers attached to solenoids with iron cores.

In the first experiments 0.08 mol/L SDS is added to a solution of 2- and 1- μm particles in concentrations of 7.7×10^7 , and 6×10^8 beads per milliliter respectively to create a system where only the larger polystyrene microparticles would tend to flocculate. However, due to the lower than usual concentration, large size of the particles, flocculation by diffusion takes a very long time to occur. *In fact*, the fluid dries long before any appreciable number of particles floc. The addition of ferrofluid (EMG 705, Ferrotec) at 0.34% by volume fraction and application of a 24-kA/m magnetic field causes rapid flocculation. Rapid formation of particle chains is observed with smaller particles generally on the outside of the chains as shown in Fig. 2(a). The flocs then settle to the bottom of the slide. When the field is removed the smaller particles rapidly diffuse away whereas, due to depletion forces, the larger particles remain floccled to each other and to the slide below. Therefore, the smaller particles can be removed by a gentle rinsing that does not disrupt the larger floccled particles. The result of this separation is shown in Fig. 2(b).

In the second set of experiments clusters are formed without any SDS micelles. Ferrofluid (EMG 705 at 0.34% volume fraction) is employed alone. This is more convenient as separating different sizes can be done by varying the field alone instead of having to alter the chemistry. The application of a uniform magnetic field induces rapid cluster formation. When this magnetic field is not rotating, the clusters form particle chains. As illustrated in Fig. 3(a), larger particles tend to stay together with other larger particles, while the smaller particles stay together with other smaller particles because chains of smaller particles take longer to form and energy is minimized by having larger particles next to each other. Once the chains are formed at 24 kA/m, the field is reduced to 3.2 kA/m. At that time, the

smaller 1- μm particles are dispersed. However, the 2- μm particles remain clustered together in chains. Complete removal of the applied field results in dispersal of the larger particle chains as well in these experiments because the ferrofluid particles are present in far too low a concentration to cause appreciable depletion forces. Separations in this case are achieved either by using gravity or the magnetic field gradient directed toward the walls of the container.

IV. CONCLUSION

This paper proposed and investigated a new method of fractionation of nonmagnetic colloidal particles using ferrofluid and a uniform external magnetic field. Experimental demonstrations confirmed that this magnetically assisted fractionation indeed occurs much faster than depletion fractionation. Moreover, the experiments carried out in this work confirmed that fractionation occurs even in the absence of SDS micelles due to magnetic interactions alone. In any of these fractionations the ferrofluid can, in principle, be reclaimed using high gradient magnetic separation.

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