Direct Measurement of Colloidal Forces

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We present a novel approach that allows us to directly determine the force-distance law between tiny colloidal particles. Our technique exploits the fact that the anisotropy of the forces between dipoles causes particles to form chains. Because chains give rise to a strong Bragg diffraction of the visible light, the interdroplet spacing is accurately measured. Moreover, because the attractive dipolar magnetic force can be varied through the intensity of the external field, the balancing repulsive force can also be measured at various spacings. We give first evidence of the feasibility of this approach by using monodisperse magnetic emulsions under magnetic field.

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The knowledge of force-distance laws between colloidal grains is of prime importance in understanding their stability and many of their properties. Unfortunately, a direct measurement of such tiny forces has been impossible both because of their magnitude and because of the difficulty in controlling the separation of colloidal particles with sufficient precision. Instead, it is only possible to infer the behavior from bulk properties such as the compressibility [1] and the phase behavior [2,3]. To date, direct measurements of force-distance laws have been limited to macroscopic flat interfaces such as mica surfaces [4,5] or to a sphere approaching a macroscopic surface [6,7], large soap films [8,9], vesicles [10], lamellar phases, clays, and parallel linear polyelectrolytes [11-13]. Here we present a novel approach that overcomes these limitations, allowing the direct measurement of both forces and distances between tiny colloidal particles. Our technique exploits the fact that the anisotropy of the forces between induced dipoles causes particles to form linear chains. The magnitude of the induced dipole can be controlled by the strength of the applied field, allowing the force to be determined precisely. Moreover, if the particles are uniform in size, light is Bragg scattered from the chains, allowing the separation to be measured precisely. The force-distance laws can thus be directly measured in a wide variety of materials, including emulsions, foams or sols.

In this paper, we demonstrate the feasibility of this technique using monodisperse magnetic emulsions. Monodisperse oil-in-water emulsions are obtained using a fractionated crystallization technique [14]. The oil is a ferrofluid [15]; the resultant droplets are paramagnetic, so that an applied field induces a magnetic dipole in each drop, causing them to form chains [16]. At low concentration, these one droplet thick chains are well separated and oriented along the field direction. As a result of the presence of this one dimensional ordered structure, surprisingly intense Bragg scattering is observed [16], enabling a precise measurement of the interdroplet spacing. Moreover, because the dipolar magnetic interaction can be calculated, the repulsive forces between droplet interfaces can be measured. By varying the intensity of the applied field, the full force-distance law can be determined. Stable magnetic droplets can be formed from many kinds of oils and surfactants; the liquid droplets can also be changed to solid spheres through polymerization or temperature controlled solidification. Here we demonstrate the accuracy of this method by studying the forces arising from the presence of ionic surfactant (sodium dodecyl sulfate or SDS) covering the droplet surfaces. These electrostatic forces are well described in the limit of low surface potential or large separation, allowing us to quantitatively test our technique.

The dispersed phase of the emulsion is an octane ferrofluid, with an oxide content of 10% by volume; the grains are single magnetic domains of Fe_2O_3 and have a size of about 100 Å. This ferrofluid dispersion remains perfectly stable in the magnetic fields under consideration [15]. In the absence of field, the properties of these ferrofluid emulsions are the same as nonmagnetic ones. By contrast, upon application of an external field, the droplets form chains; if they are very dilute, with volume fractions $\phi < 0.1\%$, the chains are only one droplet thick, and remain well separated. In Fig. 1, we show a microscope picture of these chains formed from droplets with a radius of $a = 94$ nm, as determined by quasielastic light scattering, and for an applied field strength of about 40000 A/m. This chaining causes a strong modification of the optical properties; if the sample is illuminated by a white light source, the emulsion appears beautifully colored in the backscattering direction. As the field

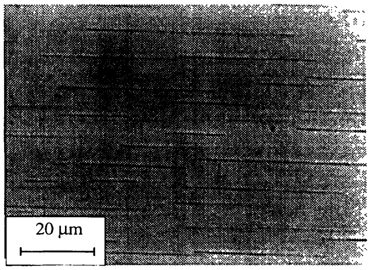

FIG. 1. Chains of particles aligned with the magnetic field.

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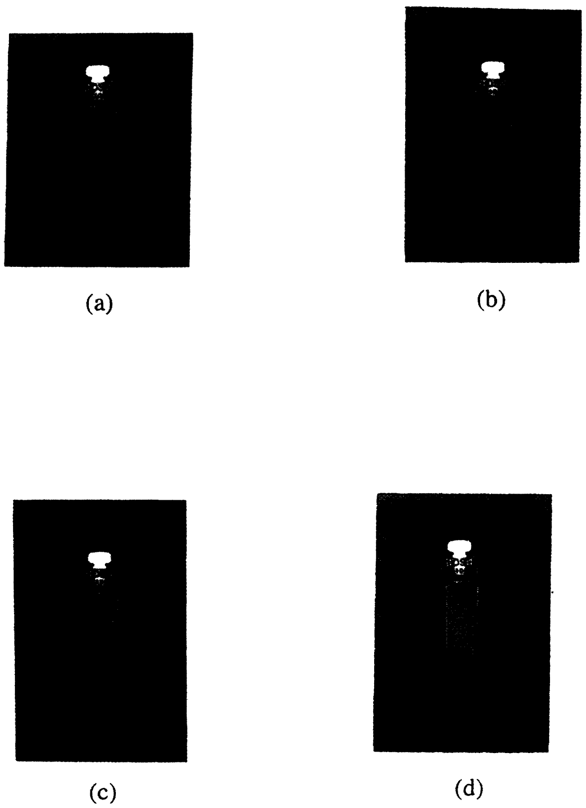
(a) (b)

(c) (d)

FIG. 2. Evolution of the color with the intensity of the magnetic field. Droplet volume fraction ~0.1%. Surfactant concentration $=3\times10^{-4}\,\mathrm{mol\,l^{-1}}$. (a) $H_{\mathrm{ext}}=0$; (b) $H_{\mathrm{ext}}=8000$; (c) $H_{\mathrm{ext}}=22000$; and (d) $H_{\mathrm{ext}}=36000$ A/m.

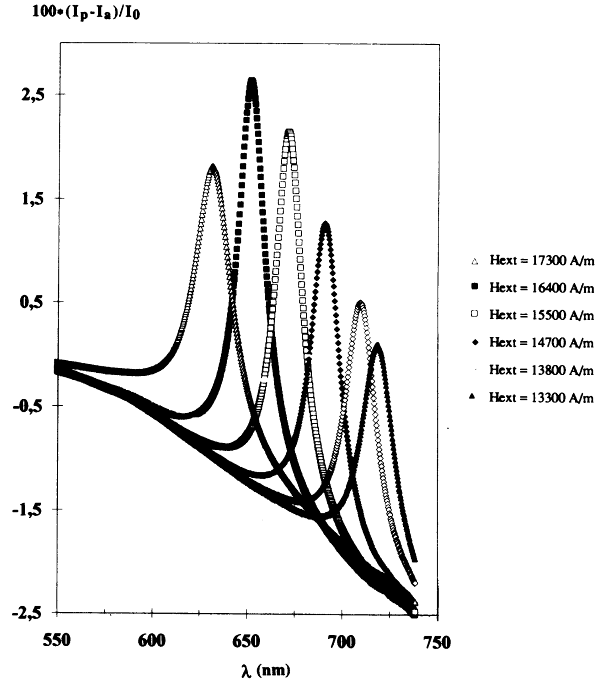

FIG. 3. Diffraction peaks at various field intensities. I_0=incident intensity; I_p=scattered intensity in the presence of field; and I_a=scattered intensity at zero field.

strength is increased, the color changes from brown to red, to yellow, and to green. We illustrate this dramatic coloring in the photograph in Fig. 2. These colors originate from Bragg diffraction and provide a straightforward measure of the spacing between droplets within the chains. We take advantage of this fascinating behavior to directly measure the force-distance law.

The spacing between droplets is directly deduced from the determination of the spectral distribution of the scattered light at a constant angle. For perfectly aligned particles with a separation d, illuminated by incident white light parallel to the chains, the first order Bragg condition reduces to

$$2d=\lambda_0/n\,, \tag{1}$$

where n is the refractive index of the suspending medium ($n=1.33$ for water), and λ_0 is the wavelength of the light Bragg scattered at an angle of 180°. Representative data of the normalized scattered intensity as a function of wavelength are shown in Fig. 3. The pronounced first order diffraction peaks are clearly observed, as expected from visual observation. The peak position moves to smaller λ_0 as the field is increased. The wavelength of the peak intensity provides a direct measure of the spacing between the drops, through Eq. (1). The width of the peaks is determined by the resolution of our optical system. Because the drops are so monodisperse and negligibly deformable owing to their large capillary pressure (~1 atm) [17], we can also determine the interfacial separation, $h=d-2a$.

The repulsive force between the droplets must exactly balance the attractive force between the dipoles induced by the applied magnetic field. Since the dipoles are aligned parallel to the field, this force can be calculated exactly and is given by [18]

$$F_m(d)=-\frac{1.202}{2\pi\mu_0}\times\frac{3m^2}{d^4}\,, \tag{2}$$

where μ_0 is the magnetic permeability of free space and m is the induced magnetic moment of each drop. The induced magnetic moment must be determined self-consistently from the intrinsic susceptibility of the ferrofluid, the spherical shape of the drops, and the presence of the neighboring drops. Thus

$$m=\mu_0\tfrac{4}{3}\pi a^3\chi_s H_T\,, \tag{3}$$

where H_T is the total magnetic field acting on each drop, and χ_s is the susceptibility of a spherical droplet. Taking into account the demagnetization effect due to polarization [19],

$$\chi_s=\frac{\chi}{1+\frac{1}{3}\chi}\,, \tag{4}$$

where χ is the intrinsic susceptibility of the ferrofluid.

This follows the classical Langevin form

$$\chi = \alpha[\coth(\beta H_{\text{ext}}) - 1/\beta H_{\text{ext}}]/H_{\text{ext}}, \qquad (5)$$

where H_{ext} is the actual applied field. We determine the coefficients, $\alpha = 3.7\times10^4$ A/m and $\beta = 1.80\times10^{-4}$ m/A from magnetic susceptibility measurements on the bulk ferrofluid using a SQUID susceptometer.

The total applied field H_T is given by the sum of the external applied field and the field from the induced magnetic moments in all the neighboring drops in the chain. This can easily be calculated for an infinite chain, assuming point dipoles, giving

$$H_T = H_{\text{ext}} + 2\times1.202\times\frac{2m}{4\pi\mu_0 d^3}. \qquad (6)$$

The magnitude of the second term makes at most a 20% correction to the externally applied field. Because the magntic moment induced in each drop is expressed in terms of the total applied field in Eq. (3), the results in Eqs. (2) and (6) represent a self-consistent calculation.

In calculating the interaction between the magnetic moments induced in the droplets, we have restricted our attention to the dipole term. Strictly speaking, the force should be written as a multipole expansion with the leading dipole term given by Eq. (2). While the uniform external field H_{ext} generates only a pure dipole moment, the nonuniform field from the other spheres generates higher order multipole moments. Nevertheless, since the susceptibility is so small, we estimate that the point-dipole approximation is sufficient for perfect spheres, since corrections due to higher order multipole moments are less than $10^{-3}F_m$ [18]. Finally, in Eq. (2), we have also assumed that the only attractive force is due to the attraction between the induced magnetic dipoles. However, other attractive interactions can also become nonnegligible when the droplets are sufficiently close. In particular, the van der Waals attraction can also make some contribution; this can be readily calculated using standard formulas, and added to the total force.

We plot the total repulsive force between colloidal particles as a function of their separation by the solid points in Fig. 4. The measurements were performed for emulsions with $\phi = 0.1\%$ and with three different concentrations of SDS in the continuous phase, ranging from 6×10^{-5} $\text{mol}\,\text{l}^{-1}$ to 10^{-2} $\text{mol}\,\text{l}^{-1}$. Changing the SDS concentration has the effect of changing the range of the repulsive Coulombic interaction between the drops by changing both their surface potential and the Debye screening length. As can be seen in Fig. 4, the range of the repulsive interaction clearly increases as the SDS concentration decreases. In obtaining the data in Fig. 4, the induced magnetic interactions dominate all other attractive interactions except for the case when the droplet separation becomes less than 150 Å; for these cases, the van der Waals contribution is about 10%, and was included through the Hamaker derivation [20] in obtaining the value of the force plotted. The data in Fig. 4 clearly illustrate the potential of our technique for performing direct force measurements between colloidal particles. In these experiments, it is the force that is controlled by the applied magnetic field; the resultant distance is set by the force-distance law of the particular interaction between the colloidal particles. The minimum force that can be measured is that required to hold the particles in a chain, so that the interaction energy overcomes the thermal energy. The maximum force is determined by the saturation field of the ferrofluid; this could be increased by about an order of magnitude by using a ferrofluid with a larger susceptibility. We are able to resolve average interfacial separation distances of about 15 Å. We are able to measure interparticle forces as small as 10^{-13} N, corresponding to the minimum force required for forming chains.

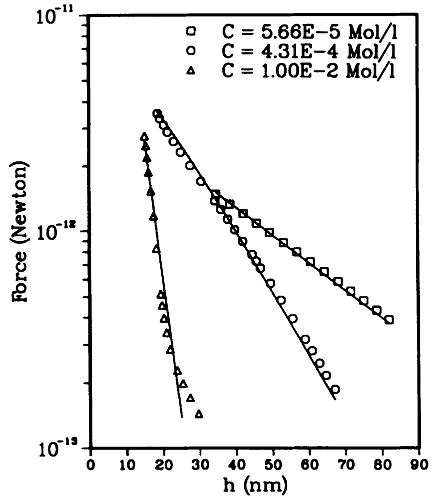

FIG. 4. Evolution of the force with the spacing h for different surfactant concentrations. Points correspond to experimental values and solid lines to theoretical predictions.

We can prove the accuracy of our new technique by comparing our experimental results with the theoretical prediction for the repulsive forces between charged interfaces. An electrostatic repulsion arises from the presence of anionic SDS molecules adsorbed on the droplets. However, it is not a simple Coulomb repulsion, since, to conserve electroneutrality, the particle charge is surrounded by a diffuse ion atmosphere forming an electric double layer with the surface charge. For the case of particles having small charge densities, the force between two particles is best represented by [21]

$$F_r(d) = 4\pi\varepsilon\psi_0^2 a^2\left(\frac{\kappa}{d} + \frac{1}{d^2}\right)\exp[-\kappa(d-2a)], \qquad (7)$$

where ε is the dielectric permittivity of the suspending medium, ψ_0 is the electric surface potential, and κ the inverse Debye length [22]. Equation (7) is valid for extended double layers where $\kappa a < 5$. If the particles have a thin double layer, $\kappa a > 5$, the alternate Derjaguin ap-

TABLE I. Variation of the surface potential with the bulk surfactant concentration.

C (mol l^{-1})	Ψ_0 (mV)
5.66×10^{-5}	-18.8
4.31×10^{-4}	-24.2
10^{-2}	-45.5

proximation [23] provides the appropriate interaction force with the assumption that ψ_0 remains constant and independent of h:

$$F_r(d)=2\pi\varepsilon\psi_0^2 a\kappa\frac{\exp[-\kappa(d-2a)]}{1+\exp[-\kappa(d-2a)]}\,. \tag{8}$$

The inverse Debye length is calculated from the ionic surfactant concentration of the continuous phase. Thus the only unknown parameter is the surface potential ψ_0; this can be obtained from a fit of these expressions to the experimental data. The theoretical values of $F_r(h)$ are shown by the continuous curves in Fig. 4, for the three surfactant concentrations. We use Eq. (7) for the lowest concentration ($\kappa a=2.3$) and Eq. (8) for the two others ($\kappa a=6.4$ and 27.6). In both cases the agreement is spectacular, confirming the inherent accuracy of our technique.

The three values corresponding to the three different surfactant concentrations are reported in Table I. We checked that incorporating higher order terms in the expression of the force [24] did not significantly change the deduced values of ψ_0. As expected, the surface potential increases with the bulk surfactant concentration as a result of the adsorption equilibrium. Consequently a higher surfactant concentration induces a larger repulsion, but is also characterized by a shorter range due to the decrease of the Debye screening length. The measured surface potentials compare fairly well with other measurements based on electrophoretic droplet mobility performed on different ionic emulsions [25].

While the forces between the particles are well described by the double layer repulsion, some deviation occurs in the case of a short screening length and low value of the force. This is most clearly evident in the data in Fig. 4 for the highest SDS concentration and at the lowest forces, just at the onset of chaining. We believe that this deviation arises from the thermal expansion of the chains which leads to a larger average spacing. This acts as an additional effective repulsive force which is entropic in origin.

This technique offers the opportunity to directly measure interaction forces between colloidal particles. We use paramagnetic particles with magnetic field but in principle it can be extended to electrical field. We believe that the knowledge of these forces will be critical in addressing many important problems in surface science. The most important application will probably be to clarify the interplay between surfactant adsorption and the resulting forces between colloids which is essential in determining their stability.

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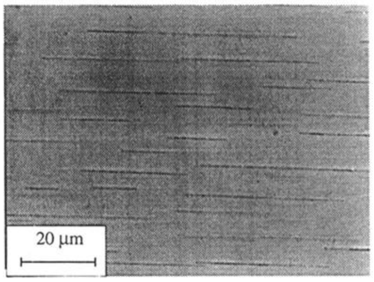

FIG. 1. Chains of particles aligned with the magnetic field.

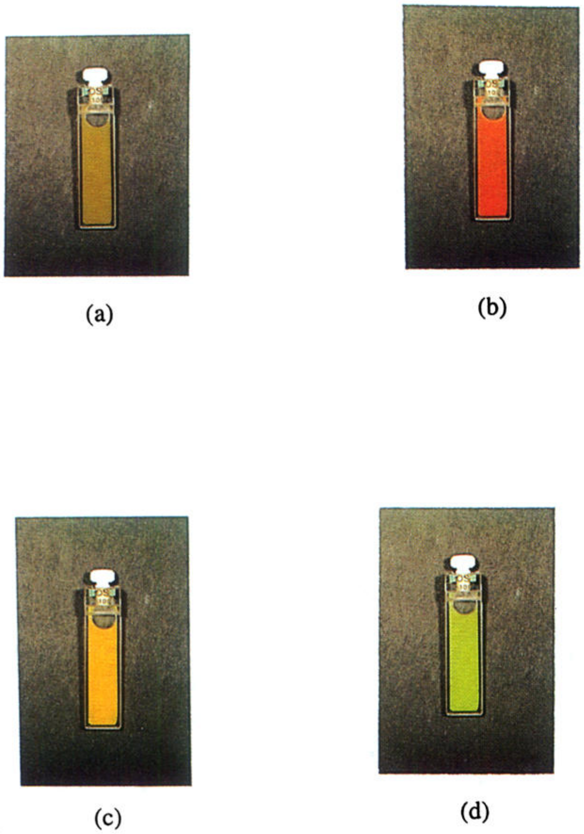

FIG. 2. Evolution of the color with the intensity of the magnetic field. Droplet volume fraction ∼0.1%. Surfactant concentration $=3\times10^{-4}$ mol l^{-1}. (a) $H_{\text{ext}}=0$; (b) $H_{\text{ext}}=8000$; (c) $H_{\text{ext}}=22\,000$; and (d) $H_{\text{ext}}=36\,000$ A/m.