

Direct Measurement of Colloidal Forces in an Anisotropic Solvent

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We present a new method to measure attractive interactions between colloidal particles, and determine the nature of the attraction between particles suspended in a nematic liquid crystal. We confine droplets filled with ferrofluid to a thin layer and apply a magnetic field to induce dipole moments that drive the droplets apart. When the field is removed, the attractive interactions pull the droplets back together. The force is determined from the velocity because the motion is viscously damped. We confirm the dipolar character of the interaction between droplets in a nematic solvent. [S0031-9007(97)04806-0]

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Anisotropic interactions between colloidal particles can have a pronounced effect on the structures that form in a suspension. Electrorheological and magnetorheological fluids are well known examples [1]; application of an external field induces electric or magnetic dipoles in the particles, and the resultant dipole-dipole interaction is anisotropic, leading to the formation of pronounced linear chains. However, higher-order moments may also play an important role [2–4], making it important to directly measure the forces between the particles to determine the nature of the interactions for practical applications. Other important anisotropic colloidal interactions arise in suspensions of particles in anisotropic host fluids, such as liquid crystals, where highly unusual structures are observed; perhaps the most spectacular structures are the long linear chains of particles observed in emulsions of water droplets suspended in a nematic liquid crystal [5]. In this case, the anisotropy arises from the orientational elasticity of the host liquid crystal. Boundary conditions force the liquid crystal molecules to be normal to the surface of the droplet; by contrast, far from the droplet, the nematic must be uniformly aligned. This mismatch in ordering is resolved through an induced topological defect; experimentally, this defect is observed to be a hyperbolic hedgehog, which accompanies each droplet. The distortion of the orientational order of the nematic has a dipolar character, and the dipole-dipole attraction of the droplet-defect pairs is believed to cause the formation of the chains. To quantify this, a model has been proposed which is based on the analogy between the director \mathbf{n} , which is a unit vector field specifying the orientation of the nematic, and an electrostatic field [5,6]. This analogy can provide considerable insight into the origin of the observed behavior and can be used for detailed calculations of the structures and long-range interactions. It is, therefore, essential to definitively confirm the accuracy of this model by testing its primary prediction, that the long-range attraction between the droplets is, in fact, dipolar in character. This can be accomplished by measuring the dependence of the attractive force on particle separation.

In this Letter, we report a new technique for making direct measurements of attractive forces between colloidal particles. We apply it to verify the dipolar nature of the attraction between particles suspended in a nematic liquid crystal, thereby confirming the theoretical approach that has been used to account for the observed behavior. We use droplets which contain an aqueous ferrofluid; the application of an external magnetic field induces a large magnetic dipole within the droplets. By confining the droplets between two slides, a repulsive interaction results forcing them apart. When the magnetic field is turned off, the long-range elastic attraction pulls the droplets back together. This force is exactly balanced by the viscous drag; thus, a measure of the droplet velocity as a function of separation provides a direct measure of the attractive force. We show that this attraction exhibits the distance dependence expected for dipolar interactions, varying as r^{-4} , where r is the separation between particle centers. We also show that the scaling with particle size of the magnitude of this attractive force is consistent with a dipolar attraction, confirming the elastic origin of the force. These results unambiguously demonstrate the validity of the electrostatic analogy in describing the elastic forces. In addition, we identify an unexpected attractive interaction which is also induced by orientational elasticity, but which is not dipolar in character. Instead, the magnitude of this attraction is independent of particle separation, reflecting the different behavior of the accompanying topological defects. While our measurement technique is utilized here to study the attractions between particles in a liquid crystal solvent, it is, in fact, more general; it provides a direct measure of attractive forces between colloidal particles on the scale of piconewtons, and thus may be useful for other applications as well.

We use an emulsion composed of aqueous ferrofluid droplets dispersed in a liquid crystal which is in the nematic phase at room temperature [7]. The droplets are stabilized by polyoxyethylene sorbitan monostearate, a surfactant which imposes normal boundary conditions of the director at the droplet surface [8]. The emulsion is

produced by shaking a mixture containing a small amount of surfactant (0.2%), ferrofluid (10%), and nematic liquid crystal; by limiting the concentration of the aqueous phase, we produce an inverted emulsion, consisting of ferrofluid droplets suspended in the liquid crystal. A thin layer of this emulsion is confined between two glass slides coated with polyimide and rubbed to establish planar anchoring of the nematic liquid crystal at the surface [9], and setting the global orientation of \mathbf{n} in the cell. We digitize the positions of the droplets with a microscope, a CCD camera, and a computer. The ferrofluid is a suspension of small iron oxide grains, which is superparamagnetic. In the absence of an applied field, there is no macroscopic magnetic dipole in the droplets. However, upon application of a uniform magnetic field parallel to the optical axis of the microscope, large magnetic dipoles are induced within the droplets, parallel to the applied field. This leads to a repulsive interaction which drives neighboring droplets apart. We focus our attention on pairs of equally sized droplets; in any sample, it is typically possible to find several suitable pairs with different sizes. By using very low droplet concentrations, aggregation is sufficiently slow to allow ample time to study droplet pairs.

In the absence of the field, droplet pairs are aligned along the direction of alignment of \mathbf{n} imposed by the slide, which we take as the z axis. The droplets are separated by a few tenths of a micron because of the presence of a hyperbolic hedgehog between them [5]. We illustrate a typical pair of droplets in Fig. 1; crossed polarizers are used to view the droplets, and the two hyperbolic hedgehog defects appear as crosses beside each droplet. The configuration of the corresponding director field is also shown in Fig. 1. An example of the experimental observations is shown directly in the pictures in Fig. 2. Application of an external magnetic field of about 100 G induces large magnetic dipoles in the droplets, forcing

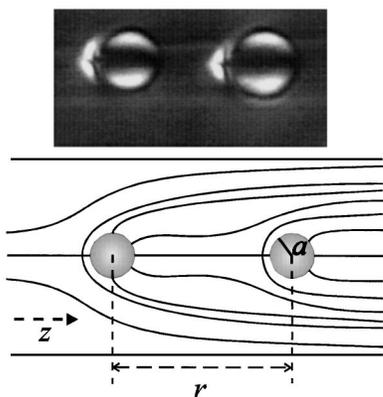


FIG. 1. Microscope picture, taken between crossed polarizers, of two ferrofluid droplets suspended in a nematic liquid crystal. The hyperbolic hedgehogs to the left of each droplet lead to a dipolar configuration for the director field, and cause an attractive interaction. A schematic of the director field is shown below.

them apart, as shown in Figs. 2(b) and 2(c). When their separation reaches about $20 \mu\text{m}$, the field is turned off, and the elastic attraction draws the droplets back together, as shown in Figs. 2(d) and 2(e). Initially, the droplets approach each other rather slowly, but their speeds increase significantly with decreasing separation. In all cases, the motion of the droplets is along the z axis, both as they are forced apart by the induced magnetic dipoles, and as they are attracted back together by the elastic interaction. This reflects the anisotropy expected for a dipolar interaction.

The separation of droplet centers, r , is measured directly from the digitized images; results for a pair of droplets with radii $a \sim 4 \mu\text{m}$ are plotted in Fig. 3, where we show the measured r a function of time after the field is turned off, t . The slow initial and rapid final change of separation is apparent. The final cessation of their motion is quite sudden, reflecting the sharpness of the short-range repulsion due to the intervening hyperbolic hedgehog; this can provide an additional mechanism to stabilize the droplets [5]. The velocity of the droplets can be determined directly from the derivative of the data in Fig. 3. In addition, we can determine the acceleration of the particles from the second derivative of these data, albeit with considerably more uncertainty.

To determine the attractive force between the droplets, $F_a(r)$, we consider the total force acting on them,

$$m\ddot{r} = 2F_a(r) - 6\pi\eta_{\text{eff}}a\dot{r}, \quad (1)$$

where m is the buoyant mass of the particles. We include the factor of 2 to ensure that $F_a(r)$ reflects the force per droplet between the pair. Here, we assume that the viscous drag is the Stokes drag for a sphere with stick boundary conditions, and recognize that the effective viscosity η_{eff} represents some combination of the five independent viscosities of the nematic liquid crystal; we

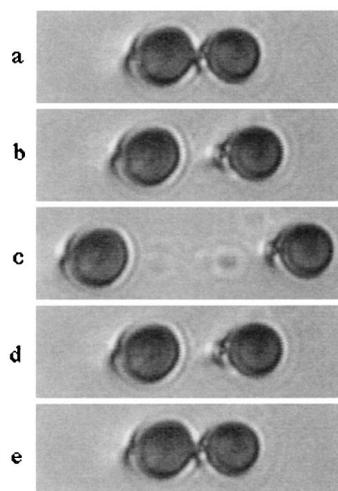


FIG. 2. Application of a magnetic field induces a repulsive interaction which drives the droplets apart in (b) and (c). When the field is switched off, in (c), the elastic attractive interaction pulls the droplets together, in (d) and (e).

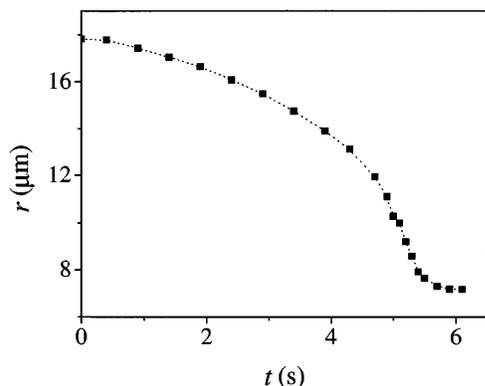


FIG. 3. Time dependence of the separation between the centers of two particles after the field is turned off, and the attractive elastic interaction pulls them together.

approximate this by the shear viscosity measured with a capillary tube, $\alpha_4 \sim 23$ cP [7]. The measured inertial force $m\dot{r}$ is much smaller than the viscous drag, being at least 7 orders of magnitude less. Thus, the total force is nearly zero, so the particle motion is viscously damped, allowing us to directly determine the attractive force from the measured velocity.

We plot the attractive force as a function of particle separation for three pairs of particles of different sizes in Fig. 4. We use a logarithmic plot to emphasize the power-law dependence of the forces; the slope of each data set is 4, as indicated by the straight lines. Thus, $F_a(r) \sim r^{-4}$, confirming the dipolar nature of the attractive force. Higher-order multipole moments may contribute to the attractive force as the droplets become very close [6]; however, observation of their contribution is precluded by the strong

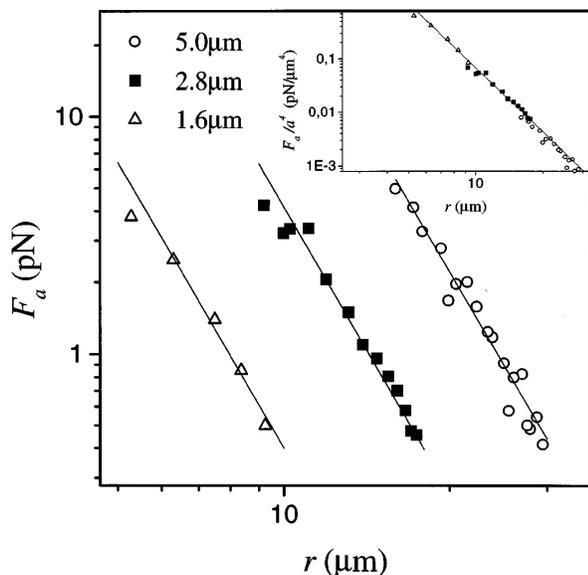


FIG. 4. Velocity v of approaching particles as a function of separation r , for three different particles. The inset shows the scaling of the force with particle size.

short-range repulsive interaction which dominates as the droplet separation approaches $\sim 3a$. The range of the attractive forces increases with particle size. We expect $F_a(r)$ to be proportional to some elastic constant of the liquid crystal, K [10]. Since $F_a(r) \sim r^{-4}$, dimensional analysis requires that it be proportional to some length to the fourth power; the droplet diameter is the only length scale in the problem, implying that $F_a(r) = CKa^4/r^4$, where C is a constant. Thus, we expect $F_a(r)/a^4$ to be independent of particle size. To test this, we plot the forces normalized by a^4 as a function of r for the three pairs of droplets in the inset of Fig. 4. The data all fall on a single, universal curve, confirming the elastic origin of the attractive force. Moreover, by taking an average of the three elastic constants, $K = 10$ pN [7], we obtain $C = 70$; given the uncertainties in the choice of the viscosity and the average elastic constant, this is in reasonable agreement with a value of $C = 300$ determined theoretically [6].

While most droplet pairs exhibit the hyperbolic defect structure shown in Fig. 1, we occasionally, but regularly, see a different structure for the defect that accompanies the two droplets. Instead of two distinct hyperbolic defects, we see narrow strings of birefringent regions between the droplets; an example of this is shown in the image in the top inset of Fig. 5, where we show two droplets observed between crossed polarizers in the absence of an external magnetic field. The birefringent strings are the lighter regions just above and below the droplets. By contrast to the dipolar case, these droplet pairs are not separated by a defect, but instead nearly touch each other.

There is still a long-range attractive interaction between these droplets, but it has a completely different character. When we apply the magnetic field, the droplets again separate along the z direction; now, however, the two birefringent strings elongate and seem to approach each other in a fashion reminiscent of stretched chewing gum, as shown in two lower images in the inset of Fig. 5. We call this a

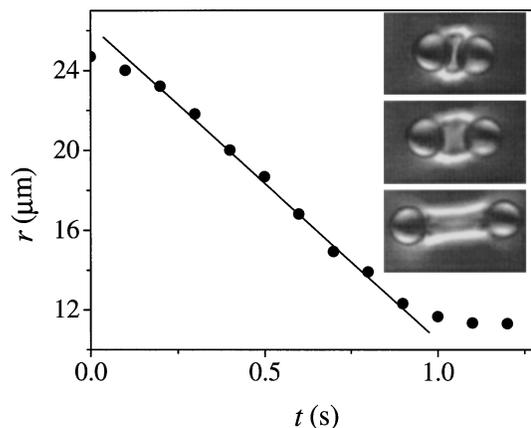


FIG. 5. Time dependence of the separation between approaching particles separated by the bubble-gum defect. The linear behavior means the force is constant, independent of droplet separation.

bubble-gum defect. We again measure the droplet separation as a function of t . As shown by the results plotted in Fig. 5, the velocity in this case is constant, independent of separation. Thus, the particles are again in the overdamped limit, but the force is constant, independent of separation.

The exact nature of these bubble-gum defects is unclear. One possibility is that they are two, distorted hyperbolic hedgehogs, each one being attached to both particles. These distorted hedgehogs could give rise to the observed birefringent strings. Regardless of their nature, we can account for the distance dependence of the attractive force from dimensional analysis. Since the defect structure is a line, the elastic energy of the distortion must be proportional to the length of the line, which is set by the separation between the particles; as a result, the attractive force must be constant, and must scale as a line tension, which we expect to be of the order of the elastic constant. Indeed, we measure the force to be $F_a \sim 1.5K$. We do expect an additional contribution to the viscous dissipation arising from the reorientation of the molecules as the defect shrinks, analogous to the dissipation observed in the coarsening of a defect line in a nematic liquid crystal. However, this viscous dissipation will still be proportional to the particle velocity, and will, therefore, modify only the magnitude, but not the scaling, of the attractive force; we have not included this effect in our estimate of the magnitude of F_a .

We have presented a new method to measure the attractive forces between colloidal particles. Other techniques for measuring forces between colloidal particles have focused on the more common occurrence of repulsive forces or very weak attractions [11,12]. Stronger attractive forces have been measured between colloidal particles joined by a single macromolecule, using laser tweezers [13]. The use of laser tweezers is not feasible in our system because of the unfavorable refractive indices. Our technique also has the advantage that it is capable of measuring forces over a large range of magnitudes. Our method should be applicable to measure attractive colloidal forces in other systems as well, and should be capable of probing forces as small as 10^{-14} N, using $10 \mu\text{m}$ particles, before Brownian motion obscures the approach velocity. Finally, we note that, to our knowledge, these are the first measurements of an

interaction between topological dipoles. The interactions between single defects, or the coarsening of disclination lines have been studied; however, topologically neutral assemblies cannot be studied in pure liquid crystals because they spontaneously annihilate. In the present work, the dipoles are stabilized by the droplets, which cannot collapse, enabling dipolar interactions to be measured.

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