

NOTE

Rotational Diffusion of Monodisperse Liquid Crystal Droplets

We have prepared monodisperse suspensions of nematic liquid crystal droplets in water. The droplets are stabilized by polyvinyl alcohol, a polymer that induces planar anchoring of the liquid crystal molecules at the surface of the droplets. The resultant particles exhibit strong optical anisotropy while having a spherical shape. As a consequence, the light scattering from the particles contains a strong depolarized component. We report a simple application of this feature by performing dynamic light scattering experiments to measure the rotational diffusion of colloidal spheres in a dilute suspension. © 1998 Academic Press

Key Words: depolarized light scattering; rotational dynamics; liquid crystal; emulsion.

Spherically isotropic, but optically anisotropic particles can be highly desirable for a wide range of purposes; their optical anisotropy allows them to serve as local probes for the rotational motion in fluid flows and for rotational diffusion in different geometries. For example, colloidal particles containing polymer microcrystallites in an amorphous host matrix (1) have been used to measure the rotational diffusion of spherical particles in a colloidal crystal or a concentrated suspension (2) and to study rotation in hydrodynamic flows (3). While these optically anisotropic particles enable many new studies of both scientific and technological interest, their applicability can be limited by the amount of their optical anisotropy. Since they are generally composed of several microcrystallites in each particle, the total optical anisotropy tends to be averaged out, limiting the total value. Moreover, being made of Teflon, these materials are difficult to synthesize. Thus, it would be highly desirable to have spherical colloidal particles that are easy to synthesize and are highly optically anisotropic.

In this note, we show that colloidal droplets of liquid crystal can form nearly ideal spherically shaped, optically anisotropic particles. These particles are simple to synthesize using standard emulsion techniques (4). Moreover, they can be purified to obtain highly monodisperse suspensions using the technique of fractionated crystallization (5). Emulsions of liquid crystals in water form the basis of an important display technology based on polymer dispersed liquid crystal electrooptical devices (6). The droplets provide a well-defined geometry of confinement, which results in the formation of topological defects and elastic distortions, which have been widely studied (6). The nature of the optical anisotropy is controlled by the alignment of the liquid crystal, and this can be varied by adjusting the boundary conditions at the surface of the droplets. This allows us to easily convert nearly optically isotropic droplets into ones that are optically anisotropic. Each of these small droplets consists of a single domain of optically anisotropic oil, maximizing their anisotropy. We demonstrate the consequences of this anisotropy by performing depolarized dynamic light scattering measurements on the droplets at dilute concentrations, and confirm that the measured values of the translational and rotational diffusion coefficients are consistent and in agreement with expectations.

We make the liquid crystal droplet using standard emulsion techniques, developed previously for isotropic oils in water; however, here we replace the isotropic oil by a liquid crystal, a mixture of organic molecules com-

posed mainly of long, rigid, and rodlike cyanobiphenyl molecules (7). Like many isotropic oils, this liquid crystal is not soluble in water. We therefore use an ionic surfactant, sodium dodecyl sulfate (SDS), to stabilize the droplets. This allows us to use standard fractionated crystallization methods to purify the crude emulsion; after four steps, we obtain monodisperse droplets about $0.6\ \mu\text{m}$ in diameter, as determined with an optical microscope. The polydispersity of the droplets is estimated to be $\Delta R/R \sim 15\%$.

At room temperature, the liquid crystal is in the nematic phase, so the molecules have a preferential orientation (7). This alignment results in the formation of a topological defect within the droplets (6). The nature of this defect depends on the anchoring conditions of the liquid crystal molecules at the surface of the droplet. When SDS is used to stabilize the droplets, the anchoring is normal to the droplet surface. This results in radial orientation of the liquid crystal, with a radial hedgehog defect in the center of the droplet. We show in Fig. 1 (top) a schematic representation of the director field, \mathbf{n} , which characterizes the direction of the alignment of the liquid crystal molecules within the droplet. We note that this structure is centrosymmetric and thus will not result in strong anisotropy in the scattering from the small particles used here.

To change the orientation of the liquid crystal molecules within the droplet, we modify the anchoring conditions. This is easily accomplished by replacing the stabilizing surfactant, SDS, by another surface-active agent, polyvinyl alcohol (PVA), which is known both to stabilize the droplets and to change the surface anchoring condition from normal to parallel (6). This is accomplished by centrifuging the emulsion to concentrate it, removing most of the excess continuous phase, and replacing it an aqueous solution containing PVA ($M_w \sim 50\text{K}$) at 0.1% by weight. After several steps, the droplets are dispersed in a PVA solution and have the same size, but completely different boundary conditions and completely different optical properties. Now the anchoring is planar, resulting in two diametrically opposed defects, called boojums, and illustrated in Fig. 1 (bottom), where we show schematically the director orientation. The droplet now has a single domain of aligned liquid crystal.

The optical properties of a liquid crystal in the nematic phase are characterized by two indexes of refraction, the ordinary one, n_o , and the extraordinary one, n_e . At room temperature, this liquid crystal has $n_o = 1.49$ and $n_e = 1.59$. The optical anisotropy is quantified by the difference between the ordinary and extraordinary indexes, $n_e - n_o = 0.10$. The global optical anisotropy of a nematic droplet also depends on the configuration of the alignment of the liquid crystal molecules. The particles with normal anchoring are small and centrosymmetric and thus are not strongly anisotropic, whereas the particles with planar anchoring should exhibit a strong optical anisotropy resulting from the nearly complete alignment of the liquid crystal. Because of such an alignment the optical anisotropy of the droplets should be approximately that of the liquid crystal molecules themselves. Moreover, because the liquid crystal droplet is composed of only a single domain, it is much more optically anisotropic than the Teflon particles, which typically consist of several, randomly oriented domains. We estimate that the optical anisotropy of the liquid crystal droplets is about a factor of 10 larger than that of the Teflon particles.

We must also consider the shape of the droplets; the orientational elasticity of the nematic phase competes with the surface energy of the droplet, and could induce deformation of the droplet shape. However, nematic droplets in

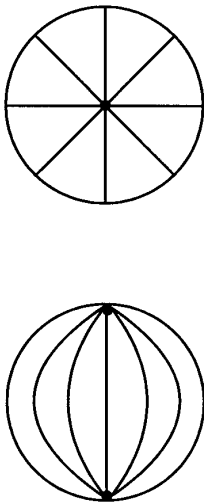


FIG. 1. Schematic representations of liquid crystal droplets stabilized with SDS (top) or PVA (bottom). The lines represent the orientation of the director field of the liquid crystal molecules. A topological defect, known as hedgehog, is located at the center of the radial droplet (top) obtained with normal boundary conditions. Such a droplet is centrosymmetric. By contrast, two surface defects, known as boojums, are located at the surface of the bipolar droplet (bottom) obtained under planar boundary conditions. This droplet is highly anisotropic.

water are known to be spherical (6). This can be simply understood by comparing the scale of the elastic energy, Ka , to the surface energy, γa^2 . Here, K is a typical elastic constant of the liquid crystal, a is the size of the droplet, and γ is the interfacial tension. For the materials used in these experiments, $K/\gamma a \sim 10^{-3}$; thus, the surface energy is much greater than the elastic energy, and the droplets remain spherical.

To measure the consequences of the optical anisotropy, we perform dynamic light scattering experiments and measure both the polarized and depolarized components. We use dilute suspensions of liquid crystal droplets: centrosymmetric droplets stabilized with SDS and optically anisotropic droplets stabilized with PVA. We use a goniometer to allow us to vary the scattering angle. The temporal autocorrelation function of the scattered light is calculated with a digital correlator. An Ar^+ ion laser operating at a wavelength of 514.5 nm is used as the excitation source. It is linearly polarized in the vertical direction. We detect the scattered intensity polarized in the same direction, I_{vv} , and in the perpendicular or horizontal direction, I_{vh} . In both cases, we determine the normalized electric field correlation functions, $g_{vv}(\tau)$ and $g_{vh}(\tau)$, as a function of scattering angle and, thus, scattering vector, $q = 4\pi n/\lambda \sin(\theta/2)$.

For isotropic particles, $g_{vv}(\tau)$ is sensitive only to translational motion and is widely used to measure particle size (8). For isotropic particles there is no depolarized scattering ($I_{vh} = 0$). By contrast, for optically anisotropic particles both the polarized and depolarized components of the scattering are large. A general theoretical description of the depolarized scattering is rather complex; we simplify this by restricting our attention to the Rayleigh approximation and treating the particles as point scatterers (8). While not exact, this approximation provides sufficient insight to properly interpret our results; moreover, it becomes increasingly accurate as the particle size and index of refraction mismatch decrease. We assume that the particles are spherically symmetric, but have an optical anisotropy, characterized by two indices of refraction, n_{\parallel} and n_{\perp} . Values of n_{\parallel} and n_{\perp} can, in principle, be determined experimentally by measuring the polarization dependence of the static light scattering as the index of refraction of the solvent is varied (1, 8, 9). Unfortunately, however, the index of refraction of the liquid crystal is so large that we were unable to attain a sufficiently large index

of refraction of the solvent to make these measurements. Thus, instead, we assume that $n_{\parallel} \approx n_e = 1.59$ and $n_{\perp} \approx n_o = 1.49$; these are reasonable assumptions because of the alignment of the liquid crystal in the droplets. The average index of refraction is then

$$\bar{n} = \left[\frac{(n_{\parallel}^2 + 2n_{\perp}^2)}{3} \right]^{1/2}, \quad [1]$$

and the optical anisotropy is $\Delta n = (n_{\parallel} - n_{\perp})$. The correlation function $g_{vv}(\tau)$ takes a simple form in the limit where $4\Delta n^2/45$ is small compared with $(n_s - \bar{n})^2$ (1, 8, 9); here $4\Delta n^2/45 \approx 10^{-3}$, while $(n_s - \bar{n})^2 \approx 4 \times 10^{-2}$. In this limit, $g_{vv}(\tau)$ reflects mainly the translational diffusion of the particles and is given by (1, 8, 9)

$$g_{vv}(\tau) = \exp\{-D_t q^2 \tau\}. \quad [2]$$

Here, the translational diffusion coefficient is $D_t = k_B T / 6\pi\eta a$, where k_B is Boltzmann's constant, T is the temperature, and η is the viscosity of the suspending fluid. For all the experiments reported here, $T \approx 300$ K and $\eta \approx 1$ cP. By contrast, the correlation function for depolarized scattering exhibits contributions from both translational and rotational diffusion. It is given by (1, 8, 9)

$$g_{vh}(\tau) = \exp\{-(D_t q^2 + 6D_r)\tau\}, \quad [3]$$

where the rotational diffusion coefficient is given by $D_r = k_B T / 8\pi\eta a^3$. Thus, to characterize our data, we use a cumulant analysis to determine the initial rates of the exponential decays, Γ_{vv} and Γ_{vh} , and plot these as a function of q^2 ; this should yield linear behavior, with the depolarized value somewhat larger than the polarized value, reflecting the added contribution of the rotational diffusion.

As expected, the depolarized component of the light scattered from the centrosymmetric particles stabilized with SDS was found experimentally to be very weak; thus, $g_{vh}(\tau)$ could not be measured. By contrast, the depolarized scattering from the droplets stabilized with PVA was much more intense, allowing $g_{vh}(\tau)$ to be measured. Typical results for both polarized and depolarized scattering are shown in Fig. 2, where we plot Γ_{vv} and Γ_{vh} as a function of q^2 . In all cases, we find that the measured correlation functions are exponential in shape, reflecting the highly mono-

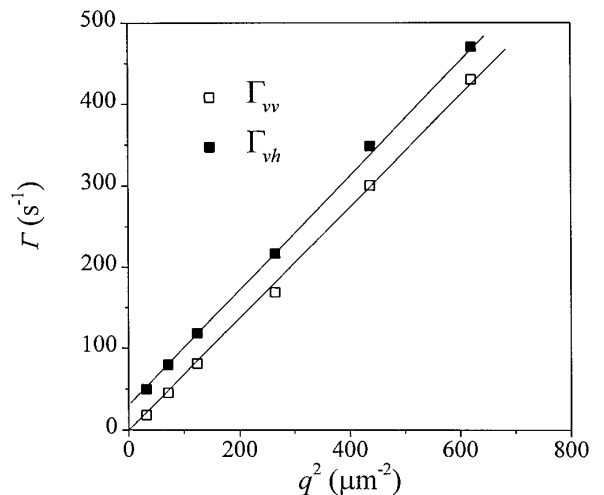


FIG. 2. Decay rates for both the polarized [Γ_{vv}] and depolarized [Γ_{vh}] scattering, determined from the autocorrelation function, plotted as a function of q^2 , for liquid crystal droplets stabilized by PVA.

disperse distribution of the droplets. The solid lines through the data in Fig. 2 are linear fits; the linearity of the data again reflects the monodisperse distribution of the particles. Moreover, the slopes of the two data sets are identical, as expected from Eqs. [2] and [3]. The slope gives the translational diffusion coefficient, $D_t \approx (7.0 \pm 0.2) \times 10^{-13} \text{ m}^2/\text{s}$. The intercept of the depolarized data provides a measure of the rotational diffusion coefficient, yielding $D_r = 4.8 \pm 0.1 \text{ s}^{-1}$. From the translational diffusion coefficient we determine the particle radius to be $a = 0.31 \text{ }\mu\text{m}$. By comparison, from the rotational diffusion coefficient we determine $a = 0.32 \text{ }\mu\text{m}$, in excellent accord with the value determined from D_t . These values also agree very well with that obtained from optical microscopy. The ratio $D_t/D_r = 4/3*a^2$ depends only on a and not on any other system parameter. This provides a direct measure of the particle size; we obtain $a = 0.33 \text{ }\mu\text{m}$ from this estimate.

To conclude, we have introduced a simple method for synthesizing highly monodisperse droplets that are spherical in shape but highly anisotropic in their optical properties. We characterize their behavior by measuring both their translational and rotational diffusion coefficients with depolarized dynamic light scattering. Because the liquid crystal is in a single domain within the droplets, their optical anisotropy is quite large. These particles are potentially useful as local probes of fluid rotation or vorticity, and will also be of use in the study of rotational effects in concentrated suspensions of particles. In addition, it may be possible to align these droplets using external electric or magnetic fields, providing additional control over their properties and increasing their potential utility. Finally, we also expect such monodisperse droplets to have important uses in electrooptical devices, providing an increased degree of control over the light because of their monodisperse distribution. The preparation of the liquid crystal emulsions is independent of the nature of the liquid crystal; thus, many systems with different optical properties can be synthesized.

ACKNOWLEDGMENTS

We gratefully acknowledge Paul Drzaic for very helpful discussions and for providing the liquid crystal used in these experiments. This work was

supported by the Materials Research Science and Engineering Center Program of NSF under Award DMR96-32539.

REFERENCES

1. Piazza, R., *et al.*, *Prog. Colloid Polym. Sci.* **81**, 89 (1990).
2. Degiorgio, V., Piazza, R., and Jones, R. B., *Phys. Rev. E* **52**, 2707 (1995).
3. Tong, P., Xia, K. Q., and Ackerson, B. J., *J. Chem. Phys.* **98**, 9256 (1993).
4. Lissant, K. J. (Ed.), “*Emulsions and Emulsion Technology*,” Marcel Dekker, New York, 1974–1984.
5. Bibette, J., *J. Colloid Interface Sci.* **147**, 477 (1991).
6. Drzaic, P. S., “*Liquid Crystal Dispersions*,” Series on Liquid Crystals 1. W. S. Publishing, 1995.
7. Collings, P. J., “*Liquid Crystals*,” Hilger, Bristol, 1990.
8. Berne, B., and Pecora, R., “*Dynamic Light Scattering*,” Wiley, New York, 1975.
9. Piazza, R., Degiorgio, V., Corti, M., and Stavans, J., *Phys. Rev. B* **R42**, 4885 (1990).

Paul Hsu
Philippe Poulin¹
D. A. Weitz

Department of Physics and Astronomy
University of Pennsylvania
209 South 33rd Street
Philadelphia, Pennsylvania 19104

Received June 23, 1997; accepted October 9, 1997

¹ Present address: CRPP/CNRS, Avenue du Dr. Schweitzer, 33600 Pessac, France. To whom correspondence should be addressed.