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Direct Observation of Rigid-Body Rotation of Cholesteric Droplets Subjected to a Temperature Gradient

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Droplets of cholesteric liquid crystals rotate their helical structure when subjected to a thermal gradient perpendicular to their helical axes. Concerning the interpretation of their dynamics, there has been an argument whether the textural rotation indicates rigid-body rotation of the droplets or pure director rotation. To clarify this, we dispersed micron-size particles in a cholesteric-isotropic coexisting sample and traced their motion, and found that the particles adhering onto a cholesteric droplet rotated together with the helix in phase. This observation provided clear evidence of the rigid-body rotation of the droplet, and we also revealed an unusual hydrodynamic flow in the coexisting phase.

Liquid crystals (LCs) possess various phases classified on the basis of symmetry, among which the second-most well-known phase is the cholesteric (Ch) phase.[1] The Ch phase is generally obtained by dissolving a small amount of chiral molecules in a nematic compound so that the nematic and Ch phases have similar contents and both behave as a uniaxially anisotropic fluid. However, their macroscopic structures in thermal equilibrium are clearly distinguished; the nematic phase favors a uniform molecular orientation whereas the Ch phase favors a helical distortion owing to the broken mirror symmetry. The chirality plays a distinctive role not only in the static structure but also in the dynamics of the Ch phase, one of which is known as the "Lehmann effect". In 1900, Lehmann found that when a Ch droplet was subjected to a thermal gradient, the constituent molecules rotated their long axes (called director) continuously and unidirectionally.[2] The Lehmann effect was understood as a typical thermo-mechanical coupling in chiral LCs and was described by a phenomenological equation by Leslie.[3] After a long interval, Oswald et al. reproduced the Lehmann's experiment about a decade ago, observing the director rotation in Ch droplets coexisting with an isotropic (Iso) phase under a temperature gradient.[4,5] Since then, the Lehmann effect has been refocused on and additional details have been investigated.[6–8] Recent studies not only promoted a deeper understanding of the phenomenon but also gave rise to a new argument. In the original work by Lehman, a Ch droplet subjected to a heat flux in the direction parallel to its helical axis exhibited director rotation unaccompanied by translational molecular motion. In contrast, Yoshioka et al. applied a thermal gradient to a Ch droplet coexisting with an Iso phase in the direction perpendicular to its helical axis, and detected a vortexlike flow in the droplet by fluorescence recovery after photobleaching (FRAP).[6] The flow indicates that the Ch droplet should rotate as a rigid body in this geometry. Soon after that, Poy and Oswald carried out the same FRAP experiment and obtained a different result from that described in Ref. 6; they confirmed that there was no hydrodynamic flow in the coexisting Iso phase near the Ch droplets in the same geometry and concluded that the droplets exhibited pure director rotation.[9] Theoretically, the molecular motion in Ch droplets should be determined to minimize dissipation. However, it is difficult to predict the dissipation when the molecules rotate while maintaining the helical structure under nonuniform torque perpendicular to the helical axis. So far, no convincing reason for the disagreement has been proposed.

In this report, we show direct evidence of the rigid-body rotation of Ch droplets under a thermal gradient perpendicular to their helical axes. To visualize a hydrodynamic flow field, we dispersed micron-size particles in a Ch-Iso coexisting sample and traced the motion of the particles. The direct observation gave an explanation for the disagreement between the previous two reports and also revealed the flow field in the Iso phase.

To fabricate a Ch sample, we mixed 4-cyano-4′-pentylbiphenyl and No. 270032 (LCC) at a weight ratio of 2 : 3, and added the chiral dopant of (*S*)-4-{[1-(methylheptyl)oxy]carbonyl}-phenyl-4-(hexyloxy)benzoate (DIC Inc.) to the host nematic with a concentration of 1.0 wt%. The phase sequences of the mixture are Ch–69.8 °C–Ch + Iso–72.2 °C–Iso. To visualize the hydrodynamic flow, we dispersed tracer particles (a gift from DIC Inc.) with an average diameter of ~1 μm in the LC compound. The mixture was then sandwiched by a cover glass and a slide glass, the distance between which was adjusted using 10-μm-diameter beads. Both substrates were treated by UV-ozone cleaning and then spin-coated with poly(methyl methacrylate) (Sigma-Aldrich) to make the surfaces slippery. To the laboratory-made LC cell, a thermal gradient was applied as shown in Fig. 1. The temperature of the bottom substrate was adjusted using a Linkam hot stage and the upper substrate was in contact with air at room temperature, so that the thermal flow was transported in the cell from the bottom to the top. The temperatures of the surfaces of the substrates were precisely measured with Pt thermocouples (Shimaden, JIS Class2), from which we calculated the temperature gradient exerted on the LC cell as $4.2 \pm 0.2\,\mathrm{mK\,\mu m^{-1}}$. For observation, an optical microscope (BX51, Olympus) equipped with white light was used.

In the Ch-Iso coexisting phase, most tracer particles formed aggregates with various sizes and adhered onto the interface between the two phases as schematically shown in Fig. 1. We found that when too many tracers adhered onto the Ch droplets, they accumulated between the droplets and the substrates, and stopped the rotation of the helix of the droplets. To avoid this side effect, we searched for the droplets having only a small number of tracers. Figure 2(a)

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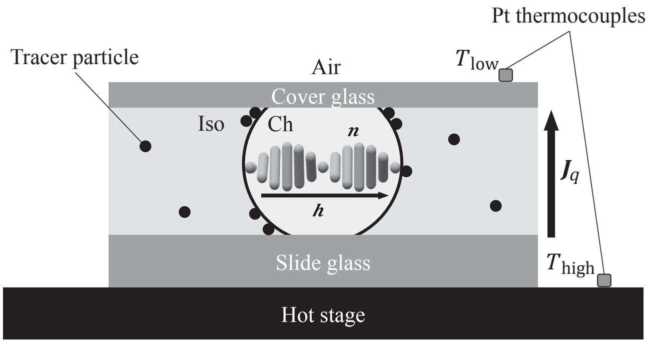

Fig. 1. Schematic figure of the LC cell (side view). $\boldsymbol{n}$, $\boldsymbol{h}$, and $\boldsymbol{J}_q$ denote the director, helical axis, and heat flux, respectively. The temperatures of the hot stage and upper substrate were $T_{high} = 70.8\,°C$ and $T_{low} = 65.9\,°C$, respectively.

shows an image sequence of one such Ch droplet. The droplet has a uniform stripe texture with a period of 6.2 μm, corresponding to half-pitch of the Ch helix, which indicates that the helical axis should be perpendicular to the stripe. The white solid arrow in Fig. 2(a) denotes the helical axis, which lies in the substrate plane and is perpendicular to the thermal gradient direction. When a heat current was transported from the back to the front of the page in Fig. 2(a), the stripe texture rotated continuously in the clockwise direction,[10] which is consistent with a previous report.[4] Since the 2π rotation took ~600 s, the rotational velocity of the helical axis was obtained as $1.0 \times 10^{-2}\,\mathrm{rad\,s^{-1}}$. In the same figure, one can notice that two aggregates of the tracer particles adhere onto the droplet and rotate about the center of the droplet together with the texture in phase. The rotation of the particles visualizes the vortexlike flow in the droplet, suggesting the rigid-body rotation of the droplet.

To quantitatively analyze the motion, let us denote the rotational angles of the helical axis and of the large aggregate measured from their initial positions by θ and θ', respectively. Figure 2(b) shows the temporal changes in θ and θ', which well overlap with each other. Tracing their motion further, we obtained a clear relationship between the angular velocities of the helical axis ($\omega_{droplet}$) and of the particles about the droplet center ($\omega_{particle}$), which is given by the open squares in Fig. 3. Clearly, $\omega_{droplet}$ and $\omega_{particle}$ are linear to each other with slope 1. The result proves that the droplet rotates as a rigid body, i.e., the LC molecules in the Ch droplet should exhibit barycentric rotation about the droplet center while maintaining the same relative orientation to each other.

Next, we focused on particles in the coexisting Iso phase. A typical observation is shown in Fig. 4(a). In the upper left of the Ch droplet in each snapshot, there is an aggregate of tracer particles, whose distance from the droplet center r is about 1.2–1.3 times the droplet radius R, i.e., $r/R = 1.2$–1.3. As shown in the sequence, the droplet rotated in the clockwise direction at an angular velocity of 3.0×10^{-2} $\mathrm{rad\,s^{-1}}$,[11] which is three times the velocity of the droplet in Fig. 2(a). The larger velocity is ascribed to the low density of the tracer particles adhering onto the droplet. In Fig. 4(a), while the droplet rotated continuously, the aggregate of the

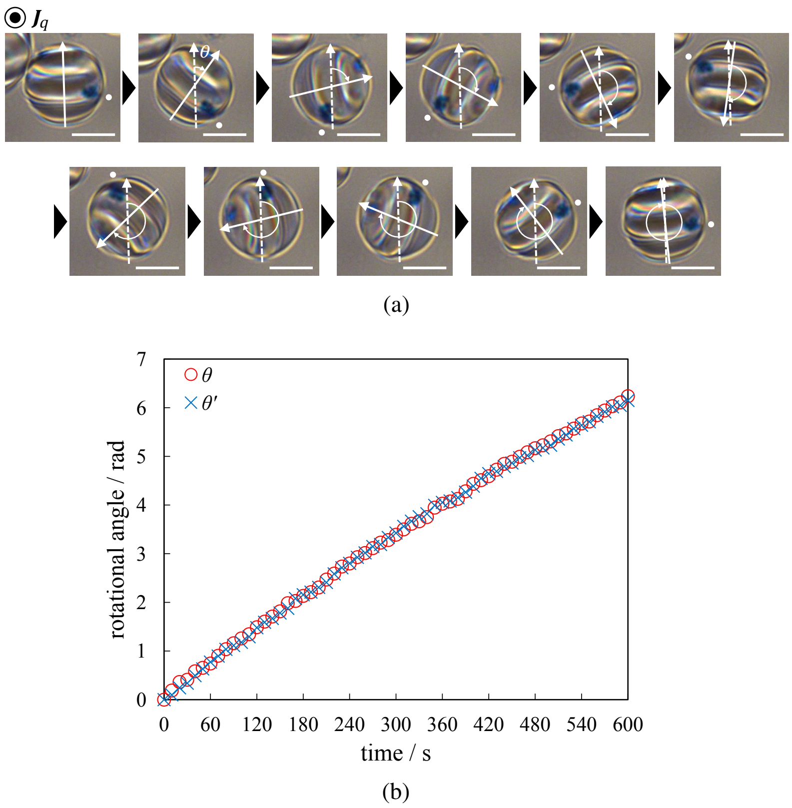

Fig. 2. (Color online) (a) Image sequence of the Ch droplet and tracer particles adhering onto the droplet in a Ch-Iso coexisting phase observed under an optical microscope. In the microscopy, the linearly polarized light was normally incident onto the sample and the transmitted light was detected without polarizers. The sample was subjected to a thermal gradient of $4.2 \pm 0.2\,\mathrm{mK\,\mu m^{-1}}$. The white solid arrow denotes the helical axis and the white dot near the large aggregate of the particles is drawn as a guide to the eye to follow the particle position. The dashed arrow gives the helical axis at $t = 0$. Images were taken every 60 s and the scale bar indicates 10 μm. (b) Temporal changes in θ and θ'.

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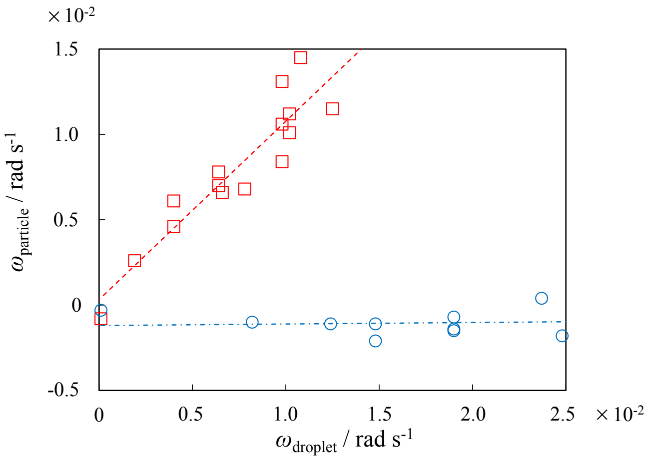

Fig. 3. (Color online) Relationship between the rotations of the Ch droplets and those of the tracer particles. The open squares give the angular velocities of the helical axes and of the particles when they adhered onto the surfaces of Ch droplets, such as the droplet shown in Fig. 2(a). The dashed line denotes the best-fitting line to the open squares, the slope of which is 1. The open circles show the angular velocities of the helical axes of Ch droplets and of the particles when they existed in the Iso phase just outside the droplets [see Fig. 4(a)]. The dashed-dotted line is the best-fitting line to the data given by the open circles.

particles near the droplet remained around the initial position with vigorous fluctuation owing to Brownian motion. Figure 4(b) quantitatively shows the motion of the aggregate, in which one can notice both a constant temporal change in θ and no change in θ' with time. Their unrelated angular velocities are also shown in Fig. 3. Since the aggregate is nearly halfway between the two substrates and vigorously fluctuating, if there is a hydrodynamic flow in the Iso phase, it can move with the flow. The results show that the rotation of the Ch droplet is not accompanied by any detectable hydrodynamic flow in the Iso phase even just outside the droplet.

The above observation gives a good reason for the disagreement between the previous two experiments.[6,9] Yoshioka et al. detected the vortexlike flow inside rotating Ch droplets by FRAP. On the other hand, Poy and Oswald measured the diffusion of bleached dyes just outside Ch droplets in the Iso phase and confirmed the absence of a hydrodynamic flow. We found that their results are not inconsistent with each other but both agree with our observation. Taking all these experimental results into account, we can conclude that Ch droplets, whose helical axes are perpendicular to the heat flux, should exhibit rigid-body rotation and that there is no detectable hydrodynamic flow in the coexisting Iso phase even near the rotating Ch droplets.

Although our observation is consistent with the previous reports, it may sound unnatural from a hydrodynamic viewpoint. If the boundary condition at the interface between the Ch and Iso phases is nonslip, the rotating droplet must induce a hydrodynamic flow in the surrounding fluid. To quantitatively estimate the flow field in the Iso phase, we carried out numerical calculations. The model system used for the calculations is shown in Fig. 5(a); a hard sphere with radius R, corresponding to a Ch droplet, is set in an isotropic fluid, and the sphere and the fluid are sandwiched by two parallel plates. Rotating the sphere at a constant angular velocity Ω, we calculated the flow field generated in the fluid. In a steady state, the incompressible Navier–Stokes equation is

$$(\boldsymbol{v} \cdot \nabla)\boldsymbol{v} = -\frac{\nabla p}{\rho} + \nu \nabla^2 \boldsymbol{v}, \qquad (1)$$

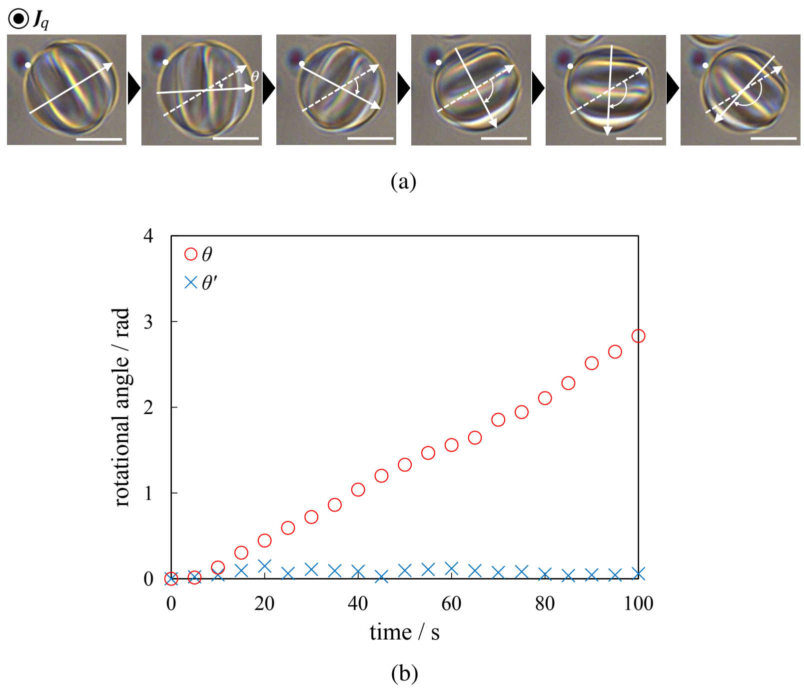

Fig. 4. (Color online) (a) Image sequence of a Ch droplet and the aggregate of the tracer particles observed under an optical microscope with linearly polarized incident light. The sample is subjected to a thermal gradient of 4.2 ± 0.2 mK μm^{-1}. In each snapshot, the white solid arrow denotes the helical axis and the white dot near the large aggregate highlights its position. The dashed arrow gives the helical axis at $t = 0$. Each image was taken every 20 s and the scale bar indicates 10 μm. (b) Temporal changes in θ and θ'.

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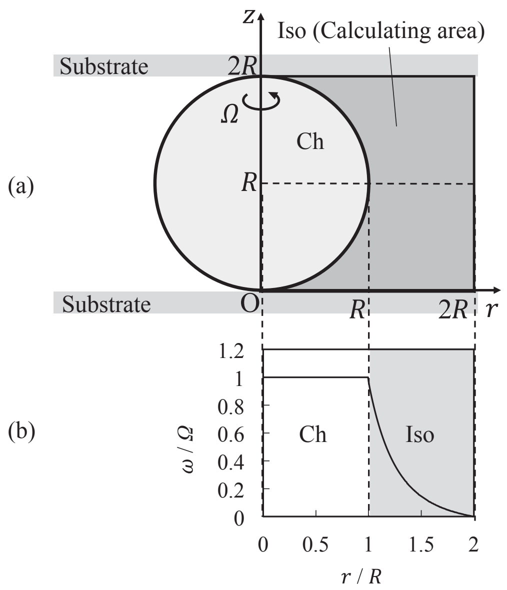

Fig. 5. (a) Side view of the geometry used for the calculation. The hard sphere with radius R rotates at an angular velocity of Ω around the z-axis in the fluid. (b) Normalized angular velocity ω/Ω [$= v_\varphi/(r\,\Omega)$] of the fluid in the $z = R$ plane, obtained by the numerical calculations described in the text.

where $\boldsymbol{v}$, p, ρ, and ν are the velocity, hydrostatic pressure, density, and viscosity of the fluid, respectively. It is convenient to use the cylindrical coordinate system (r, φ, z) as shown in Fig. 5(a) with the z-axis taken to be perpendicular to the substrates and through the center of the sphere. From the symmetry, $\boldsymbol{v}$ and p are independent of φ, and the assumption of $\nabla \cdot \boldsymbol{v} = 0$ requires that the components of $\boldsymbol{v}$ in the r- and z-directions should be zero. Then, the Navier–Stokes equation results in the simple differential equation of v_φ given as

$$\frac{\partial^2 v_\varphi}{\partial r^2} + \frac{1}{r}\frac{\partial v_\varphi}{\partial r} + \frac{\partial^2 v_\varphi}{\partial z^2} - \frac{v_\varphi}{r^2} = 0. \qquad (2)$$

We assumed the following boundary conditions: (1) At the surfaces of the sphere and the substrates, the nonslip boundary condition is satisfied; (2) v_φ is zero at $(2R, \forall\varphi, \forall z)$, which corresponds to the experimental condition that the shortest distance between the nearest Ch droplets is about $2R$ on average and the velocity should be zero at the middle of the two rotating droplets. The result of the calculations is shown in Fig. 5(b), in which the angular velocity of the fluid, $\omega = v_\varphi/r$, in the plane of $z = R$ is plotted against the normalized distance r. The calculation indicates that the vortexlike flow in the isotropic fluid slowly decreases with increasing r/R in the region of $r/R > 1$, which disagrees with the experimental result that the particles at $r/R = 1.2$–1.3 did not show any directional motion. The disagreement between the calculation and the experiment could be ascribed to our assumptions; the nonslip boundary condition may not be satisfied at the Ch-Iso interface, and/or the viscosity in the Iso phase is not uniform but may take a lower value in the vicinity of the droplet than that in the bulk. The particularity of the Ch-Iso interface may play a role in the unusual flow field, but it is beyond the scope of this study and further investigation will be necessary.

In summary, we investigated the Lehmann effect, focusing on the rotation of Ch droplets subjected to a thermal gradient perpendicular to their helical axes. By dispersing micron-size tracer particles in a Ch-Iso coexisting sample, we observed the motion of the particles. Aggregates of the particles adhering onto a Ch droplet surface rotated about the droplet center at the same angular velocity as that of the helical texture, which proves that the Ch droplet exhibited rigid-body rotation under the heat flux. On the other hand, particles dispersed in the coexisting Iso phase did not show any directional motion but only fluctuated, suggesting that the hydrodynamic flow in the Iso phase was undetectably weak even in the vicinity of the rotating Ch droplets. Our result is consistent with two previous reports that appeared to produce contradictory results, and helps to settle the argument about the interpretation of the rotating helix. The unusual flow field near the Ch-Iso boundary will be investigated in the near future.

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10) (Supplemental Material) Movie (movie1.avi), showing the Ch droplet and tracer particles adhering onto the droplet subjected to a temperature gradient of $4.2 \pm 0.2\,\mathrm{mK\,\mu m^{-1}}$ [corresponding to Fig. 2(a)], is provided online played at 50 times speed.
11) (Supplemental Material) Movie (movie2.avi), showing the Ch droplet and tracer particles in the Iso phase subjected to a temperature gradient of $4.2 \pm 0.2\,\mathrm{mK\,\mu m^{-1}}$ [corresponding to Fig. 4(a)], is provided online played at 40 times speed.

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