

Lehmann rotation of cholesteric droplets: Role of the sample thickness and of the concentration of chiral molecules

Patrick Oswald* and Guilhem Poy

Université de Lyon, Ecole Normale Supérieure de Lyon, Laboratoire de physique, 46 Allé d'Italie, 69364 Lyon, Cedex 07, France

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We study the role of the sample thickness d and of the concentration C of chiral molecules during the Lehmann rotation of cholesteric droplets of radius R subjected to a temperature gradient \vec{G} . Two configurations are studied depending on how the helix is oriented with respect to \vec{G} . The first result is that, at fixed C and R , the rotation velocity ω increases with d when the helix is parallel to \vec{G} , whereas it is independent of d when the helix is perpendicular to \vec{G} . The second result is that, for a given C , $\omega_0 = \lim_{R \rightarrow 0} \omega(R)$ is the same for the two types of droplets independently of d . This suggests that the, as yet unknown, physical mechanism responsible for the droplet rotation is the same in the two types of droplets. The third result is that the Lehmann coefficient $\bar{\nu}$ defined from the Leslie-like relation $\omega_0 = -\bar{\nu}G/\gamma_1$ (with γ_1 the rotational viscosity) is proportional to the equilibrium twist q . Last, but not least, the ratio $\bar{R} = \bar{\nu}/q$ depends on the liquid crystal chosen but is independent of the chiral molecule used to dope the liquid crystal.

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I. INTRODUCTION

In 1900 Lehmann [1] observed the continuous rotation of the internal texture of cholesteric droplets when subjected to a temperature gradient. The experiment was first reproduced in 2008 by using a compensated cholesteric (mixture of octyloxycyanobiphenyl and cholesteryl chloride in equal proportions) [2,3] and one year later by using diluted cholesteric mixtures (i.e., a nematic phase doped with a small amount of chiral molecules) [4]. In these experiments, the droplets coexist with their isotropic liquid and have a banded texture in natural light, indicating that the helical axis is perpendicular to the temperature gradient. Previous systematic measurements [2–5] showed that their rotation velocity ω_{\perp} could reasonably be described by a relation of the type

$$\omega_{\perp} = -\frac{\bar{\nu}G}{\gamma_1}[1 + f(qR)]^{-1}, \quad (1)$$

where γ_1 is the bulk rotational viscosity, q is the equilibrium twist, and $f(qR)$ is a strictly increasing even function of the dimensionless radius qR :

$$f(qR) = \frac{\iint_{\text{drop}} [\vec{e}_z \cdot \frac{\partial \vec{n}}{\partial \theta} \times \vec{n} + (\frac{\partial \vec{n}}{\partial \theta})^2] dV}{\iint_{\text{drop}} [\vec{e}_z \cdot \frac{\partial \vec{n}}{\partial \theta} \times \vec{n} + 1 - (\vec{e}_z \cdot \vec{n})^2] dV}. \quad (2)$$

In this expression, \vec{e}_z is the unit vector parallel to the temperature gradient and θ is the polar angle. This function depends on the texture inside the droplet and on the shape of the droplet [5] and so should *a priori* depend on the sample thickness d , but it always tends to 0 when $R \rightarrow 0$. This relation was used to define the Lehmann coefficient $\bar{\nu}$. In the model used in Ref. [2] based on the Leslie explanation of the Lehmann effect, $\bar{\nu}$ identifies with the Leslie thermomechanical coefficient ν . This equality was obtained by equilibrating the viscous torque (proportional to γ_1) with the Leslie thermomechanical torque,

of expression [6]

$$\vec{\Gamma}_{\text{Leslie}} = \nu \vec{n} \times (\vec{n} \times \vec{G}), \quad (3)$$

while neglecting the backflow effects. Although this calculation seemed correct at first sight, precise measurements, in both compensated and diluted mixtures [5], have shown that $\bar{\nu}$ was much larger than ν and had even sometimes an opposite sign [7]. In addition, $\bar{\nu}$ was found to be proportional to q in diluted and compensated cholesteric mixtures [4,5,8] contrary to ν found independent of q [7] (in particular, ν does not vanish at the compensation point of the cholesteric phase [9,10], contrary to $\bar{\nu}$ that vanishes to within the experimental errors at this point [5]). These results show that the Lehmann rotation is of structural origin and is not due (except, perhaps, for a very slow residual rotation; see Ref. [8]) to the Leslie thermomechanical coupling of microscopic origin. These conclusions were recently confirmed by the crucial observation that each droplet with a banded texture seems to rotate as a rigid body in contradiction with the Leslie explanation [11].

Other types of droplet exist. In some of them the helix orients parallel to the temperature gradient. In this case, the bands disappear and the droplet presents a texture made of concentric circles between crossed polarizers (CC droplets in the following). Droplets of this type spontaneously form in the mixtures studied by Yoshioka *et al.* [11]. Nonetheless, we noted that they easily transform in our samples into banded droplets when their size decreases, which indicates that the helical axis easily tilts from vertical to horizontal position. One way to avoid this transformation is to force the helix to orient along the vertical direction by submitting the sample to a large vertical AC electric field. This technique works on the condition to use a liquid crystal of negative dielectric anisotropy [12]. In that case, the droplet seems to no longer rotate when illuminated in natural light. Nevertheless, an observation between crossed polarizers shows that the helix rotates with an angular velocity ω_{\parallel} proportional to qG and inversely proportional to R . This dependence is quite different from that described by Eq. (1) suggesting that another

*patrick.oswald@ens-lyon.fr

mechanism is perhaps responsible for the helix rotation in this geometry. This conclusion is reinforced by the fact that no flow was observed in these droplets [11]. For this reason, the authors of Ref. [11] proposed that the Leslie mechanism might be responsible for the rotation of the helix. But this explanation is disturbing because it predicts a far too small value of ω_{\parallel} . In addition, it fails to explain why ω_{\parallel} decreases when R increases because $f(qR) = 0$ in Eq. (1). This comes from the fact $\frac{\partial \bar{n}}{\partial \theta} = 0$ since the contrast of the CC droplets is axisymmetric around the z axis (see Fig. 4 below).

This short outline shows that the Lehmann effect is still unexplained and that additional experiments are necessary. So far a number of parameters have been varied to try to understand this effect. Among them are the droplet radius and the concentration of chiral molecules. On the other hand, the sample thickness d has never been systematically changed. The aim of this paper is to show that this parameter is important, in particular in the case of the CC droplets. For the sake of completeness, we will reanalyze the role of the concentration of chiral molecules, in particular in the limit $R \rightarrow 0$. This study will prove useful to better characterize what we called before the Lehmann coefficient $\bar{\nu}$ (not to be confused with the Leslie thermomechanical coefficient ν).

II. EXPERIMENTAL PROCEDURE

We refer to Ref. [2] for a full description of the experimental setup. In brief, the sample is sandwiched between two ovens regulated to within $\pm 1/100^{\circ}\text{C}$ which impose a temperature gradient G given by $G = \frac{\Delta T}{4e} \frac{\kappa_g}{\kappa_{LC}}$, where ΔT is the temperature difference between the top and bottom ovens, e is the thickness of the glass plates (1 mm), and κ_g (respectively, κ_{LC}) is the thermal conductivity of the glass (respectively, of the liquid crystal). Because the measurements are performed in the coexistence region, we shall use for κ_{LC} the thermal conductivity of the isotropic liquid at the transition temperature. In practice, the thermal conductivities of the two liquid crystals studied (MBBA or *p*-methoxybenzilidene-*p*-*n*-butylaniline and 7CB or 4,4'-*n*-heptyl-cyanobiphenyl, both purchased at Frinton Laboratories, USA) are very similar, of the order of 0.14 W/m/K (for MBBA, see Refs. [13,14] and for 7CB, see Ref. [15]) while the glass conductivity is close to 1 W/m/K [16]. This gives $G = a\Delta T$ with $a \approx 1800 \text{ m}^{-1}$. Note that, in this formula, we neglected the thickness d of the liquid crystal layer ($< 70 \mu\text{m}$) with respect to the thickness of the glass plates (4 mm).

The sample are prepared between two parallel glass plates covered with an ITO layer (when necessary) and a ~ 20 nm-thick polymercaptan layer. This surface treatment insures a sliding anchoring and a much better reproducibility of the results concerning the rotation velocity of the droplets. Nickel wires of calibrated diameter are used as a spacer. The sample thickness d is measured with a spectrometer to within $\pm 0.1 \mu\text{m}$ before each experiment. The chiral molecules used to prepare the cholesteric sample are R811 (from Merck, Germany) and the cholesteryl chloride (CC from Sigma-Aldrich, Germany). The concentration (or weight fraction) C of chiral molecules is measured with an accuracy of $\pm 1\%$.

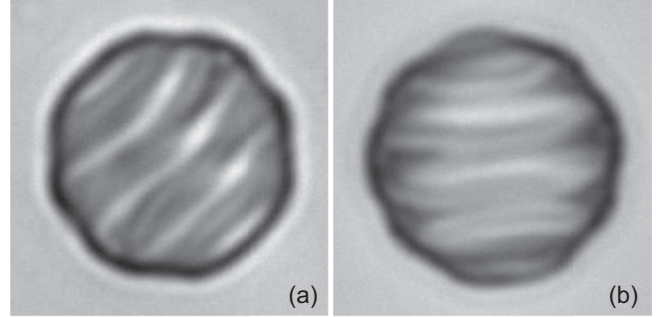


FIG. 1. Two striped droplets of similar radii ($\approx 15 \mu\text{m}$) observed under natural light in two samples of different thicknesses. In (a), $d = 20.1 \mu\text{m}$ and in (b) $d = 68.8 \mu\text{m}$ (MBBA + 1% R811, $\Delta T = 5^{\circ}\text{C}$).

III. ROLE OF THE SAMPLE THICKNESS

This study was performed with MBBA doped with 1% of R811. In this mixture, the rotation vector of the droplets and the temperature gradient are oriented in opposite directions, which means that the Lehmann coefficient is positive.

We first systematically measured the rotation period $\Theta_{\perp} = 2\pi/|\omega_{\perp}|$ of the striped droplets (Fig. 1) as a function of their radius R . Measurements were performed at different temperature gradients (for $\Delta T = 5, 10$, and 15°C) and thicknesses ranging between 6.8 and $70 \mu\text{m}$). Our data are shown in Fig. 2. This figure shows that all the measurements reasonably collapse on the same master curve when the product $\Theta_{\perp}\Delta T$ is plotted as a function of the radius R . As a consequence, the rotation velocity of the droplets is independent of the sample thickness within the experimental dispersion. The latter is mainly due to a pollution of MBBA with the polymercaptan. Indeed, we observed that the rotation velocity can decrease by a factor of 2 during the day. This variation could come from a viscosity increase due to the dissolution of the polymercaptan in MBBA. But earlier measurements of the rotational viscosity of MBBA in similar conditions have shown that it does not increase by more than 20% during the day. This suggests that the viscosity

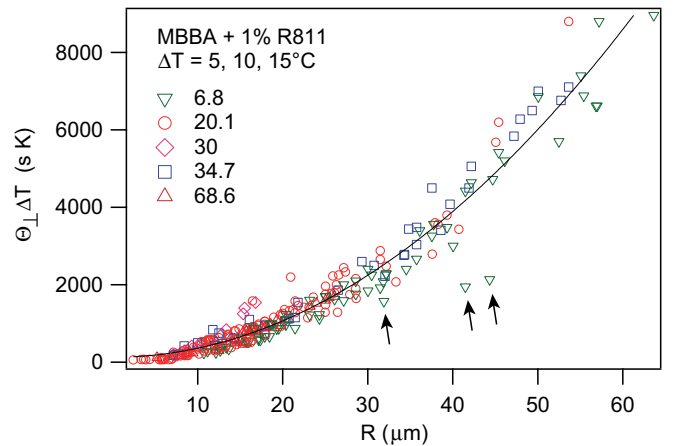


FIG. 2. (Color online) Product $\Theta_{\perp}\Delta T$ of the period of rotation times the temperature difference as a function of the droplet radius R . Each symbol corresponds to a different thickness given in μm on the graph. All the points correspond to banded droplets, except the three points marked by an arrow referring to droplets with a different texture (see the main text).

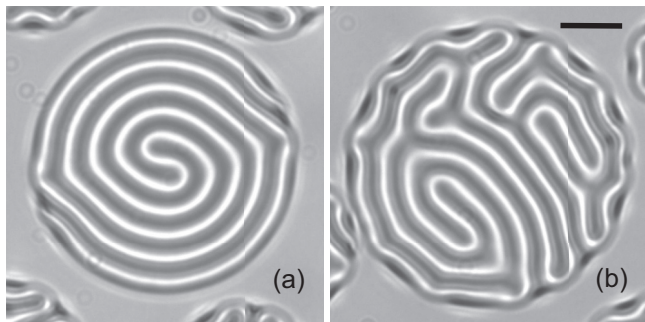


FIG. 3. Two types of droplet observed under natural light in the $6.8 \mu\text{m}$ -thick sample. In (a) the bands form a double spiral, and in (b) they form a labyrinth. The bar is $20 \mu\text{m}$ long (MBBA+1% R811).

increase is not alone responsible for the slowing down of the droplets. The reader will further note that three points marked with an arrow in Fig. 2 shifts significantly from the master curve. These three points correspond to droplets observed in a very thin sample ($d = 6.8 \mu\text{m}$) in which the texture is different from the usual one. This time the bands are no longer rectilinear but form a double spiral as can be seen in Fig. 3(a). This is a new confirmation that the rotation velocity strongly depends on the internal texture of the droplet (another example is given in Ref. [4]). Note that in this very thin sample, the bands are rarely parallel to each other, in particular in big droplets in which they rather form a labyrinth as shown in Fig. 3(b). Despite this, the rotation velocities of the labyrinthine droplets fall on the master curve. On the other hand, we did not observe similar droplets in the thicker samples.

Second, we systematically measured the rotation period $\Theta_{\parallel} = 2\pi/|\omega_{\parallel}|$ of the helix inside droplets oriented with a large 10 kHz electric field (typically $1 \text{ V}/\mu\text{m}$). Because MBBA is of negative dielectric anisotropy, the molecules orient perpendicular to the electric field so that the helix is parallel to the temperature gradient. At this frequency there is no convective instabilities, and the heating of the sample by the ITO layers is negligible. It is important to emphasize that Θ_{\parallel} is independent of the amplitude and the frequency of the electric field once the droplets are well oriented [12]. Two droplets of similar radii observed between crossed polarizers in two samples of different thicknesses (21.6 and $70 \mu\text{m}$) are shown in Fig. 4. In the two cases, the bands disappear and the droplets display a typical concentric circles texture, indicating that the director field has now the symmetry of revolution around the temperature gradient. The measurement was performed by recording the transmitted intensity between crossed polarizers in the middle of the droplets. In these conditions, the intensity oscillates with the period $\Theta_{\parallel}/4$. An important point is to note that, here again, the rotation vector of the helix and the temperature gradient point in opposite directions. Our results are shown in Fig. 5, where the product $\Theta_{\parallel}\Delta T$ is plotted as a function of the radius R for different values of the sample thickness d . In agreement with our previous measurements published in Ref. [12], we find that in each sample:

(1) The points obtained at $\Delta T = 5, 10,$ and $15 \text{ }^{\circ}\text{C}$ fall on the same curve, indicating that the rotation velocity ω_{\parallel} is proportional to the temperature gradient.

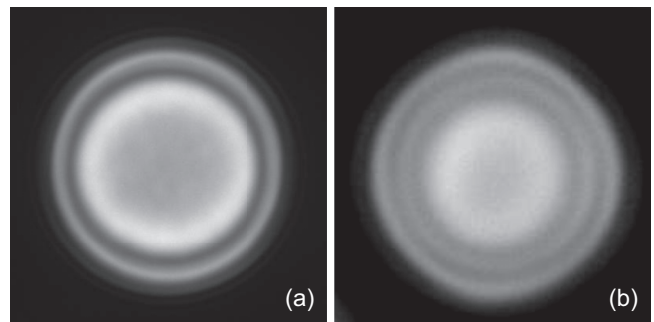


FIG. 4. Two droplets of similar radii ($\sim 11.5 \mu\text{m}$) observed between crossed polarizers in two samples of different thicknesses. The helix is oriented parallel to the temperature gradient by applying a 10 kHz electric field. In (a), $d = 21.6 \mu\text{m}$, $V = 25 \text{ Vrms}$ and in (b) $d = 70 \mu\text{m}$, $V = 80 \text{ Vrms}$. (MBBA+1% R811, $\Delta T = 10 \text{ }^{\circ}\text{C}$).

(2) The product $\Theta_{\parallel}\Delta T$ linearly increases with the radius of the droplets.

This dependence is different from that recently reported by Yoshioka *et al.* [11], who find rather a constant rotation

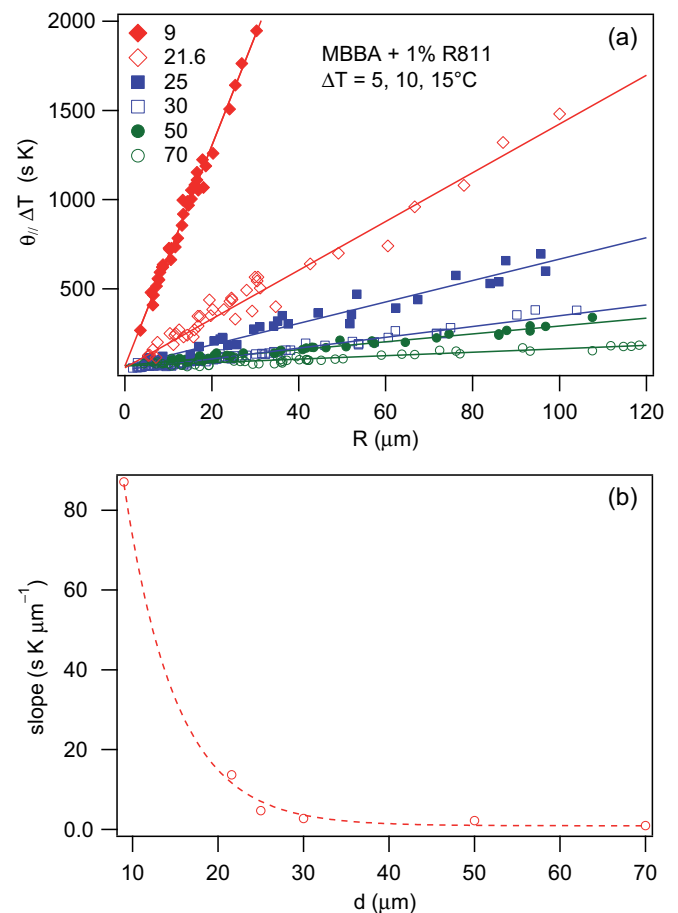


FIG. 5. (Color online) (a) Product $\Theta_{\parallel}\Delta T$ of the period of rotation times the temperature difference as a function of the droplet radius R and their best linear fits. Each symbol corresponds to a different thickness given in μm on the graph. (b) Slope of the straight lines as a function of the sample thickness d . The dashed line is only a guide for the eye.

velocity. But this is perhaps due to the relatively small range of radii studied by these authors or to a texture effect. Indeed, the symmetry of revolution is slightly broken in their droplets, as can be seen in the video shown in the supplementary material of Ref. [11].

On the other hand, the slope of each of these straight lines increases when the thickness decreases as shown in Fig. 5(b). That means that, at fixed radius, the helix rotates faster in thick samples than in thin samples. This result strongly contrasts with the behavior of the striped droplets for which the rotation velocity is independent of the sample thickness.

IV. ROLE OF THE CONCENTRATION OF CHIRAL MOLECULES

For completeness, we studied the role of the concentration of the chiral molecules on the rotation velocity of the striped droplets in the diluted cholesteric liquid crystals. Our goal is to determine whether the Lehmann coefficient $\bar{\nu}$ defined from Eq. (1) depends on the liquid crystal. Indeed, we already know that, for a given liquid crystal, $\bar{\nu}$, like the equilibrium twist q , is proportional to C [4]. This led us to define the Lehmann rotatory power $LRP = \bar{\nu}/(2\pi C)$ by analogy with the helical twisting power $HTP = q/(2\pi C)$ [8]. In addition, it was shown that the ratio $\bar{R} = \bar{\nu}/q = LRP/HTP$ was independent of the chiral molecule chosen. On the other hand, we do not know yet whether this ratio depends on the liquid crystal itself.

To test this point, we systematically measured the product $\Theta_{\perp} \Delta T C$ as a function of the dimensionless radius qR for different concentrations of R811 in two different liquid crystals: MBBA and 7CB. According to Eq. (1) the extrapolation to $qR = 0$ of these curves gives the reciprocal of the LRP to within the multiplicative factor γ_1/a (where a is defined from the relation $G = a\Delta T$). Our experimental results are shown in Fig. 6. As expected all the curves obtained at the different concentrations extrapolate to a constant value of the order of 0.2 s K in 7CB and of the order of 0.6 s K in MBBA. This allows us to estimate the LRP of the two liquid crystals by taking $a = 1800 \text{ m}^{-1}$ (see Sec. II) and for γ_1 the value measured at the transition temperature under rotating magnetic field [17]: $\gamma_1(7CB) = 0.02 \text{ Pa s}$ and $\gamma_1(\text{MBBA}) = 0.023 \text{ Pa s}$. Note that our value of γ_1 in MBBA is 25% larger than the value given in Ref. [17]. We applied this correction to take into account the fact that during the measurements the polymercaptan dissolves in MBBA, resulting in a systematic decrease of 3 to 4 °C of its transition temperature. This correction was determined by noticing that γ_1 typically increased of 50% when the MBBA is saturated in polymercaptan. In that case, its transition temperature decreases of about 7 °C, which is about twice larger than in the present experiment. With these values of γ_1 , we calculate

$$\begin{aligned} LRP(\text{MBBA}) &\approx 2.1 \cdot 10^{-5} \text{ N m}^{-1} \text{ K}^{-1}, \\ LRP(7CB) &\approx 5.6 \cdot 10^{-5} \text{ N m}^{-1} \text{ K}^{-1}. \end{aligned}$$

In a previous work [7], we measured the HTP of the R811 in 7CB and MBBA at the transition temperature: $HTP(\text{MBBA}) \approx 10.2 \mu\text{m}^{-1}$ and $HTP(7CB) \approx 12.1 \mu\text{m}^{-1}$. From these values and the previous values of the LRP, we can calculate the \bar{R}

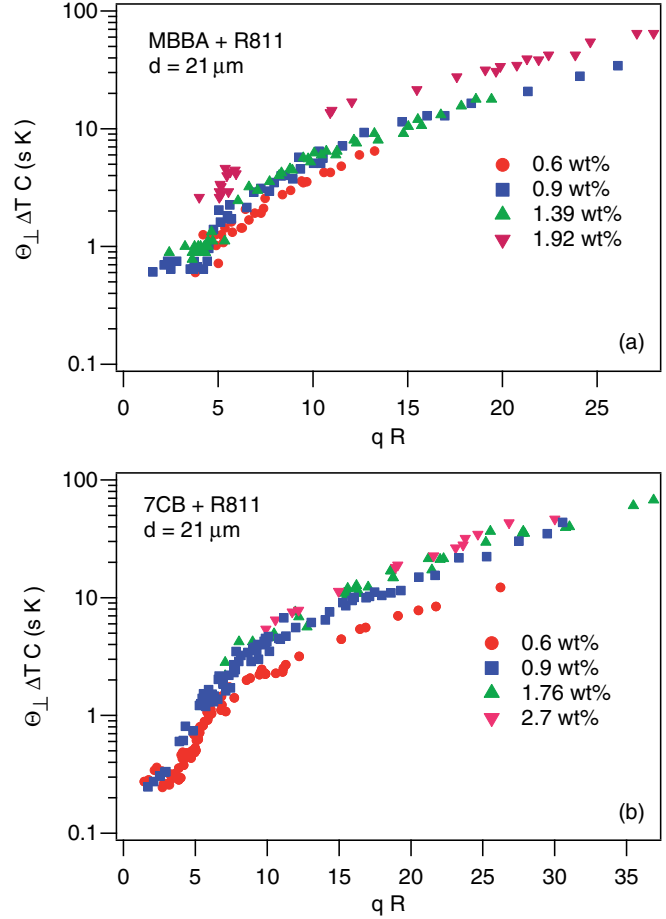


FIG. 6. (Color online) (a) Product $\Theta_{\perp} \Delta T C$ of the period of rotation times the temperature difference times the concentration as a function of the dimensionless radius qR . The host liquid crystal is MBBA in (a) and 7CB in (b). The chiral molecule is R811.

ratio :

$$\begin{aligned} \bar{R}(\text{MBBA}) &\approx 2.1 \text{ pN K}^{-1}, \\ \bar{R}(7CB) &\approx 4.6 \text{ pN K}^{-1}. \end{aligned}$$

These values are clearly not equal, even if they are of the same order of magnitude. This new measurements show that the \bar{R} ratio depends on the liquid crystal chosen, whereas it does not depend on the chiral molecule used to dope the liquid crystal as previously shown in Ref. [8].

V. DROPLET BEHAVIOR AT ZERO RADIUS

An interesting point is to compare the velocity of the helix extrapolated at zero radius in the CC droplets with the velocity of the striped droplets in the same limit. To obtain this limit, we reproduce in Fig. 7(a) a graph already published in Ref. [12] showing measurements of the product $\Theta_{\parallel} \Delta T C$ as a function of the radius R in 30 μm -thick samples of MBBA doped with R811 at three different concentrations ($C = 0.5, 1,$ and 1.5 wt\%). This graph shows that the limit is close to 0.6 s K, as in the case of the striped droplets. One may wonder whether this limit depends on the thickness of the sample. To answer

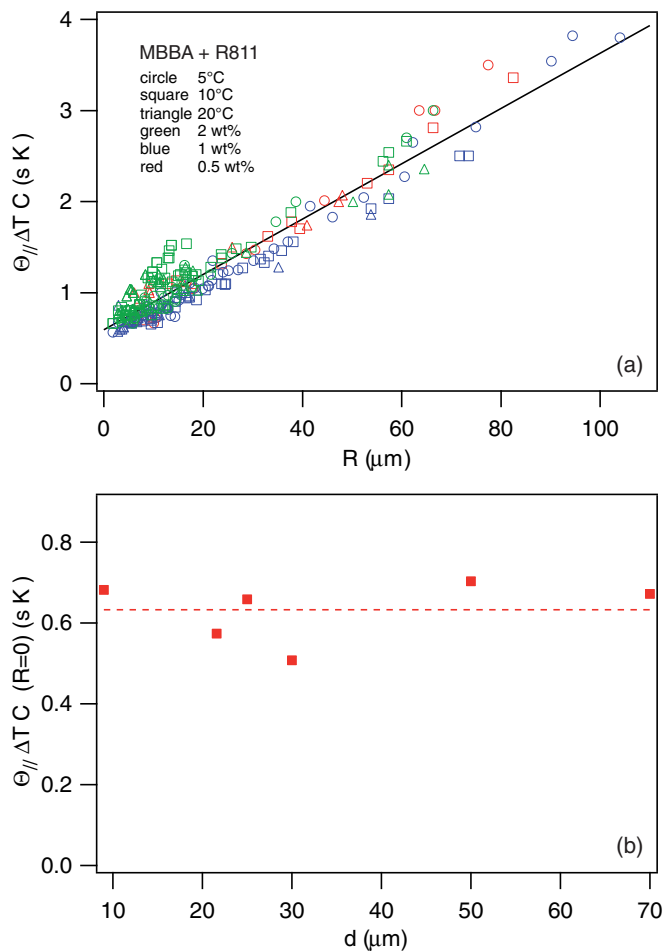


FIG. 7. (Color online) (a) Product $\Theta_{\parallel} \Delta T C$ of the period of rotation times the temperature difference times the concentration as a function of the radius R . MBBA+R811, $d = 30 \mu\text{m}$. The different symbols correspond to different concentrations (from Ref. [12]). (b) Extrapolation at radius $R = 0$ of the product $\Theta_{\parallel} \Delta T C$ as a function of the thickness d . These values are deduced from the data shown in Fig. 5(a). The dashed line gives the average value, close to 0.6.

this question, we plotted in Fig. 7(b) the extrapolation to 0 of this product as a function of the thickness. This extrapolation is obtained from the linear fits of the data reported in Fig. 5(a).

Although these values are very imprecise due to the dispersion of the points, they are all close to 0.6 s K. That means that all the droplets, irrespective of their internal texture, rotate at the same velocity in the limit $R \rightarrow 0$. This result suggests that the same driving mechanism is involved in all the droplets, at least in this limit.

VI. CONCLUSION

We have shown that the rotation velocity of the striped droplets is independent of the sample thickness. By contrast, the rotation velocity of the CC droplets stabilized with an electric field is highly dependent on the thickness and systematically larger than that of the striped droplets, at equal radii. These results show the importance of the internal texture of the droplets, what we already knew. The shape of the droplets might also play a role to explain the difference of behavior of the two types of droplets when the sample thickness is changed. For instance, one sees in Fig. 4, just by observing the spatial distribution of the concentric circles and the extend of the central homogeneous zone, that the droplet in the $70 \mu\text{m}$ -thick sample seems to be more spherical than the one observed in the $21.6 \mu\text{m}$ -thick sample. In comparison, the striped droplets seems rather similar in all the samples, at least as long as their radius is smaller than the thickness (see Fig. 1). This could qualitatively explain why the striped droplets are less sensible to the thickness than the CC droplets. The flows could also play a role in the thickness effects, but our results seem to be in contradiction with the recent findings of Yoshioka *et al.* [11]. Indeed, according to these authors, the striped droplets rotate as a rigid body, whereas no flow is detected in the vicinity of the CC droplets. As a consequence, the striped droplets should produce a flow around them and accelerate when the sample thickness increases, whereas the CC droplets should be insensitive to the sample thickness. This is exactly the contrary of what we observe. Finally, we have shown that all the droplets tend to rotate at the same velocity when their radius tends to 0. This result suggests that a single mechanism, still unknown, is involved in this limit.

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