Temperature dependence of droplet breakup in 8CB and 5CB liquid crystals

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Droplet breakup of many Newtonian fluids is well described by current experiments, theory, and simulations. Breakup in complex fluids where interactions between mesoscopic structural features can affect the flows remains poorly understood and a burgeoning area of research. Here, we report on our investigations of droplet breakup in thermotropic liquid crystals. We investigate breakup in the smectic, nematic, and isotropic phases of 4-cyano 4-octylbiphenyl (8CB) and the nematic and isotropic phases of 4-cyano 4-pentylbiphenyl (5CB). The experiment consists of varying the ambient temperature to control liquid crystalline phase and imaging breakup using a fast video camera at up to 110 000 frames/s. We expand on previous work [John R. Savage *et al.*, Soft Matter **6**, 892 (2010)] that shows breakup in the smectic phase is symmetric, producing no satellite droplets, and is well described by a similarity solution for a shear-thinning power-law fluid. We show that in the nematic phase the breakup occurs in two stages. In the first stage, the breakup is symmetric and the power-law exponent for the minimum radius dependence on the time left to breakup is $1.2 < n < 1.9$. In the second stage the drop develops two minima and the minimum radii shrink with a power-law exponent $0.6 < n < 1$. We find that the exponents vary with temperature across the nematic phase. These results are surprising because rheological measurements of 8CB and 5CB in the nematic phases indicate Newtonian behavior that cannot account for the observed breakup dynamics. Finally, in the isotropic phase, the exponents are consistent with theoretical predictions and experiments for Newtonian fluid breakup in the inertial viscous regime.

I. INTRODUCTION

Droplet dispersal is a ubiquitous phenomenon with rich scientific underpinnings and many industrial applications. It is not only relevant to the beautiful shapes formed by water droplets as they drip from a faucet [1] or the elegant threads formed by honey oozing from a bottle, but is critical for controlling the size distribution of droplets formed in various ink-jet printing and flow cytometry applications. As the droplets break the minimum radius decreases to zero and the curvature diverges. Since the pressure is proportional to the curvature, a finite time singularity in the pressure develops at the point of breakup. Often the gradients in the pressure are also singular so that extreme flows develop within the breakup region [2,3]. Thus, droplet breakup exposes the response of a fluid on increasingly shorter length scales and higher flow velocities, extreme conditions not accessible in normal bulk rheology.

The fluid instability leading to the breakup of Newtonian fluids in air has been the subject of scientific investigation for over a century [4,5]. Over the past two decades, however, scientists have developed, with the aid of high speed imaging and numerical computation, methods that also allow for studying and predicting the shapes and flows near the singularity [2,3,6,7]. In particular, they have shown that there are various scaling relations that determine how the characteristic lengths and flow velocities depend on time. These scaling relations allow for constructing similarity solutions that capture the entire breakup process down to the molecular scale [8,9].

They also serve as an excellent starting point for determining the resulting satellite droplet distribution. Several different similarity solutions have been found in which either stress due to inertia, viscosity, or both balance the stresses arising from the pressure gradients in the flows [6,7,10–14].

However, many scientifically important fluids are non-Newtonian, displaying long-range ordering or unusual flow characteristics such as shear thickening or shear thinning [3,15–19]. Moreover, the industrial importance of understanding the dripping characteristics of complex fluids continues to grow. The technology of ink-jet printing, for example, is expanding beyond traditional inks to print structured fluids and materials [20]. Thus, there is a growing need to better understand how droplet breakup dynamics are modified in structured fluids. Liquid crystals (LCs) offer an ideal starting point for this type of investigation. Their ubiquitous usage in modern technology provides not only good motivation for understanding their dynamics, but has provided a good understanding of their equilibrium phase behavior and the defect structures that control their mechanical response.

Thermotropic liquid crystals such as 8CB and 5CB, for example, possess an underlying order that can be controlled by varying the temperature and gives rise to their viscoelastic flow characteristics [21,22]. A schematic illustrating the phase behavior of 8CB is shown in Fig. 1. In addition to the crystalline phase and isotropic liquid phase, there are two intermediate "mesophases" that are important to this study. The smectic phase is characterized by one-dimensional positional ordering that results in layering of the molecules, while the nematic phase is characterized by molecules oriented in the same direction but without any positional order. Regions where
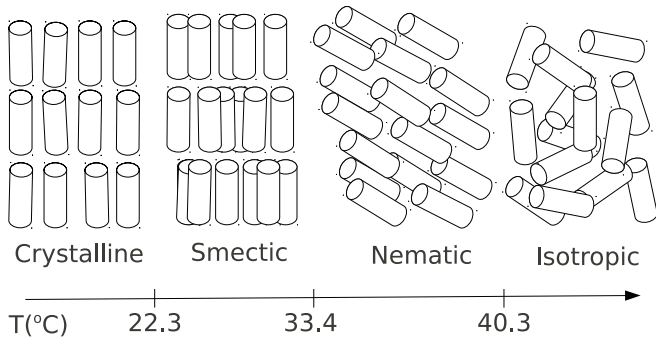
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FIG. 1. Phase diagram for 8CB. The molecules within the liquid crystal are "rodlike." This figure illustrates the ordering of the four relevant liquid crystalline phases (crystalline, smectic, nematic, isotropic) including the temperatures at which phase transitions occur in 8CB. 5CB has a similar phase diagram but does not experience a smectic phase.

these molecules are all oriented in the same direction are referred to as domains, and the size of these regions is typically highly dependent on the sample prehistory. Radial and axial length scales characterizing the drop are often large enough to accommodate many domains with different orientations in the initial stages of breakup, but decrease to subdomain scales at breakup. While the equations of motion for a uniform LC domain are well established [23], the domain interactions at high flow rates that lead to the observed bulk behavior of the drop are still poorly understood.

Naively, since the equations governing flows within each LC domain are rather daunting, one might expect that the equations governing bulk flows in the drop, which take into account the interactions between LC domains, are even more complex. Recent experiments on the breakup of surfactant systems and LCs in the smectic phase, however, have shown that the bulk flows during breakup are well described by the equations of motion for a simple viscous liquid with a rate varying viscosity $\mu \sim |\dot{\gamma}|^n$, where $\dot{\gamma}$ is the shear rate [24]. Moreover, these measurements showed that as predicted for power-law fluids [2], the minimum radius, characterizing the radial length scales, decreases in time with the same exponent so that $R_{\min} \sim \tau^n$, where τ is the time left to breakup. In these previous experiments the exponent was measured to be $n \approx 0.6$ at room temperature. Here we extend these studies and measure the temperature dependence of the power-law exponent n throughout the phases of the thermotropic liquid crystal systems 4-cyano 4-octylbiphenyl (8CB) and 4-cyano 4-pentylbiphenyl (5CB).

II. EXPERIMENT

The systems we investigate are the thermotropic liquid crystals 8CB and 5CB from Frinton Laboratories, Inc. 8CB is a rodlike liquid crystal with four phases; it exhibits a transition from crystal to smectic at 22.3 °C, from smectic to nematic at 33.4 °C, and from nematic to isotropic at 40.4 °C. 5CB is a rodlike liquid crystal with three phases; it exhibits a transition from crystal to nematic at 18 °C and from nematic to isotropic at 35 °C. Bulk rheology reveals that 8CB is a shear-thinning fluid in the smectic phase, and that both 8CB and 5CB
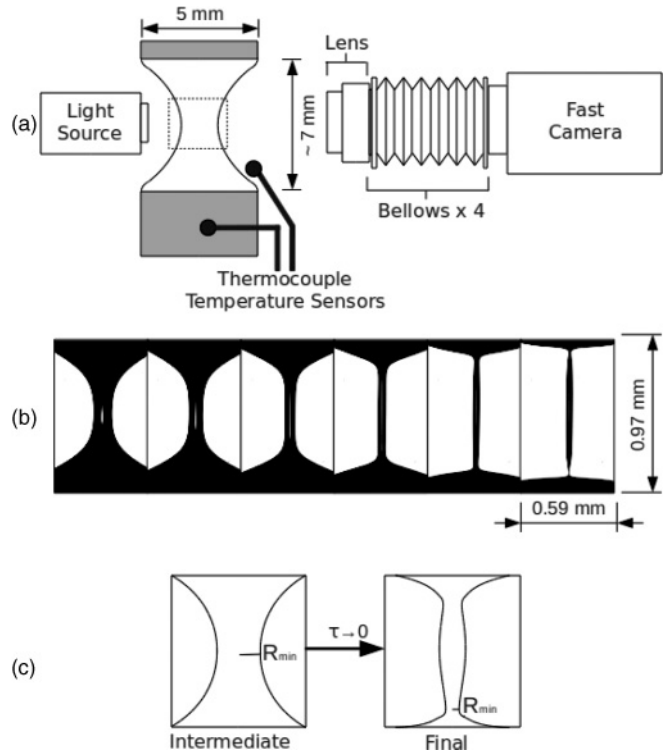

FIG. 2. (a) Liquid bridge geometry, imaging apparatus, and thermocouple placement. (b) Droplet profile images for 8CB in the nematic phase at $T = 38$ °C. Images showing the intermediate regime (first three frames) and the transition to the final regime (final three frames). Contrast enhanced in all droplet images. (c) Droplet profiles for intermediate and final regimes.

are Newtonian fluids with a temperature dependent viscosity varying between 20 and 30 cSt in the nematic and isotropic phases [17,25]. The accessible transition temperatures of 8CB and 5CB facilitate investigation of the phase dependent droplet breakup of these complex fluids.

To investigate breakup, we used a liquid bridge geometry [Fig. 2(a)]. This geometry simplified the imaging since the breakup region remained fixed during successive experiments and allowed for recycling of the fluid for multiple runs. We sandwiched a small amount of fluid between two glass disks of radius 5 mm, and changed the distance between the plates by adjusting the height of the top plate. The liquid bridge apparatus was enclosed in a temperature controlled box, and the ambient temperature was measured using two thermocouples. By placing one thermocouple near the fluid and another in contact with the bottom plate we were able to ensure that temperature gradients in the measuring volume were smaller than 1 °C. We use a Phantom 7.1 fast camera to capture videos of the droplet profiles near breakup, and a macro lens coupled to a bellows to magnify the images. The profiles were illuminated from behind by a projector bulb, allowing us to produce videos of dark profiles on a light background, at a frame rate of up to 110 000 frames/s and a pixel resolution ranging between 2.0 μm/pixel and 0.86 μm/pixel. In the experiments the apparatus and sample were heated to the desired temperature. The plates were slowly drawn apart until the liquid bridge between the plates became unstable and broke. A series of images depicting a breakup

event for an 8CB drop in the nematic phase at $T = 38$ are shown in Fig. 2(b).

From these images we can observe and compare the shapes of the drops close to breakup. We quantify the drop evolution by measuring how the minimum radius changes with the time left to breakup $\tau = t - t_0$, where t_0 is the breakup time [7]. Due to limitations of the fast cameras, the slow, large-scale dynamics and much faster, small-scale dynamics could not be imaged with the same frame rate and image size. Consequently, data from multiple videos with different frame rates needed to be stitched together to obtain a complete measurement of the entire breakup process. The droplet breaks at time t_0, which lies between two successive video frames. Thus, t_0 was chosen within this range and used as a fitting parameter to maximize the overlap between curves obtained in different breakup runs. Using this procedure we obtained R_{min} versus τ curves for 8CB and 5CB for temperatures ranging between roughly 25 °C and 45 °C.

III. RESULTS

We find that the breakup dynamics for 8CB vary substantially with liquid crystalline phase. In Fig. 3, we plot R_{min} versus τ and show images of the region of breakup for one temperature in the smectic phase, $T = 28$ °C. In this regime the breakup of 8CB is symmetric about a single minimum [24]. We find that minimum radius decreases as $n = 0.63 \pm 0.06$ for temperatures ranging between 25 °C and 33.4 °C. In Fig. 4, we plot R_{min} versus τ and show images of breakup for one temperature in the nematic phase, $T = 35$ °C. Qualitatively, the breakup is divided into two regimes: an intermediate regime where the drop pinches with its minimum radius
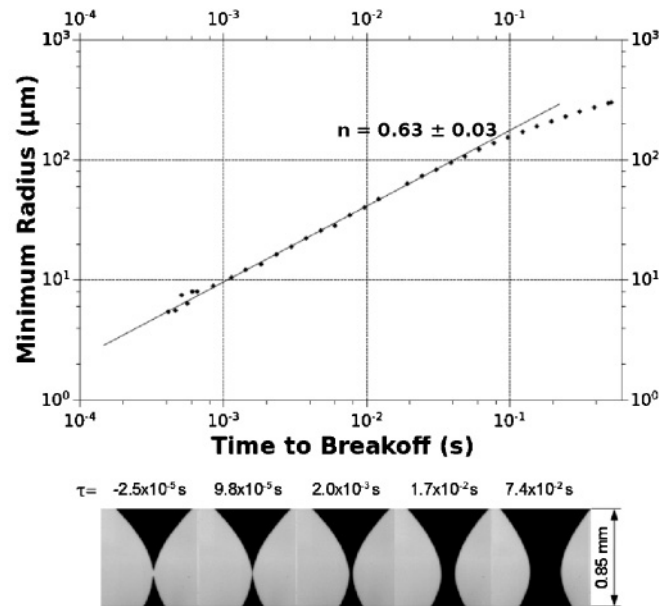

FIG. 4. R_{min} as a function of τ and droplet profile images for 8CB in the lower range of the nematic phase (35 °C).

roughly midway between the two plates, and a final regime where the drop pinches near both the top and bottom plates so that satellite droplets are formed. The intermediate regime proceeds with $n \approx 1.7$, and the final regime with $n \approx 0.66$. As the temperature is increased, we find similar qualitative behavior. However, we do observe that the satellite droplets increase in size and that the exponents for the intermediate regime decrease. Finally, in Fig. 5, we plot R_{min} versus τ

FIG. 3. Breakup of 8CB in the smectic phase. (a) R_{min} versus τ for the smectic phase at $T = 28$ °C. The solid line corresponds to a power-law fit to the data between $R_{min} = 100$ μm and 10 μm with an exponent $n = 0.63$. Errors in the measurement are approximately 3 μm and correspond to the scatter in the data. (b) Successive droplet profile images for 8CB in the smectic phase.
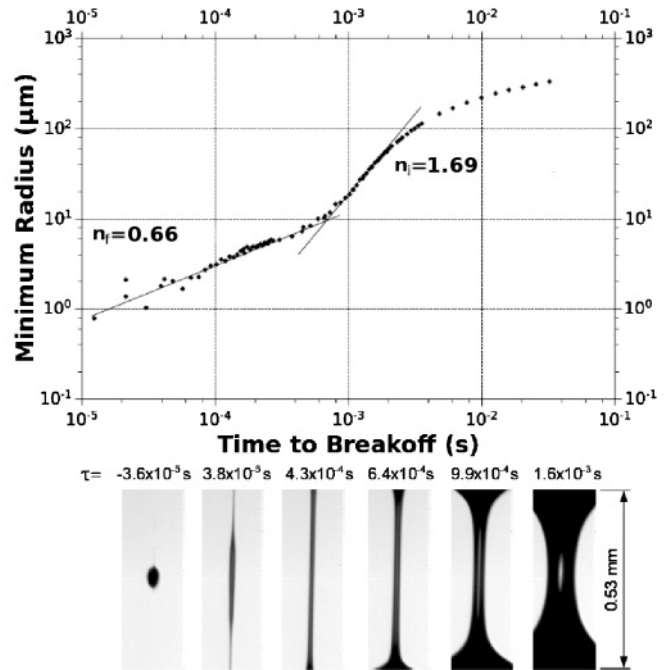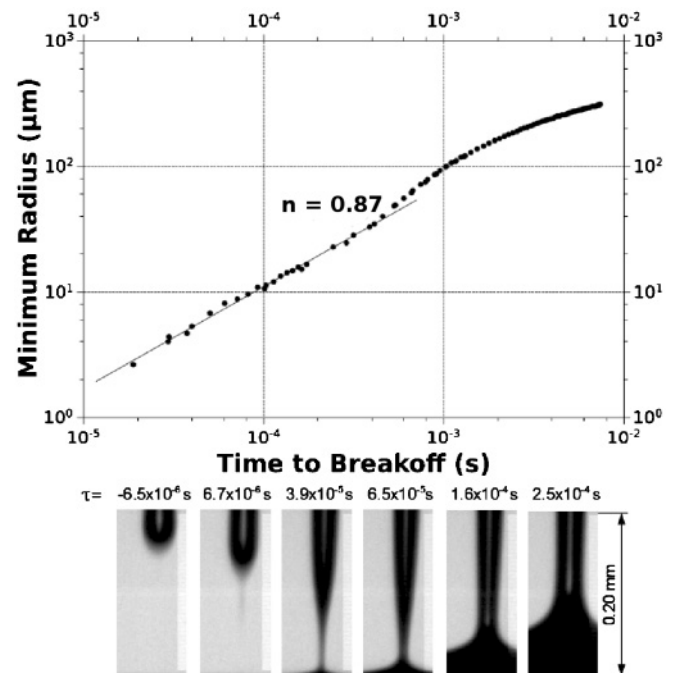

FIG. 5. R_{min} as a function of τ and images of the lower half of droplet profile for 8CB in the isotropic phase (46 °C).
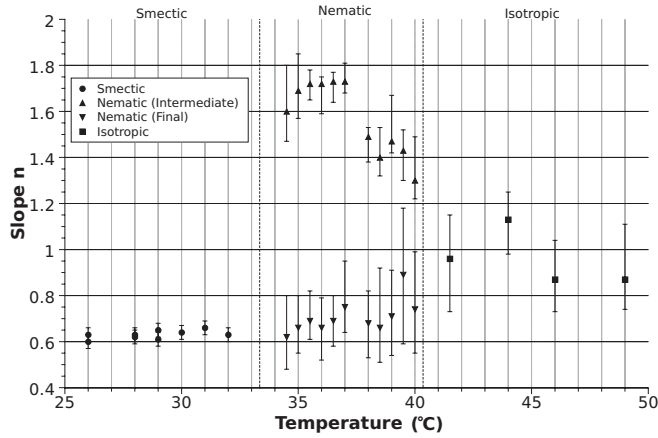
FIG. 6. Logarithmic slope n for 8CB at various temperatures throughout its three liquid phases. Results show agreement with power-law exponents of $n = 0.67$ in the smectic phase and deviation from the expected $n = 1$ in the nematic phase, with different n in the intermediate and final regimes.

and show images of breakup for one temperature in the isotropic phase, $T = 46\,^{\circ}$C. Here, we find that the drop rapidly transitions to the final regime with minima close to the bottom and top plate. Thus we only report on the exponent for the final breakup regime. Measurements of $R_{\min}$ versus τ indicate breakup dynamics consistent with those characterizing an inertial-viscous Newtonian fluid where $n = 1$. These results are summarized in the plot of the power-law exponent n versus temperature (Fig. 6).

Similarly, we found that breakup dynamics for 5CB also vary substantially with liquid crystalline phase. Qualitatively, the breakup in the nematic phase is similarly divided into a symmetric intermediate regime and a final regime with two minima. The intermediate regime proceeds with n between ≈ 1.7 and 1.1, and the final regime with n between ≈ 0.9 and 0.5. As the temperature is increased, we find similar qualitative behavior to breakup in the nematic phase of 8CB with increased satellite droplet size and decrease in intermediate regime exponents. Finally, the isotropic regime is also consistent with breakup of an inertial-viscous Newtonian
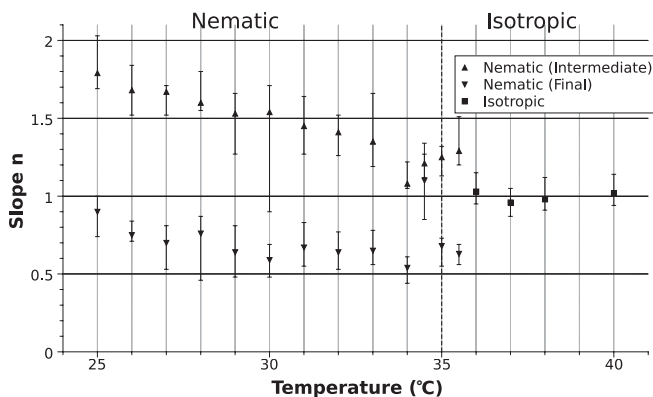
fluid. These results are summarized in the plot of n versus temperature (Fig. 7).

IV. CONCLUSIONS

Collectively, these measurements identify a set of scaling relations for droplet breakup in liquid crystals that are distinct from those observed in the breakup of Newtonian fluids. For breakup in the smectic regime scaling relations for both the radial and axial components of the droplet evolution have been shown to lead to similarity solutions where successive drop profiles could be scaled onto a single curve [24]. Both the rheology and similarity solution for breakup in this regime were found to correspond to those for a rate-thinning power-law fluid. [2]. The power-law scalings reported here for 8CB and 5CB in the nematic regime strongly suggest universal dynamics characterized by similarity solutions. These observed scalings are distinct from those found for Newtonian fluids in three ways. First, we find that the scaling exponents are different in the intermediate and final regimes indicating distinct rheologies. Second, the measured exponents in the intermediate regimes are different from those measured for all other Newtonian fluids breaking in air. Finally, while the radial exponents in the final asymptotic breakup regime are close to 2/3 the shape of the drop is long and thin indicating that the axial scaling exponent is much smaller than 2/3. This behavior is distinct from that in Newtonian breakup in the inertial regime where both the radial and axial scaling exponents are 2/3 and the drop profile is conical [11]. Together, these differences indicate a non-Newtonian rheology of these liquid crystals throughout their smectic and nematic phases.

Interestingly however, the measured shear rheology for 8CB and 5CB in the nematic phase is Newtonian [17,25]. Such measurements imply that either the droplet breakup experiments are probing a different flow regime inaccessible to bulk rheological measurements, or that the shear rheology in these systems is insufficient to capture the breakup dynamics. More specifically, the rapid extensional flows and changing drop geometry may induce structural changes in the domain configurations that lead to non-Newtonian behaviors distinct from those observed in bulk rheology measurements. Such hypotheses are consistent with interpretations of electrorheological measurements and *in situ* x-ray studies that show that 8CB molecules can exhibit tumbling or rolling behavior depending on the alignment of the LC domain with the shear flows [16,21,26,28].

Overall, these observations form the basis for developing a class of similarity solutions that are necessary for describing breakup in the nematic phase. To make progress, it will be necessary to gather further data relating to the internal flows that govern the breakup dynamics. For example, using cross polarizer measurements to image the domain distribution and alignment in more transparent samples will lead to the development of models for the rate dependent extensional and shear viscosities. Alternatively, experiments where the domains are aligned prior to breakup could be used to determine how molecular orientation affects breakup. [27,28] These measurements also highlight the subtleties in using

FIG. 7. Logarithmic slope n for 5CB at various temperatures throughout its two liquid phases. Results are similar to 8CB, however, 5CB exhibits no smectic phase.

breakup to measure the rheology of structured fluids. For example, the different scalings observed in the intermediate and final regimes indicate that the radial evolution of the entire profile needs to be tracked in order to capture the spectrum

of rheological behaviors. Thus, using a capillary breakup extensional rheometer (CaBER) for example, [29] will not be sufficient to fully characterize this increasingly important class of fluids.

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