

Self-Propulsion of Nematic Drops: Novel Phase Separation Dynamics in Impurity-Doped Nematogens

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We report a novel phase separation dynamics, mediated by self-propelled motion of the nucleated drops, in a mixture of a nematogen and an isotropic dopant. We show that surface flow, induced by the gradient in the concentration of the dopant expelled by the growing drops, provides the driving force for the propulsion of nematic droplets. While the liquid crystal-isotropic transition is used here to demonstrate the phenomenon, self-propulsion should be observable in many other systems in which the dynamics of a conserved order parameter is coupled to a nonconserved order parameter.

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Nondiffusive transport of objects such as vesicles and aggregates plays a fundamental role in biological systems. Understanding different mechanisms leading to such directed motion is also of importance in materials processing. Motivated by these, many processes that can lead to such motion have been predicted [1–9]. Examples are conversion of chemical energy to mechanical work [5], osmotic work obtained by transporting solvent molecules along the gradient [10], and gradients in solute concentration resulting from a chemical reaction catalyzed by the particle surface [6]. However, there are very few experimental observations of such self-driven transport, in non-biological systems [5,10,11]. Here we report the very first observation of a growth process mediated by self-driven drops nucleating in a mixture containing a small amount of impurity and a nematogen.

Phase separation dynamics in nematic liquid crystals has received considerable attention for the past many years, both experimentally [12–15] and theoretically [16,17]. Theoretical investigations were also carried out on phase ordering kinetics in mixtures of nematogen and nonmesogenic (isotropic) components [18]. On the contrary, there are no systematic experimental investigations of nucleation and growth of nematic domains, mainly because in pure nematogens the isotropic-nematic (I - N) transition is only weakly first order, and the coexistence range is very small. The latter can be widened considerably by adding non-mesogenic impurities to the sample. In this Letter, we show that this makes the dynamics surprisingly rich.

In the past, unusual coalescence mechanisms of droplets were observed in the spinodal decomposition of simple fluid mixtures [19]. The explanation for such domain growth, which is faster than that due to diffusive coalescence, was provided by the coalescence-induced coalescence mechanism and attraction due to the overlap of concentration fields of nearby drops [20]. More recently, it was predicted, in the context of nucleating clusters, that a

flow along the droplet surface, resulting from the nonuniform distribution of solutes around it, can lead to directed motion of the clusters [2]. The phenomena we report in this Letter is distinctly different from these two. We show here, to the best of our knowledge for the first time, a growing fluid domain, moving because of the surface flow induced by the asymmetric concentration of an expelled impurity.

The experiments were performed on asymmetric mixtures of common liquid crystals and isotropic dopants (10–20 wt %). We used two different dopants: fluorescent perylene labeled polystyrene oligomers and the hardener of the commercially available epoxy Araldite. The “impurity” lowers the I - N transition temperature in a concentration dependent manner. Glass cells of about 1 cm \times 1 cm area and 18 μ m gap were filled with the mixtures in their completely mixed isotropic state. The temperature was controlled to better than 0.1 $^{\circ}$ C using a homemade hot stage with computer control. Observations were made using a Zeiss Axiovert 135 microscope configured for polarized light microscopy and images were recorded using a CCD camera. A high gain EM-CCD camera (Hamamatsu-C9100) was used for fluorescence microscopy. All the quantitative measurements were performed using 4-octyloxy-4'-cyano-biphenyl (8OCB) doped with 20 wt % of the hardener of Araldite (Standard Resin, Huntsman Advanced Materials). This mixture shows a 70–63 $^{\circ}$ C nematic range.

When a uniform mixture is cooled across its I - N transition temperature, nematic droplets start nucleating throughout the sample cell. These nematic drops exhibit a novel and remarkable coalescence dynamics. Small droplets drift towards bigger domains until they coalesce resulting in a few fast growing domains (see supporting movie 1 [21]). The coalescence phenomenon is much more spectacular when a sample with a radial concentration profile, in its isotropic phase, is cooled. Such a profile is obtained by melting a large nematic domain as described

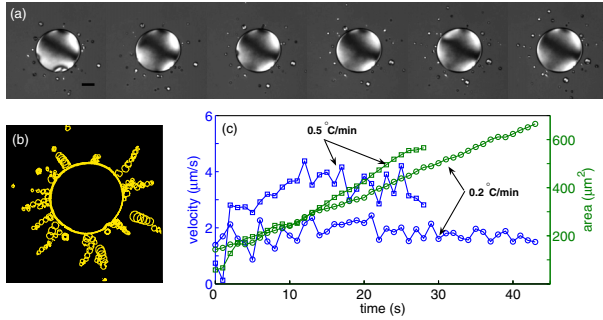


FIG. 1 (color online). (a) Image sequence (6 s/frame) showing radial drift of small nematic droplets toward a big drop, in a sample with radial concentration gradients, when cooled at $0.2\text{ }^{\circ}\text{C}/\text{min}$. The scale bar is $50\text{ }\mu\text{m}$. (b) The radial drift and growth of droplets is illustrated by stacking the detected boundaries of drops from a sequence of images. (c) A typical plot of the variation of the projected area and velocity of drops for cooling rates of 0.2 and $0.5\text{ }^{\circ}\text{C}/\text{min}$.

later. In this case, the first nematic drop nucleates almost exactly where the previous domain had existed. Moreover, this drop appears at a temperature close to that of I - N transition of the pure liquid crystal, suggesting a nonuniform impurity concentration field (the I - N transition temperature is lower for higher impurity concentrations). As cooling is continued, nematic nuclei form all around and progressively away from this central drop. These freshly nucleated droplets exhibit an inward radial drift until they coalesce with the drop at the center, as shown in Figs. 1(a) and 1(b). This radial motion of drops is best visualized in supporting movie 2 [21]. This process of nucleation and drift continues as long as the sample is being cooled. For a fixed cooling rate, the drop velocity remains almost constant while it grows at a constant rate as shown in Fig. 1(c). However, if the cooling is stopped, the motion as well as the growth of the drop ceases. Resumption of cooling results in fresh droplet nucleations and motion as before.

The nucleation pattern mentioned above suggests that fast cycling through the N - I - N transitions results in a nonuniform concentration profile in the sample. In order to verify this, we performed fluorescence microscopy by taking advantage of the fact that the dopant produces slight autofluorescence when excited by blue light. We find that nematic domains appear as dark circular patches, indicating clearly that the dopant is almost completely expelled from these domains, as shown in Fig. 2(a). When quickly reheated, the nematic domain melts leaving behind the circular dark patch which takes several minutes to an hour to disappear, depending on its size, as can be seen in the sequence in Fig. 2(a). These patches show a clear radial gradient of the dopant concentration. The time dependence of this gradient is shown in Fig. 2(b). On cooling, new nematic droplets form and travel down this radial concentration gradient giving rise to the radial motion described earlier (see movie 3 in the supporting material [21]).

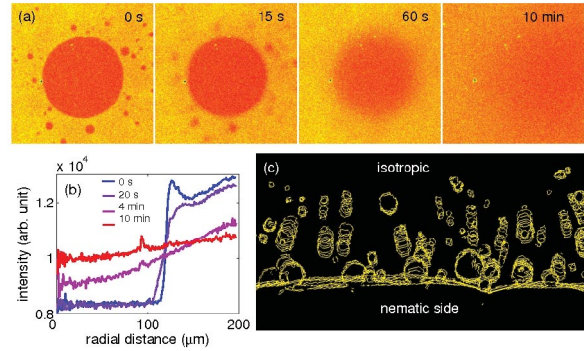


FIG. 2 (color). (a) Fluorescence images (in pseudocolor) showing a nematic domain with surrounding droplets (0 s) and the diffusion of the dopant after the sample was heated to its isotropic state ($t > 0$ s). (b) Evolution of the angular-averaged radial intensity distribution after the central domain was melted. An almost linear gradient is set up after a sufficiently long time. The intensity dip for the 0 s curve, just outside the interface, is largely due to the small droplets around it. (c) Stack of detected boundaries of droplets moving in an almost unidirectional gradient obtained using a contact preparation (see text). The droplets move away from the pure dopant side (above) and towards the slowly advancing I - N interface.

The connection between the concentration gradients and the directionality of the drift is further verified by preparing a sample with a unidirectional gradient. For this, the pure nematogen and the pure dopant were injected into the glass cell from two opposite sides, so that they make an almost straight interface. This “contact preparation” was then heated above the I - N transition temperature of the nematogen and held for about 45 minutes. This results in the formation of a broad mixed region with a concentration gradient normal to the initial interface. The concentration varies continuously from pure nematogen at one end of the cell to pure dopant at the other. This results in a straight I - N interface when this sample is cooled to the transition temperature of the pure nematogen. When the sample is cooled further, nucleation of nematic drops begins to occur in the mixed region. The droplets nucleating in this region move towards the I - N interface and coalesce with it as shown in Fig. 2(c) (see supporting movie 4 [21]). This experiment, along with observations of uniformly mixed samples mentioned earlier, rules out any possibility of temperature gradients giving rise to the observed phenomenon. It is noteworthy that many moving drops reach sizes larger than the cell thickness and, hence, become disk shaped. Experiments using glass plates treated for specific alignment of the nematic show that such treatments have no aligning effect, suggesting the presence of a thin wetting layer of the dopant at the nematic-glass interface.

From the experiments described above, we draw the following conclusions: (i) The dopant is very effectively and quickly expelled from the growing nematic drops. The diffusion of the expelled dopant is very slow compared to the expulsion rate. (ii) The nematic drops move down the

impurity gradient as revealed by fluorescence imaging and contact preparation. (iii) The drift velocity increases with increasing cooling rates. (iv) There is no drift of the droplets if the sample is heated. In this case, the droplets shrink and disappear while remaining stationary. The above facts rule out a number of mechanisms. Dipolar interaction between the drops is ruled out because the motion stops when the cooling is stopped. We also exclude the possibility of convective currents carrying the drops since there is no hydrodynamic flow field away from the moving drops. This has been verified by observing micron sized, freely suspended particles. For a given sample, we can repeat the experiment any number of times. So any chemical reaction driving the drops is ruled out.

One possible mechanism for the motion of drops is the dependence of the I - N interfacial tension on the dopant concentration, which is similar to that proposed by Karpov and Oxtoby [2]. A nematic droplet expels the dopant as it grows. This results in a high dopant concentration at the I - N interface, resulting in an increase in the interfacial energy. In the presence of a background gradient of the concentration, this leads to an asymmetric concentration profile around the drops as shown in Fig. 3(a). This results in an asymmetric interfacial tension which sets up a surface flow (Marangoni flow), from the region of low dopant concentration to high dopant concentration, which propels the drop forward. The surface flow is evident in the motion of a micron sized particle as shown in Fig. 3(d) (see movie 5 in the supporting material [21]). When the cooling is stopped, the growth of the droplet, the expulsion of the impurity, and the movement of the drop stop. This is because the accumulated dopant diffuses away, leading to

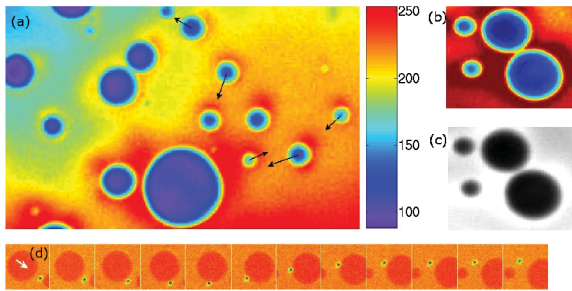


FIG. 3 (color). (a) Pseudocolor fluorescence image obtained using labeled polystyrene oligomer as the dopant. The sample was cooled from a state with arbitrary concentration gradients. The dopant concentration has a local maximum close to the drop interface, which is asymmetric in the case of moving drops. The arrows indicate directions of motion. (b),(c) Gray-scale and pseudocolor images of drops which are about to coalesce. The concentration profiles overlap at short distances even before the interfaces coalesce. (d) Sequence of images (4 s/frame) showing the motion of a dust particle along the surface of a moving drop. The arrow indicates the direction of motion of the drop. The dust particle flows only when in contact with the interface due to surface flow.

a drastic reduction in the average interfacial tension and, hence, also the net force acting on the drop, even though the background gradient remains almost the same. This means that the background gradient by itself does not generate any significant motion.

In samples with a radial concentration profile, the small drops coalesce with the large domain at the center, resulting in its growth. However, this growing central domain does not significantly alter the preexisting background profile because (i) the central domain is formed in a region of minimal dopant concentration, (ii) the flux of impurity expelled decreases as the drop grows at a constant rate, and (iii) the growth of the central domain is mainly due to the merging of drops already devoid of the dopant. Thus, the gradient of dopant due to expulsion affects the background gradient significantly only very close to the big drop and may result in a decrease in the velocity of the approaching drop. It should also be pointed out that, when the drops are very close to each other, the local concentration profiles overlap [see Figs. 3(b) and 3(c)] and there may be other forces that come into play [19].

In order to test the proposed mechanism, we conducted numerical calculations using a model in two dimensions. To describe the isotropic-nematic transition, we employ the following free energy: $\mathcal{F}_{\text{IN}} = \frac{1}{2}a(\phi)S^2 - \frac{1}{3}wS^3 + \frac{1}{4}uS^4$ [22], where $a(\phi) = a_0[\phi^* - \tanh(a_1 * \phi)]$ and $\phi = (\rho_n - \rho_i)/(\rho_n + \rho_i)$, with ρ_n being the nematogen concentration and ρ_i the concentration of isotropic component. ϕ^* sets the threshold concentration above which nematic ordering takes place and S is the “nematic order parameter” [22]. $a(\phi)$ provides the coupling between the concentration field and the nematic order parameter. This term models both the effect of impurity on the nematic isotropic transition and the action of nematic order, as a local field [23], to expel the impurity. Mixing and demixing of the phases are described by the following free energy: $\mathcal{F}_{\text{mix}} = \frac{1}{2}b\phi^2 + \frac{1}{2}[(1 + \phi)\log(1 + \phi) + (1 - \phi)\log(1 - \phi)]$ [18]. The total free energy functional of the system is then $\mathcal{F} = \mathcal{F}_{\text{IN}} + \mathcal{F}_{\text{mix}} + \frac{1}{2}(\sigma_0 + \sigma_1\phi)(\nabla S)^2$. Here σ_0 and σ_1 determine the concentration independent and dependent parts of the interfacial tension, respectively, given by the integral of the last term across the boundary. The parameter $\phi^*(T)$ sets the critical concentration for the I - N transition at a temperature T . $a_0(T)$, a_1 , w , u , and b are phenomenological coefficients. The equations of motion for ϕ and S are then given by $\Gamma_S^{-1} \frac{\partial S}{\partial t} = -\frac{\delta \mathcal{F}}{\delta S}$ and $\Gamma_\phi^{-1} \frac{\partial \phi}{\partial t} = \nabla^2 \frac{\delta \mathcal{F}}{\delta \phi} - \nabla \cdot (\vec{V}\phi)$. The Navier-Stokes equations for the velocity field, in the overdamped limit, are solved in the Fourier space to obtain the velocity components as $v_{k_\alpha} = [F(k)_\beta / \eta k^2][\delta_{\alpha\beta} - (k_\beta k_\alpha / k_\alpha k_\alpha)]$, with the force given by $F = -\frac{\delta \mathcal{F}}{\delta \phi} \nabla \phi$ [23]. We discretize the equations of motion in space and time and solve them numerically using an explicit Euler scheme. The calculations show the movement of the drop in the presence of a background gradient.

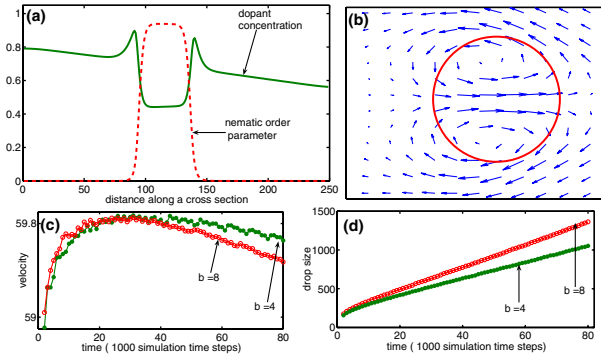


FIG. 4 (color online). Results from the numerical solution of the equations of motion with $\sigma_0 = 40$, $\sigma_1 = -20$, $\phi_c = 1.0$, $a_0 = 18$, $a_1 = 3$, $w = 20$, and $u = w - a_0[\phi_c - \tanh(a_1)]$. (a) The variation of the order parameter S and the dopant concentration along a line through the center of the drop in the direction of motion (left to right). (b) The velocity field in and around the moving drop (red circle) for $\sigma_1 = 1$. (c) Drop velocity for two values of the dopant diffusivity: Slower diffusion results in faster motion. (d) The drop size vs time showing growth rate is smaller when the dopant diffusion is small. We also verify that the interfacial tension is larger at the back on the drop than the front (data not shown).

The main results are summarized in Fig. 4. The motion of the drops in a background concentration with a hill at the center and a valley at the center are shown in supporting movies 6 and 7, respectively [21]. We believe that the nematic curvature elastic energy does not play a major role in its movement here as the medium between the drops is isotropic. A detailed mechanism for the change in surface tension as a function of dopant concentration is unclear. However, it is likely that the anchoring energy of the nematic director at the N - I boundary is a function of the dopant concentration and may contribute to the interfacial tension.

It is important to note that, unlike in spinodal decomposition, where attractive interaction between drops due to overlap of broad interfaces has been proposed [19], in the present experiment, the interface width is small [24]. We thus provide a very clear experimental demonstration of a new mechanism for self-propelled motion of nematic drops nucleating from a mixture. This mechanism adds a completely new route to coarsening in multicomponent fluids. This phenomenon may be important in material processing as, for example, in the preparation of polymer dispersed liquid crystals [25] and other composites.

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- [21] See EPAPS Document No. E-PRLTAO-97-036637 for movies on (1) coalescence of drops, (2) radial motion of drops, (3) nucleation and motion of drops along the concentration gradient, (4) motion of drops in the contact preparation, (5) motion of dust particle along the surface of the drop, and (6),(7) drop motion seen in the numerical simulations. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
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