Air tube formation at the freezing transition in nematic liquid crystals

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(Received 1 June 2006; revised manuscript received 6 December 2006; published 6 March 2007)

A phenomenon is presented, which changes the shape of gas bubbles in liquid crystals and also creates long gas tubes. The system consists of air bubbles which are injected into a nematic liquid crystal host. The shape of these air bubbles changes from spherical to ellipsoidal by initiating freezing of the sample. Furthermore, long gas tubes are formed from the air which was formerly dissolved in the liquid crystal. The gas tubes are created by the progression of the crystalline-liquid interface. Their length can reach up to 40 times their diameter. The diameter of the tubes depends on the pressure applied to the system, as well as on the interface velocity.

DOI: 10.1103/PhysRevE.75.031702 PACS number(s): 64.70.Md, 61.30.Gd, 61.30.−v, 42.70.Df

Liquid crystalline emulsions, consisting of small colloidal particles suspended in a liquid crystal, have been studied for about a decade. In particular, spherical droplets in nematic bulk phases [1–3] have been extensively investigated. In nematic bulk phases, droplets and defects form topological dipoles, which interact by the director field deformations, as has been shown in models for nematic phases [4–6]. In addition to spherical inclusions, recently the behavior of isolated rods in a nematic liquid crystal has been studied [7].

In this paper, a phenomenon is presented, which changes the shape of gas inclusions from spherical to ellipsoidal at the freezing transition. The term "freezing transition" is used to describe the transition between the nematic phase and the crystalline phase of the thermotropic liquid crystal. Since the crystallization of the sample is initiated at one location, an interface between the nematic and the crystalline phase is formed. This interface then moves over the sample, thereby transforming the nematic phase into the crystalline phase. In addition to changing the shape of the gas bubbles from spherical to ellipsoidal, by this method also long gas tubes are created. The leading front of the air tubes is pinned to the interface and is pulled through the sample. Thereby the tubes are formed, whose length can reach up to 40 times their diameter.

As experimental system, the thermotropic nematic liquid crystal host 4-pentyl-4′cyanobiphenyl (5CB by Merck) is used which has the phase sequence Cryst. 22 °C nematic 35 °C isotropic. The setup is the same as the one used in Ref. [8]. The nematic liquid crystal is put into a sandwich cell consisting of two circular glass plates, separated by a spacer in the center of the cell, thus keeping the periphery open for bubble injection. The gap between the glass plates is about 300 and 900 μm for two sandwich cells. Air bubbles are injected into the liquid crystal through a heat-drawn microaperture (1–20 μm) of a 100 μm diameter quartz capillary (Moritex) connected to an air pump, see Fig. 1. The stable injection of air bubbles is achieved by creating a constant relative motion between the capillary tip and the liquid crystal realized by rotation of the cell. The air flow through the capillary is regulated, for a particular capillary, by using a massflow controller (Lintex MC-3000E) or by varying the length of the capillary according to Hagen-Poiseuille's law $\frac{dV}{dt} \propto \frac{\Delta p}{l}$, where $\frac{dV}{dt}$ is the volume flow through the capillary, l is the capillary length, and Δp is the pressure difference.

After air injection, the sandwich cell is put into a high-pressure chamber with optical view ports to allow the application of high pressure of up to about 1 MPa. The textures are observed with an optical microscope (Olympus BX50) in transmission mode.

The injected air bubbles gradually rise to the top of the sandwich cell due to their buoyancy. However, we assume that the small air bubbles do not directly touch the glass substrates but are likely to be kept at an equilibrium distance, since the alignment is randomly planar at the glass substrates, and the anchoring is homeotropic at the bubble surface.

Utilizing the freezing transition, the shape of the initially spherical air bubbles can be controlled: After the injection of the air bubbles into the nematic matrix, the freezing of the sample is initiated by decreasing the temperature of the sample. After the freezing is initiated at one nucleation point at one location in the sample, the interface between the crystalline and the nematic phase moves across the sample, thereby freezing the entire sample. When the interface moves over an air bubble, the air of the bubble is pinned to the

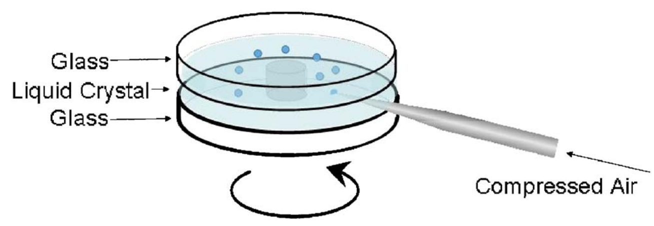

FIG. 1. (Color online) Experimental setup: Gas bubbles are injected through a capillary into the liquid crystal which is contained in a rotating sandwich cell.

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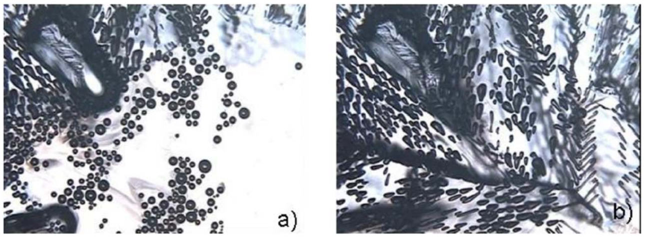

FIG. 2. (Color online) The crystalline-liquid interface moves over gas inclusions within the liquid crystal and changes their shape from spherical (a) to ellipsoidal (b). The width of the images is 1.75 mm.

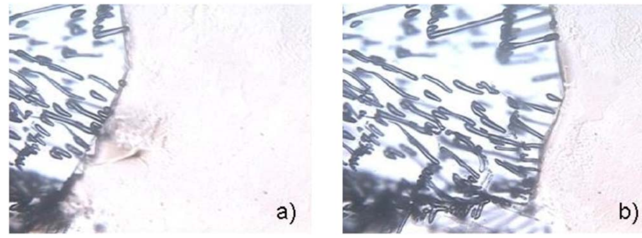

FIG. 4. (Color online) The crystalline-liquid interface moves over the liquid crystal, and from the air dissolved in the liquid crystal (a) long gas tubes are created (b) through the freezing transition at the freezing interface. The width of the images is 1.75 mm.

interface and is pulled in the direction in which the interface moves. In this way, the bubbles are elongated, and the formerly spherical bubbles form ellipsoids, see Fig. 2.

In order to analyze the shape change from spheres to ellipsoids, the aspect ratio, i.e., the ratio between the major and the minor axis of an ellipse equivalent to the bubble shape, has been calculated. The major (minor) axis is determined as the length of the major (minor) axis of an ellipse with the same first and second order moments as the object. For many different experimental runs, the aspect ratio has been calculated. Figure 3 shows the mean aspect ratio as a function of interface velocity. This analysis reveals that the shape change of a bubble from a spheroid to an ellipsoid is independent of the interface speed. Alternatively, the roundness of the object has been calculated, given as roundness$=(\text{perimeter}^2)/(4\times\pi\times\text{area})$. This roundness parameter shows no dependence on the interface velocity either (data not shown). In a different analysis, the bubble shape has been analyzed as a function of initial bubble size. No dependence of the bubble shape after freezing on the initial bubble size is found (data not shown).

The elongation of the bubbles occurs in the direction in which the interface moves. As long as the sample remains frozen, the elongated ellipsoidal shape of the bubbles is fixed.

The phenomenon of the pinning of the air in the liquid crystal to the moving interface can be utilized in order to create long air tubes. Therefore, air is dissolved in the liquid crystal until the liquid crystal is almost saturated with air. No visible air bubbles are present in the liquid crystalline matrix. Freezing of the sample is again initiated at one nucleation point in the sample, and the interface between the nematic and the frozen phase moves through the sample. In the crystalline phase, the solubility of the air decreases compared to the nematic phase. Therefore, when the crystalline-liquid interface moves through the sample and thereby freezes the sample, the air solubility decreases, and air is pinned to the interface. In this way, long air tubes are pulled through the sample by the movement of the interface. Figure 4 shows the process of the gas tube formation. Since the air tubes are aligned in the direction of the movement of the interface, they arrange in a parallel pattern (see Fig. 5).

The length of the tubes depends on the density of air tubes: The higher the tube density, the smaller the amount of air which is available for the creation of a tube, and the earlier the tube is terminated. Also, the higher the saturation of the liquid crystal with air, the longer the air tubes can grow. The length of the tubes can so far reach up to 40 times their diameter. As long as the sample remains frozen, the air tubes remain unchanged.

The diameter of the air tubes can be varied by applying high hydrostatic pressure to the sample, while the air tubes

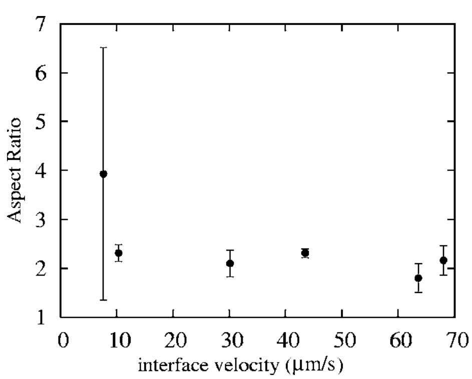

FIG. 3. Mean aspect ratio between the major and the minor axis of an ellipse equivalent to the bubble shape. The error bars give the standard deviation.

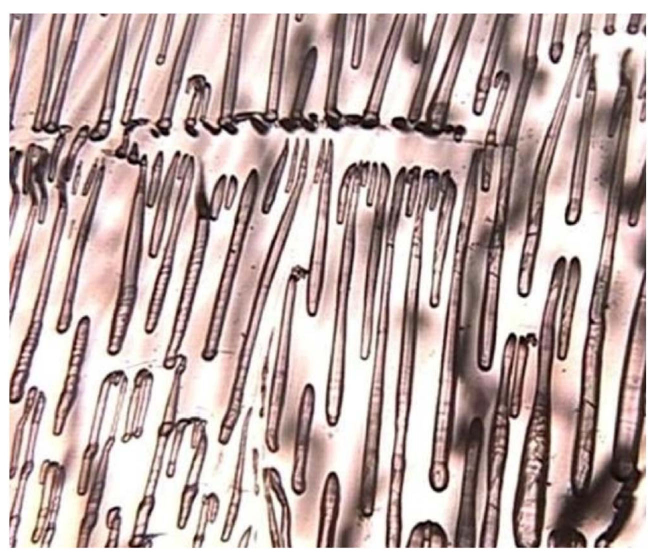

FIG. 5. (Color online) Parallel gas tubes, contained in a frozen nematic liquid crystal, formed by the air formerly dissolved in the liquid crystal. The width of the image is 1.33 mm.

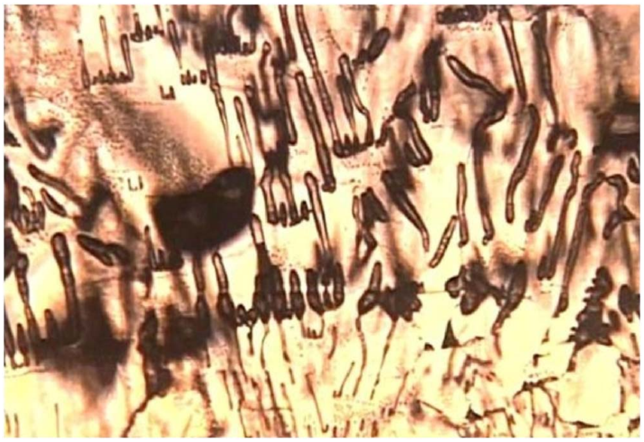

FIG. 6. (Color online) Control of tube diameter by varying the pressure applied to the sample: High pressure (450 kPa, bottom of the image) reduces the diameter; releasing the pressure (100 kPa, top of the image) increases the tube diameter. The width of the image is 1.75 mm.

are formed. Therefore the sample is put into the high-pressure chamber. This effect of changing the diameter of the air tubes by applying high hydrostatic pressure is shown in Fig. 6.

In order to compare the shrinking of the tubes due to the external pressure for many different runs, the shrinking factor has been calculated as the ratio of the tube diameter at normal pressure of 100 kPa and the tube diameter at the selected pressure p_2. The average shrinking factor has been plotted as a function of p_2, and is shown as Fig. 7. The higher the pressure p_2 applied to the sample, the smaller the diameter of the air tubes and the bigger the shrinking factor.

The dependence of the shrinking factor on the pressure p_2 can qualitatively be explained by a simple model: According to Boyle-Mariotte's law for gases, the volume Δvol of the gas supplied to the tube in a unit time is inversely proportional to the pressure p, $\Delta\text{vol} \propto 1/p$, and with $\Delta\text{vol} \propto d^2 \cdot \Delta l$, where d is the diameter of the tube and Δl is the increase of the length of the tube for a unit time determined by the freezing speed of the front, follows $1/d \propto \sqrt{p}$. This dependence is plotted together with the experimental data in Fig. 7.

Besides depending on the applied pressure, the width of

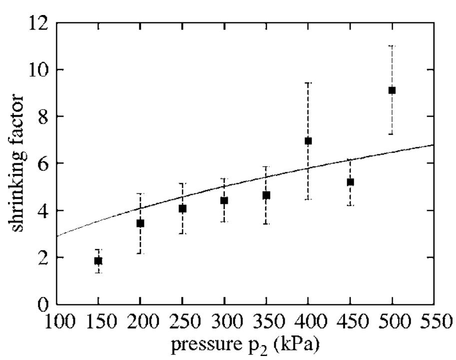

FIG. 7. Mean shrinking factor, the ratio of the tube diameter at normal pressure of 100 kPa and at the selected pressure p_2, plotted as a function of p_2. The error bars give the standard deviation.

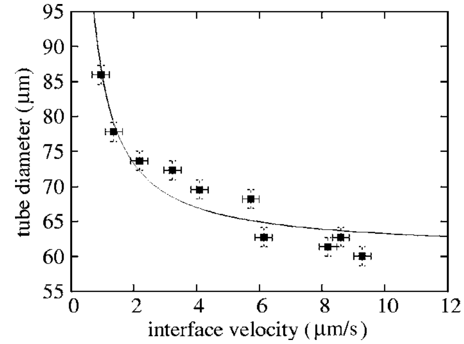

FIG. 8. Tube diameter as a function of interface velocity.

the tubes at constant pressure also depends on the interface speed. This dependence has been analyzed and is shown in Fig. 8. The lower the interface velocity, the longer the time for the collection of the air into the tube and hence the larger the range from where air is collected into the tube. This means, more air can contribute to the tube, and therefore the lower the interface velocity, the bigger the width of the tube.

The dependence of the tube width on the interface velocity can more quantitatively be explained by a simple model: Around the air tube there exists a cylindrical volume, which contributes air to the tube. This cylindrical volume has a radius R. Assuming homogeneous air distribution in the liquid crystal, R is given by $R=D/v$, where D is the diffusion coefficient of air in the liquid crystal, and v is the interface velocity. The equation for the mass flow per time interval is given by $\alpha\pi R^2 v=\beta\pi(d/2)^2 v$, where α is the air density in the nematic phase, β is the air density in the frozen tube, and d is the tube diameter. Combining this with $R=D/v$, it follows that $d \propto 1/v$. Although this relation is qualitatively consistent with the decreasing tube diameter with increasing velocity, this dependence does not describe the experimental data well. To better describe the data, an offset is needed according to $d \propto 1/v+\text{offset}$. This qualitative dependency is shown in Fig. 8, together with the experimental data. The offset implies, that even for an infinite interface velocity, the tube diameter does not vanish, but remains finite.

We should note here that the argument for $d \propto 1/v$ holds only when the length of air tubes is uniform. In reality, this assumption does not hold, especially at high interface velocities. For high tube densities at the beginning of the tube growth at high interface velocities, usually there is not enough air dissolved in the liquid crystal to support the growth of all tubes at a constant tube radius. Instead, either the radius of the air tubes must decrease, or the number of tubes per area must decrease. In the experiments, however, the first effect, that all air tubes in a dense air tube region keep growing with a reduced tube radius, is usually not realized. Instead, usually the second effect is realized: Just a few tubes continue growing at a constant radius while other tubes are terminated. This behavior might be responsible for the offset. However, for a more profound understanding of this effect, more experimental and theoretical investigations are necessary.

In order for a tube to continue to grow, a sufficient supply of air from the liquid crystal host is needed. When finally the

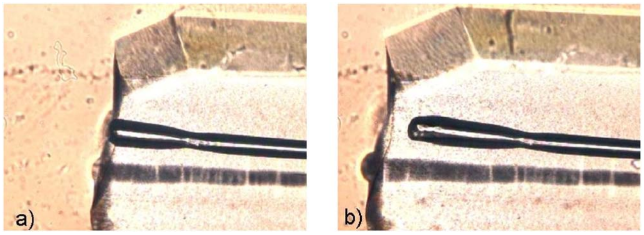

FIG. 9. (Color online) (a) and (b) Termination of air tube: When the inward flow of air from the surrounding liquid crystal into the tube is insufficient, the tube is unpinned from the interface and falls behind the interface, and the growth of the tube is terminated. The width of the images is 870 μm. The images show a second tube in a different layer, which is unfocused.

supply becomes inadequate for further elongation of the tube, the tube is terminated. Figure 9 shows the termination of such an air tube.

In order to reveal the crystalline structure of the frozen liquid crystal, polarizers were used for the observation of the freezing process. The results show that the frozen phase is not a monocrystal but consists of different crystallites. During the freezing process, each crystallite has had a separate interface to the nematic phase with a different orientation, giving rise to a different tube orientation. The direction of the movement of the interface does not only orient the air tubes, but at the same time orients the molecules in the liquid crystal. Figure 10 shows a section of the sample consisting of four crystallites with each having a different crystalline orientation, as can be seen from the different colors, as well as a different tube orientation. The grain boundaries between the different crystallites are clearly visible as dark lines.

Different from the work by Killawee *et al.* [9], who observed the formation of air tubes at the freezing of water, we use an anisotropic host medium. We assume that the orientation of the director in the direction of the movement of the freezing front supports the creation of the air tubes and helps direct the dissolved air in the direction of the tube. However, the effect of the anisotropy of the system on the freezing transition needs to be further investigated.

FIG. 10. (Color online) Frozen liquid crystalline sample consisting of four crystallites with different crystalline structure. The width of the image is 4.38 mm.

In conclusion, experiments at the freezing transition in liquid crystals have been performed. The system consists of air bubbles which are injected into a nematic liquid crystal host. By initiating freezing of the sample, the interface between the nematic and the crystalline phase is formed and moves across the sample, thereby changing the shape of air bubbles from spherical to ellipsoidal. By this method also long air tubes can be created from the air formerly dissolved in the liquid crystal. The difference in the solubility of air in the melt phase and in the crystalline phase of the liquid crystal, as well as the anisotropy of the direction of the freezing interface, are needed for the formation of the parallel gas tubes. The length of the gas tubes can reach up to 40 times their diameter. The diameter of the tubes can be varied by controlling the pressure, as well as controlling the interface velocity.

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