Circular flow formation triggered by Marangoni convection in nematic liquid crystal films with a free surface

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We demonstrate a circular flow formation at a surface in homeotropically oriented nematic liquid crystals with a free surface by a focused laser beam irradiation. Under a weak laser power, a pit together with an associated circular bulge is formed; the Marangoni effect. Here a diverging molecular flow from the pit (thermocapillary flow) also induces the director tilt to the radial direction. With increasing the laser power, the pit becomes deeper, and eventually evolves to a circular flow associated with a deeper pit and subsidiary circular bulge or valley structures. This phenomenon is induced by escaping from excess deformation energy due to a bend deformation of the director. Actually, we confirmed that the circular flow is never formed in the isotropic phase. The handedness of the vortex cannot be controlled by circular polarisation, but is controllable by doping with chiral molecules. This rotational motion (a nematic micro-rotor) is a unique phenomenon exhibited only by anisotropic liquid, and is expected to be applied for novel devices.

Introduction

A liquid crystal (LC), which appears between the isotropic liquid and solid crystal phases by changing temperature, is an interesting material, since it has both properties of fluidity and anisotropy. In the nematic LC (NLC) phase molecules rotate freely about their long axis and orient along a particular direction, director, so that the system is optically uniaxial. The director field can be easily deformed by external stimuli, such as electromagnetic, optical, mechanical, thermal, and interfacial fields, because of the long-range orientational order and a restoring force to minimise the deformation energy, which makes various applications, such as displays and sensors, possible. Towards the further applications of NLCs as beyond-the-display materials, photo-induced phenomena have been widely studied.[1-3] The majority of studies has been related to the photo-isomerisation using molecules possessing azo groups.[4-7] Here we report a unique circular flow formation initiated by thermocapillary flow (Marangoni effect) in simple NLC films with a free surface.

Marangoni convection is defined as the movement of mass through the interface of two matters in a different condition due to surface tension gradient.[8] If a surface tension gradient arises due to the difference in temperature, so-called thermocapillary convection occurs. A rise in temperature normally causes a decrease in surface tension. Consequently, if a laser beam is incident normally on a sample surface, an axisymmetric temperature distribution generates the axisymmetric surface tension distribution with the temperature maximum and the surface tension minimum at the laser-beam axis. Then outward mass transfer occurs radially in the free liquid surface; The liquid molecules are transferred from the centre to the periphery of the heated region and the high local density instability at the periphery turns the mass flow toward the direction of the heated region. The outward surface flow is much faster than the inward return flow. As a result, a pit is observed with a bulge around the periphery on the liquid surface. In a film, the feature of the pit formed by the thermocapillary flow changes depending on a variety of conditions such as the thickness, the surface tension of the film and the energy of the incident laser beam, etc.[9-11] In fact, the formation of a pit may depends upon temperature field and specification of materials like Marangoni number, Rayleigh number, viscosity, and etc.[12,13] The pit formation in liquid was widely studied experimentally[14] and theoretically.[10,15] However, the study of the Marangoni effect in NLCs is scarce. We can find only a few theoretical works[16-18] and only one experimental work.[19] Particularly, the experimental work was made using rather weak laser power and on a surface with a planarly anchoring condition. Physical phenomena observed in NLCs critically depend on surface conditions. Here, we demonstrate the Marangoni effect in a homeotropically aligned NLC mixture by using focused laser beam irradiation along the surface normal, and more importantly the evolution from an axisymmetrical thermocapillary flow (Marangoni flow) to a circular flow about the laser beam axis for the first time.

Experimental

The sample used was a NLC mixture ZLI-2293 (Merck) doped with 0.028 wt% of disperse red 1 dye (λ_{max}=502 nm) to induce the thermal effect by absorbing incident laser light. The clearing point of ZLI-2293 was 85°C, and ordinary and extraordinary refractive indices are n_o=1.499 and n_e=1.6312, respectively. We doped the NLC sample with some inclusions; borosilicate glass microspheres of a diameter 5.1 μm and silica micro-particles of a diameter 0.5 μm without any surface treatment to clearly observe laser-induced flow. The sample was dropped and spread on the cover glass on which a polyimde layer of JALS-204 (JSR Corp.) was spin-coated to achieve homeotropic alignment. Because of a free surface interfaced with air and the homeotropically treated surface, NLC molecules were vertically aligned. The sample thickness measured by a piezo-motor stage was 1-30 μm.

The schematic of the experimental setup is shown in Fig. S1. We used an optical manipulation system consisting of a laser, an inverted microscope, and CCD. The laser beam we used was a linearly-polarized TEM00-mode continuous wave from a semiconductor laser (Coherent, SF 532, 532 nm wavelength). An inverted microscope (Nikon, Ti-U) attached with a CCD camera (QImaging Micropublisher and Point Grey Research) were used for observation. By inserting a filter cube consisting of Exciter ZET532/10x, emitter ET542lp, and dichroic mirror ZT532rdc-UF1 (Chroma technology) in the inverted microscope, we avoid the green laser beam from being incident to CCD. An optical manipulation was done using a 50x microscope objective (NA=0.45) and was also used for heating micro-domain on the free surface of the LC layer, where a pit was formed by thermocapillary-driven flow. The temperature rise was estimated as about 5 K per 0.01 GW/m^2, and the measurements were made mostly at room temperature (more than 60 K below the clearing temperature). Hence, the central part of the sample under laser irradiation was never at the isotropic phase.

The image simulation was carried out at normal incidence of microscope illumination to the sample by software ImageJ.[20] The image simulation using this software was carried out based on the data taken at normal incidence of microscope illumination to the sample (Fig. 1(c)). The 3D surface plot plug-in of the software ImageJ converts the luminance of an image to the relative height profile. A micro-particle was also used to obtain the absolute length.

Results and discussion

We first show main results obtained using a vertically aligned NLC film (about 10-μm thickness) at room temperature. A linearly-polarised laser beam focused into a radius of 7 μm was cast upon the sample along the normal direction (Fig. S1 in ESI[+]).

Fig. 1 shows four series of pictures with increasing laser power (1.26, 2.80, 3.29, and 4.70 mW); (a1-a4) top views through crossed polarisers under vertical light illumination, (b1-b4) top views without polarisers under oblique light illumination (about 15 degrees from the surface normal), (c1-c4) top views without polarisers under vertical light illumination, and (d1-d4) surface views simulated by using (c1-c4) and a software ImageJ.[20] While the images in the a-series are useful to draw the two-dimensional director maps, the images in the b- and c-series clearly show three-dimensional (3-D) topographic structures (d-series). To see the 3D structures clearly, the images in d-series are shown in a reversed fashion between up and down. Namely, for instance, a bump in the images is actually a pit. We can clearly recognise two stages in the a-series; (a1) an extinction cross is observable, (a2) the extinction cross starts to curve, and (a3) and (a4) characteristic spiral patterns are stabilised and developed. Within the sample thickness range from 1 to 30 microns, the phenomenon we can observe in films is qualitatively the same under a certain laser power density except for the following quantitative difference; (1) the size of the defect structures, (2) the threshold laser power density from Marangoni to circular motion, and (3) the frequency of the circular rotational motion.

For more details of the dynamic motions, you can refer to movies in ESI[+] for a- and b-series. In the absence of laser light irradiation, the director was normal to the flat sample surface, so a complete dark image under crossed polarisers were observed. When the irradiation started, mass transportation (thermocapillary flow) from the laser spot position to radial outward directions occurred. Then the director tilted toward the radial direction, resulting in bright regions due to the induced birefringence as shown in Fig. 1(a1). The first dark ring appears when the retardation is equal to π. The estimate of the director tilt from the surface normal is not easy because of the variation of the tilt along the thickness direction and non-uniform sample thickness including a circular bulge with a small pit at the centre (Fig. 1(d1)). But we can roughly estimate the tilt angle as about 30 degrees by assuming uniform tilt and sample thickness. The defect size increases with increasing laser power. The evolution to the second stage (a2-a4) indicates the catastrophic formation of a circular flow, which will be more clearly shown by the movement of inclusions (See Fig. 3 later). Though extensive efforts have been devoted to study peculiar thermocapillary flows induced by laser irradiation both experimentally and theoretically, such circular flow formation through the thermocapillay convection has never been reported. The structure characterisation and the formation mechanism of the vortex is the main topic of this paper, which will be described in the following.

Fig. 2 shows an evolution process from the first (simple pit with bulge) to the second (circular flow motion) stages; (a1) and (a2) the polarising microscope images between crossed polarisers, (b1) and (b2) the director map overlaid on the (a1) and (a2) images, and (c1) and (c2) the corresponding surface profiles. The positional correspondence can be identified by the same colored points in the (a) and (c) series. As the laser power gradually strengthened, thermocapillary convection nature changes from the radial flow to the circular flow associated with the drastic change of both the director orientation and surface topograpy. Namely, a clear extinction cross shown in Fig. 2(a1) became curved and coiled (Fig. 2(a2)), indicating a drastic director orientation change from radial (Fig. 2(b1)) to spirals (Fig. 2(b2)). As one can see that curved dark brushes have opposite handednesses in Fig. 2(a2), the director field is suggested to have two domains, i.e., inner and outer spirals with opposite handednesses, as shown in Fig. 2(b2). In between these spirals, the tilt direction of the director sharply changes with an acute angle, so that at least one of the directors in vortices is neither parallel nor perpendicular to the polarisers, which makes almost continuous bright ring between inner and outer spirals. These director map suggests the formation of circular flow along the bright ring, which will be experimentally proved (see later). Fig. 2(c1) and (c2) clearly shows that this drastic orientational and thermocapillary flow changes are associated with the formation of subsidiary circular bulge structures and a deeper valley (Fig. 2(c2)). Comparison between red points in Fig. 2(a2) and (c2) suggests that the circular flow occurs in the valley. It is not easy to distinguish between cause and effect, since the circular flow and the deep valley are almost simultaneously formed. More detailed obseration and theoretical consideration are necessary to define the causal relationship. The result will be reported in the near future.

Let us now discuss how the evolution from the first radial flow to the second circular flow occurs. With increasing laser power, the pit becomes deep and the bulge becomes sharp, resulting in large bend deformation along radial direction at the surface. As a result, the deformation energy becomes larger, since the bend elastic constant is the largest elastic constants. Then, orientational instability occurs and the director tends to be deflected with respect to the radial direction, resulting in the formation of a circular flow. Conceptual images along with the change are shown in Fig. S2 of ESI^{+}. At this stage, the thermocapillary flow changes the direction from radial to circular, as shown in Fig. 2(b1) and (b2). The circular flow, which is counterclockwise (CCW) in the present case, makes the director field deformed because of their coupling. The director map shown in Fig. 2(b2) is consistent with this consideration. Note that the sense of the molecular flows induced by this circular flow (CCW) inside and outside of the bright ring (Fig. 2(a2)) or a valley (Fig. 2(c2)) is the same (CCW), although the director map shows spirals with opposite handednesses. This consideration including the elastic energy is supported by the experimental fact that the vortex structure never emerges in the isotropic phase.

It is important to comment on the handedness of the flow. Clear curved extinction (spiral) observed in the vicinity of the pit has a handedness of clockwise (CW) both in Figs. 1 and 2. However, we observed those with both handednesses, CW and CCW. Although the present measurements were made using linearly polarised light, we confirmed that the results were not influenced by using circularly polarised light. This means that the vortex formation does not originate from the transfer of the angular momentum of light.[21] It is important to note that a small amount (less than 0.5 wt%) of chiral dopant is effective to control the handedness of the flow; i.e., S811 (Merck, S-form) and CB15 (Merck, R-form) induced CCW and CW rotations, respectively. In chiral systems, the molecular tilt along the radial direction (Fig. 2(b1)) is perturbed by the chiral dopants to make a slight twist along the radial direction, in which the twist sense is determined by the chirality handedness of the chiral dopants. This twist governs the sense of the circular flow motion.

Next, we observed dynamic motions of inclusions. If CW and CCW circular flows exist, the rotations of the inclusions (borosilicate glass microspheres of a diameter 5.1 μm) around the pit must be observed along CW and CCW directions, respectively. Different movements of the inclusions corresponding to the radial and circular flows were clearly observed in Fig. 3 (a) and (b), respectively. A weak convection movement of the inclusions by the thermocapillary radial flow was observed under weak laser irradiation as red dots in Fig. 3(a). In contrast, an orbital motion of the inclusions was observed under higher laser light irradiation, as shown in Fig. 3(b). Videos are avaliable in ESI.[+] Such orbital motion is generally impossible in the convection observed in normal isotropic liquid, so it is the very unique phenomenon observed in NLCs, which have a long-range orientational order and the resultant deformation energy.

The detailed observation of the inclusion motion was made to study the relationship between the laser power and the frequency of the orbital movement. The measurements were made using a laser beam focused into 8 μm in radius onto a NLC sample of about 7-μm thick including inclusions of 0.5 μm in diameter. As shown in Fig. 4, the revolving frequency of the inclusion in NLC micro-rotor linearly increases with increasing incident laser power density with a threshold of about 0.013 GW/m^2, which is the threshold power density for the catastrophic change from radial to circular thermocapillary flows. The evolution of the defect structure with increasing incident laser power density is also shown in Fig. 4.

Summary

We have shown characteristic topographical defect formations and unique flows associated with molecular motions in NLC films with a free surface by focused laser beam incidence normal to the films. Radial movement observed under low laser power is reminiscent of Marangoni effect. Characteristic circular flows were observed for the first time with increasing laser power, which were identified by the destorted director orientations and the movements of inclusions. Qualitative explanation for the evolution from the radial to the circular flow was given based on the elastic deformation energy, which never arises in isotropic liquids and solid films. This kind of induced defect structures enable us to collect and rotate inclusions in NLC media using opto-thermal tweezers.

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Figure Captions

Fig. 1 Typical defect structure changes with increasing laser power (7 μm in radius) observed in a NLC film (10 μm thick) with a free surface at RT. (a1)-(a4) a-series: polarising microscope images between crossed polarisers, that show the evolution of defect structures; (a1) 1.26 mW, (a2) 2.80 mW, (a3) 3.29 mW, and (a4) 4.7 mW. (b1)-(b4) b-series: microscope images without polarisers using obliquely incident light illumination. (c1)-(c5) c-series: microscope images without polarisers using normally incident light illumination for topographic simulation. (d1)-(d5) d-series: surface profile (topographic) images simulated by using software (ImageJ) for each state. Videos are available in ESI[+] for the dynamic motion about the evolutional changes, i.e., a- and b-series.

Fig. 2 (a1) and (a2): Polarising microscope images under (a1) low (1.26 mW) and (a2) high (3.30 mW) laser powers. (b1) and (b2): Corresponding director maps overprinted on the image (a1) and (a2), respectively. (c1) and (c2): Corresponding surface profiles simulated by the imageJ software. The sample thickness was 10 μm, and the measurements were made at RT.

Fig. 3 Movement of inclusions under (a) low (0.9 mW) and (b) high (1.4 mW) laser powers. Dots show the locations (5.1 μm borosilicate glass microspheres) of inclusions taken every 1/30 s intervals. In (a), convection along the radial direction can be seen. In contrast, in (b), an inclusion shows a simple rotation. The movement directions are indicated by thick arrows. See videos in ESI[+] for the dynamics. The sample thickness was 15 μm, and the measurements were made at RT.

Fig. 4 The rotational frequency of an inclusion of 0.5 μm in diameter in NLC micro-rotor as a function of incident laser power density. The sample thickness was 7 μm, and the measurements were made at RT using an incident laser beam with the beam radius of 8 μm.