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Equation (3), which gives the deformation profile of a cell moved at the edges, has unfortunately been mistyped; in its printed form it does not fulfill the requirement for cell symmetry, and it does not satisfy the boundary condition at the edges [$Z(\pm L/2) = S$].

The correct Equation (3) should read: $\beta(x) = 3\left(\frac{2\,|x|}{L}\right)^2 - 2\left(\frac{2\,|x|}{L}\right)^3$.

P H Y S I C A L   R E V I E W   L E T T E R S

Giant Flexoelectricity of Bent-Core Nematic Liquid Crystals

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Flexoelectricity is a coupling between orientational deformation and electric polarization. We present a direct method for measuring the flexoelectric coefficients of nematic liquid crystals (NLCs) via the electric current produced by periodic mechanical flexing of the NLC's bounding surfaces. This method is suitable for measuring the response of bent-core liquid crystals, which are expected to demonstrate a much larger flexoelectric effect than traditional, calamitic liquid crystals. Our results reveal that not only is the bend flexoelectric coefficient of bent-core NLCs gigantic (more than 3 orders of magnitude larger than in calamitics) but also it is much larger than would be expected from microscopic models based on molecular geometry. Thus, bent-core nematic materials can form the basis of a technological breakthrough for conversion between mechanical and electrical energy.

The flexoelectric effect—or coupling between electric polarization and elastic flexure—in nematic liquid crystals (NLCs) was first predicted almost 40 years ago [1]; this effect has the potential to serve as the basis for a wide variety of technologies relying on electromechanical coupling, including strain gauges, actuators, and micropower generators. A flexoelectric polarization $\vec{P}_f$ can arise in a normally apolar NLC when the average direction for orientational order or director $\vec{n}$ is subjected to splay or bend deformations. The effect is enhanced for molecules which possess a permanent dipole moment and shape anisotropies, specifically pear-shaped or banana-shaped molecules. In these cases, orientationally deformed structures having nonzero $\vec{P}_f$ have both closer molecular packing and lower free energy than nonpolar arrangements. The flexoelectric polarization of a standard uniaxial nematic can be expressed in terms of two flexoelectric coefficients e_1 and e_3, corresponding to splay and bend deformations, respectively:

$$\vec{P}_f = e_1 \vec{n}(\text{div}\vec{n}) + e_3(\text{curl}\vec{n}) \times \vec{n}. \qquad (1)$$

In this Letter, we describe a new, direct method for measuring flexoelectric coefficients and apply it to a bent-core nematic (BCN) material. We find that the value of e_3 is about 3 orders of magnitude greater in the BCN than in conventional calamitic (rod-shaped) nematics, making BCNs a potentially viable technology for mechanical to electrical energy conversion.

A molecular statistical approach [2,3] to estimate the flexoelectric coefficients predicts that the bend flexoelectric constant e_3 of a banana-shaped molecule can be related to the kink angle θ_0 in the molecular core [Fig. 1(a)]:

$$e_3 = \frac{\mu_\perp K_{33}}{2k_B T} \theta_0 \left(\frac{b}{a}\right)^{2/3} N^{1/3}. \qquad (2)$$

In this expression, $\mu_\perp$ is the molecular dipole perpendicu-

lar to the molecular long axis, a and b are the length and width of a molecule, respectively [Fig. 1(a)], T is the absolute temperature, N is the number density of the molecules, and K_{33} is the bend elastic constant. This approach assumes that the molecules fluctuate independently. For rod-shaped molecules, $\theta_0 < 1°$, and the flexoelectric coefficients of such NLCs are estimated to be 1–10 pC/m, in reasonable agreement with measured values [4,5]. For typical banana-shaped molecules, however, $\theta_0 \sim 60°$, and thus, all other factors being roughly equal, one might expect BCNs could have e_3 up to 100 times larger due to their distinctive shape. On the other hand, a recent Monte Carlo simulation [6], which also assumes independent molecules (i.e., no clustering or other microstructural organization), indicates no significant flexoelectric enhancement for BCNs. The wide discrepancy in these predictions compels an experimental investigation.

To date, flexoelectric coefficients have been measured mainly using indirect methods, i.e., analyzing optical effects produced by electric field induced director distortions, and typically only either the sum or the difference of the coefficients can be obtained [5]. These methods require knowledge of various material parameters (e.g., birefringence, dielectric and elastic constants, anchoring energies), which ideally should be independently measured, and various authors have obtained different values from the same experimental data sets using different evaluation techniques. Our new method for measuring the flexoelectric coefficient is directly based on the definition, Eq. (1). We induce an oscillatory bend deformation by periodically flexing a thin layer of NLCs contained between nonrigid conducting surfaces and then measure the induced electric current. The method is validated by obtaining literature values on a standard calamitic material. Our experimental setup is sketched in Fig. 1(b). The sample was placed in a temperature regulated box, which has a fixed bottom plate with two vertical, cylindrical posts and
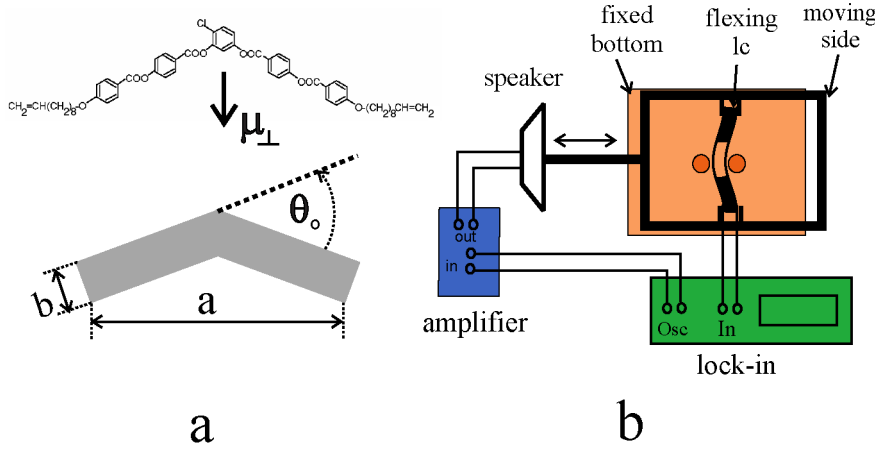
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FIG. 1 (color online). (a) Molecular structure of the bent-core material and its simplified geometrical model. (b) Schematics of the experimental setup.

movable side walls having vertical slots. The LC is confined between flexible electrodes, and this assembly is inserted between the slots and the cylindrical posts as shown. Flexing is achieved by periodically translating the side walls using an audio speaker cone driven by a Regent home theater system model HT-391 amplifier with an input signal from the built-in oscillator of a Perkin Elmer 7265 lock-in amplifier. In order to achieve smooth and uniform motion, the speaker's position was critical and, hence, was adjusted using two perpendicular micropositioners. With this arrangement, the walls of the box oscillate and the NLC sample flexes at the same frequency and amplitude as the speaker.

The electrodes of the liquid crystal cell are connected to the current input of the lock-in amplifier. The precision with which the electric polarization current could be measured using this technique was a few pA. The amplitude of the applied oscillatory deformation was measured with 0.2 mm precision either by mechanical detection or by measuring the intensity of a laser diode through a neutral optical gradient filter fixed to the moving rod connecting the box to the speaker. The temperature of the box was regulated with $\Delta T < 1\,°C$ precision between room temperature and 160 °C. The present setup is limited to oscillation frequencies $f = 1$–10 Hz and amplitudes $S = 0.2$–2 mm. This apparatus allows simultaneous measurement of the temperature, amplitude, and frequency dependence of the current, from which we directly determine the flexoelectric coefficient. Assuming strong planar anchoring boundary conditions of the director at the cell substrates, the periodic flexing of the cell results in a periodic bend distortion of the director, which allows us to measure e_3.

Our cell geometry is shown in Fig. 2. The cell of total length $L_x + 2D$ and width L_y is initially located in the x-y plane; the mechanical displacement occurs along z. The cell is symmetric with respect to its center, so the deformation profile of the substrates is given by an even function $Z(x)$. The current induced by the flexoelectric polarization is $I = \frac{d}{dt} \iint P_f dA$, where dA is the surface area element and

the integration should extend over the whole active area $(X \times Y)$ of the cell. In the planar geometry, only the bend term contributes, so after integration one obtains $I = e_3 Y \frac{d}{dt}[n_z(x = X/2) - n_z(x = -X/2)]$. In case of the small deformations considered here, n_z corresponds to the tangent of the substrates, i.e., $n_z(x) = \frac{\partial Z(x)}{\partial x}$, where $Z(x)$ describes the displacement of the substrates and the sample. The mechanical deformation depicted in Fig. 2 corresponds to the classical problem of "bending an elastic sheet" found in standard texts. These reveal $Z(x) = S\beta(x)$, where

$$\beta(x) = \frac{1}{4}\left\{3\left(\frac{2x}{L_x}\right)^2 - \left(\frac{2x}{L_x}\right)^3\right\}. \tag{3}$$

So, taking into account that the direction is fixed at the edges by the slots, the flexoelectric current becomes $I = e_3 Y \frac{dS}{dt} \frac{d\beta}{dx}\big|_{-X/2}^{X/2} = e_3 Y \frac{dS}{dt}(6X/L_x^2)$. With periodic flexing ($S = S_0 \sin\omega t$), the flexoelectric coefficient can then be determined in terms of the rms induced current I_{rms} as

$$|e_3| = \frac{\sqrt{2}I_{rms}}{6X\omega S_0} \frac{L_x^2}{Y}. \tag{4}$$

As flexible substrates, we first used transparent, 150 μm thick polycarbonate sheets with indium tin oxide conduc-
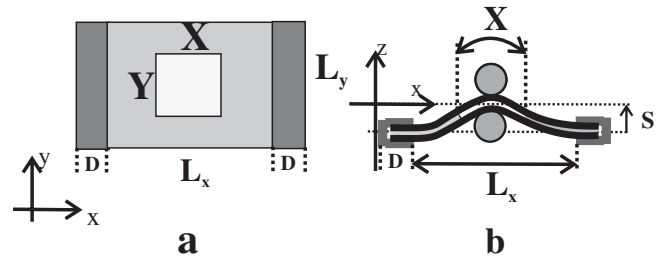

FIG. 2. Model of the sample geometry and deformation of the flexible cell during the periodic vibration driven by the speaker. (a) The geometry of the cell in the xy plane. (b) The cell structure during the deformation.

tive coating sputtered onto their inner surfaces; these were then spin-coated with a polyimide layer and rubbed unidirectionally to achieve uniform planar alignment of the LC director. 20 μm thick samples of the recently characterized [7,8] bent-core NLC 4-chloro-1,3-phenylene bis 4-[4'-(9-decenyloxy) benzoyloxy] benzoate (ClPbis10BB) [9], whose molecular structure is shown in Fig. 1(a), were loaded into cells constructed from these substrates. This material has a monotropic nematic phase during cooling between 78 and 70 °C, but it may be supercooled below 60 °C before crystallization occurs. A typical example of the displacement dependence (parameters: $L_x = 32$ mm, $L_y = 15$ mm) of the induced current for $f = 5$ Hz in a sample at 74 °C, which initially exhibited poor alignment, is shown in Fig. 3(a). One observes that for $S < 1.5$ mm the slope (which determines the flexoelectric constant) is much smaller than for $S > 1.5$ mm. This may indicate a possible improvement of the alignment as a result of flow occurring during periodic flexing (in analogy to flow induced orientation [10]). In this figure, we have also added a point ($\otimes$) which shows the induced current in a well-aligned sample. As the dashed line indicates, the data from zero through this point extrapolate into agreement with the initially poorly aligned sample at sufficiently large $S(\sim 3$ mm). The temperature dependence of the flexoelectric constant $|e_3|$, as calculated from Eqs. (3) and (4) with $S_0 = 0.7$ mm and $f = 5$ Hz on the well-aligned sample, is shown in Fig. 3(b).

The temperature dependence of the flexoelectric response shows a sharp increase at the transition from the isotropic to the nematic phase, having a maximum at the transition of 62 nC/m at 70 °C, before the crystallization starts. This value is over *1000 times larger* than usual for calamitic NLCs and more than 10 times larger than is predicted from calculations based upon molecular shape [2].

The polycarbonate cells yielded unambiguous measurements of the flexoelectric current in the bent-core NLC material and also permitted optical inspection of the alignment before and after making measurements. However, we
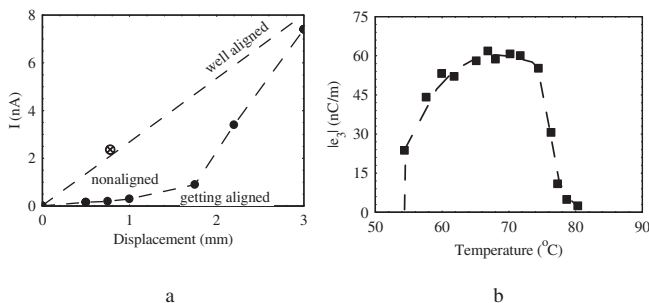
need to have a reference measurement on a standard calamitic nematic liquid crystal to verify the validity of the new measurement technique. For this, we chose 4-cyano-4'-*n*-pentyl-biphenyl (5CB) [11], because it is one of the few nematics that are both stable and for which published values of both e_1 and e_3 exist [12]. Moreover, they are both relatively large and in the same order of magnitude (in spite of the mainly longitudinal dipole); therefore, the measured flexoelectric signals are not sensitive to the alignment in the cell. Unfortunately, however, on the polycarbonate cells the weak flexoelectric signal from 5CB was not measurable due to a 100 pA background current, which we believe to be caused by electrostatic charging of the plastic. Moreover, at the elevated temperatures necessary for the bent-core NLC, the material leaked out after a large number of flexing cycles. For this reason, we also encased the bent-core compound and 5CB between 0.1 mm thick brass plates with 25 μm Mylar spacers interposed between them; the LC remained in a 1 cm × 1 cm area in the center of the plates. The inner surfaces of this cell were rubbed unidirectionally to promote uniform alignment along the rubbing direction. With this construction, no NLCs leaked out of the brass cell over repeated measurements, and the sensitivity of the experiment was great enough so that the flexoelectric current in a rod-shaped control nematic material could be measured.

The relative temperature dependences of the bend flexoelectric constants of both ClPbis10BB and 5CB (measured with $S_0 = 2$ mm and $f = 3.2$ Hz for ClPbis10BB and $S_0 = 1.5$ mm and $f = 5$ Hz for 5CB) are plotted in Fig. 4. On the same overall scale, we see that the flexoelectric constant of 5CB is practically zero compared to that of the BCN material ClPbis10BB, which on cooling attains a peak value of roughly 35 nC/m about 2.5 °C

FIG. 3. (a) Displacement dependence of flexoelectric current (in rms values) of ClPbis10BB at 74 °C; (b) the temperature dependence of $|e_3|$ of a well-aligned cell measured at 5 Hz in 15 mm × 15 mm active area plastic cells.
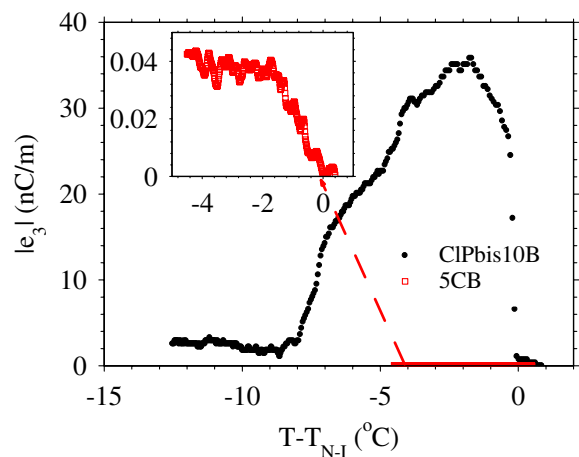

FIG. 4 (color online). Variation of the flexoelectric coefficient on a relative temperature scale $T - T_{N-I}$ for the bent-core liquid crystal ClPbis10BB and for the calamitic liquid crystal 5CB measured in cells of $A = 1$ cm^2 active areas. The inset shows part of the figure ($|e_3|$ of 5CB) at a magnified scale.

below the isotropic-nematic transition. In the inset, it is seen that the flexoelectric coefficient e_3 of 5CB is clearly larger than the measurement error and increases from zero to about 40 pC/m on cooling into the nematic phase. Available literature data for the flexoelectric coefficients of 5CB, obtained by electro-optical techniques using hybrid aligned cells [12,13], give $e_1 - e_3 = 25$ pC/m and $e_1 + e_3 = 11$ pC/m at 25 °C [12]. The reasonable agreement between the magnitudes of the flexoelectric coefficient of 5CB measured electro-optically in previous work and directly in the present work validates our new technique for flexoelectric measurements.

The peak value of $|e_3|$ for the bent-core material measured in the brass cell is $|e_3| = 35$ nC/m, about half of that we have measured in the well-aligned plastic cell. Comparing this value with those measured on an initially unaligned plastic cell as a function of amplitude [see Fig. 3(a)], we see good agreement at the same 2 mm displacement used in the brass cell. This indicates the alignment in the brass cell is due to the bending related flow. Comparing the flexoelectric coefficient with other calamitic compounds such as N-(p-methoxybenzylidene)-p'-buthylaniline ($e_3 = 3$–20 pC/m depending on the technique used [5(b),5(c),14–16]), which like ClPbis10BB has a transverse molecular dipole, we see that the flexoelectric response of our very first bent-core nematic is truly gigantic, over 3 orders of magnitude larger than of typical rod-shaped nematics.

All of our attempts to measure the flexoelectric response of ClPbis10BB with the classical method in hybrid aligned cells failed, as the resulting alignment was almost planar even near the homeotropically aligned surface. Given the results shown above, this is perfectly understandable, since in hybrid cells flexoelectric polarization results in an internal dc electric voltage [5] $U_e = [-(e_1 + e_3)/2\varepsilon_0\varepsilon_a] \times \ln(\varepsilon_{||}/\varepsilon_{\perp})$. While in calamitics $|U_e|$ is in the order of a few volts, for BCN it becomes a few kilovolts, which due to the negative dielectric anisotropy of the material induces planar alignment in the vast majority of the volume.

Since the models or simulations based on ''independent'' molecules that we are aware of cannot account for the enormous flexoelectric effect observed in our bent-core nematic, we propose that the arrangement of molecules with respect to each other on the nanoscopic scale must play a decisive role. We estimate that an arrangement in which molecules are grouped together in polar ''clusters'' containing a few tens of molecules would be sufficient to explain the results. In fact, the results of a recent dynamic light scattering study [7] of the nematic phase of ClPbis10BB are consistent with local clustering or association of the molecules.

In summary, we have demonstrated a new, electromechanical method to detect flexoelectric current in NLCs. In

principle, this technique is capable of measuring the individual flexoelectric coefficients by selecting planar alignment for e_3 and homeotropic alignment for e_1. We have applied the method to measure, for the first time, the flexoelectricity of bent-core liquid crystals, which was found to be 3 orders of magnitudes larger than in a standard calamitics. Based on this giant flexoelectric effect, bent-core nematic materials must be viewed as a highly promising platform for a new breakthrough in technology for conversion of mechanical to electrical energy at the molecular scale.

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