

Overlooked Ionic Phenomena Affecting the Electrical Conductivity of Liquid Crystals [†]

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Abstract: Liquid crystal devices such as displays, various tunable optical components, and sensors are becoming increasingly ubiquitous. Basic physical properties of liquid crystal materials can be controlled by external physical fields thus making liquid crystal devices dynamically reconfigurable. The tunability of liquid crystals offers exciting opportunities for the development of new applications, including advanced electronic and photonic devices, by merging the concepts of flat optics, tunable metasurfaces, nanoplasmonics, and soft matter biophotonics. As a rule, the tunability of liquid crystals is achieved by applying an electric field. This field reorients liquid crystals and changes their physical properties. Ions, typically present in liquid crystals in minute quantities, can alter the reorientation of liquid crystals through the well-known screening effect. Because the electrical conductivity of thermotropic liquid crystals is normally caused by ions, an understanding of sources of ion generation in liquid crystals is of utmost importance to existing and emerging technologies relying on such materials. That is why measurements of electrical conductivity of liquid crystals is a standard part of their material characterization. Measuring the electrical conductivity of liquid crystals is a very delicate process. In this paper, we discuss overlooked ionic phenomena caused by interactions of ions with substrates of the liquid crystal cells. These interactions affect the measured values of the DC electrical conductivity of liquid crystals and make them dependent on the cell thickness.

Keywords: liquid crystals; liquid crystal devices; ions; ion generation; electrical conductivity

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1. Introduction

Liquid crystals continue to be at the heart of modern technologies. They include ubiquitous liquid crystal displays (LCD) and liquid crystal on silicon (LCoS) displays for virtual and augmented reality [1], polarization and phase control devices (waveplates and retarders) [2,3], tunable components of biomedical equipment (lenses, filters for hyperspectral imaging) [4,5] and reconfigurable elements of plasmonic [6] and meta-devices [7], diffractive optical elements [8], spatial light modulators and beam-steering devices [9], light shutters [10,11,12], smart windows [13,14], various tunable signal processing devices operating at microwave and millimeter wave frequencies [15], and countless others.

As a rule, the tunability of the aforementioned devices is achieved by exploiting the electric-field induced reorientation of liquid crystal materials [9]. This reorientation can be altered by the electric field screening effect caused by ions normally present in liquid crystals in minute quantities [16,17]. In the case of displays, ions in liquid crystals can lead to many undesirable effects including image flickering, image sticking, reduced voltage holding ratio, and overall slow response [16,17]. There are also liquid crystal applications

relying on ions. For example, liquid crystal shutters [10-12] and smart windows [13,14] are receiving increasing attention these days.

An importance of ions in liquid crystal materials has been recognized since the early 1960s [16,17]. Since that time numerous reports have been published aimed at broadening our understanding of mechanisms of ion generation in liquid crystal materials [16,17,18 and references therein].

Typically, information about ions in liquid crystals is obtained by performing electrical measurements [19,20,21,22]. Such measurements utilize sandwich-like liquid crystal cells [19-22]. The obtained experimental results are used to extract the value of the DC electrical conductivity, ion mobility, and their bulk concentration [19-22]. In the majority of the reports, electrical measurements are performed at only a single value of cell thickness [23]. At the same time, a very limited number of measurements carried out using several cells with different thickness reveal an important experimental fact that the measured electrical parameters of liquid crystals in general can depend on the cell gap [20,21,24,25]. Unfortunately, only a very limited set of experimental data is available. An analysis of the dependence of the electrical conductivity of liquid crystals on the cell thickness is still missing. In this paper, we discuss how interactions between ions and substrates of the liquid crystal cell make their DC electrical conductivity dependent on the cell thickness.

2. Model

In the case of molecular thermotropic liquid crystals, their finite DC electrical conductivity λ_{DC} is caused by ions. It can be written as (1):

$$\lambda_{DC} = \sum_i q_i \mu_i n_i \tag{1}$$

where q_i is the charge of the i -th ion, μ_i is the mobility of the i -th ion, and n_i is its volume concentration [16,17]. In the case of two types of symmetric monovalent ions ($q_i = |e|$ ($i = 1,2$), $n_1^+ = n_1^- = n_1$, $\mu_1 = \mu_1^+ + \mu_1^-$, $n_2^+ = n_2^- = n_2$, $\mu_2 = \mu_2^+ + \mu_2^-$) the electrical conductivity can be rewritten as (2)

$$\lambda_{DC} = |e|(\mu_1 n_1 + \mu_2 n_2) \tag{2}$$

where $|e| = 1.6 \times 10^{-19} C$.

The bulk concentration of ions can be computed by applying a recently developed model [26,27]. This model considers the possibility of both ion capturing and ion releasing regimes in liquid crystal cells. The ion releasing regime takes place if substrates of a liquid crystal cell are contaminated with ions prior to filling the cell with liquid crystals. In this case contaminated substrates act as sources of ion generation in liquid crystals. The trapping of ions by the substrates (in the simplest case via physical or chemical adsorption) results in the ion capturing regime. The processes of ion capturing and ion generation are described by rate equation (3):

$$\frac{dn_j}{dt} = -k_{Sj}^{a\pm} n_j \frac{\sigma_{Sj}}{d} (1 - \theta_{S1}^{\pm} - \theta_{S2}^{\pm}) + k_{Sj}^{d\pm} \frac{\sigma_{Sj}}{d} \theta_{Sj}^{\pm} \tag{3}$$

where the subscript j stands for the dominant type of symmetric ions in liquid crystals ($j = 1,2$); $k_{Sj}^{a\pm}$ is the effective rate constant of the ion capturing process of n_j^+ and n_j^- ions on the surface of substrates, and $k_{Sj}^{d\pm}$ is the effective rate constant of the ion releasing process of n_j^+ and n_j^- ions from the substrates; and θ_{Sj}^{\pm} is the fractional surface coverage

of substrates defined for the j -th ions; σ_{sj} is the surface density of all surface sites of the liquid crystal substrates; n_j is the concentration (volume density) of mobile ions of the j -th type ($j = 1,2$); d is the thickness of the cell [26,27].

The conservation of the total number of ions of the j -th type can be written as Equation (4):

$$n_{0j} + \frac{\sigma_{sj}}{d} v_{sj} = n_j + \frac{\sigma_{sj}}{d} \theta_{sj}^{\pm} \tag{4}$$

where v_{sj} is the contamination factor of substrates [26,27]. The applicability of Equations (3) and (4) to describe ion capturing and ion generating processes in liquid crystals was discussed in several recent papers [26,27].

3. Results

DC electrical conductivity of liquid crystal cells as a function of their thickness was computed using equations (2)-(4). Table 1 lists values of basic physical parameters used to generate graphs shown in Figures 1-2. As a rule, electrical measurements of liquid crystals are carried out using liquid crystal cells. The presence of substrates can lead to several ionic processes. The capturing of ions by substrates results in the ion capturing regime whereas the use of contaminated substrates leads to the ion releasing regime. Normally, ions which are already present in the liquid crystal bulk prior to filling an empty cell get captured by the substrates once the cell is filled. This scenario is shown in Figures 1(a) and 2(a). At the same time, if substrates of the empty cell are contaminated with ions, these ions contaminate liquid crystal materials upon filling the cell as can be seen in Figures 1(b) and 2(b). The combination of these two, ion-releasing and ion-capturing, processes can result in a non-trivial dependence of the electrical conductivity on the cell thickness (Figures 1(c) and 2(c)).

Table 1. Values of physical parameters used to model DC electrical conductivity.

Physical parameter	Value
$K_1 = \frac{k_{S1}^a}{k_{S1}^d}$	10^{-21} m^3
$K_2 = \frac{k_{S2}^a}{k_{S2}^d}$	10^{-22} m^3
$K_3 = \frac{k_{S3}^a}{k_{S3}^d}$	10^{-23} m^3
$K_4 = \frac{k_{S4}^a}{k_{S4}^d}$	10^{-21} m^3
$\sigma_{S1} = \sigma_{S2}$	$5 \times 10^{16} \text{ m}^{-2}$
$\mu_1 = \mu_2$	$10^{-10} \text{ m}^2/\text{Vs}$
v_{S1}	0
v_{S2}	10^{-3}
n_{01}	$6 \times 10^{18} \text{ m}^{-3}$
n_{02}	0

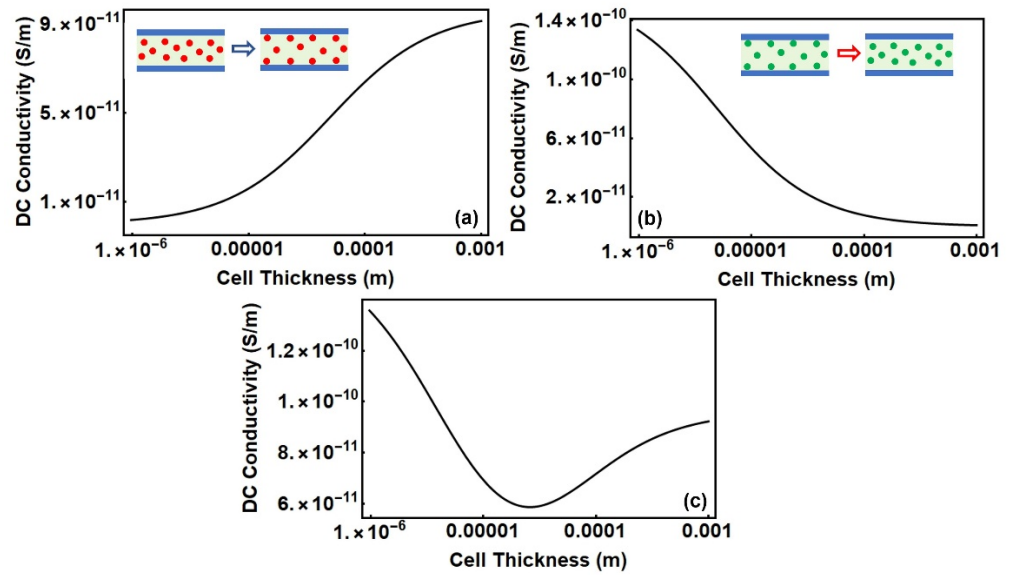


Figure 1. DC conductivity of liquid crystals as a function of the cell thickness. (a) DC conductivity caused by ions already present in liquid crystals. Values of parameters used in simulations are listed in Table 1 ($n_{01}, \nu_{S1}, \mu_1, \sigma_{S1}, K_1$). (b) DC conductivity due to ions originated from contaminated substrates of the liquid crystal cell. Values of parameters used in simulations are listed in Table 1 ($n_{02}, \nu_{S2}, \mu_2, \sigma_{S2}, K_2$). (c) DC conductivity caused by the combination of ion-capturing and ion-releasing processes shown in Figure 1(a) and Figure 1(b). Values of parameters used in simulations are listed in Table 1 ($n_{01}, n_{02}, \nu_{S1}, \nu_{S2}, \mu_1 = \mu_2, \sigma_{S1} = \sigma_{S2}, K_1, K_2$).

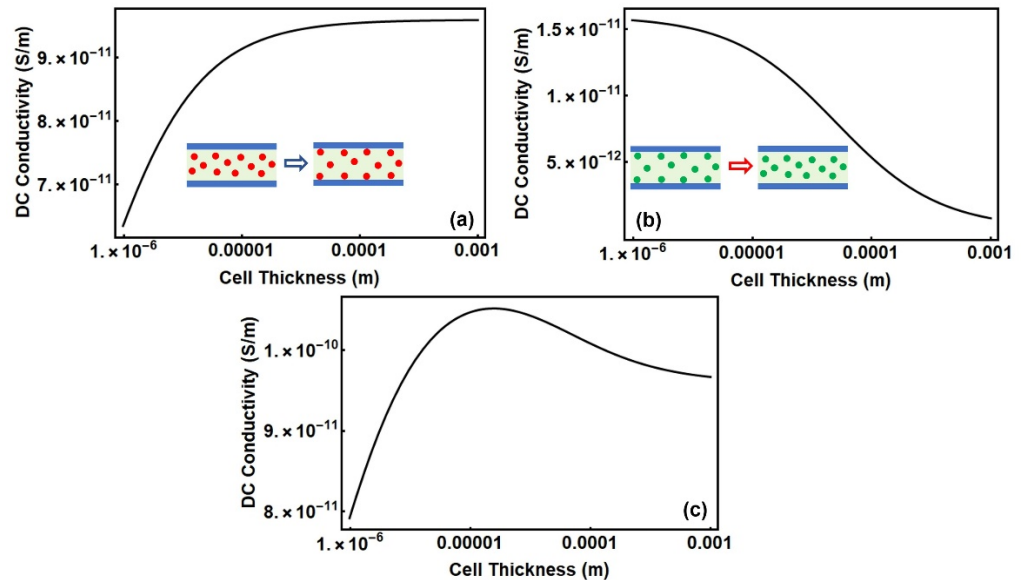


Figure 2. DC conductivity of liquid crystals as a function of the cell thickness. (a) DC conductivity caused by ions already present in liquid crystals. Values of parameters used in simulations are listed in Table 1 ($n_{01}, \nu_{S1}, \mu_1, \sigma_{S1}, K_3$). (b) DC conductivity due to ions originated from contaminated substrates of the liquid crystal cell. Values of parameters used in simulations are listed in Table 1 ($n_{02}, \nu_{S2}, \mu_2, \sigma_{S2}, K_4$). (c) DC conductivity caused by the combination of ion-capturing and ion-releasing processes shown in Figure 1(a) and Figure 1(b). Values of parameters used in simulations are listed in Table 1 ($n_{01}, n_{02}, \nu_{S1}, \nu_{S2}, \mu_1 = \mu_2, \sigma_{S1} = \sigma_{S2}, K_3, K_4$).

4. Conclusion

The dependence of DC electrical conductivity on cell thickness shown in Figures 1 and 2 has important practical implications. It suggests an importance to consider interactions between ions and substrates of the liquid crystal cell. These interactions can result in the combination of ion capturing and ion releasing effects. A striking manifestation of this interplay between ionic processes is a non-monotonous dependence of the conductivity on the cell thickness exhibiting either minimum (Figure 1(c)) or maximum (Figure 2(c)). It should be noted that ionic processes caused by the presence of substrates get weaker and become almost negligible if very thick (> 100 μm) cells are used (Figures 1 and 2). Because typical cells used in experiments are normally much thinner (1 – 20 μm), the consideration of the dependence of DC electrical conductivity on the cell thickness is very important and should not be ignored. Electrical measurements of this type allow for the correct evaluation of the true values of the electrical parameters of liquid crystal materials. Moreover, they can also reveal possible sources of ionic contamination of substrates of liquid crystal cells.

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