Research

Importance of the Critical Point in Thermotropic Nematic Liquid Crystals in Terms of Their Sensitivity

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Abstract:
The critical point (*CP*) of liquid crystals has proven to be of immense significance in terms of their sensitivity and their ability to respond to even the slightest external stimuli, such as surface interactions and applied electric or magnetic fields. In this article we focus on the mathematical approach to achieving the the minimal free energy potential of a ther-motropic liquid crystal - which we prove to happen at the *CP* - via an applied external electric field and surface interactions caused by biomolecules at the interface. We graph-ically present the free energy behavior, which can be simplified to a 4th order polynomial. We also explain how this phenomenon could be used to achieve extremely high sensitivity in liquid crystalline sensors, based on nematic liquid crystal droplets (temperature sensors, biodetectors, light-sensitive sensors). We also give a few plausible causes and mechanisms responsible for heightened sensitivity directly related to the *CP* in general.

Keywords: Critical point; Liquid crystal sensors; Mesoscopic modeling

1. Introduction

Liquid crystals (LCs) have been present in complex biological organisms for millennia; however, the soft matter has been relatively thoroughly studied and explained in the last two centuries. Liquid crystalline formations (liquid crystal matter) are essential for the survival of most living creatures, including ourselves, homo sapiens sapiens, the modern human. The first liquid crystal to be discovered was myelin, which is a substance found in nerve cells and is responsible for the isolation and transmission of electrical impulses across nerves.

LCs are also building blocks of most cell membranes in form of phospholipid molecules. These, when exposed to water, turn their hydrophobic tails in a way as to make a construction commonly referred to as the lipid bilayer membrane, which exhibits LC behaviour (Seddon & Templer, 1991). This type of construction is energetically most stable. Primitive cell membranes can easily be formed with a combination of oil and water. This is useful for research purposes, and the classification of the properties exhibited by liquid crystals.

In this article, we shall take a deeper look at the fundamental physical properties of thermotropic LCs and how they react to external stimuli, such as an applied electric or magnetic field, and surface interactions caused by biomolecules such as phospholipids at the interface. We will mathematically explain the behaviour of the free energy potential and why the critical point is important for the sensitivity of liquid crystal sensors that use liquid crystal droplets as their means of sensing.

2. Liquid Crystal Sensors

The usefulness of LCs in terms of sensing is shown in an example of a thermotropic LC in an aqueous environment, where the long range orientational order is described by the order parameter $\boldsymbol{S}$. In the isotropic phase, the order parameter is equal to $\boldsymbol{S} = \boldsymbol{0}$ and, in the nematic phase, is equal to $\boldsymbol{S} = \boldsymbol{1}$, meaning we have complete order, and the long axes of LC molecules are oriented in a single direction. We call this a uniaxial state. A phase transition from an isotropic to nematic state is a symmetry-breaking phenomenon, and LCs in the low-temperature nematic phase become immensely sensitive to external perturbations. If we add organic molecules to an NLC in water, we notice this impacts the local change in the nematic director field $\hat{\boldsymbol{n}}$, especially when LC droplets are present (Kaučič et al., 2004). The change in the nematic field orientation is directly correlated to the type of organic molecules the LC (or LC droplet) interacts with. We choose the type of LC based on the type of interaction between the LC and the organic molecules, which either classifies whether they are compatible or incompatible for a desired type of sensor (Lowe & Abbott, 2011). The conjuction of the properies of LCs (softness and directional order, susceptibility to external fields) and the properties of organic molecules (affinity to adhere to surfaces through polar interactions and their chemical similarity to other LCs) makes an effective sensory system. A system such as that described above is well known, however if we take into account the critical point, which is well defined by the phase behavior of water when pressure and temperature are not fixed variables, it is possible to enhance the sensitivity of such sensory systems to an unprecedented accuracy. The critical point is the point above which phase transitions are no longer discontinuous: they become phase transitions of the 2nd order. The enthalpy of a continuous phase transition above the critical point is negligible (Zid et al., 2024). At the critical point the free energy is highly dependent on the order parameter, which is proven by the extremely shallow energy potential in the vicinity of a steady state. When the system is at the critical point, in our case, the first three derivatives of the free energy function in terms of order parameter are equal to zero.

3. Mathematical Model

To mathematically describe the behavior of LCs at the critical point and their free energy potential, we begin by defining a traceless and symetric tensor $\boldsymbol{Q}$ as follows:

$$Q = S\left(\hat{\boldsymbol{n}} \otimes \hat{\boldsymbol{n}} - \frac{I}{3}\right), \tag{1}$$

where $\underline{I}$ is the identitiy tensor, S the order parameter and $\hat{\boldsymbol{n}}$ the unit length of the nematic director $\vec{\boldsymbol{n}}$. If we add organic molecules such as phospholipids to the LC, the volume concentration ϕ is:

$$\phi = \frac{N_{om} v_{om}}{V}, \tag{2}$$

where N_{om} is the number of organic molecules in a volume V and v_{om} the average volume of an organic molecule. Considering the symmetrically relevant energy contributions obtained by the Taylor series, we write the free energy ($\boldsymbol{F}$) of the system as:

$$F = \int_V f_v \; d^3\vec{\boldsymbol{r}} + \sum_j \oint f_i^{(j)} \, d^2\vec{\boldsymbol{r}}, \tag{3}$$

where the voulmetric free energy density ($f_v = f_c + f_e + f_f$) contains the energy contributions of condensation, elasticity and field, respectively. $f_i^{(j)}$ represents the free energy density at the organic molecule-LC interface and measures the local interaction strength of the j^{th} organic molecule and the closest LC molecule. We assume a spatially homogenious nematic field along which we apply an external electric field, and we assume the structural equivalence of all organic molecules, meaning each of them has the same surface free energy contribution. In this case, we write the energy contributions as:

$$f_c = \frac{3}{2}a_0(T - T^*)TrQ^2 - \frac{9}{2}b(TrQ^3) + \frac{9}{4}c(TrQ^2)^2, \tag{4a}$$

$$f_e \sim 0, \tag{4b}$$

$$f_p = -\frac{3}{2}\varepsilon_0 \Delta\varepsilon \vec{\boldsymbol{E}} \cdot Q\vec{\boldsymbol{E}}, \tag{4c}$$

and

$$f_i^{(j)} = -\frac{3}{2}w^{(j)} \;\; \hat{\boldsymbol{e}}_{\boldsymbol{i}} \cdot Q\hat{\boldsymbol{e}}_{\boldsymbol{i}}. \tag{\boldsymbol{4d}}$$

In subEqs. (4) the parameters a_0, b and c represent the Taylor series coefficients, whereas $T^*$is the lowest supercooling metastable isotropic phase temperature (Zid et al., 2024), which is similar to the lowest water vapor temperature in the temperature region, where liquid phase is stable. $w^{(j)}$ is the anchoring energy density of an organic molecule along the unit vector $\hat{\boldsymbol{e}}_{\boldsymbol{i}}$. The local nematic field orientation is closely dictated by the interaction between the LC and an external electric field $\vec{\boldsymbol{E}}$, which is described by subEq. (4c). In the subEq. (4c) we use a Legendre polynomial of the 2nd order $P_2(cos\theta) = (3\cos^2\theta - 1)/2$, where θ is the angle between $\vec{\boldsymbol{E}}$ and $\hat{\boldsymbol{n}}$. To clarify, let us expand the final scalar product in subEq. (4c):

$$\vec{\boldsymbol{E}} \cdot Q\vec{\boldsymbol{E}} = \left(\hat{\boldsymbol{E}} \cdot \hat{\boldsymbol{n}}\right)^{\boldsymbol{2}} - \frac{E^2}{3} = \frac{2E^2}{3}P_2(cos\theta), \tag{5a}$$

which is the same as:

$$\left(\hat{\boldsymbol{E}} \cdot \hat{\boldsymbol{n}}\right)^{\boldsymbol{2}} - \frac{E^2}{3} = \frac{2E^2}{3}P_2(cos\theta). \tag{5b}$$

We notice that the value of the expression in subEq. (5a) is highest when $\theta = 0°$. Subsequently the term $\boldsymbol{\Delta\varepsilon}$ in subEq. (4c) enforces a nematic field orientation along the electric field's orientation. A few important average values of the 2nd order Legendre polynomial are 0, 1 and -1/2. Values 0 and 1 are extreme values and mean that we may have complete alignement of LC molecules with the direction of an applied electric field or no alignment at all. In subEq. (4d) they also measure the angle between organic molecules and the surface of an LC droplet. We express the average free interaction energy of organic molecules (F_i) as:

$$F_i = N_{om}a_{om}\bar{f}_i^{(j)}, \tag{6}$$

where $\bar{f}_i^{(j)} = w^{(j)}S\overline{P_2}$ is the average interaction free energy of one organic molecule and $\boldsymbol{a_{om}}$ the area of the organic molecule. If we take into consideration Eqs. (2) and (4d), we can rewrite Eq. (6) as follows:

$$F_i = -V\phi\frac{a_{om}}{v_{om}}w^{(j)}S\overline{P_2}. \tag{7}$$

Considering the relation $F_i/V \ = \bar{f}_\iota$, we can expand the average interaction free energy densitiy as:

$$\bar{f}_\iota = -\phi\frac{a_{om}}{v_{om}}w^{(j)}S\overline{P_2}. \tag{8}$$

Now, the system's effective free energy ($\tilde{f}_v$) is approximately expressed as $\tilde{f}_v \sim F/V$, which is the same as:

$$\tilde{f}_v \sim \bar{f}_c + \bar{f}_f - \phi\frac{a_{om}}{v_{om}}w^{(j)}S\overline{P_2(\vec{\boldsymbol{e}_\iota} \cdot \vec{\boldsymbol{n}})}. \tag{9}$$

We assume that all organic molecules take up the same area and $\overline{P_2(\vec{\boldsymbol{e}_\iota} \cdot \vec{\boldsymbol{n}})}$ is the average orientation of an organic molecule at the interface. $\vec{\boldsymbol{e}_\iota}$ is the anchoring direction, locally enforced by the organic molecule. For general purposes we now switch to a dimensionless notation by introducing the dimensionless order parameter s as follows:

$$s = \frac{S}{S_0}, \tag{10}$$

where $S_0 = b/2c$. We then rewrite the subEq. (4a) like so:

$$f_c = a_0(T - T^*)S^2 - bS^3 + cS^4 \tag{11}$$

and, while taking into account Eq. (10) also as:

$$f_c = cS_0^4\left[\frac{a_0(T - T^*)}{cS_0^2}s^2 - \frac{b}{cS_0}s^3 + s^4\right]. \tag*{(12}$$

Considering the expression $S_0 = b/2c$ and Eq. (12), we can define the reduced temperature r^{ef} as:

$$r^{ef} = \frac{a_0(T - T^*)4c}{b^2}, \tag{13}$$

which also satisfies the phase transition condition at the value $r^{ef} = 1$. Eq. (13) can otherwise be expressed as:

$$r^{ef} = \frac{T - T^*}{T_{IN} - T^*}. \tag{14}$$

We now obtain a relation $T_{IN} = T^* + b^2/(4a_0c)$, which is the phase transition temperature from an isotropic to nematic phase in a thermotropic liquid crystal and it's droplets, formed at the interface. The sum of $\overline{f_f}$ and $\overline{f_\iota}$ can be writen as:

$$\overline{f_f} + \overline{f_\iota} = \left[-\varepsilon_0 \Delta\varepsilon E^2 - \phi w \frac{a_{om}}{v_{om}}\right] \overline{P_2} S, \tag{15}$$

Which is equal to:

$$\overline{f_f} + \overline{f_\iota} = a_0(T_{IN} - T^*) S_0^2 [-\sigma_E - \sigma_w] \overline{P_2} s, \tag{16}$$

where the following relations hold:

$$\sigma_E = \frac{\varepsilon_0 \Delta\varepsilon E^2 S_0}{a_0(T_{IN} - T^*) S_0^2} \tag{17a}$$

and

$$\sigma_w = \frac{\phi w a_{om} S_0}{v_{om} a_0(T_{IN} - T^*) S_0^2}. \tag{17b}$$

From Eq. (17b) it's clear, that the value of the parameter σ_w is heavily dependent on the geometry (a_{om} and v_{om}) of the organic molecule (can also be a nanoparticle or other impurity), material properrties (a_0, T_{IN}, T^* and S_0) and the concentration of oorganic molecules (ϕ). The effective control parameter is now $\sigma^{ef} = \sigma_E + \sigma_w$. Considering Eqs. (12) and (13), we can rewrite Eq. (9) as:

$$\widetilde{f_v} = f_0(r^{ef} s^2 - 2s^3 + s^4 - \sigma^{ef} s). \tag{18}$$

We now introduce the dimensionless effective free energy density $\tilde{f} = \widetilde{f_v}/f_0$, where $f_0 = a_0(T_{IN} - T^*)S_0^2$, as:

$$\tilde{f} = r^{ef} s^2 - 2s^3 + s^4 - \sigma^{ef} s. \tag{19}$$

Eq. (19) can be expanded as:

$$\tilde{f} = A(s - s_1)^2 (s - s_2)^2 + B, \tag{20}$$

where A and B are constants, and s_1 and s_2 the effective free energy function zero values. If we equate the the coefficients in Eqs. (19) and (20), we obtain the next relations:

$$\sigma^{ef} = 2A(s_1^2 s_2 + s_1 s_2^2), \tag{21a}$$

$$r^{ef} = A(s_1^2 + 4s_1s_2 + s_2^2), \tag{21b}$$

$$s_1 = 1 - s_2 \tag{21c}$$

And

$$A = 1. \tag{21d}$$

We now minimize the system's free energy by demanding that the first derivative of function given by Eq. (19), being $\tilde{\boldsymbol{f}}(\boldsymbol{s})$, is equal to zero. We now obtain three possibilities: a minimum, a maximum or curve. The minimum is determined by the second derivative condition $\partial^2\tilde{f}/\partial s^2 > 0$. The third derivative gives the rate of change in curvature and at the *CP* it hold, that it is also equal to zero, meaning it's a flat line. The conditions which are unequivocally true at the *CP* are as follows:

$$\frac{\partial^2\tilde{f}}{\partial s^2} = 0 \tag{22a}$$

and

$$\frac{\partial^3\tilde{f}}{\partial s^3} = 0. \tag{22b}$$

The 1st order pahse transition conditions are given by:

$$r^{ef} = 1 + \sigma^{ef} \tag{23a}$$

And

$$\sigma^{ef} < \sigma_{cp}^{ef}. \tag{23b}$$

At the *CP* it then holds: $r_{cp}^{ef} = 1 + \sigma_{cp}^{ef}$ and $\sigma^{ef} = \sigma_{cp}^{ef}$. When conditions given by subEqs. (23) are realised, the following is also true:

$$s_c^{(-)} = \frac{1 - \sqrt{1 - 2\sigma^{ef}}}{2} \tag{24a}$$

and

$$s_c^{(+)} = \frac{1 + \sqrt{1 - 2\sigma^{ef}}}{2}, \tag{24b}$$

where $s_c^{(-)}$ and $s_c^{(+)}$ are the minima of the $\tilde{f} = \tilde{f}(s)$ function. The relation $s_c(\sigma^{ef})$ is shown in **Figure 1**.

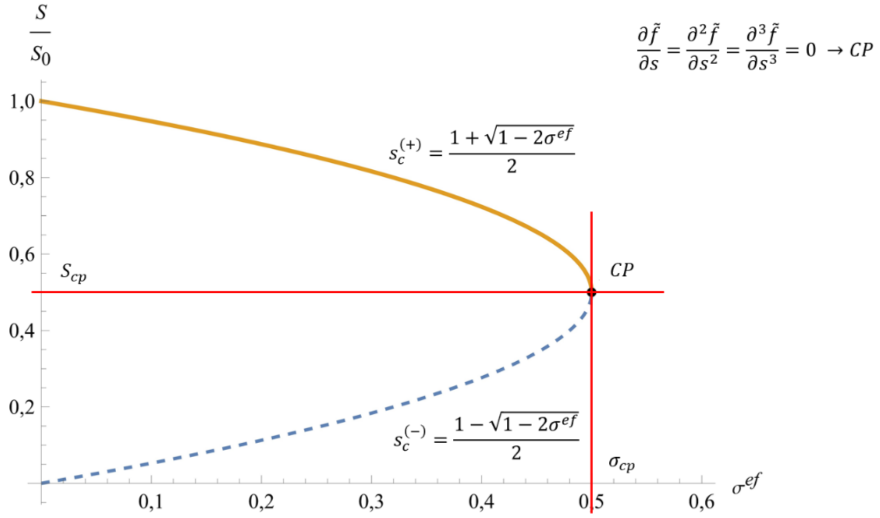

Figure 1. The relation between the normalized order parameter s and the effective control parameter σ^{ef}. The orange curve represents values of $s_c^{(+)}$ and the blue one the values of $s_c^{(-)}$. The black dot marks the critical point *CP* which has the coordinates (1/2, 1/2). S_{cp} is the critical value of the order parameter S and σ_{cp} the critical value of the effective control parameter σ^{ef}. Red lines help in marking the CP's coordinates.

The minimization of the effective free energy, as shown in this example, can only be used when the system is completely homogenious; the parameters in Eqs. (15-17b) are spatially unrelated. At the *CP* the condition $s_c^{(+)} = s_c^{(-)}$ is true. Higher values of σ^{ef} than σ_{cp}^{ef} cause a supercritical phase behavior (Immanuel et al., 2019). Our system is at the *CP* when the following is true:

$$\sigma_{cp}^{ef} = \frac{1}{2}, r_{cp}^{ef} = \frac{3}{2} \quad , s_{cp} = \frac{1}{2}. \tag{25}$$

Normalized values of the free energy density function $\tilde{\boldsymbol{f}}(\boldsymbol{s})$ are shown in **Figure 2**.

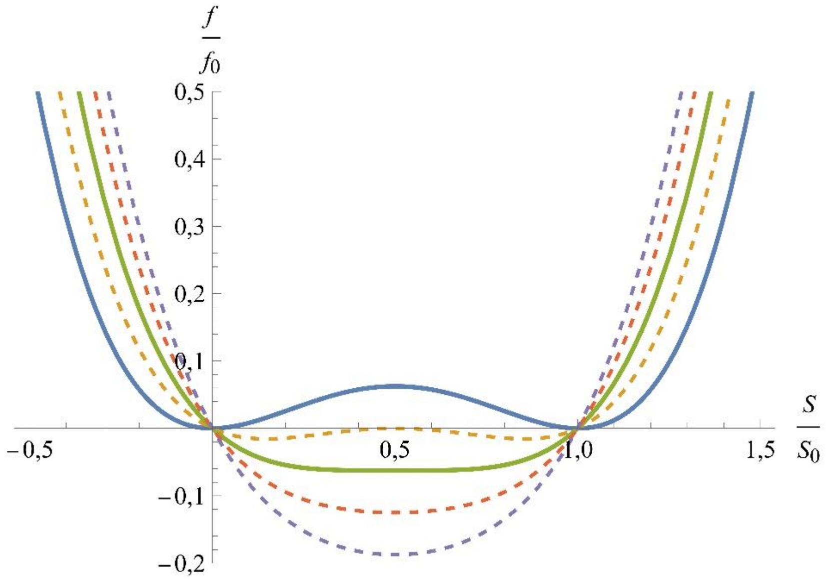

Figure 2. Free energy density during phase transition. Dark blue curve: $\sigma^{ef} = 0$, orange slitted curve: $\sigma^{ef} = 0{,}25$, green curve: $\sigma^{ef} = 0{,}5$, red slitted curve: $\sigma^{ef} = 0{,}75$, purple slitted curve: $\sigma^{ef} = 1$.

We observe that the potential becomes incredibly flat at the *CP*. Subsequently, this enables strong fluctuations in the LC molecule orientation, which in turn gives a very sensitive system, the phase of which can be changed by the slightest external perturbation, which can easily be observed qualitatively. Similar techniques and phenomena could be useful in future sensory systems, where precision and sensitivity are of utmost importance (in medicine for dosing antibiotics, in food industry for dosing aditives or in biology for measuring the concentrations of biomolecules present in a sample).

4. Experimental Relevance

Experimentally, the sensitivity of LC droplets is usually measured in an aqueous environment where liquid crystal droplets have formed. We may introduce low-wavelenght light or impurities such as nanoparticles or biological molecules into such an environtment. We then observe at what intensity of light or concentration of impurities the LC droplets reconfigure form usually bipolar to radial configuration and obtain an effective measuring system that can further be used in real-scenario sensors that are sensitive to light or different molecular structures. If, in such experiments, the LC was at its critical point, the sensitivity would cerainly be higher, because the free energy pottential for a phase transition is already at it's minimum, which causes the energy difference between competing structural configurations to also be minimized. In the following paragraphs, we shall discuss additional causes for enhanced sensitivity at the *CP*.

At the *CP*, a few very important mechanisms are responsible for enhancing the sensitivity of LC droplets and LCs in general. The first one is the divergence of correlation length. This is the distance over which fluctuations in molecular alignment are correlated. Because these distances become large, the result is the collective mollecular behavior over macroscopic distances, making discussed sensory systems highly responsive to small perturbations in temperature, external fields and stress (Nicastro, 1984).

The relaxation time for fluctuations increases dramatically at the *CP*, meaning the system takes longer to return to equilibrum state after being perturbed. This phenomenon amplifies the effects of external perturbations, acting as a magnifying glass in terms of sensitivity. We call this critical slowing down (Zid et al., 2024).

Thermal fluctuations in order parameter (***S***), such as the degree of molecular alignment in LCs, are amplified and make the system more sensitive to external forces, which can significantly alter the phase state that the system is in.

Finally, at the *CP*, the response of an LC to external fields oftern becomes nonlinear, due to the system's inherent instability and the competition between different phases.

5. Conclusion

Liquid crystal formations have been around for millenia, and while incredibly important for living beings, they are also very useful in sensory systems. Their susceptibility to exxternal magnetic and electric fields or impurities makes them excellent candidates for electrical appliances such as LC displays. It also makes them great test subjects in environments, where our goal is to measure a certain concentraion of nanoparticles or biomolecules in an aqueous environment and the sensitivity of certain electric fields and magnetic fields.

The mathematical model is very important in determining what mainly causes an LC to change its phase and how to finely tune its sensitivity through the mentioned perturbations. It also shows that a complex free energy system can easily be generalized by a 4th order polynomial to show the change in its potential below, at and above the critical point. Through this we can easily determine where the system is the most sensitive.

Conflicts of Interest: The author declares no conflict of interest.

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