Research

Volume and Surface Phase Transitions in Confined Nematic Liquid Crystals

Švajger Blaž[1],*, Pal Kauskih[2], Kralj Samo[1]

1. University of Maribor, Faculty of Natural Sciences and Mathematics, Department of Physics, Maribor, Slovenia
2. University Centre for Research and Development (URCD), Department of Physics, Chandigarh University, Mohali, India

* Correspondence: Blaž Švajger; blaz.svajger1@gmail.com

Abstract:
We study bulk and surface phase transitions in confined nematic liquid crystals exhibiting 1st order isotropic-nematic phase transition in bulk systems. We demonstrate analytically that confinement could in general quantitatively and even qualitatively modify phase behavior. Furthermore, we show that confining substrates could enable surface phase transitions. Studied phase behaviors could be applied also to other condensed matter systems displaying 1st order continuous symmetry order-disorder phase transition if the relevant order parameter amplitude is linearly coupled to a local surface ordering field.

Keywords: Liquid crystals; Phase transition; Confined nematic liquid crystal; Surface phase transition

Citation: Švajger B, Pal K, Kralj S. Volume and surface phase transitions in confined nematic liquid crystals. Proceedings of Socratic Lectures. **2025,**12(II), 120-125. https://doi.org/10.55295/PSL.12.2025.II12

1. Introduction

Liquid crystals (LCs) exhibit both liquid and crystal-type of order (Kleman & Lavrentovich, 2004). They consist of weakly interacting anisotropic molecules in which relatively fast noncollective fluctuations average out microscopic details. The resulting system exhibits orientational or even translational order that could be well theoretically described by mesoscopic order parameter fields. Due to microscopic averaging the resulting phase behaviour on varying a relevant control parameter (temperature, pressure, concentration of LC molecules…) often exhibits several universal features, which depend mostly on the symmetry properties of order parameter.

In this contribution we focus on thermotropic nematic LCs consisting of rod-like molecules which in bulk systems (where confinement effects could be neglected) exhibit on varying temperature 1st order isotropic (I) – nematic (N) phase transition. The isotropic phase possesses liquid-like isotropic behavior, where all directions in space are equivalent. This phase is stable at relatively high temperatures. On decreasing temperature, the nematic phase is formed which in bulk equilibrium exhibits spatially homogeneous uniaxial order along a single symmetry breaking direction. On the other hand, the center of mass of molecules could flow like in a liquid. Note that due to the continuous symmetry breaking any spatial direction could be chosen. For this reason, the system could exhibit the so-called Goldstone modes (Kleman & Lavrentovich, 2004), due to which LC order could be relatively easily excited by various perturbations. Because of this susceptibility to various stimuli, LCs are also referred to as soft materials. Furthermore, uniaxial orientational order of transparent LC molecules yield optic anisotropy. Therefore, nematic LCs are particularly useful for sever applications which rely on fast enough external electric or some other field driven optical changes.

In this contribution we illustrate analytically how a confinement of nematic LC within a plan-parallel cell could affect its phase behavior which could be quantitatively and even qualitatively different from bulk behavior.

2. Material and Methods

We use a minimal model to describe the impact of confinement on the I-N phase behaviour. We use a Landau-de Gennes type modelling where one determines the nematic orientational order by the scalar order parameter S and the nematic director field $\hat{\boldsymbol{n}}$. This unit vector defines a local uniaxial direction of nematic order, where the states $\pm\hat{\boldsymbol{n}}$ are physically equivalent. The amplitude S determines the degree of nematic order and S=1 corresponds to the maximal nematic order, where LC molecules would be firmly aligned along $\hat{\boldsymbol{n}}$.

In our approximate treatment we allow spatial variations along a single coordinate, say x-axis of the Cartesian coordinate system (x,y,z). We use a one-dimensional system which is enough to identify key mechanisms that can impact I-N phase behavior. For simplicity we parametrize the director as $\hat{\boldsymbol{n}}=(\sin\theta,\cos\theta,0)$. In terms of $S(x)$ and $\hat{\boldsymbol{n}}(\boldsymbol{x})$ we express the free energy of the system, where LC is confined between parallel plates placed at $x = 0$ and $x = h$, where h stands for the cell thickness. The free energy F per surface area A is given by (Ranjkesh et al., 2014)

$$\frac{F}{A}=\int_0^h\left[f_c+f_e+f_f\right]dx+f_i(x=0)+f_i(x=h) \tag{1}$$

in terms of the condensation (f_c), elastic (f_e), external field (f_f), and interfacial (f_i) free energy densities. Here we assume that an external electric field $\vec{\boldsymbol{E}}=E\hat{\boldsymbol{e}}$ is also present, enforcing orientation parallel to $\hat{\boldsymbol{e}}$. The condensation term determines S in bulk equilibrium, the elastic terms penalize spatial variations in orientational order, the field term tends to align LC molecules along the external field direction for LCs with positive dielectric anisotropy, and the interfacial term determines conditions at LC confining substrates. We express the free energy densities in the simplest form, where we include only the key terms affecting the LC phase behavior. It follows (Ranjkesh et al., 2014)

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

$$f_e = \frac{L}{2}\left(\frac{\partial S}{\partial x}\right)^2 + \frac{LS^2}{2}\left(\frac{\partial \theta}{\partial x}\right)^2 , \tag{2b}$$

$$f_f = -\frac{\Delta\varepsilon\varepsilon_0 E^2}{2} S P_2(\hat{n}.\hat{e}), \tag{2c}$$

$$f_i = -\frac{wS}{2}. \tag{2d}$$

Here a_0, T^*, b, c, L are positive material parameters, $P_2(x) = (3x^2 - 1)/2$, ε_0 is the vacuum permittivity and $\Delta\varepsilon$ is the LC dielectric anisotropy. We set that the interfacial term locally supports nematic, order. Consequently, the interaction (wetting) strength constant w is positive. For simplicity we set that the conditions at both confining substrates are the same.

3. Results

3.1. *Spatially homogeneous system*

Firstly, we consider systems in which w is relatively weak. To simplify the problem, we neglect spatial variations in S and set $P_2 = 1$ (i.e., $\hat{\boldsymbol{n}}$ is aligned along $\vec{\boldsymbol{E}}$). Furthermore, we rewrite the free energy into a dimensionless form. For this purpose, we introduce scaled quantities

$$s = \frac{S}{S_0}, u = \frac{x}{h}, r = \frac{T - T^*}{T_{IN} - T^*}. \tag{3}$$

where $S_0 = b/(2c)$ is the equilibrium order parameter at the bulk I-N phase transition temperature $T_{IN} = T^* + \frac{b^2}{4a_0 c}$. Here *s*, *u* and *r* stand for the scaled nematic order parameter, dimensionless Cartesian coordinate and temperature, respectively.

Furthermore, we introduce the material dependent lengths (Kleman & Lavrentovich,2004) that characterise the nematic response to different perturbations:

$$\xi_e = \sqrt{\frac{L{S_0}^2}{\Delta\varepsilon\varepsilon_0 E^2 S_0}}, \xi_{IN} = \sqrt{\frac{L}{a_0(T_{IN} - T^*)}}, d_e = \frac{LS_0}{w}. \tag{4}$$

Here ξ_e, ξ_{IN} and d_e stand for the external electric field extrapolation length, nematic order correlation length and interface extrapolation length. All these distances characterise bulk LC responses and could be measured. They are temperature dependent and for this reason we express them at T_{IN}.

Taking this into account we obtain the following expression for the scaled free energy

$\tilde{f} = \frac{F}{A\ \ a_0(T_{IN} - T^*){S_0}^2 h}$:

$$\tilde{f} = r_{eff} s^2 + 2s^3 + s^4 - \sigma_{eff} s. \tag{5}$$

In this expression we introduced the scaled effective temperature r_{eff} and the scaled effective interaction σ_{eff}:

$$r_{eff} = r + \frac{\xi_{IN}^2}{h^2}\tilde{g}_e, \tag{6}$$

$$\sigma_{eff} = \frac{\xi_{IN}^2}{\xi_e^2} + \frac{\xi_{IN}^2}{h\ \ d_e}, \tag{7}$$

where

$$\tilde{g}_e = \int_0^1 \left(\frac{\partial \theta}{\partial u}\right)^2 du \tag{8}$$

One can obtain phase transition conditions analytically by assuming that at a phase transition the free energies of the competing phases are equal. Therefore, $\tilde{f}$ could be expressed as

$$\tilde{f} = A(s - s^{(+)})^2 (s - s^{(-)})^2 + B \tag{9}$$

where $s^{(+)}$ and $s^{(-)}$ determine equilibrium values of order parameter just above and below the phase transition. By equating Eq.(5) and Eq.(9) we got a system of equations by requiring that coefficients in front of s, s^2, s^3 and s^4 are equal. The resulting phase transition conditions read

$$r_{eff}^{(c)} = r_c + \frac{\xi_{IN}^2}{h^2} \tilde{g}_e = 1 + \sigma_{eff}, \tag{10a}$$

$$s^{(-)} = \frac{1 + \sqrt{1 - 2\sigma_{eff}}}{2}, \tag{10b}$$

$$s^{(+)} = \frac{1 - \sqrt{1 - 2\sigma_{eff}}}{2} \tag{10c}$$

providing the effective interaction σ_{eff} is weak enough:

$$\sigma_{eff} < \sigma_c = 0.5. \tag{11}$$

Here $r_{eff}^{(c)}$ and r_c determine values of r_{eff} and r at the transition. In the supercritical regime, where $\sigma_{eff} > \sigma_c$, the phase transition is replaced by gradual variation of orientational order on varying the temperature.

3.2. *Nonhomogeneous system*

Next, we consider regime where w is relatively large. Consequently, we assume that above each confining substrate a thin surface layer (we refer to it as an *interface*) exists where the degree of order is larger than in the remaining LC volume (i.e., *volume* in continuation). We set that $s \sim s_i$ and $s \sim s_v$ in the *interface* and *volume* part of the system. Furthermore, we assume that the *interface* width is roughly given by the nematic correlation length ξ.

The average dimensionless free energy in the *volume* part of the system is roughly given by

$$\tilde{f}_V \sim r_{eff}^{(v)} s_v^2 - 2s_v^2 + s_v^2 - \sigma_{eff}^{(v)} s_v, \tag{12}$$

where

$$r_{eff}^{(v)} = r + \frac{\xi_{IN}^2}{h^2} \tilde{g}_e^{(v)}, \sigma_{eff}^{(v)} = \frac{\xi_{IN}^2}{\xi_e^2}. \tag{13}$$

On the other hand, the phase behaviour of *interfaces* is roughly described by

$$\tilde{f}_i \sim \Delta u \left[r s_i^2 - 2s_i^3 + s_i^4 + s_i^2 \tilde{g}_e^{(i)} \frac{\xi_{IN}^2}{h^2} - s_i \frac{\xi_{IN}^2}{\xi_e^2} \right] - s_i \frac{\xi_{IN}^2}{d_e h}, \tag{14}$$

where $\Delta u \sim \xi / h$. It follows

$$\frac{\tilde{f}_i}{\Delta u} \sim r_{eff}^{(i)} s_i^2 - 2s_i^2 + s_i^2 - \sigma_{eff}^{(i)} s_i. \tag{15}$$

$$r_{eff}^{(i)} = \frac{T - T^*}{T_{IN} - T^*} + \frac{\xi_{IN}^2}{h^2} \tilde{g}_e^{(i)}, \sigma_{eff}^{(i)} \sim \frac{\xi_{IN}}{d_e}. \tag{16}$$

In expressing $\sigma_{eff}^{(i)}$ we assumed $\xi_{IN} \sim \xi$.

Phase behaviours in the *volume* and *interface* part can be solved analytically as described in the previous subsection. In the *volume* part subcritical behaviours are obtained for $\sigma_{eff}^{(v)} < \sigma_c \equiv 0.5$. In this regime a *volume* 1st phase transition occurs when the condition

$$r_{eff}^{(v,c)} = \frac{T_c - T^*}{T_{IN} - T^*} + \frac{\xi_{IN}^2}{h^2}\tilde{g}_e^{(v)} = 1 + \sigma_{eff}^{(v)} \qquad (17)$$

is fulfilled. If $\sigma_{eff}^{(v)} > \sigma_c$ the *volume* LC exhibits noncritical behaviour, i.e., s_v varies gradually on varying the temperature.

Similarly, the *interfacial* part exhibits a 1st order phase transition if $\sigma_{eff}^{(i)} < \sigma_c$ and the phase transition is determined by

$$r_{eff}^{(i,c)} = \frac{T_c - T^*}{T_{IN} - T^*} + \frac{\xi_{IN}^2}{h^2}\tilde{g}_e^{(i)} = 1 + \sigma_{eff}^{(i)}. \qquad (18)$$

4. Discussion

We analyzed analytically phase behavior is system where the surface interaction is relatively weak or strong. In the first case one sensibly assume a homogeneous order in the whole system and the effective free energy is given by Eq.(5). Minimization of free energy reveals that the system exhibits 1st order phase transition only in the regime $\sigma_{eff} < 0.5$. In this case the phase transition temperature T_c is given by Eq.(10a), yielding

$$\Delta T_c = (T_{IN} - T^*)\left(\frac{\xi_{IN}^2}{\xi_e^2} + \frac{\xi_{IN}^2}{h\ d_e} - \frac{\xi_{IN}^2}{h^2}\tilde{g}_e\right), \qquad (19)$$

where $\Delta T_c = T_c - T_{IN}$ measures the temperature shift with respect to the bulk system. One sees that the external electric field and the surface wetting interaction tend to increase the phase transition temperature. Note that the surface contribution scales with $1/h$. Hence, its impact increases on decreasing h. Furthermore, elastic distortions decrease T_c. Furthermore, in the subcritical regime (i.e., $\sigma_{eff} < \sigma_c$) the system exhibits finite ordering also above T_c providing $\sigma_{eff} > 0$, to which one commonly refers as the *paranematic* order. Values of nematic and paranematic order just below and above T_c are given by Eq.(10b) and Eq.(10c), respectively. Note that for $\sigma_{eff} = 0$ it holds $s^{(-)} = 1$ and $s^{(+)} = 0$, where the paranematic phase is replaced by isotropic order.

In the supercritical regime, where $\sigma_{eff} > \sigma_c$, the phase transition is replaced by a gradual variation of orientational order on varying the temperature. The condition separating critical and subcritical regime is determined by

$$\frac{\xi_{IN}^2}{\xi_e^2} + \frac{\xi_{IN}^2}{h\ d_e} = 0.5. \qquad (20)$$

This condition can be reached either by a strong enough electric field or by a large enough surface interaction strength, where in the latter case the critical interaction strength decreases with decreasing h.

On the other hand, if w is relatively strong then one should distinguish between volume and interface LC contribution. In general, they could exhibit different phase behaviour what has been also experimentally observed (Boamfa et al., 2003). In such cases the volume part exhibits a 1st order phase transition if $\frac{\xi_{IN}^2}{\xi_e^2} < 0.5$ (see Eq.(13)) where

$$\Delta T_c^{(v)} = (T_{IN} - T^*)\left(\frac{\xi_{IN}^2}{\xi_e^2} - \frac{\xi_{IN}^2}{h^2}\tilde{g}_e^{(v)}\right). \qquad (21)$$

If $\frac{\xi_{IN}^2}{\xi_e^2} > 0.5$ systems exhibit gradual evolution of order on varying the temperature.

On the contrary, interfaces exhibit 1st order phase transitions if $\frac{\xi_{IN}}{d_e} < 0.5$ (see Eq.(17)) where it holds

$$\Delta T_c^{(i)} = (T_{IN} - T^*)\left(\frac{\xi_{IN}}{d_e} - \frac{\xi_{IN}^2}{h^2}\tilde{g}_e^{(i)}\right). \qquad (22)$$

For $\frac{\xi_{IN}}{d_e} > 0.5$ interfaces exhibit gradual phase behaviour.

Note that in such cases $T_c^{(v)}$ and $T_c^{(i)}$ (i.e., volume and interface phase transitions) are in general different. Furthermore, it might happen, for example, that the volume part exhibits the noncritical behaviour and the interface subcritical behaviour.

5. Conclusions

In this contribution we addressed phase behavior in confined nematic liquid crystals using a minimal model. We focused on key features that quantitatively or even qualitatively alter the bulk discontinuous I-N phase transition. Note that the approach shown could be applied also to other systems in which order parameter could exhibit different symmetries. For example, nematic LC possesses an axial symmetry and similar approach could be used to model ferromagnetic or ferroelectric systems, where one can use a vector field for the mesoscopic order parameter field. The following conditions need to be fulfilled to apply the illustrated approach to a different system: (i) the system should in bulk exhibit 1st order phase transition, (ii) continuous symmetry breaking should be realized in the phase transition (i.e., the symmetry broken phase should exhibit infinity different but equivalent ground states), (iii) the order parameter amplitude, measuring the strength of order (i.e. S in our illustration) should be linearly coupled to the relevant ordering field.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Boamfa MI, Kim MW, Maan JC, Rasing T. Observation of surface and bulk phase transitions in nematic liquid crystals. Nature. 2003;421(6919):149-152. DOI:10.1038/nature01331
2. Kleman M, Lavrentovich O. Soft Matter Physics: An Introduction; Springer Science & Business Media: New York, 2004. DOI: 10.1007/b97416
3. Ranjkesh A, Ambrožič M, Kralj S, Sluckin TJ. Computational studies of history dependence in nematic liquid crystals in random environments. Phys. Rev. 2014; E 89, 022504. DOI: 10.1103/PhysRevE.89.022504