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Binary Mixture Composed of Nematic Liquid Crystal and Carbon Nanotubes: A Theoretical Description

Vlad Popa-Nita and Robert Repnik

Abstract

Based on the phenomenological model first presented by van der Schoot et al., which predicts the alignment of carbon nanotube (CNT) dispersions in thermotropic nematic liquid crystals, we present the extensive results concerning the phase diagram and the orientational properties of the mixture in this chapter.

Keywords: liquid crystal, carbon nanotube, phase transition

1. Introduction

A method to obtain aligned CNTs (necessary for applications) is to disperse them into liquid crystals (LCs) [with their self-organization (long-range orientational order) and fluidity] [1–9]. The thermotropic [10–13] and the lyotropic LCs [14–17] have been used to align CNTs parallel as well as perpendicular to average direction of alignment of long axes of LC molecules called the director. As a consequence, the orientational order parameter of CNTs could have the values between 0.6 and 0.9. The study of mixture composed by LCs and CNTs is also important due to the influence of CNTs on the physical properties of LCs (increased dielectric anisotropy, decreased threshold voltage, much accelerated electrooptical response) [18–25].

The main hypothesis used in the theoretical study of the collective behavior of CNTs dispersed in the isotropic solvents [26–28] as well as in LCs [29–36] is that they can be considered as rigid rod polymers [37].

Using the density functional theory, the isotropic-liquid crystal phase transition has been analyzed considering the van der Waals attractive interactions [26]. Onsager theory of rigid rods [38] was used to study the phase behavior of CNTs dispersed into organic and aqueous solutions [27]. Also, the Onsager model including length polydispersity and solvent-mediated interaction was considered to study the dispersions of CNTs in superacids [28]. These theoretical studies lead to the conclusion that to obtain orientational order of CNTs at room temperature it is necessary that the van der Waals interactions must be screened out, i.e., the CNTs must be dispersed in a good solvent. In the case of a non-good solvent, no liquid crystalline phases of CNTs form at room temperature because only dilute solutions are thermodynamically stable.

Matsuyama [29, 30] used a mean field theory to analyze the phase behavior of a mixture composed of low-molecular-weight liquid crystal and a rigid rod-like polymer such as CNTs. The free energy is constructed on the basis of Onsager model for excluded volume interactions, the Maier-Saupe model for orientational-dependent attractive interactions, and the Flory-Huggins theory for binary mixtures.

In the previous papers [31, 32, 34–36], we have presented a phenomenological theory to describe the alignment of CNT dispersions in thermotropic nematic LCs. We combined the Landau-de Gennes [39, 40] free energy for thermotropic ordering of the LC solvent and the Doi free energy [41–43] for the lyotropic orientational order of CNTs. Because the CNT is much thinner than the elastic penetration length, the alignment of CNTs in the nematic solvent is caused by the coupling of the LC director field to the anisotropic interfacial tension of the CNTs. This is true only for very dilute solutions without large aggregates [33]. Density functional calculations [44] show that CNT alignment mechanism in LC is associated with a strong interaction due to surface anchoring with a binding energy of -2eV for $\pi - \pi$ electron stacking between LC molecules and CNT.

In the present chapter, we extend this model to generalize the anisotropic interaction form between a CNT and the liquid crystal molecules including the possibility of perpendicular alignment.

The remainder of this chapter is organized as follows. In Section 2, we describe the model. In Section 3, we illustrate the results and finally give the main conclusions in Section 4.

2. Model

The free energy density of the binary mixture composed of CNTs and thermotropic nematic LC contains three terms:

$$f = f_{CNT} + f_{LC} + f_{CNT/LC} \quad (1)$$

where f_{CNT} represents the Doi free energy density of CNTs, f_{LC} represents the Landau-de Gennes free energy density of the nematic liquid crystal order, and $f_{CNT/LC}$ takes into account the interaction of these two components.

2.1 Free energy of carbon nanotubes

At the mesoscopic level of description, the free energy of CNTs can be written in the following form [31]:

$$f_{CNT} = k_B T \left[\frac{1}{v_{LC}} (1 - \phi) \ln (1 - \phi) + \frac{1}{v_{CNT}} \phi \ln \phi \right] + k_B T \frac{L \phi^2}{6 v_{CNT}} \left[\left(\frac{3}{L \phi} - 1 \right) S_{CNT}^2 - \frac{2}{3} S_{CNT}^3 + S_{CNT}^4 \right] \quad (2)$$

where the first two terms represent the entropy of isotropic mixing of CNTs and LC components [45] and the third one is obtained from the Onsager theory [38] using the Smoluchowski Equation [41, 42]. In this form, the van der Waals attractions between CNTs are neglected. The long-ranged intermolecular attractions between CNTs were considered in [36]. $v_{LC} \approx \pi l d^2 / 4$ represents the volume of one LC molecule with length $l \approx 3 \text{ nm}$ and diameter $d \approx 0.5 \text{ nm}$, and $v_{CNT} \approx \pi L_0 D^2 / 4$ is the volume of one CNT with length $L_0 \approx 400 \text{ nm}$ and diameter $D \approx 2 \text{ nm}$. The values cited

above are those used in this paper. In Eq. (2), k_B is the Boltzmann constant, T is the absolute temperature, ϕ represents the volume fraction of CNTs, $1 - \phi$ defines the volume fraction of the LC, and $L = L_0/D$ is the aspect ratio of a CNT.

Eq. (2) defines a first-order isotropic-nematic phase transition of CNTs with the equilibrium values of the order parameters $S_{CNT,iso} = 0$ and $S_{CNT,nem} = 0.3365$ and of the volume fractions, respectively, $\phi_{iso} = 0.01349$ and $\phi_{nem} = 0.01351$. These equilibrium values of the parameters are obtained minimizing the free energy (2) with respect to S_{CNT} and equating the chemical potentials of CNTs ($\mu_{CNT} = v_{CNT} [f_{CNT} + (1 - \phi)\partial f_{CNT}/\partial \phi]$) and of LC ($\mu_{LC} = v_{LC} (f_{CNT} - \phi\partial f_{CNT}/\partial \phi)$) in the two phases. The model predicts a relative variation of the volume fraction of CNTs (the Flory “chimney”) at the transition of 0.19%, while the prediction of Onsager and Flory [38, 46] for monodisperse lyotropic LC is about 1%, and the experimental results obtained by the polarized light microscopy for an aqueous dispersion of multiwall carbon nanotube indicate a biphasic region that range between 1 and 4% [47, 48]. The discrepancy is due to polydispersity, as well as the possibility of segregation which the model does not consider.

2.2 Free energy of thermotropic liquid crystal

To characterize the isotropic-nematic phase transition of thermotropic LC, we use the Landau-de Gennes [39] free energy:

$$f_{LC} = (1 - \phi) \left[\frac{3}{2} a (T - T^*) S_{LC}^2 - \frac{3}{4} B S_{LC}^3 + \frac{9}{4} C S_{LC}^4 \right] \quad (3)$$

where T^* is the undercooling limit temperature of stability of the isotropic phase and the constant coefficients a , B , and C depend on the material. Later, in our numerical calculations presented in Section 3, we consider the following values: $T^* = 307.55$ K, $a \approx 3.5 \cdot 10^4$ J · m⁻³ · K⁻¹, $B \approx 7.1 \cdot 10^5$ J · m⁻³, and $C \approx 4.3 \cdot 10^5$ J · m⁻³ [40, 49–51], values specific for pentylcyanobiphenyl (5CB). For this nematogen, the first-order isotropic-nematic phase transition takes place at temperature $T = T_{NI} = T^* + B^2/24aC = 308.95$ K with $S_{LC,iso} = 0$ and $S_{LC,nem} = B/6C = 0.2752$.

2.3 The coupling free energy

The condition of weak anchoring limit of the interaction between the two components is $D \ll \xi$, where the diameter of a CNT is $D \approx 2$ nm and $\xi = K/W \approx 10^{-5}$ m is the elastic penetration length ($K \approx 10^{-11}$ N is a typical elastic constant, and $W \approx 10^{-6}$ N/m is a typical anchoring energy).

The coupling free energy has been explained in [31], and it has the following form:

$$f_{CNT/LC} = -\gamma \phi S_{LC} S_{CNT} \left(1 - \frac{1}{2} S_{CNT} \right) \quad (4)$$

where $\gamma \equiv \frac{4}{3} W/D$ defines the coupling parameter. Thus, for the same anchoring energy, the coupling parameter in the case of thin rods is larger than that of the thick one. From the experimental results, we find that the value of the coupling parameter can be between $10^{-3} - 10^3$ N · m⁻². In the limit of large coupling $\gamma \rightarrow \infty$, the orientational order of CNTs is perfect $S_{CNT} \rightarrow 1$.

We note that positive values of γ characterize a parallel alignment of LC molecules to CNTs. In this chapter we extend our analysis considering also negative

values of γ which characterize a perpendicular alignment. Depending on the orientational order parameters S_{CNT} and S_{LC} , two nematic phases could be defined: (i) the N_1 phase with $S_{CNT} > 0$ and $S_{LC} > 0$ (parallel alignment of CNT and LC molecules) and (ii) the N_2 phase with $S_{CNT} < 0$ and $S_{LC} > 0$ (perpendicular alignment of CNT and LC molecules). These two phases are experimentally obtained depending on the surface treatment of the CNTs.

2.4 The total free energy density of the binary mixture

Finally, the total free energy density of the binary mixture (1) is the sum of the free energy densities of CNTs (2), thermotropic LC (3), and interaction between nematic CNTs and nematic LC (4):

$$\begin{aligned}
 f = & k_B T \left[\frac{1}{v_{LC}} (1 - \phi) \ln (1 - \phi) + \frac{1}{v_{CNT}} \phi \ln \phi \right] \\
 & + k_B T \frac{L\phi^2}{6v_{CNT}} \left[\left(\frac{3}{L\phi} - 1 \right) S_{CNT}^2 - \frac{2}{3} S_{CNT}^3 + S_{CNT}^4 \right] \\
 & + (1 - \phi) \left[\frac{3}{2} a (T - T^*) S_{LC}^2 - \frac{3}{4} B S_{LC}^3 + \frac{9}{4} C S_{LC}^4 \right] \\
 & - \gamma \phi S_{LC} S_{CNT} \left(1 - \frac{1}{2} S_{CNT} \right)
 \end{aligned} \tag{5}$$

3. Results

We present the main results concerning the phase behavior of the CNT-LC binary mixture as a function of temperature, volume fraction ϕ of CNTs, and coupling strength γ .

3.1 Positive γ : critical point of CNT phase transition

The positive value of the interaction parameter γ defines the nematic N_1 phase with $S_{CNT} > 0$ and $S_{LC} > 0$ (the rod and the LC molecules are parallel to each other). The isotropic phase of CNTs is transformed into a nematic phase with a small degree of order which is called paranematic phase (by analogy with the magnetism). The phase transition nematic-paranematic of the CNTs is first order for small values of the interaction parameter (so-called subcritical regime of CNTs). For large values of γ , the phase transition of CNTs becomes continuous. The critical point is given by the equations $\partial f / \partial S_{CNT} = \partial^2 f / \partial S_{CNT}^2 = \partial^3 f / \partial S_{CNT}^3 = 0$, giving $S_{CNT,c} = 1/6$ and the effective volume fraction $(L\phi)_c = 2.592$, while the critical value of the interaction parameter is given by the equation:

$$\gamma_c = \frac{k_B T}{125 v_{CNT} S_{LC,c}}. \tag{6}$$

The dependence of γ_c as a function of temperature is shown in **Figure 1**.

In the nematic phase of the liquid crystal, the critical interaction parameter is relatively small (because $S_{LC,c}$ has relatively large values between 0.28 and 0.8), while in the isotropic phase of the liquid crystal, the value of the order parameter is very small ($\simeq 10^{-4}$), and the values of γ_c are relatively large. As a consequence there is a jump of γ_c at T_{NI} .

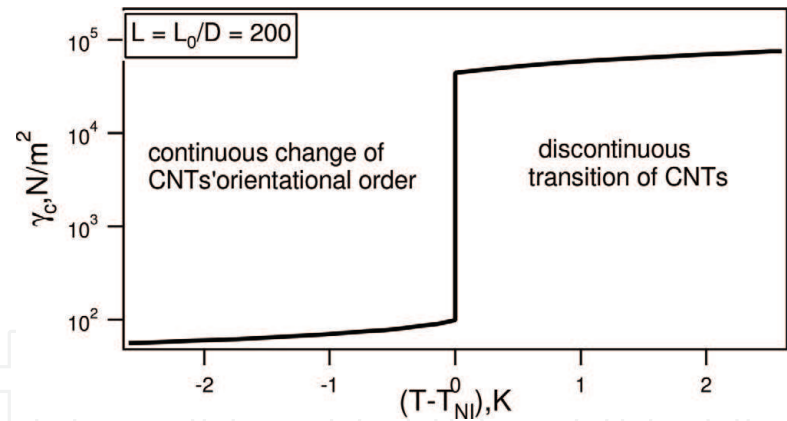


Figure 1.
 The critical value of the coupling parameter γ_c as a function of temperature.

The dependence of γ_c on the lengths of CNTs for a fixed value of the temperature is shown in **Figure 2** (we mention that for the value of the temperature shown ($T - T_{NI} = -1.4K$) the LC is in the nematic phase). The critical value of the coupling parameter decreases when the length of CNTs increase, meaning that the continuous paranematic-nematic transition of CNTs is favored.

In **Figure 3** the volume fractions of CNTs at the transition as a function of the coupling parameter for a fixed value of the temperature are shown. For negative values of γ (region I in the figure, perpendicular alignment), the volume fraction

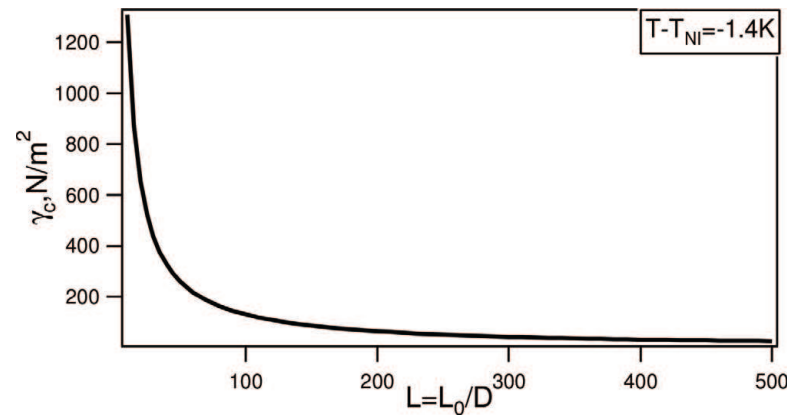


Figure 2.
 The critical value of the coupling parameter γ_c as a function of the lengths of CNTs for a fixed temperature in the nematic region of the liquid crystal.

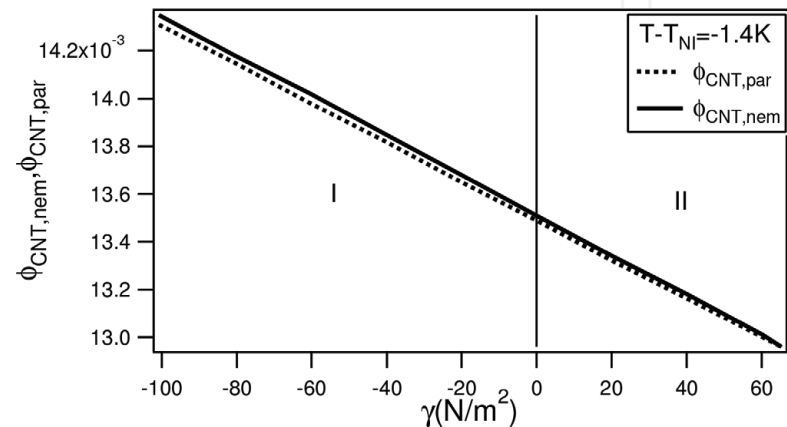


Figure 3.
 The volume fractions of CNTs at the transition as a function of coupling parameter for a fixed value of temperature in the nematic region of LC.

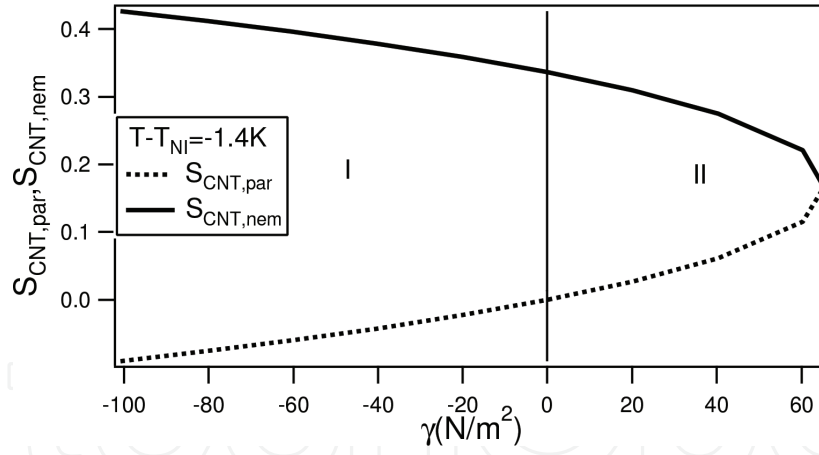


Figure 4.

The order parameter of the two phases of CNTs at the transition as a function of the coupling parameter for a fixed value of the temperature in the nematic region of LC.

gap of CNTs remains practically constant, while for positive values (region II in the figure, parallel alignment), the volume fraction gap decreases with increasing γ until it cancels for critical value γ_c .

The CNT order parameters at the transition as a function of the coupling parameter for a fixed value of the temperature are plotted in **Figure 4**. For negative values of the coupling parameter (the region I in the figure), the first-order phase transition of CNTs takes place between a paranematic phase with a negative order parameter (perpendicular alignment) and a nematic phase with a positive order parameter (parallel alignment). For positive values of γ (region II in the figure), the transition takes place between a paranematic phase and a nematic phase, both with positive order parameters (parallel alignment). If the coupling increases the degrees of alignment of the two phases become smaller until the critical value of the coupling parameter when they are identical.

3.2 Phase diagram

The equilibrium phase diagram can be obtained by minimizing the free energy with respect to S_{CNT} and S_{LC} :

$$\frac{\partial f}{\partial S_{CNT}} = \frac{\partial f}{\partial S_{LC}} = 0 \quad (7)$$

and equating the chemical potentials of CNTs and LC in the two phases. The chemical potentials are given by

$$\begin{aligned} \mu_{CNT} &= v_{CNT} \left[f + (1 - \phi) \frac{\partial f}{\partial \phi} \right] \\ \mu_{LC} &= v_{LC} \left(f - \phi \frac{\partial f}{\partial \phi} \right) \end{aligned} \quad (8)$$

where the free energy density is given by Eq. (5).

3.2.1 Positive coupling constant

A positive coupling parameter corresponds to a paranematic ($S_{CNT,par}$ very small and positive) and nematic ($S_{CNT,nem}$ large and positive) phase transition of CNTs. The corresponding $T(\phi)$ phase diagram is shown in **Figure 5**, where the

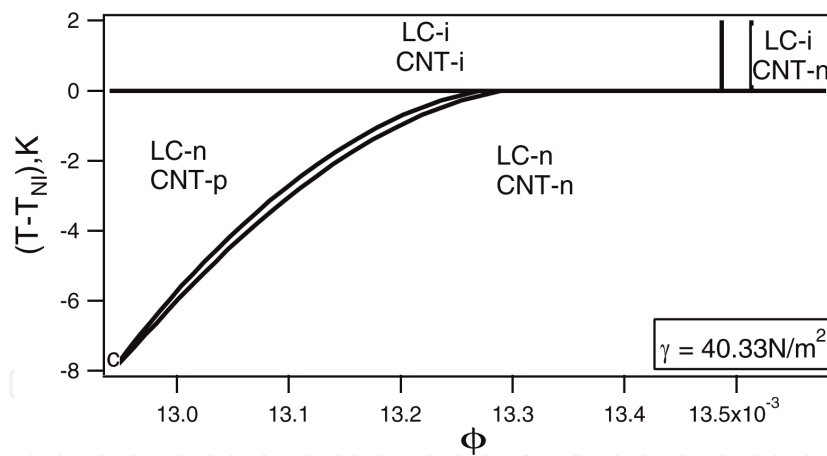


Figure 5. The $T(\phi)$ phase diagram for a constant positive coupling parameter. The horizontal line shows the isotropic-nematic phase transition of LC.

smaller case letters i, p, and n stand for isotropic, paranematic (parallel alignment), and nematic phases, respectively.

For $T < T_{NI}$, LC is in the nematic phase, and the paranematic-nematic phase transition of CNTs is first order. With decreasing temperature, the bi-phase region (the Flory “chimney” [45]) becomes smaller and cancels at the critical point (for the value $\gamma = 40.33 \text{ N/m}^2$, the critical temperature is given by $T_c - T_{NI} = -7.84 \text{ K}$). On the contrary, for $T > T_{NI}$, LC is in the isotropic phase. The isotropic-nematic phase transition of CNTs is first order with a constant Flory “chimney” that does not depend on temperature (because $S_{LC} = 0, f_{LC} = f_{CNT/LC} = 0$, and the problem is equivalent with the dispersion of CNTs in an isotropic solvent). The triple points are the intersection points between the CNT phase transition equilibrium curves and LC phase transition equilibrium curve (the horizontal lines).

To see in more detail the orientational order of the two components, in **Figure 6**, we have plotted the order parameter profiles S_{LC} and S_{CNT} along the binodal lines as a function of temperature.

The transition between the isotropic and nematic phases of LC is first order (see **Figure 6a**), and the values of the LC order parameter depend only on temperature and are not influenced by CNT phase transition (because of $v_{CNT} \gg v_{LC}$, the concentration of LC component is much larger than for CNTs). But each particle contributes with $k_B T$ to the free energy, so that the free energy of LC is significantly larger than that of CNTs. The order parameters of CNTs as functions of temperature are shown in **Figure 6b**. Lowering the temperature, the jump of the order parameters cancels at the critical temperature. In the isotropic phase of LC ($T > T_{NI}$), the jump of the CNT order parameter remains constant independent on temperature (see the discussion of the results plotted in **Figure 5**).

3.2.2 Negative coupling constant

The negative coupling parameter corresponds to a paranematic ($S_{CNT,par}$ very small and negative) and nematic ($S_{CNT,nem}$ large and positive) phase transition of CNTs. The corresponding $T(\phi)$ phase diagram is shown in **Figure 7**, where the smaller case letters i, p, and n stand for isotropic, paranematic (perpendicular alignment), and nematic phases, respectively.

For $T < T_{NI}$, LC is in the nematic phase, and the paranematic (perpendicular)-nematic (parallel) phase transition of CNTs is first order. Contrary to the positive coupling parameter, here with decreasing temperature, the bi-phase region (the Flory “chimney” [45]) becomes larger. For $T > T_{NI}$, the characteristic of the phase

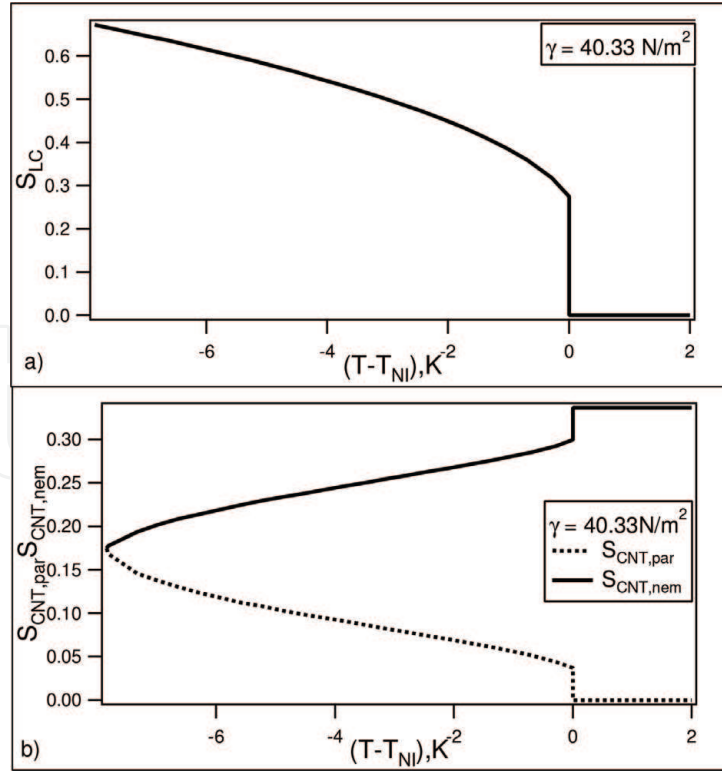


Figure 6.

The order parameters along the binodal lines for a constant positive coupling parameter. (a) The LC order parameter and (b) the CNT order parameters.

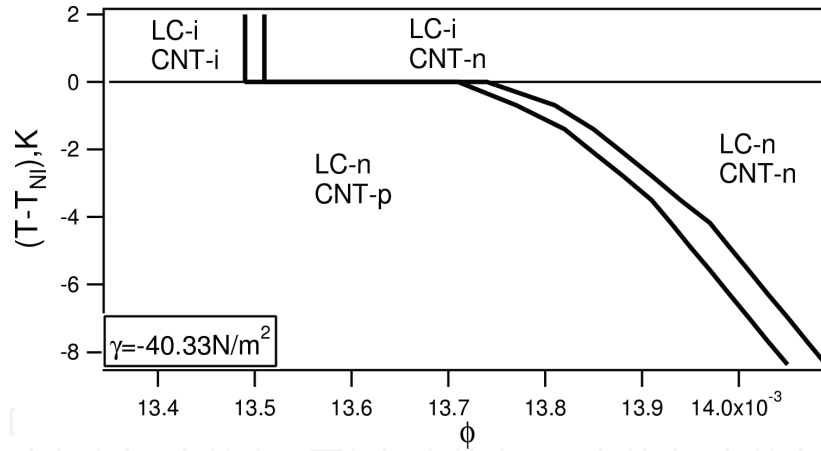


Figure 7.

The $T(\phi)$ phase diagram for a constant negative coupling parameter. The horizontal line shows the isotropic-nematic phase transition of LC.

diagram remains the same; because LC is in the isotropic phase, the isotropic-nematic phase transition of CNTs is first order with a constant Flory “chimney” that does not depend on temperature.

The order parameter profiles S_{LC} and S_{CNT} along the binodal lines as a function of temperature are plotted in **Figure 8**.

Again the transition between the isotropic and nematic phases of LC is first order (see **Figure 8a**), and the values of the LC order parameter depend only on temperature. The behavior of CNT orientational order with temperature is shown in **Figure 8b**. In the nematic phase of LC ($T < T_{NI}$), the CNT jump of the order parameters at transition slowly decreases with increasing temperature, while in the isotropic phase of LC ($T > T_{NI}$), the jump of the CNT order parameter remains constant independent on temperature.

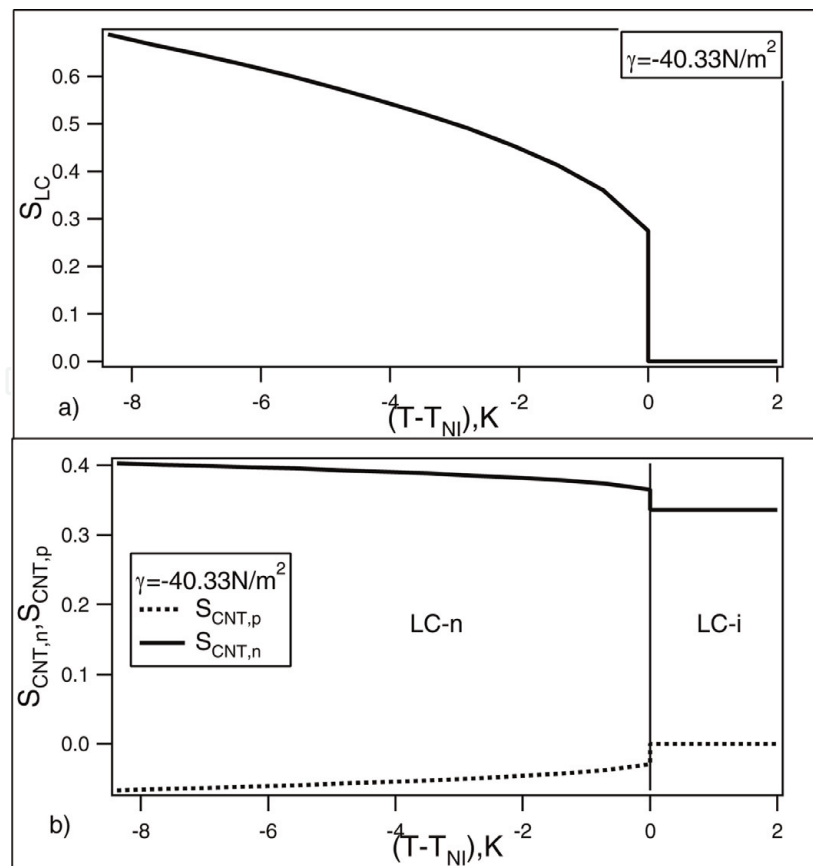


Figure 8.
The order parameters along the binodal lines for a constant negative coupling parameter. (a) The LC order parameter and (b) the CNT order parameters.

4. Conclusions

In the present chapter, we have extended the previous mesoscopic phenomenological model [31, 32, 34–36] (used to describe the phase behavior of a binary mixture composed of CNTs and thermotropic nematic LC) to include the possibility of a perpendicular alignment of CNTs to LC molecules. The model contains the CNT free energy density (2), the Landau-de Gennes free energy (3) for thermotropic LC order, and an interaction term between the nematic CNTs and nematic LC (4). This interaction term generates the possibility of existence of two nematic phases of CNTs: (i) the mean direction of orientation of CNTs is parallel with the direction of the director of LC molecules, when $S_{CNT} > 0$ and $S_{LC} > 0$, and (ii) the two direction of orientation are perpendicular with each other, $S_{CNT} < 0$ and $S_{LC} > 0$. It is to be mentioned that the order parameter of CNTs can be negative (perpendicular alignment) only for a paranematic phase for which the degree of orientational order is very low. The model predicts in this case a first-order paranematic (perpendicular alignment)-nematic (parallel alignment) phase transition of CNTs. When the coupling constant is positive, the first-order paranematic (parallel alignment)-nematic (parallel alignment) phase transition of CNTs cancels at a critical point, when the transition becomes continuous.

The phase behavior and orientational properties of the mixture are discussed considering different values of temperature T , volume fraction of CNTs ϕ , and coupling strength γ .

The theoretical model we have presented describes quite well (comparing with experimental results) the phase properties of the CNTs into thermotropic

nematic LC. The model could be improved by considering the polydispersity of the CNT component and by considering, in more detail, the form of the interaction energy between the two components.

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Author details

Vlad Popa-Nita^{1*} and Robert Repnik²

1 Faculty of Physics, University of Bucharest, Bucharest, Romania

2 Faculty of Natural Sciences and Mathematics, University of Maribor, Maribor, Slovenia

*Address all correspondence to: v.popanita@gmail.com

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