Alignment of Carbon Nanotubes in Nematic Liquid Crystals

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The self-organizing properties of nematic liquid crystals can be used to align carbon nanotubes dispersed in them. Because the nanotubes are so much thinner than the elastic penetration length, the alignment is caused by the coupling of the unperturbed director field to the anisotropic interfacial tension of the nanotubes in the nematic host fluid. In order to relate the degree of alignment of the nanotubes to the properties of the nematic liquid crystal, we treat the two components on the same footing and combine Landau−de Gennes free energies for the thermotropic ordering of the liquid crystal and for the lyotropic nematic ordering of carbon nanotubes caused by their mutually excluded volumes. The phase ordering of the binary mixture is analyzed as a function of the volume fraction of the carbon nanotubes, the strength of the coupling and the temperature. We find that the degree of ordering of the nanorods is enslaved by the properties of the host liquid and that it can be tuned by raising or lowering the temperature or by increasing or decreasing their concentration. By comparing the theory to recent experiments, we find the anchoring energy of multiwalled carbon nanotubes to be in the range from 10^{-10} to 10^{-7} N m^{-1}.

1 Introduction

Carbon nanotubes or CNTs can be produced in a number of different ways, including arc discharge,[1] chemical vapor deposition,[2] and laser ablation.[3] One usually distinguishes two kinds of carbon nanotubes, referred to as single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). The former consist of a single sheet of carbon rolled up into a cylinder with a diameter of about one nanometer, while the latter are built up of multiple carbon sheets producing rods with diameters ranging from a few to tens or even hundreds of nanometers. Aspect ratios of CNTs vary from, say, one hundred to many thousands.

Upon dispersion in fluid media, e.g., by means of sonication and with the aid of stabilizers such as surfactants, isotropic dispersions of CNTs have been produced that act as the starting point of technological applications such as conducting polymer composites.[4] In some cases sufficiently stable dispersions were obtained to observe the spontaneous orientational ordering of the nanotubes in a nematic liquid crystalline state, caused by the highly anisotropic excluded-volume interaction between them.[5−9] However, the tendency of CNTs to cluster and form gels even at quite low concentrations often precludes the formation of ordered phases.

For many applications it is nevertheless essential to obtain a uniformly aligned CNT dispersion. Methods that have been proposed to align CNTs dispersed in a fluid are shearing,[10] field-assisted alignment,[11−13] and molecular combing[14] processes. Still, high degrees of alignment seem difficult to achieve in this way. An alternative route to long-range orientational order would be to use the self-organizing properties of liquid crystals. Indeed,

thermotropic[16,17] as well as lyotropic nematic liquid crystals or NLCs[18] have been successfully applied as CNT-aligning solvents. The preferred axis of the nematic solvent can be controlled by application of suitable alignment (or "rubbing") layers or by means of electric and magnetic fields.

It appears that in a nematic solvent CNTs orient parallel to the director with an orientational order parameter between 0.6 to 0.9 depending on the system and conditions.[16−18] This is quite remarkable considering that the orientational order of the molecules in the nematic solvents typically is quite a bit smaller than 0.6. This implies that there is no obvious connection between the degree of ordering of the nematic solvent and that of the dispersed carbon nanotubes, even though the width (but not the length) of the nanotubes is comparable in size to the nematogens. Hence, it would seem that carbon nanotubes cannot be used as simple gauges for the degree of order in nematic liquid crystals albeit they can be used to visualize director fields.[19,20]

The question arises what precisely can be learned from the degree of alignment of CNTs dispersed in a nematic fluid. Theoretically, the problem of a rod-like particle immersed in a nematic liquid crystal has been addressed at different levels of description and in different limits.[21−25] For our purposes, the most relevant work seems to be that of Burylov and Raikher,[21] in particular, because they allow for the weak coupling limit in which the director field couples only weakly to the surfaces of the particles. Depending on the penetration length $\xi \equiv K/W$, where K is some average of the Frank elastic constants and W that of the polar and azimuthal anchoring energies of the nematic molecules at the CNT surface, and on the preferred type of homeotropic or planar anchoring, different director field structures can develop around a single CNT.[21]

If the diameter D of the CNT is small and $D \ll \xi$, one would presume the anchoring to be so weak as to not be able to produce

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large deformations in the surrounding nematic matrix. In contrast, when $D \gg \xi$, rigid anchoring can be assumed to hold and topological singularities result from this, giving rise to a strong interaction between the dispersed nanotubes.[24] As we shall see below, for CNTs, the limit $D \ll \xi$ typically applies, suggesting that the surface tension anisotropy determines whether the rods prefer to be aligned along or perpendicular to the director field.

It follows that by considering the orientational order of CNTs in nematics information can be gotten on the surface anchoring energies of these particles and their dependence on the temperature and, hence, on the strength of their coupling to the nematic fluid. This is a problem quite straightforwardly dealt with in the limit of vanishing CNT concentrations, but at nonzero concentrations, interactions between them influence this coupling, making the issue much more involved. We shall see that excluded-volume interactions strongly enhance the alignment, explaining in part the experimental observations. Still, the behavior of the CNTs in the nematic fluid seems to be enslaved by the nematic host that even in the weak coupling limit acts like a strong external field.

In this paper, we present a phenomenological theory for predicting the alignment of CNTs dispersions in thermotropic liquid crystals. We treat the two components in the mixture on an equal footing and combine a Landau−de Gennes free energy for the thermotropic ordering of the liquid crystal solvent and a Landau−de Gennes free energy for the lyotropic nematic ordering of carbon nanotubes caused by excluded-volume interactions between them. The interaction between the carbon nanotubes and liquid crystal molecules is thought to be sufficiently weak to not cause any director field deformations in the nematic host fluid. We analyze the phase ordering of the binary mixture as a function of the volume fraction of the carbon nanotubes, the strength of the coupling, and the temperature.

The remainder of this paper is organized as follows. First, in Section 2 we consider the coupling of a test rod to a nematic host liquid, presuming that it operates via an anisotropic surface tension. This allows us to predict the order parameter of the dispersed rods as a function of the polar and azimuthal anchoring strengths. In the next Section 3, we introduce the free energy of a binary mixture of CNTs and a NLC. Our calculations show that the NLC fluid dictates the behavior of the CNTs on account of its very much larger free energy density. The reason is that there are very many more NLC molecules per unit volume than there are CNTs. In Section 4, we illustrate our results and give the main conclusions to be drawn from them.

2 Noninteracting CNTs in a NLC

Let us first consider a single carbon nanotube in a liquid crystal solvent. For values of the elastic constant $K \approx 10^{-11}$ N and anchoring energy $W \approx 10^{-6}$ N/m usually taken as typical, the penetration length $\xi = K/W$ should be vastly in excess of a micron. Because the diameter of CNTs is at or below the micron scale, this then implies that $D \ll \xi$ and only the weak-anchoring limit needs to be considered. This was in fact also recently concluded by Lynch and Patrick.[16] (As we shall see, the anchoring energy of CNTs is actually quite bit smaller than 10^{-6} N/m, so our estimate of the penetration length is actually quite conservative.)

It seems reasonable to presume the anchoring of the NLC molecules to the CNT surface to obey a Rapini−Papoular type of expression for the surface energy.[26] In our case, we need to distinguish polar from azimuthal anchoring, so the surface energy W per unit area can be written as

$$W = W_0 + W_\theta (\vec{q} \cdot \vec{n})^2 + W_\phi (\vec{u} \cdot \vec{n})^2 \qquad (1)$$

where W_0, W_θ, and W_ϕ are the isotropic, polar, and azimuthal anchoring energies, respectively, and $\vec{q}$, $\vec{u}$, and $\vec{n}$ stand for the surface normal, the tangent vector along the main axis of the rod, and director of the NLC, respectively. The schematic representation of a CNT orientation is shown in Figure 1. If $W_\theta > 0$, the NLC favors parallel alignment to the surface of the rods, while for $W_\phi < 0$, this parallel alignment is preferentially along their main axis.

If we integrate this surface energy over the surface of a single rod, we obtain for the total surface free energy, F_{nem}, an expression that can be cast into the following simple form

$$F_{nem}(\theta) = \pi L D W_{nem} - \frac{\pi}{3} L D W P_2(\cos\theta) \qquad (2)$$

Here, $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynomial, L and D stand for the length and width of the test rod, respectively, $W_{nem} = W_0 + {}^2/_3 W_\theta + {}^1/_3 W_\phi$ is the isotropic part of the surface energy, and $W = W_\theta - W_\phi$ is the net surface anchoring energy. Finally, $\theta = \arccos(\vec{u} \cdot \vec{n})$ denotes the angle between the long axis of the test CNT, $\vec{u}$, and the nematic director axis, $\vec{n}$, that we presume to be prescribed. If $W > 0$, the test rod favors alignment parallel to the director, while for $W < 0$, it favors perpendicular alignment.

Interestingly, a similar expression for the free energy of the alignment of rod in a nematic $F_{nem}(\theta) = F_{||} + (F_{||} - F_\perp) \cos^2\theta$ has been suggested to be valid for the *strong* anchoring case, where the ordering is driven by a director field deformation and not the surface tension.[21] (See, however, ref 25.) Here, $F_{||}$ and $F_\perp$ are effective alignment energies. Recent measurements on the alignment of MWMTs in the liquid crystal 5CB bear out this functional form.[16] Inserting the fitted value for $(F_{||} - F_\perp) = -(\pi/2)LDW$ of $-3.8\ k_B T$, where k_B is Boltzmann's constant and T the absolute temperature, and the estimated length of $L \approx 2.7\ \mu$m and width of $D \approx 20$ nm, we find for the anchoring strength an estimated value of $W \approx 10^{-7}$ N m^{-1}. This confirms that the CNTs in NLCs must indeed adhere to the weak anchoring condition, as was also concluded in ref 16.

The equilibrium distribution of the noninteracting rods in the NLC follow from straightforward Boltzmann statistics, $P(\theta) \propto \exp(-\beta F_{nem})$, where $P(\theta)$ is the distribution over the angles θ and $\beta = 1/k_B T$. A simple calculation then shows that the orientational order parameter S_{CNT} of the CNTs in the NLC is given by

$$S_{CNT} = \langle P_2(\cos\theta) \rangle = \sum_{-1}^{+1} d(\cos\theta) P(\theta) P_2(\cos\theta)$$

$$= -\frac{1}{2} - \frac{3}{2\pi\beta L D W}$$

$$+ \sqrt{\frac{9}{2\pi^2 \beta L D W}} \times \frac{\exp(\pi\beta L D W/2)}{[\mathrm{erf}(i\ \sqrt{\pi\beta L D W/2})/i]} \qquad (3)$$

where $\mathrm{erf}(x)$ is the usual error function and i the imaginary unit. This expression relates the observed order parameter to the dimensionless surface energy $\beta L D W$ as a dependence shown in Figure 2. For weak surface anisotropy $|\beta L D W| \ll 1$, this somewhat unwieldy expression reduces to

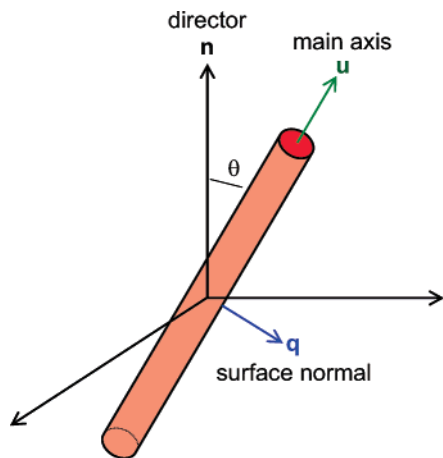$$S_{CNT} \sim \frac{\pi}{15} \beta L D W \qquad (4)$$

Figure 1. Schematic representation of a test CNT in a nematic host with director field $\vec{n}$. Indicated are the orientation $\vec{u}$ of the main axis of the CNT and the surface normal $\vec{q}$.
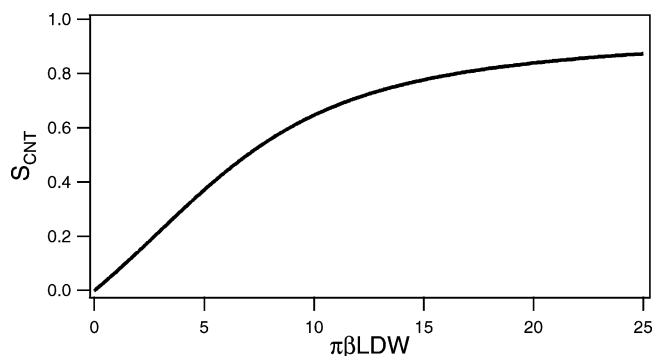

Figure 2. Order parameter of noninteracting CNTs dispersed in a nematic host fluid as a function of the dimensionless surface energy.

If we compare our prediction with the measured value of $S_{CNT} \approx 0.9$ for *bundles* of MWNTs in the liquid crystal E7,[17] we obtain a value for the dimensionless group βLDW of about 11. Inserting the estimated $L \approx 20\ \mu m$ and $D \approx 3\ \mu m$ then produces a surprisingly low value of $W \approx 10^{-10}$ N m^{-1}. Again, the weak anchoring limit seems to hold.

As our aim is to study the interplay of the ordering of the NLC and the CNTs, and relate the degree of order S_{NLC} of the NLC to that of the CNTs, S_{CNT}, we need to formulate a free energy that couples these two quantities. As a fist step, we note that if we average the free energy of a test rod over the angle θ we obtain a surface energy per CNT as

$$\langle F_{nem} \rangle = \pi LDW_{nem} - \frac{\pi}{3} LDW\, S_{CNT} \qquad (5)$$

This has to be compared with the free energy F_{iso} of a CNT in the isotropic phase of the nematogen

$$F_{iso} = \pi LDW_{iso} \qquad (6)$$

where W_{iso} is the associated surface tension. In principle $\langle F_{nem} \rangle \neq F_{iso}$, implying different solubilities of the CNTs in the isotropic and nematic phases of the nematogen.

One would expect the presence of CNTs should to cause a shift in the isotropic−nematic transition temperature of the NLC. In the strong coupling limit, the impact of the surfaces of the particles on the nematic director is so strong that it leads to their expulsion from the nematic liquid.[27] The fact that we find

the weak anchoring limit to hold for the CNTs suggests that we need not consider differences in solubilities in the two phases. So, for simplicity and in the spirit of the Landau−de Gennes theory, we put $W_{nem} = W_{iso}$ and retain only the coupling between the degrees of order of the NLC and the CNTs. The influence of the coupling on the isotropic−nematic transition temperature will prove minute on account of the large difference in densities of the two components.

The second step we take is to make use of the asymptotic relation $W \sim wS_{NLC}$ for weak ordering of the NLC near a hard flat interface, where w is again a surface energy.[28] From this, we can already conclude that only if the degree of order of the CNTs is weak there is a simple relation between the order parameters of the two components: $S_{CNT} \sim (\pi/15)\beta LDW \sim (\pi/15)\beta LDwS_{NLC}$.

The overall surface free energy is the sum of the surface free energies of all the rods. If the volume of the mixture is V, this then suggests within a Boltzmann description for the coupling between the N CNTs and the NLC host liquid a free energy per unit volume of the following form

$$\frac{F_{CNT/NLC}}{V} = -\frac{4W}{3D}\phi S_{CNT} = -\gamma\phi S_{NLC}S_{CNT} \qquad (7)$$

where $\phi \equiv Nv_{CNT}/V$ is the volume fraction of rods in the dispersion and $v_{CNT} \approx (\pi/4)LD^2$ is the volume of a single CNT of length $L \gg D$ and width D. The relevant coupling parameter is apparently given by $\gamma \equiv {}^4/_3 w/D$.

It transpires that the coupling parameter depends only on the width of the CNTs and not on their length and is inversely proportional to it. Hence, in the weak coupling limit, thin rods are in some sense more strongly influenced by the nematic host fluid than the thick ones are. From our comparison with the experiments on MWNTs and extrapolation to SWNTs that have much smaller widths D, we find that the value of the coupling parameter γ can range widely from, say, $10^{-3} - 10^3$ N m^{-2}.

In the next section, we use this free energy to connect the free energies of the NLC and the CNTs, where we shall no longer presume that the CNTs are dilute and do not interact.

3 Interacting CNTs in a NLC

Our aim is to write down a free energy for the CNT−NLC mixture. In the theory of thermotropic nematic liquid crystals, it is customary to do this at the level of a phenomenological Landau−de Gennes description in terms of an expansion in powers of the orientational order parameter.[29] Here, we choose to treat the CNTs and the NLC on an equal footing, implying that we also describe the anisotropic interactions between the CNTs at the level of a Landau−de Gennes theory.[30] Although in principle not as accurate as Onsager's second virial theory for hard rods,[31] we have to keep in mind that CNTs are not quite the idealized monodisperse, infinitely rigid, and straight rods envisaged in that theory. For our more qualitative purposes, a phenomenological theory will therefore do.

The free energy per unit volume $f \equiv F/V$ of the mixture consist of three contributions

$$f = f_{CNT} + f_{NLC} + f_{CNT/NLC} \qquad (8)$$

coming from the CNTs dispersed in a fluid, f_{CNT}, from thermotropic NLC, f_{NLC}, and from the coupling of these two components, $f_{CNT/NLC}$. The last contribution was discussed in the previous section albeit that it has to be amended if used in a Landau-type description. We first discuss the two main

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contributions f_{CNT} and f_{NLC} and then return to $f_{CNT/NLC}$ at the end of this section.

Presuming the fluid to be incompressible, we write for the free energy of the CNTs what may perhaps be seen as an interpolation between the Onsager theory and a Flory-type theory valid for all volume fractions, ϕ, of dispersed CNTs[32−35]

$$f_{CNT}/k_B T = v_{NLC}^{-1}(1 - \phi) \ln(1 - \phi) + v_{CNT}^{-1} \phi \ln \phi + v_{CNT}^{-1} \phi \left[\frac{1}{2} \left(1 - \frac{u}{3} \right) S_{CNT}^2 - \frac{u}{9} S_{CNT}^3 + \frac{u}{6} S_{CNT}^4 \right] \quad (9)$$

where the third term accounts for the gain in free volume and the loss of orientational entropy upon ordering of the rods. Here, $v_{NLC} \ll v_{CNT}$ is the volume of the thermotropic nematogen and $u \equiv \varsigma \phi L/D$ a scaled volume fraction, with ς a constant close to unity. Note that because $v_{CNT} \approx (\pi/4)LD^2$, with typical values of $L \approx 400$ nm and $D \approx 2$ nm, and $v_{NLC} \approx (\pi/4)ld^2$, with length $l \approx 3$ nm and $d \approx 0.5$ nm, for nematogens such as E7, we find that the ratio $R_v \equiv v_{CNT}/v_{NLC}$ of molecular volumes must be equal to $R_v \approx 2 \times 10^3$. Due to this large value of R_v, the number of particles per unit volume is much larger for the NLC than for the CNTs. Each particle contributes of order $k_B T$ to the free energy, therefore the contribution of the NLC to the overall free energy of the mixture vastly overwhelms that of the CNTs. It is for this reason that the CNTs are enslaved by the NLC. Without loss generality, we shall in our numerical calculations below fix the parameters R_v and L/D at the values of 2×10^3 and 200, respectively.

If there were no coupling to the order parameter of the NLC, the equilibrium between an isotropic phase, with $S_{CNT} = 0$, and an nematic phase, with $S_{CNT} > 0$, can be established by equating the chemical potentials $\mu_{CNT} = (\partial f_{CNT}/\partial \phi)_T$ and the grand potentials (or pressures) $g_{CNT} = f_{CNT} - \phi \mu_{CNT}$ in the two phases and optimizing S_{CNT} by minimizing the free energy, i.e., by putting $(\partial f_{CNT}/\partial S_{CNT})_{T,\phi} = 0$. This gives in the limit $L/D \rightarrow \infty$ for the conditions of coexistence between the nematic and isotropic phases of the rods $u_{nem} = 27/10$, $S_{CNT} = 1/3$, and $u_{iso}/u_{nem} - 1 = -1/18(1 + R_v \phi_{nem})^{-1} \ll 1$ and for the limits of stability of the isotropic and nematic phases $u_* = 3$ and $u_+ = 8/3$. If we set $\varsigma = 4/3$, we obtain for the stability limit of the isotropic phase the same result as that from the Onsager theory.[35,31] The dimensionless quantity $R_v \phi_{nem} \approx (27/10)D^3/ld^2$ does not depend on the length of the CNTs and is equal to 29 for our choice of parameters $R_v = 2 \times 10^3$ and $L/D = 200$.

So, the phase gap within our description is very narrow indeed and in fact much less than the 30% or so predicted for monodisperse, perfectly straight hard rods.[31] For CNTs, the phase gap can be as large as 300%, plausibly caused by the very large polydispersity in length and width.[7] This does not concern us too much, however, because, as we shall see below, even for quite small values of the coupling parameter γ the first-order transition disappears in favor of a more gradual crossover, in what essentially is a paranematic dispersion of rods.

For the free energy of the NLC, we invoke the usual expression[29]

$$f_{NLC} = (1 - \phi) \left[\frac{3}{2} a(T - T^*) S_{NLC}^2 - \frac{3}{4} B S_{NLC}^3 + \frac{9}{4} C S_{NLC}^4 \right] \quad (10)$$

where the $(1 - \phi)$ accounts for the part of the volume not taken up by NLC. Here, T^* denotes the spinodal temperature of the isotropic phase of the pure liquid crystal, a material parameter, and a, B, and C are material-dependent coefficients. For 5CB

or pentylcyanobiphenyl, for example, $T^* = 306$ K and $a \approx 3.5 \times 10^4$ J m^{-3} K^{-1}, $B \approx 7.1 \times 10^5$ J m^{-3}, and $C \approx 4.3 \times 10^5$ J m^{-3}.[36,37] We shall take these values in our numerical calculations presented in the next section. For this particular nematogen, a nematic phase with an order parameter $S_{NLC} = B/6C = 0.28$ and an isotropic phase with order parameter $S_{NLC} = 0$ coexist at a temperature of $T = T_{NI} = T^* + B^2/24aC = 307.5$K.

Finally, we need to write down a form of the coupling free energy $f_{CNT/NLC}$ that in the limit of vanishing concentration of rods $u \rightarrow 0$ reproduces the results of the Boltzmann analysis of the previous section. The simplest free energy inspired by eq 7 that approximately does just that is

$$f_{CNT/NLC} = -\frac{1}{5} \gamma \phi S_{NLC} S_{CNT} \left(1 - \frac{1}{2} S_{CNT} \right) \quad (11)$$

Here, the $1/5$ makes certain that in the limits $\gamma \rightarrow 0$ and $u \rightarrow 0$ we find $S_{CNT} \sim 1/5 \beta \gamma v_{NLC} S_{NLC}$ in agreement with the Boltzmann analysis. The term in the brackets ensures that $S_{CNT} \rightarrow 1$ in the limit of large couplings $\gamma \rightarrow \infty$, as it should.

As already advertised, because of the large difference in the densities of the NLC and CNTs, the temperatures T^* and T_{IN} are only marginally impacted upon by the presence of the CNTs and may for all intents and purposes be considered as constants. The same, in fact, is true for the order parameter S_{NLC}, which also is only exceedingly weakly dependent on the amount of CNT present, unless the coupling parameter is unrealistically large. Because of this, we shall focus on temperatures below T_{NI} where the NLC is in its nematic phase, characterized by an order parameter $S_{NLC} > 0$, and investigate under what conditions the CNTs dispersed in it undergo a nematic−isotropic phase transition. Note that the isotropic phase of the CNTs is actually a paranematic one on account of the coupling to the nematic host.

Provided the CNTs do undergo this transition, a system of average composition ϕ splits into a nematic phase of CNTs characterized by the relevant order parameters (ϕ_{nem}, S_{NLC}, $S_{CNT_{nem}}$) and a paranematic phase characterized by (ϕ_{iso}, S_{NLC}, $S_{CNT_{iso}}$). The values for the concentrations ϕ_{iso} and ϕ_{nem} at coexistence are as before fixed by the equalities of chemical potentials $\mu_{CNT} = \mu_{CNT}(\phi, S_{NLC}, S_{CNT}) = (\partial f/\partial \phi)_T$ and grand potentials $g = g(\phi, S_{NLC}, S_{CNT}) = f - \phi \mu_{CNT}$ in the coexisting phases. The order parameters S_{NLC} and S_{CNT} are obtained by minimizing the free energy density f with respect to S_{NLC} and S_{CNT}, respectively. We emphasize again that in both phases the value of the order parameter S_{NLC} of the NLC host fluid is (for all intents and purposes) the same, i.e., the nematic background acts like a temperature-dependent external field to the CNTs.

In the next section, we present the results of our calculations. Here, we shall for reasons of convenience introduce the reduced temperature $\tau \equiv (T - T^*)/(T_{NI} - T^*)$, where by definition $\tau = \tau^* = 0$ at the undercooling limit of the isotropic phase while $\tau = \tau_{NI} = 1$ at the nematic−isotropic phase transition temperature of the NLC.

4 Results and Discussion

For very small values of the coupling parameter γ, the nematic−isotropic phase transition of the CNTs is first order and the order parameter jumps at the transition from zero to some nonzero value depending on the value of this coupling parameter. With increasing coupling to the NLC host fluid, that is, with increasing γ, the transition becomes continuous at some tricritical value γ_t. The tricritical point where the discontinuous phase transition becomes continuous can be found by solving
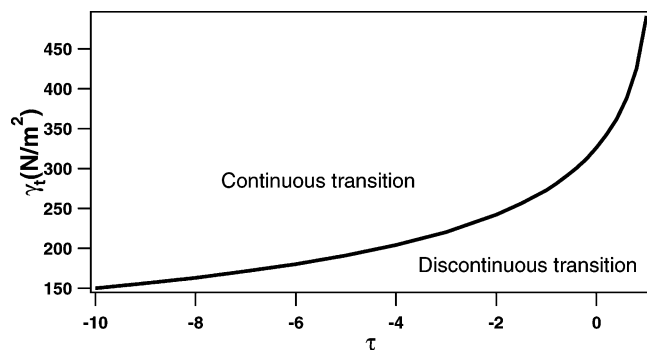
Figure 3. The tricritical value of the coupling parameter γ_t as a function of the reduced temperature τ calculated for CNTs of length 400 nm and width 2 nm in the nematic 5CB.

the equations $\partial^2 f/\partial S_{NLC}^2 = \partial^3 f/\partial S_{NLC}^3 = 0$, giving at the tricritical point universal values for the order parameter $S_{CNT} = {}^1/_6$, the scaled concentration $u_t = \varsigma\phi_t L/D = 2.592$, and the dimensionless coupling parameter $\beta\gamma_t v_{CNT} S_{NLC} = 0.04$. The tricritical value of the coupling parameter γ_t as a function of the reduced temperature τ is presented in Figure 3. This demonstrates that with decreasing the temperature, as S_{NLC} increases, the external field felt by the CNTs increases and the nematic–isotropic phase transition of CNTs becomes continuous for increasingly lower values of interaction parameter γ.

We conclude that for $\beta LDW > 3/25\pi \approx 0.038$ the isotropic–nematic transition is no longer observable albeit the excluded-volume interactions do enhance the degree of order of the CNTs in the NLC. We have seen in Section 2 that for the two cases tested βLDW is quite larger than unity, suggesting that in practice we should always be under the strong-ordering conditions, even though in the weak-anchoring limit. Indeed, scaling arguments tell us that $W \approx k_B T/ld$[28,38] apart from a numerical constant that could well be small, indicating that we should find $\beta LDW \approx LD/ld \gg 1$ to hold in almost all cases.

To illustrate how in the limit of weak couplings the isotropic–nematic transition of the CNTs is affected by the NLC host fluid, the phase diagram of the coexisting concentrations as a function of the coupling parameter is plotted in Figure 4. In Figure 4a, the binodal is presented for a reduced temperature $\tau = 0$ that corresponds to the undercooling limit temperature of the isotropic phase of the pure NLC. The phase gap decreases with increasing the coupling constant and becomes zero for $\gamma = \gamma_t$. The isotropic–nematic phase transition of CNTs takes place at increasingly lower concentration with increasing coupling constant. Figure 4b shows how temperature impacts upon the ordering transition of the rods. Indicated are the cases for reduced temperature $\tau = 1$ corresponding to nematic–isotropic phase transition temperature of the nematic phase of the pure liquid crystal, for $\tau = 0$ at undercooling limit of the isotropic phase of the pure liquid crystal, and for somewhat below that for $\tau = -5$.

To see in more detail the influence of temperature on the order parameter of CNTs, we have plotted in Figure 5 the order parameter profiles S_{CNT} of the CNTs for a small value of the coupling parameter $\gamma < \gamma_t$ for two different temperatures, one at the nematic transition temperature of the NLC and one a few degrees below that. For this choice of coupling parameter, even though small, we still see a large effect of the NLC on the ordering of the rods.

First, we observe that the isotropic phase of CNTs at low concentrations is not isotropic but paranematic with some nonzero degree of orientational order. This, of course, is a characteristic of a nematic–isotropic phase transition in an
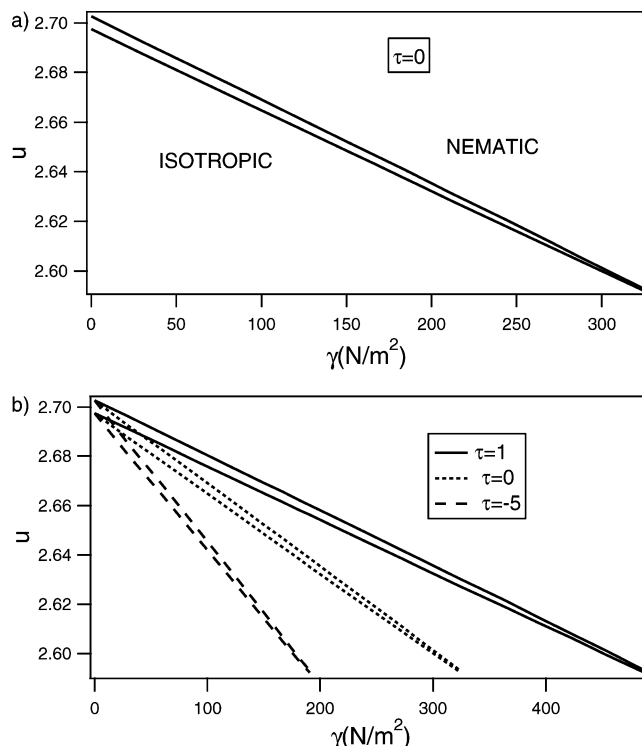

Figure 4. (a) Phase diagram of CNTs of length 400 nm and width 2 nm in a nematic host fluid of 5CB at a reduced temperature $\tau = 0$ and varying coupling strength γ. Indicated are the coexisting scaled volume fractions u in the isotropic and nematic phases discussed in the main text. (b) As in (a) for three different temperatures: $\tau = 1$, continuous line; $\tau = 0$, dotted line; $\tau = -5$, dashed line.
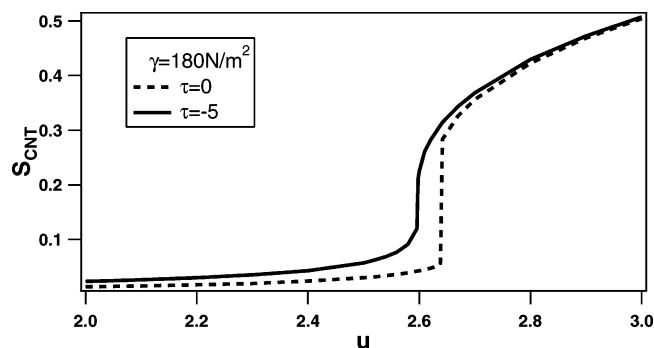

Figure 5. Orientational order parameter of CNTs as a function of the scaled volume fraction u for two different temperatures for small values of the coupling parameter: dashed line, reduced temperature $\tau = 0$; continuous line, $\tau = -5$. Parameters correspond to rods of length 400 nm and width 2 nm in the nematic 5CB.

external field. Second, with decreasing temperature, the discontinuity of the transition reduces, as in fact is to be expected from the results of Figure 3. Third, with decreasing temperature, the volume fraction at which the transition takes place diminishes, as was in fact also clear from the results of Figure 4. All in all, this allows us to conclude that the CNTs can be aligned more easily at low volume fractions the lower the temperature of the NLC.

In Figure 6, we have plotted the order parameter profiles of the CNTs at the undercooling limit of the isotropic phase of the pure liquid crystal, so $\tau = 0$, for two more realistic values of the coupling parameter corresponding to values of βLDW of 5 (drawn line) and 10 (dashed line). These values correspond to coupling strengths of $\gamma = 1.76 \times 10^4$ N m^{-2} and $\gamma = 3.52$

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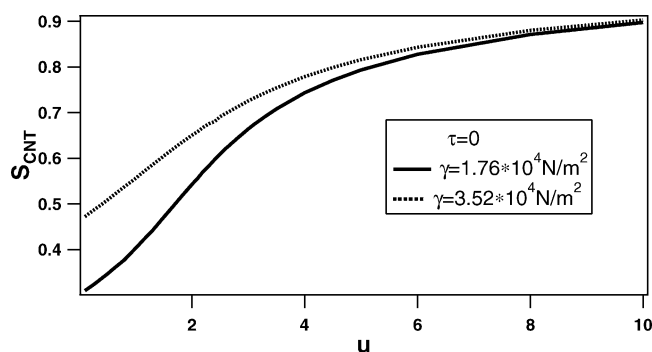*J. Phys. Chem. B, Vol. 112, No. 15, 2008* **4517**

Figure 6. Orientational order parameter of CNTs as a function of the scaled volume fraction u for two large values of the coupling parameter. Indicated are results for reduced temperature $\tau = 0$. Parameter values are chosen to correspond to rods of length 400 nm and width 2 nm in the nematic 5CB.

$\times 10^4$ N m^{-2}, if $L = 400$ nm and $D = 2$ nm. Because the two values of interaction parameter correspond to strong coupling limit ($\gamma > \gamma_t$), the alignment of the rods is a continuous function of the concentration. In both cases, the degree of the orientational order saturates at volume fractions $\phi \gtrsim 4D/L$, which is in fact still very low because $L/D \gg 1$.

It is important to stress that without any information on the volume concentration of the rods we are not able to calculate the strength of the coupling the way we have done in Section 2. Hence, the values quoted there should, in principle, be regarded as upper bounds. On the other hand, for these two cases the degree of order is already very large at very low concentrations and the crossover from weak to strong coupling taking place roughly when $\beta LDW \gtrsim 1$. (See also Figure 2.) This suggests that the quoted upper bounds cannot be off by more than a factor of 2.

To summarize, in this paper we have theoretically investigated the alignment of carbon nanotubes in a thermotropic liquid crystal. Our study was motivated by recent experimental observations indicating that carbon nanotubes can be aligned to a high degree of orientational order in a thermotropic liquid crystal, much more so than by external fields in an isotropic fluid dispersant.[17,39,40] For instance, Dierking and co-workers[17] observed a degree of order of $S_{CNT} \approx 0.3$ for flow-aligned MWNTs in glycerine, while Islam and co-workers[39] obtained a value of $S_{CNT} \approx 0.14$ for surfactant-stabilized SWNTs in water in an external magnetic field of 7 T, in comparison to values between 0.6 and 0.9 in liquid crystals.[16–18]

5 Conclusions

Our main conclusions are as follows.

(1) The coupling between the CNTs and a NLC seems to be dominated by an anisotropic surface tension and not by any deformation of the director field because the rods are thin on the scale of the extrapolation length. This means that CNTs dispersed in NLCs are in the weak-anchoring limit.[16]

(2) The first-order nematic−isotropic phase transition of CNTs dispersed in a NLC disappears for a strong enough coupling to the nematic host fluid. A tricritical point can be defined that within the Landau−de Gennes model exhibits universal characteristics if expressed in the right dimensionless variables.

(3) Although in the weak-anchoring limit, the coupling between the CNTs and the NLC host is so strong that in practice one should expect CNTs always to be in the strong-coupling limit, i.e., above the tricritical point. This means CNTs in NLCs are always strongly paranematic.

(4) The degree of alignment of CNTs in NLCs can be tuned by varying the CNT concentration or the temperature.

Finally, we point out the mesoscopic model presented here is only a first and rather approximate attempt to understand theoretically the properties of dispersions of CNTs in NLCs. In future work, we intend to study the important influence of length and width polydispersities on the ordering of CNTs in nematic fluids.

References and Notes

(1) Iijima, S. *Nature* **1991**, *354*, 56.
(2) Endo, M.; Takeuchi, K.; Igarashi, S.; Kobori, K.; Shiraishi, M.; Kroto, H. W. *J. Phys. Chem. Solids* **1993**, *54*, 1841.
(3) Colbert, D. T.; Zhang, J.; McClure, S. M.; Nikolaev, P.; Chen, Z.; Hafner, J. H.; Owens, D. W.; Kotula, P. G.; Carter, C. B.; Weaver, J. H.; Rinzler, A. G.; Smalley, R. E. *Science* **1994**, *266*, 1218.
(4) Grossiord, N.; Loos, J.; Koning, C. E. *J. Mater. Chem.* **2005**, *15*, 2349.
(5) Islam, M. F.; Alsayed, A. M.; Dogic, Z.; Zhang, J.; Lubensky, T. C.; Yodh, A. G. *Phys. Rev. Lett.* **2004**, *92*, 088303.
(6) Badaire, S.; Zakri, C.; Maugey, M.; Derré, A.; Barisci, J. N.; Wallace, G.; Poulin, P. *Adv. Mater.* **2005**, *17*, 1673.
(7) Song, W.; Kinloch, I. A.; Windle, A. H. *Science* **2003**, *302*, 1363; Song, W.; Windle, A. H. *Macromolecules* **2005**, *38*, 6181.
(8) Zhang, S.; Kinloch, I. A.; Windle, A. H. *Nano Lett.* **2006**, *6*, 568.
(9) Davis, V. A.; Ericson, L. M.; Nicholas, A.; Parra-Vasquez, G.; Fan, H.; Wang, Y.; Prieto, V.; Longoria, J. A.; Ramesh, S.; Saini, R. K.; Kittrel, C.; Billups, W. E.; Adams, W. W.; Hange, R. H.; Smalley, R. E.; Pasquali, M. *Macromolecules* **2004**, *37*, 154.
(10) Wang, H.; Christopherson, G.; Xu, Z.; Porcar, L.; Ho, D.; Fry, D.; Hobbie, E. *Chem. Phys. Lett.* **2005**, *416*, 182.
(11) Casavant, M.; Walters, D.; Schmidt, J.; Smalley, R. *J. Appl. Phys.* **2003**, *93*, 2153.
(12) Fisher, J. E.; Zhou, M.; Vavro, J.; Liaguno, C.; Guthy, C.; Haggenmueller, R.; Casavant, M.; Walters, D. E. *J. Appl. Phys.* **2003**, *93*, 2157.
(13) Kamat, P. V.; Thomas, K. G.; Barazzouk, S.; Girishkumar, G.; Vinodgopal, K.; Meisel, D. *J. Am. Chem. Soc.* **2004**, *126*, 10757.
(14) Gerdes, S.; Ondarcuhu, T.; Cholet, S.; Joachim, C. *Europhys. Lett.* **1999**, *48*, 292.
(15) Rai, P. K.; Pennink, R. A.; Parra-Vasquer, A. N. G.; Davis, V. A.; Schmidt, H. K.; Hauge, R. A.; Smalley, R. E.; Pasquali, M. *J. Am. Chem. Soc.* **2006**, *128*, 591.
(16) Lynch, M. D.; Patrick, D. L. *Nano Lett.* **2002**, *2*, 1197.
(17) Dierking, I.; Scalia, G.; Morales, P. *J. of Appl. Phys.* **2005**, *97*, 044309.
(18) Lagerwall, J.; Scalia, G.; Haluska, M.; Dettlaff-Weglikowska, U.; Roth, S.; Giesselmann, F. *Adv. Mater.* **2007**, *19*, 359.
(19) Jian, K.; Hurt, R. H.; Sheldon, B. W.; Crawford, G. p. *Appl. Phys. Lett.* **2006**, *88*, 163110.
(20) Ko, H.; Tsukruk, V. V. *Nano Lett.* **2006**, *6*, 1443.
(21) Burylov, S. V.; Raikher, Yu. L. *Phys. Lett.* **1990**, *A149*, 279; Burylov, S. V.; Raikher, Yu. L. *Phys. Rev. E* **1994**, *50*, 358.
(22) Andrienko, D.; Allen, M. P.; Skacej, G.; Žumer, S. *Phys. Rev. E* **2002**, *65*, 041702.
(23) Andrienko, D.; Tasinkevych, M.; Patricoi, P.; Telo da Gamma, M. M. *Phys. Rev. E* **2003**, *68*, 051702; Andrienko, D.; Tasinkevych, M.; Patricoi, P.; Telo da Gamma, M. M. *Phys. Rev. E* **2004**, *69*, 021706; Andrienko, D.; Tasinkevych, M.; Dietrich, S. *Europhys. Lett.* **2005**, *2005*, *70*, 95.
(24) Hung, F. R.; Guzman, O.; Gettelfinger, B. T.; Abbott, N. L.; de Pablo, J. J. *Phys. Rev. E* **2006**, *74*, 011711.
(25) Brochard, F.; de Gennes, P. G. *J. Phys. Paris* **1970**, *31*, 691.
(26) Rapini, A.; Papoular, M. *J. Phys. Colloq. Paris* **1969**, *30*, C4−54.
(27) Meeker, S. P.; Poon, W. C. K.; Crain, J.; Terentjev, E. M. *Phys. Rev. E* **2000**, *61*, R6083; Anderson, V. J.; Terentjev, E. M.; Petrov, P.; Meeker, S. P.; Crain, J.; Poon, W. C. K. *Eur. Phys. J. E* **2001**, *4*, 11.
(28) Okano, K. *Jpn. J. Appl. Phys.* **1983**, *22*, L343.
(29) de Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*; Oxford University Press: Oxford, 1993.
(30) Doi, M.; Edwards, S. F. *Theory of Polymer Dynamics*; Clarendon: Oxford, 1989.

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(31) Vroege, G. J.; Lekkerkerker, H. N. W. *Rep. Prog. Phys.* **1992**, *55*, 1241; Lekkerkerker, H. N. W.; Vroege, G. J. *Philos. Trans. R. Soc. London, Ser. A* **1993**, *344*, 419.

(32) Doi, M. *J. Polym. Sci., Part B: Polym. Phys.* **1981**, *19*, 229; Kuzuu, N.; Doi, M. *J. Phys. Soc. Jpn.* **1983**, *52*, 3486.

(33) Olmsted, P. D.; Lu, C.-Y. D. *Phys. Rev. E* **1999**, *60*, 4397.

(34) Flory, P. J. *Proc. R. Soc. Lonon, Ser. A* **1956**, *243*, 73.

(35) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 727.

(36) Oswald, P.; Pieranski, P. In *Nematic and Cholesteric Liquid crystals; concepts and physical properties illustrated by experiments;* Liquid Crystals Book Series; CRC Press: Boca Raton, FL, 2005.

(37) Faetti, S.; Palleschi, V. *J. Chem. Phys.* **1984**, *81*, 6254; Faetti, S.; Palleschi, V. *Phys. Rev. A* **1984**, *30*, 3241; Faetti, S.; Palleschi, V. *J. Phys. Lett. (France)* **1984**, *45*, L313.

(38) van der Schoot, P. *J. Phys. Chem. B* **1999**, *103*, 8804.

(39) Islam, M. F.; Milkie, D. E.; Torrens, O. N.; Yodth, A. G.; Kikkawa, J. M. *Phys. Rev. B* **2005**, *71*, 201401.

(40) Somewhat higher values of $S_{CNT} \approx 0.64$ have been achieved upon crystallizing a dispersion of CNTs in a polystyrene melt in the presence of a magnetic field of 2.4 T. See Takahashi, T.; Yonetake, K.; Koyama, K.; Kikuchi, T. *Macromol. Rapid Commun.* **2003**, *24*, 763.