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Derivation of extended Maxwell Garnett formula for carbon-nanotube-doped nematic liquid crystal

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A numerical effort for modelling the dielectric behaviour of the novel binary mixture of nematic liquid crystal and carbon nanotube (NLC:CNT) has been carried out using the Maxwell Garnett theory. The CNTs are treated as conductive anisotropic inclusions while the NLCs as dielectric isotropic or anisotropic matrix depending on temperature. Thus, the numerical expressions for the dielectric anisotropy for the scenarios of aligned CNTs in the NLC matrix of either nematic or isotropic phases have been derived, and the results show that the Debye parameter of CNT at optic limit seems to be the decisive factor in the enhancement of the dielectric anisotropy of the nematic system.

Keywords: nematic liquid crystal; carbon nanotube; Maxwell Garnett theory; dielectric anisotropy

1. Introduction

Many researchers have been at the vanguard of studying binary mixtures of nematic liquid crystals (LCs) and carbon nanotubes in recent years, primarily motivated by their common high geometric aspect ratios and anisotropic physical properties. Among them, Lee et al. [1,2] observed a great nonlinear-index-change coefficient enhanced by CNTs as a dopant in nematic films. Lynch and Patrick [3] discovered that CNTs can be orientationally ordered by LC when dispersed in a nematic matrix. Theoretical details in reference to this parallel alignment of CNT obtained by dispersion in a self-organising NLC was also studied by Popa-Nita and Kralj [4]. On the other hand, Dierking and colleagues [5] confirmed the guest–host effect exhibited in a LC:CNT sandwiched glass cell, in which CNTs are oriented cooperatively with LC molecules if a sufficient electric field is applied. With potential for display applications, improved electro-optical performances [6–8] and memory responses [9–11] of LCs doped with CNTs were also disclosed by various research groups. Regarding the interaction between an LC molecule and a single-walled CNT (SWCNT), Park et al. [12] calculated the electrostatic binding energy of a LC molecule on a SWCNT sidewall to be up to —2 eV (much stronger than the typical van der Waals interaction or that of the physisorption energy). Recently, more efforts were made by Basu and Iannacchione [13] to investigate the dielectric behaviour of a dilute 5CB:CNT suspension, and the characteristic local *pseudonematic* domains stabilised by the strong anchoring force were experimentally demonstrated. Along with the recent progresses and studies [14,15] related to the LC:CNT composite, it is almost evident that doping CNTs into NLCs would enhance the dielectric anisotropy of nematic liquid crystals; yet, analysis in terms of theoretical or numerical modelling towards this physical phenomenon still seems in need.

2. Modelling the dielectric behaviour of the binary mixture

Although scientists in the recent years have made progress in searching the effective permittivity of particle-filled composite for material design applications, (for example, Jylhä et al. [16] developed a differential mixing equation as a new effective medium theory which combines the small volume filling ratio properties of the Maxwell Garnett equation to the percolation properties of the Bruggeman symmetric equation, Shelestiuk et al. [17] constructed a theoretical model of the dielectric properties of a ferroelectric LC nanosuspension using a generalised Maxwell Garnett picture), the numerical effort based on the Maxwell Garnett theory which is devoted to the LC:CNT research community is missing.

In the classical mean-field approach for the effective dielectric constant of a heterogeneous mixture, it is assumed that the vector fields (D and E) are averaged

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over a volume sufficiently large to 'smear out' the heterogeneity (thus the action is so-called homogenisation), but still small with respect to the incident wavelength. It involves a set of the following equations:

$$\langle \boldsymbol{D} \rangle = \varepsilon \langle \boldsymbol{E} \rangle$$

$$\langle \boldsymbol{D} \rangle = (1-f) \langle \boldsymbol{D}_{\mathbf{e}} \rangle + f \langle \boldsymbol{D}_{\mathbf{i}} \rangle$$

$$\langle \boldsymbol{E} \rangle = (1-f) \langle \boldsymbol{E}_{\mathbf{e}} \rangle + f \langle \boldsymbol{E}_{\mathbf{i}} \rangle , \qquad (1)$$

where the subscripts e and i stand for the host environment and the embedded inclusion, respectively; and f is the volume fraction the inclusion occupies in the mixture. In addition, a relation between the field strengths in the inclusion and the host medium, i.e., $\langle \boldsymbol{E}_{\mathbf{i}} \rangle = K \langle \boldsymbol{E}_{\mathbf{e}} \rangle$, is required for giving the effective permittivity of the heterogeneous mixture [18]

$$\varepsilon_{\text{eff}} = \frac{(1-f)\,\varepsilon_e + f\varepsilon_i K}{1-f+fK}, \qquad (2)$$

where ε_{eff} is the effective permittivity of the mixture, ε_{e} is the permittivity of the environment which may not necessarily be vacuum, ε_{i} is the inclusion permittivity. However, inasmuch as CNT which is classified as a metal or a semiconductor depending on 'how strong' the CNTs are rolled from graphite, [19] the field *inside* the metallic body vanishes according to the macroscopic electrostatic theories, the answer needed for the ratio between the internal and external field for our case is unfortunately not a numerically easy problem to be resolved, otherwise, needs to be determined experimentally. Therefore, this *paper,* otherwise, follows the traditional Maxwell Garnett type approach [20] to analyse the dielectric property of the inhomogeneous NLC:CNT mixture. It is applicable when one of the components, NLC, is considered as a host in which a *minute* amount of CNT is embedded therein as an inclusion.

Among the mixing rules which are labelled like Maxwell Garnett, Rayleigh, and Bruggeman, and earlier leading scientists (Mossotti, Clausius, Lorenz, and Lorentz), the Maxwell Garnett approximation (MGA) which is an application of the Clausius–Mossotti model for polarisable particles embedded in a dielectric host, enjoys a time-honoured reputation as a correct effective medium theory in predicting the dielectric properties of a dilute biphasic or even multiphasic composite in the quasi-static or low-frequency regime.[21] For the biphasic case of isotropic-sphere-in-isotropic-matrix mixture, the MGA has an elegant look of

$$\varepsilon_{\text{eff}} = \varepsilon_{\text{e}} + 3f \frac{\varepsilon_{\text{i}} - \varepsilon_{\text{e}}}{\varepsilon_{\text{i}} + 2\varepsilon_{\text{e}} - f(\varepsilon_{\text{i}} - \varepsilon_{\text{e}})} \varepsilon_{\text{e}}. \qquad (3)$$

If the isotropic environment contains anisotropic inclusions which are conventionally treated in geometry as ellipsoids, then Equation (3) should be modified in the way the effective permittivity is represented by a diagonalised three-dimensional array of numerical values in a linear symmetric system ($\varepsilon_{\text{eff},i,j}$) where $\varepsilon_{\text{eff},i,j} = 0$ if $i \neq j$, $\forall i,j \in \{1,2,3\}$. In the global coordinate system, each individual component of ($\varepsilon_{\text{eff},i,j}$) reads

$$\varepsilon_{e\text{ff},x,y.z} = \varepsilon_{\text{e}} + f \frac{\varepsilon_{\text{i}} - \varepsilon_{\text{e}}}{\varepsilon_{\text{e}} + (1-f) N_{x,y,z} (\varepsilon_{\text{i}} - \varepsilon_{\text{e}})} \varepsilon_{\text{e}}, \qquad (4)$$

where $N_{x,y,z}$ is the geometrical or the so-called depolarisation factor that depends only on the shape of the ellipsoid in an isotropic host. In this *paper*, the dyadic notation of $\overline{\overline{\varepsilon}}_{\text{eff}}$ is adopted as convention to represent the linear system. Thus, according to Sihvola [22], one can generalise the Maxwell Garnett formula of (4) by simply retaining its expression and otherwise replacing the scalar permittivities ε_{eff}, ε_{e}, ε_{i} and the depolarisation factor N with their dyadic counterparts $\overline{\overline{\varepsilon}}_{\text{eff}}$, $\overline{\overline{\varepsilon}}_{\text{e}}$, $\overline{\overline{\varepsilon}}_{\text{i}}$ and $\overline{\overline{N}}$. However, for the special case of anisotropic-inclusion-in-anisotropic-host mixtures for which NLC:CNT is an example, one should be extra careful not to use the MG formula by merely interchanging N with $\overline{\overline{N}}$, since the depolarisation factor is also affected by the anisotropic environment (as indicated in [22]). Nevertheless, it is fortuitous (as shown in [23]) that one can still proceed with the Maxwell Garnett algorithm, bypassing the effect of anisotropy of the environment in the first place, and finish with modification of the final expression with an affinely transformed depolarisation dyadic $\overline{\overline{N'}}$. In addition, one advantage to mention the MG mixing formula is its applicability to complex permittivities for both guest and host materials.[24]

Here, consider the heterogeneous NLC:CNT composite in which the anisotropic inclusions of CNT are mixed with the anisotropic host of NLC, and the CNT inclusions are regarded as conductive or lossy dielectric materials. In order to validate the applicability of MGA for this specific mixture, some assumptions should be made as follows:

(1) The applied field frequency ω is some radio frequency within 10–10^5 Hz that is widely adopted for display facilities and related researches. Thus, the corresponding wavelength is so great in contrast to the size of CNTs and a quasi-static approximation is suitable analysing the mixture.

(2) The mixture sufficiently dilutes to the extent that the volume fraction of CNT in NLC is under the limit of MGA's applicability, which is approximately 30%, [25] and, therefore, the interaction among CNTs can herein be ignored.
(3) The percolation limit and the excluded volume condition are assumed, i.e., CNT grains are prohibited from contact, overlap or interpenetrating among each other and thereby the isolated CNTs in the dielectric NLC matrix can be safely regarded as a 'source-free' medium such that: Physically, the real-part permittivity value of the mixture here can be assumed much larger than the imaginary-part at the applied frequency ω and, numerically, the Laplace equation can be found in solving the internal field of the inclusion in quasi-static approximation.
(4) The CNTs are approximated by ellipsoids with semi-axes a, b and c in the orthogonal coordinate directions; a, b are the minor axes and c is the major axis with $c >> a, b$ and with $a = b$ as for the elongated spheroids (i.e., ellipsoids of revolution) with aspect ratio $a(b)/c$. In addition, the CNT ellipsoids are assumed to be dielectrically uniaxial, i.e., $\varepsilon_a = \varepsilon_b \neq \varepsilon_c$. The size of the ellipsoids can be different, but the geometry, i.e., the aspect ratios, should be the same.

2.1 The nematic mixture with aligned CNTs

For the scenario in which CNTs are doped in the NLC matrix under the nematic$\longleftrightarrow$isotropic transition temperature $T_{N\text{–}I}$, the composite is an anisotropic-inclusion-in-anisotropic-matrix mixture and the effective permittivity is dyadic. The CNTs are aligned uniformly in orientation, but may be random in position, and, thus, their corresponding axes are parallel. Now, since the background medium which is NLC is anisotropic, the effect of the anisotropic background is that the depolarisation factors become different in different directions and depend not only on the shape of the Lorentz cavity but also on the degree of anisotropy of the background medium.[26]

According to [26], the depolarisation dyadic modified through affine transformation for the case of isotropic inclusions of spheres in anisotropic uniaxial matrix is reproduced here as

$$N'_x = N'_y = \frac{1}{2\,(1-\gamma)}\left(1-\gamma\frac{\arctan\sqrt{\gamma-1}}{\sqrt{\gamma-1}}\right)$$

$$N'_z = \frac{\gamma}{\gamma-1}\left(1-\frac{\arctan\sqrt{\gamma-1}}{\sqrt{\gamma-1}}\right), \qquad (5)$$

where γ is the degree of anisotropy of the anisotropic medium which can be the uniaxial NLC material here and thus should be defined as $\gamma = \varepsilon_{lc,z}/\varepsilon_{lc,x} = \varepsilon_{lc,z}/\varepsilon_{lc,y} = \varepsilon_{||}/\varepsilon_{\perp}$, note that for positively anisotropic NLCs: $\gamma > 1$. In specific, for the case which is anisotropic ellipsoidal inclusions loaded in uniaxial NLC host, we derived the transformed dyadic components as

$$N'_x = N'_y = \frac{c}{2\left(c^2-\gamma a^2\right)}\left(c-\frac{\gamma a^2}{\sqrt{c^2-\gamma a^2}}\tan\ \mathrm{h}^{-1}\right.$$
$$\left.\times\left(\frac{\gamma a^2}{\sqrt{c^2-\gamma a^2}}\right)+j\left(\frac{\pi\gamma a^2}{2\sqrt{c^2-\gamma a^2}}\right)\right)$$

$$N'_z = \frac{-1}{\left(c^2-\gamma a^2\right)}\left(\gamma b^2-\frac{c}{\sqrt{c^2-\gamma a^2}}\tan\ \mathrm{h}^{-1}\right.$$
$$\left.\times\left(\frac{c}{\sqrt{c^2-\gamma a^2}}\right)+j\left(\frac{\pi c}{2\sqrt{c^2-\gamma a^2}}\right)\right) \qquad (6)$$

When the ellipsoidal inclusion degenerates to a sphere, i.e., $c = a$, Equation (6) is reduced to Equation (5). Moreover, if the major axis c of the inclusion is prolonged to infinity ($c \to \infty$), which is one of the extreme cases of ellipsoid as a 'needle', intriguingly in Equation (6), the two transverse depolarisation factors N'_x and N'_y would numerically be equal to 1/2 and N'_z to 0, independent of γ, and if the degree of anisotropy of the nematic host is very large, say, $\gamma \to \infty$, then N'_x and N'_y would be equal to 0 and N'_z to 1, independent of the aspect ratio of any shape of the inclusion, and the sum rule for the depolarisation factors ($N'_x + N'_y + N'_z = 1$) still holds. Thus, with Equation (6), the extended Maxwell Garnett formula for the NLC:CNT mixture is [26]

$$\overline{\overline{\varepsilon}}_{\text{eff\_nematic}} = \overline{\overline{\varepsilon}}_{\text{lc}} + f\overline{\overline{\varepsilon}}_{\text{lc}}\cdot\left[\frac{\overline{\overline{\varepsilon}}_{\text{cnt}}-\overline{\overline{\varepsilon}}_{\text{lc}}}{\overline{\overline{\varepsilon}}_{\text{lc}}+(1-f)\overline{\overline{N'}}\cdot\left(\overline{\overline{\varepsilon}}_{\text{cnt}}-\overline{\overline{\varepsilon}}_{\text{lc}}\right)}\right]. \qquad (7)$$

Since the effective permittivity depends on how well the inclusions are aligned, [27] it should be reminded that Equation (7) is under the assumption that the CNTs are idealised as uniaxial ellipsoids with the same geometry and orientation aligned in the uniaxial NLC host.

On the other hand, since the CNT inclusion is considered a conductive material, the dielectric behaviour that is characterised by the complex permittivity has the form of [28]

$$\overline{\overline{\varepsilon}}_{\text{i}} = \overline{\overline{\varepsilon}}_{\text{cnt}} = \overline{\overline{\varepsilon'}}_{\text{cnt}} - j\overline{\overline{\varepsilon''}}_{\text{cnt}} = \overline{\overline{\varepsilon'}}_{\text{cnt}} - j\frac{\overline{\overline{\sigma}}}{\omega} \qquad (8)$$

where $\overline{\overline{\varepsilon'}}_{\rm cnt}$ is the real-part permittivity of CNT, ω is applied angular frequency $\omega = 2\pi\nu$, $\overline{\overline{\sigma}}$ is the conductivity of CNT and can be related to the CNT's dielectric properties by $\overline{\overline{\sigma}} = \omega\overline{\overline{\varepsilon''}}_{\rm cnt}$ [see Appendix about the physical propriety of adopting Equation (8) for CNTs, since CNTs are of nano-sized materials and one may ask whether Equation (8) that is generally for bulk lossy dielectrics can be applicable for CNTs or not]. In addition, the biphasic mixture can be characterised by the Debye model if the concentration of CNT is sufficiently low (<0.05 wt%).[14] Although there is not a perfect numerical relationship between the Maxwell Garnett approximation and the Debye model, an equivalent or 'Debye-like' expression can still be developed to describe the dielectric behaviour of the mixture as indicated by Paulis et al.[24] as

$$\overline{\overline{\varepsilon}}_{\rm eff}(\omega) = \overline{\overline{\varepsilon}}_{{\rm eff},\infty} + \frac{\overline{\overline{\varepsilon}}_{{\rm eff},s} - \overline{\overline{\varepsilon}}_{{\rm eff},\infty}}{1 + j\omega\overline{\overline{\tau}}}, \tag{9}$$

where $\overline{\overline{\tau}}$ is the characteristic relaxation time, $\overline{\overline{\varepsilon}}_{{\rm eff},s}$ and $\overline{\overline{\varepsilon}}_{{\rm eff},\infty}$ are the d. c. and optic-limit effective permittivity values, respectively. To connect MGA with this first-order Debye-like expression, it is to achieve the Debye parameters $\left(\overline{\overline{\varepsilon}}_{{\rm eff},\infty}, \overline{\overline{\varepsilon}}_{{\rm eff},s}, \overline{\overline{\tau}}\right)$ in Equation (9) and we adopt the procedure described by Paulis [24]:

Step 1: Take the multi-dimensional limits of the real part of Equation (7) with respect to $\overline{\overline{\varepsilon}}_{\rm lc}$ and $\overline{\overline{\varepsilon}}_{\rm cnt}$ to evaluate $\overline{\overline{\varepsilon}}_{{\rm eff},s}$ and $\overline{\overline{\varepsilon}}_{{\rm eff},\infty}$.

Since the permittivity variance (a measure of how far a set of permittivity data spread out against frequency) of CNT, [29] seems much more than that of NLC, [14,30] i.e., $\mathrm{Var}(\varepsilon_{\rm cnt}) >> \mathrm{Var}(\varepsilon_{\rm lc})$, the permittivity of the nematic host $\overline{\overline{\varepsilon}}_{\rm lc}$ can be viewed invariant relative to the inclusion permittivity $\overline{\overline{\varepsilon}}_{\rm cnt}$ in the dielectric spectrum. So far, this is for calculative simplicity and a more rigorous analysis which treats the host as a dispersive material and thus the effective permittivity of the mixture should be a superposition of the two Debye terms is underway. Thus, we assume the NLC:CNT composites have constant host permittivity and inclusion permittivity which is described in Equation (8). Then, by substituting Equation (8) into Equation (7), taking the static- and optic-limit of Equation (7), the Debye parameters of the mixture can be derived as

$$\overline{\overline{\varepsilon}}_{{\rm eff},s} = \frac{\overline{\overline{\varepsilon}}_{\rm lc} \cdot \left(f\overline{\overline{N'}} - \overline{\overline{N'}} - f\right)}{\overline{\overline{N'}}\,(f-1)}$$

$$\overline{\overline{\varepsilon}}_{{\rm eff},\infty} = \frac{\overline{\overline{\varepsilon}}_{\rm lc} \cdot \left[\overline{\overline{\varepsilon}}_{\rm lc} \cdot \left(f\overline{\overline{N'}} - \overline{\overline{N'}} - f + 1\right) - \overline{\overline{\varepsilon}}_{{\rm cnt},\infty} \cdot \left(f\overline{\overline{N'}} - \overline{\overline{N'}} - f\right)\right]}{\overline{\overline{\varepsilon}}_{\rm lc} \cdot \left(f\overline{\overline{N'}} - \overline{\overline{N'}} + 1\right) - \overline{\overline{\varepsilon}}_{{\rm cnt},\infty} \cdot \left(f\overline{\overline{N'}} - \overline{\overline{N'}}\right)}, \tag{10}$$

Step 2: Substitute $\overline{\overline{\varepsilon}}_{eff,s}$ and $\overline{\overline{\varepsilon}}_{eff,\infty}$ into the equivalent Debye model [Equation (9)] and set equal to the MGA formula (7) for $\overline{\overline{\tau}}$, we evaluated the relaxation time at the quasi-static d. c. limit ($w \to 0$) (it is also because most of real parts of the Debye profiles have a look of step function and the steps occur at frequencies much beyond the validity of the Maxwell Garnett approximation)

$$\overline{\overline{\tau}} = \frac{\overline{\overline{\varepsilon}}_{\rm lc} \cdot \left(\overline{\overline{N'}} - f\overline{\overline{N'}} - 1\right) + \overline{\overline{\varepsilon}}_{{\rm cnt},\infty} \cdot \overline{\overline{N'}}\,(f-1)}{\sigma\overline{\overline{N'}}\,(f-1)}. \tag{11}$$

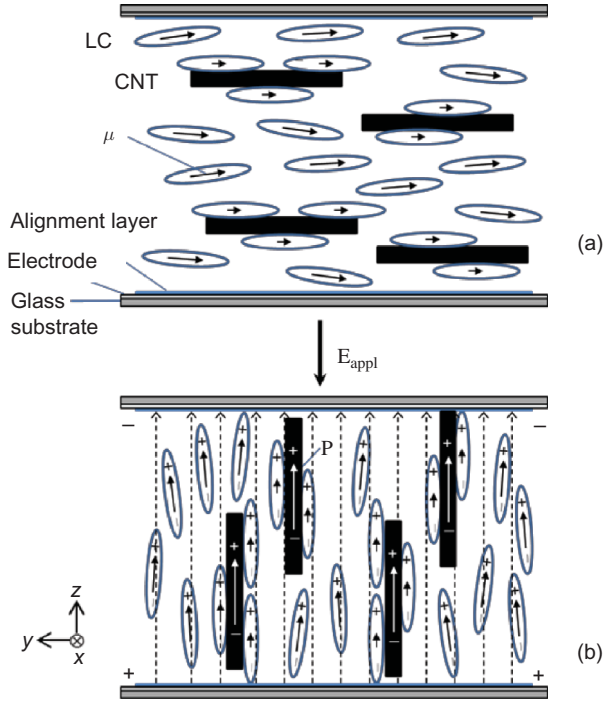

Figure 1. (colour online) (Not to scale) Schematic illustration of presumably nonpolar CNTs dispersed in NLCs with a permanent dipole moment μ.[31] The heterogeneous LC:CNT mixture is confined between a parallel-antiparallel rubbed glass cell with electrodes on both of the substrates. The CNTs and NLCs are mutually aligned as referred to [3] and [5] no matter before (a) or after (b) the threshold of the Fréedericksz transition. The applied field induces an additional dipole moment from CNTs **p** [21] in (b), and no ion impurity which not only deteriorates the electro-optical performance of the cell due to screening effect [6] but also complicates the numerical analysis exists in this idealised mixture. The laboratory coordinate is indicated in the animation.

Through Equations (9) to (11), the effective permittivity dyadic of the mixture is completely defined. Interestingly, since $\overline{\overline{N'}}$ involves the degree of anisotropy of the NLC host γ which implicitly interrelates the depolarisation components N_x, N_y and N_z according to Equation (6), the effective permittivity components are cross-coupled through the depolarisation factors and $\overline{\overline{\varepsilon}}_{\text{eff\_nematic}}$, indeed, depends not only on the operation frequency but also on the degree of anisotropy of the nematic matrix. Thus, $\overline{\overline{\varepsilon}}_{\text{eff\_nematic}}$ in Equation (9) should be thought of as $\overline{\overline{\varepsilon}}_{\text{eff\_nematic}}(\omega,\gamma)$, whereas we drop (ω,γ) tacitly, because whenever we discuss $\overline{\overline{\varepsilon}}_{\text{eff\_nematic}}$, it is clear for its dependency on frequency and the host medium's degree of anisotropy.

Case i) Below the threshold of the Fréedericksz transition of the NLC:CNT mixture, where the long axes of NLCs and CNTs are mutually aligned in the y-direction as depicted in Figure 1(a):

$$\begin{aligned}\overline{\overline{\varepsilon}}_{\text{eff\_nematic}} &= \begin{bmatrix} \varepsilon_{\text{eff},x} & 0 & 0 \\ 0 & \varepsilon_{\text{eff},y} & 0 \\ 0 & 0 & \varepsilon_{\text{eff},z} \end{bmatrix} \\ &= \begin{bmatrix} \varepsilon_{\text{eff},\perp} & 0 & 0 \\ 0 & \varepsilon_{\text{eff},||} & 0 \\ 0 & 0 & \varepsilon_{\text{eff},\perp} \end{bmatrix}\end{aligned} \tag{12}$$

where the effective permittivity components are described by

$$\varepsilon_{\text{eff},\perp} = \varepsilon_{\text{eff},x,z} = \frac{\varepsilon_{\text{lc},\perp}\left[\varepsilon_{\text{lc},\perp}\left(fN'_{x,z} - N'_{x,z} - f + 1\right) - \varepsilon_{\text{cnt},\perp,\infty}\left(fN'_{x,z} - N'_{x,z} - f\right)\right]}{\varepsilon_{\text{lc},\perp}\left(fN'_{x,z} - N'_{x,z} + 1\right) - \varepsilon_{\text{cnt},\perp,\infty}\left(fN'_{x,z} - N'_{x,z}\right)}$$

$$+ \frac{\dfrac{\varepsilon_{\text{lc},\perp}\left(fN'_{x,z} - N'_{x,z} - f\right)}{N'_{x,z}(f-1)} - \dfrac{\varepsilon_{\text{lc},\perp}\left[\varepsilon_{\text{lc},\perp}\left(fN'_{x,z} - N'_{x,z} - f + 1\right) - \varepsilon_{\text{cnt},\perp,\infty}\left(fN'_{x,z} - N'_{x,z} - f\right)\right]}{\varepsilon_{\text{lc},\perp}\left(fN'_{x,z} - N'_{x,z} + 1\right) - \varepsilon_{\text{cnt},\perp,\infty}\left(fN'_{x,z} - N'_{x,z}\right)}}{1 + j\omega\left[\dfrac{\varepsilon_{\text{lc},\perp}\left(-fN'_{x,z} + N'_{x,z} - 1\right) + \varepsilon_{\text{cnt},\perp,\infty}N'_{x,z}(f-1)}{\sigma N'_{x,z}(f-1)}\right]}$$

and

$$\varepsilon_{\text{eff},||} = \varepsilon_{\text{eff},y} = \frac{\varepsilon_{\text{lc},||}\left[\varepsilon_{\text{lc},||}\left(fN'_{y} - N'_{y} - f + 1\right) - \varepsilon_{\text{cnt},||,\infty}\left(fN'_{y} - N'_{y} - f\right)\right]}{\varepsilon_{\text{lc},||}\left(fN'_{y} - N'_{y} + 1\right) - \varepsilon_{\text{cnt},||,\infty}\left(fN'_{y} - N'_{y}\right)}$$

$$+ \frac{\dfrac{\varepsilon_{\text{lc},||}\left(fN'_{y} - N'_{y} - f\right)}{N'_{y}(f-1)} - \dfrac{\varepsilon_{\text{lc},||}\left[\varepsilon_{\text{lc},||}\left(fN'_{y} - N'_{y} - f + 1\right) - \varepsilon_{\text{cnt},||,\infty}\left(fN'_{y} - N'_{y} - f\right)\right]}{\varepsilon_{\text{lc},||}\left(fN'_{y} - N'_{y} + 1\right) - \varepsilon_{\text{cnt},||,\infty}\left(fN'_{y} - N'_{y}\right)}}{1 + j\omega\left[\dfrac{\varepsilon_{\text{lc},||}\left(-fN'_{y} + N'_{y} - 1\right) + \varepsilon_{\text{cnt},||,\infty}N'_{y}(f-1)}{\sigma N'_{y}(f-1)}\right]}, \tag{13}$$

Notwithstanding the adoption of the dyadic notation has seemingly become pretty common in electromagnetic researches plausibly due to its calculability with some easily memorisable algebraic rules and its advantage, that is, the dyadic algebra is independent of any coordinate system whereas the components in a matrix may vary even if its coordinate basis is changed globally, the matrix notation may still look more familiar. Thus, along with Equations (10) and (11), Equation (9), here, is represented by a 3×3 diagonal matrix comprising with ω- and γ- dependent components in the orthogonal x, y and z-directions for the following scenarios:

where (N'_x, N'_y, N'_z) are defined in Equation (6).

Case ii) Above the Fréedericksz transition's threshold, where the long axes of NLCs and CNTs are both tipped by the electric field to the z-direction as shown in Figure 1(b), the extraordinary term $\varepsilon_{||}$ now appears in the z-direction:

$$\begin{aligned}\overline{\overline{\varepsilon}}_{\text{eff\_nematic}} &= \begin{bmatrix} \varepsilon_{\text{eff},x} & 0 & 0 \\ 0 & \varepsilon_{\text{eff},y} & 0 \\ 0 & 0 & \varepsilon_{\text{eff},z} \end{bmatrix} \\ &= \begin{bmatrix} \varepsilon_{\text{eff},\perp} & 0 & 0 \\ 0 & \varepsilon_{\text{eff},\perp} & 0 \\ 0 & 0 & \varepsilon_{\text{eff},||} \end{bmatrix}\end{aligned}, \tag{14}$$

where

$$\varepsilon_{\text{eff},\perp} = \varepsilon_{\text{eff},x,y} = \frac{\varepsilon_{\text{lc},\perp}\left[\varepsilon_{\text{lc},\perp}\left(fN'_{x,y} - N'_{x,y} - f + 1\right) - \varepsilon_{\text{cnt},\perp,\infty}\left(fN'_{x,y} - N'_{x,y} - f\right)\right]}{\varepsilon_{\text{lc},\perp}\left(fN'_{x,y} - N'_{x,y} + 1\right) - \varepsilon_{\text{cnt},\perp,\infty}\left(fN''_{x,y} - N'_{x,y}\right)}$$

$$+ \frac{\dfrac{\varepsilon_{\text{lc},\perp}\left(fN'_{x,y} - N'_{x,y} - f\right)}{N'_{x,y}(f-1)} - \dfrac{\varepsilon_{\text{lc},\perp}\left[\varepsilon_{\text{lc},\perp}\left(fN'_{x,y} - N'_{x,y} - f + 1\right) - \varepsilon_{\text{cnt},\perp,\infty}\left(fN'_{x,y} - N'_{x,y} - f\right)\right]}{\varepsilon_{\text{lc},\perp}\left(fN'_{x,y} - N'_{x,y} + 1\right) - \varepsilon_{\text{cnt},\perp,\infty}\left(fN'_{x,y} - N'_{x,y}\right)}}{1 + j\omega\left[\dfrac{\varepsilon_{\text{lc},\perp}\left(-fN'_{x,y} + N'_{x,y} - 1\right) + \varepsilon_{\text{cnt},\perp,\infty}N'_{x,y}(f-1)}{\sigma N'_{x,y}(f-1)}\right]}$$

and

$$\varepsilon_{\text{eff},||} = \varepsilon_{\text{eff},z} = \frac{\varepsilon_{\text{lc},||}\left[\varepsilon_{\text{lc},||}\left(fN'_{z} - N'_{z} - f + 1\right) - \varepsilon_{\text{cnt},||,\infty}\left(fN'_{z} - N'_{z} - f\right)\right]}{\varepsilon_{\text{lc},||}\left(fN'_{z} - N''_{z} + 1\right) - \varepsilon_{\text{cnt},||,\infty}\left(fN'_{z} - N'_{z}\right)}$$

$$+ \frac{\dfrac{\varepsilon_{\text{lc},||}\left(fN'_{z} - N'_{z} - f\right)}{N'_{z}(f-1)} - \dfrac{\varepsilon_{\text{lc},||}\left[\varepsilon_{\text{lc},||}\left(fN'_{z} - N'_{z} - f + 1\right) - \varepsilon_{\text{cnt},||,\infty}\left(fN'_{z} - N'_{z} - f\right)\right]}{\varepsilon_{\text{lc},||}\left(fN'_{z} - N'_{z} + 1\right) - \varepsilon_{\text{cnt},||,\infty}\left(fN'_{z} - N'_{z}\right)}}{1 + j\omega\left[\dfrac{\varepsilon_{\text{lc},||}\left(-fN'_{z} + N'_{z} - 1\right) + \varepsilon_{\text{cnt},||,\infty}N'_{z}(f-1)}{\sigma N'_{z}(f-1)}\right]}. \quad (15)$$

Thus, a closed-form dielectric mechanism in the dielectric measurement for the NLC:CNT mixture is expressed in Equations (12) and (14) with their components in Equations (13) and (15), respectively. Although Equations (13) and (15) look rather complicated, substantial simplification can be done by adopting one of the extreme cases for ellipsoid, in which CNTs are further approximated as a 'needle' and the depolarisation factors of Equation (6) are as calculated $N'_{\text{longitudinal}} = 0$ and $N'_{\text{transverse}} = 1/2$ depending on field directions. Thus, the depolarisation factors (N'_x, N'_y, N'_z) in Cases i) and ii) are (1/2, 0, 1/2) and (1/2, 1/2, 0), respectively, and this approximation leads to for Case i) as

$$\varepsilon_{\text{eff},\perp} = \varepsilon_{\text{eff},x,z} = \frac{\varepsilon_{\text{lc},\perp}\left[\varepsilon_{\text{lc},\perp}(1-f) + \varepsilon_{\text{cnt},\perp,\infty}(1+f)\right]}{\varepsilon_{\text{lc},\perp}(1+f) + \varepsilon_{\text{cnt},\perp,\infty}(1-f)}$$

$$+ \frac{\varepsilon_{\text{lc},\perp}\left[\dfrac{1+f}{1-f} - \dfrac{\varepsilon_{\text{lc},\perp}(1-f) + \varepsilon_{\text{cnt},\perp,\infty}(1+f)}{\varepsilon_{\text{lc},\perp}(1+f) + \varepsilon_{\text{cnt},\perp,\infty}(1-f)}\right]}{1 + j\omega\left[\dfrac{\varepsilon_{\text{lc},\perp}(1+f) + \varepsilon_{\text{cnt},\perp,\infty}(1-f)}{\sigma(1-f)}\right]} \quad (16a)$$

$$\varepsilon_{\text{eff},||} = \varepsilon_{\text{eff},y} = \varepsilon_{\text{lc},||}(1-f) + \varepsilon_{\text{cnt},||,\infty}f, \quad (16b)$$

and for Case ii), the effective permittivity components of the mixture are in the same form only with the subscripts y and z interchanged

$$\varepsilon_{\text{eff},\perp} = \varepsilon_{\text{eff},x,y} = \frac{\varepsilon_{\text{lc},\perp}\left[\varepsilon_{\text{lc},\perp}(1-f) + \varepsilon_{\text{cnt},\perp,\infty}(1+f)\right]}{\varepsilon_{\text{lc},\perp}(1+f) + \varepsilon_{\text{cnt},\perp,\infty}(1-f)}$$

$$+ \frac{\varepsilon_{\text{lc},\perp}\left[\dfrac{1+f}{1-f} - \dfrac{\varepsilon_{\text{lc},\perp}(1-f) + \varepsilon_{\text{cnt},\perp,\infty}(1+f)}{\varepsilon_{\text{lc},\perp}(1+f) + \varepsilon_{\text{cnt},\perp,\infty}(1-f)}\right]}{1 + j\omega\left[\dfrac{\varepsilon_{\text{lc},\perp}(1+f) + \varepsilon_{\text{cnt},\perp,\infty}(1-f)}{\sigma(1-f)}\right]} \quad (17a)$$

$$\varepsilon_{\text{eff},||} = \varepsilon_{\text{eff},z} = \varepsilon_{\text{lc},||}(1-f) + \varepsilon_{\text{cnt},||,\infty}f. \quad (17b)$$

Finally, if one sets $f = 0$, then obviously the results of Equations (16a,b) and (17a,b) will be reduced to the pristine liquid crystals and satisfy $\varepsilon_{\text{eff}} = \varepsilon_{\text{lc}}$ for all the components in the effective permittivity matrix.

2.2 The isotropic mixture with aligned CNTs

For the scenario, when CNTs are doped in the NLC matrix above T_{N-I}, NLC is isotropic and the NLC:CNT composite is either an anisotropic-inclusion-in-isotropic-matrix or an utterly isotropic

mixture, depending on whether the CNT inclusions are aligned or randomly dispersed in the NLC host. For the specific system which is the isotropic NLC matrix with aligned CNT inclusions, it is due to the existence of pseudonematic domains indicated [13] such that CNTs can possibly be aligned in the isotropic NLC matrix if a sufficient external field is applied. However, since the pseudonematic domains around the nanotubes are presumably in the scale of a few angstroms, the pseudonematic domains are electromagnetically ignored throughout this *paper*; otherwise, the inclusions should be considered as two-layered anisotropic ellipsoids and the generalisation for this complicated heterogeneity is essential.

Thus, the effective permittivity here is described by [26]

$$\overline{\overline{\varepsilon}}_{\text{eff\_isotropic}} = \varepsilon_{\text{lc}}\overline{\overline{I}} + f\varepsilon_{\text{lc}} \cdot \left[\frac{\overline{\overline{\varepsilon}}_{\text{cnt}} - \varepsilon_{\text{lc}}\overline{\overline{I}}}{\varepsilon_{\text{lc}}\overline{\overline{I}} + (1-f)\overline{\overline{N}} \cdot \left(\overline{\overline{\varepsilon}}_{\text{cnt}} - \varepsilon_{\text{lc}}\overline{\overline{I}}\right)} \right], \tag{18}$$

where the permittivity of the isotropic NLC should be the mean permittivity of $\varepsilon_{\text{lc}} = \left(\varepsilon_{||} + 2\varepsilon_{\perp}\right)/3$, and the effective permittivity dyadic of this mixture is, likewise, defined by Equations (9), (10) and (11) except that $\overline{\overline{\varepsilon}}_{\text{lc}}$ should be reduced to ε_{lc} due to the annihilation of the NLC director and the affinely transformed depolarisation factor $\overline{\overline{N'}}$ should be resumed to the ordinary $\overline{\overline{N}}$.

3. Discussion

As derived in Section 2.1 for a simplified case when carbon nanotubes are regarded as infinitely thin ellipsoids, interesting Equations (16b) and (17b) can be found for all frequencies, the effective permittivity of the mixture in the NLC's/CNT's long axis is partially (due to the presence of f) a linear superposition of the frequency-dependent $\varepsilon_{\text{lc},||}$ and the constant-valued $\varepsilon_{\text{cnt},||,\infty}$. Since [7,13] the acquirements of LC:CNT's $\Delta\varepsilon$ rely on measuring $\varepsilon_{\perp}$ and $\varepsilon_{||}$ of the mixture before and after the Fréedericksz transition, respectively, Equations (16a) and (17b), simultaneously, can be adopted to explain the composite's enhanced $\Delta\varepsilon$. In particular, for dilute mixtures where $f \to 0$ (note that $0 \le f \le 1$), both Equations (16a) and (17b) accord with $\varepsilon_{\text{eff},\perp} = \varepsilon_{\text{eff},x,z} \cong \varepsilon_{\text{lc},\perp}$ and $\varepsilon_{\text{eff},||} = \varepsilon_{\text{eff},z} \cong \varepsilon_{\text{lc},||} + \varepsilon_{\text{cnt},||,\infty} f$, respectively, and leading to $\Delta\varepsilon_{\text{eff\_nematic}} \cong \Delta\varepsilon_{\text{lc}} + f\varepsilon_{\text{cnt},||,\infty}$. Thus, if the transvers ($\varepsilon_{\text{lc},\perp}$) and longitudinal ($\varepsilon_{\text{lc},||}$) permittivities of the nematic host are *not* altered by the introduction of CNT, then one can tell that the observed increase of the dielectric anisotropy of the mixture can basically be attributable to the existence of the fractional permittivity of CNT along its tubular direction at the high frequency limit, i.e., the $f\varepsilon_{\text{cnt},||,\infty}$. However, since it is well-known that the dielectric anisotropy is positively proportional to the order parameter of NLC, the last factor we should study is the order parameter of the NLC host S, whether it is changed or not. Thus, the investigation into the impact of CNTs on the order parameter of NLCs is performed by differential scanning calorimetry (DSC) which unambiguously traced the prepared highly dilute 5CB: multi-walled CNT (MWCNT) (<0.01 wt%) samples that underwent various endothermic processes (Figure 2) in spite of the thermoanalyses of NLC:CNT with relatively higher concentrations (0.01–0.1%), in which the CNT *aggregates* are considered as quasi-macroscopic particles in the nematic matrix which has been conducted previously.[32]

Despite the little discrepancy in the peak values of phase transition temperature $T_{N\text{–}I}$ among the samples, an independent optical examination of $T_{N\text{–}I}$'s which was carried out microscopically under crossed polarisers on a thermo stage (Linkham PE94, precision: 0.1°C), and with an additional 0.02 wt% 5CB:MWCNT sample which is measured to be 33.5°C,

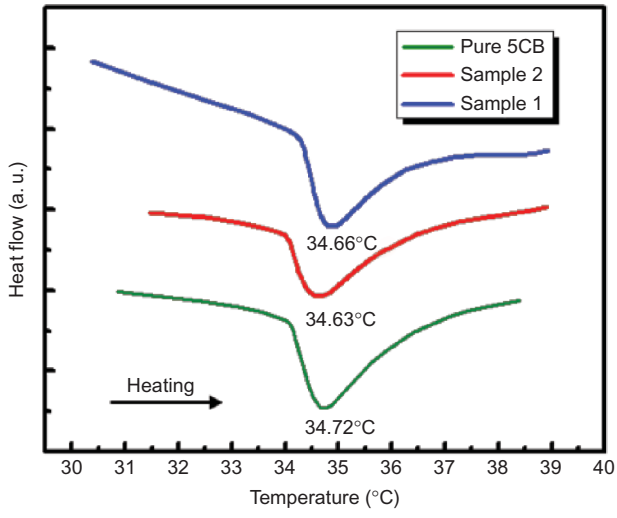

Figure 2. (colour online) DSC thermograms of pure 5CB and doped counterparts. The highly dilute samples were prepared using the ultracentrifugation technique (by which the samples were extracted from the supernatant). Sample 2 differs from Sample 1 only in the duration of ultracentrifugation, which is 15 min shorter than for Sample 1, inferring higher CNT concentration. The thermoanalysis was performed with the samples in hermetically sealed pans in temperature range between 20 and 40°C and with a heating and cooling rate of 10°C/min.

exhibited the same trend that CNT as impurity decreases T_{N-I} of pure LC and that the more the CNT content the lower the transition temperature of the mixture, presumably due to the entropic gain in origin.[33] The drop in T_{N-I} implies that the CNT dopant induced disruption of the long-range order of the 5CB matrix, according to the semi-empirical formula for the order parameter $S = \left(1 - T/T_{N-1}\right)^{\beta}$, where the exponent β is a fitting parameter for LC materials and T is temperature.[34]

The dielectric anisotropy of the NLC:CNT mixture is increased as observed by previous researchers, whereas a decrease in the order parameter observed here is detrimental to the dielectric anisotropy of the NLC matrix. Clearly, one can thus state that $f\varepsilon_{\mathrm{cnt},||,\infty}$, which is related to the stored energy within CNTs at the high frequency limit, plays an important role in the enhancement of the effective dielectric anisotropy of carbon-nanotube-doped nematic liquid crystal.

On the other hand, since the depolarisation factors of the NLC:CNT mixtures of aligned CNTs in nematic and isotropic NLCs have the same values, i.e., $N_{\mathrm{longitudinal}} = N'_{\mathrm{longitudinal}} = 0$ and $N_{\mathrm{transverse}} = N'_{\mathrm{transverse}} = 1/2$ when CNT's shape is approximated as of a needle, both kinds of the mixtures have the same form of formula as $\Delta\varepsilon_{\mathrm{eff}}$= (17b) – Re(16a) with only one difference that is between $\varepsilon_{\mathrm{lc}}$ and $\overline{\overline{\varepsilon}}_{\mathrm{lc}}$. Accordingly, we analyse the effective dielectric properties of both mixtures at the quasi-static limit as plotted in Figure 3.

In general, the effective dielectric anisotropies ($\Delta\varepsilon_{\mathrm{eff}}$) of both kinds of the NLC:CNT mixtures

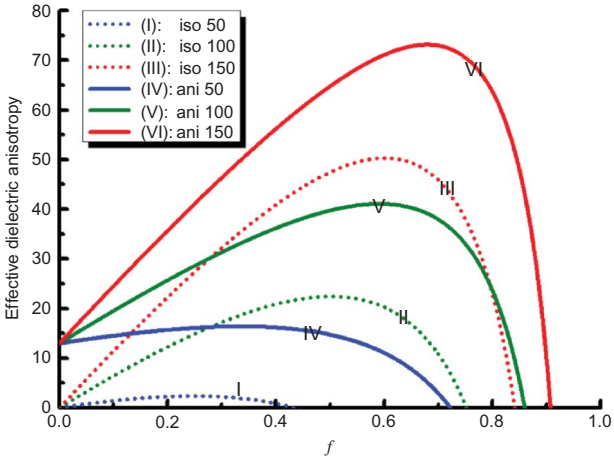

Figure 3. (colour online) Calculated effective dielectric anisotropies as a function of the volume fraction f of the binary mixtures of aligned CNTs of various longitudinal dielectric constants $\varepsilon_{\mathrm{cnt},\|}$ in the isotropic (dotted lines: I, II, III) and anisotropic (solid lines: IV, V, VI) NLC hosts. The blue (I, IV), green (II, V) and red (III, VI) lines denote the representative values of $\varepsilon_{\mathrm{cnt},\|}$ set equal to 50, 100 and 150, [35] respectively.

increase as the volume fraction increases. In addition, it can be seen in Figure 3 that the introduction of the CNT inclusion gives rise the dielectric anisotropy to the isotropic NLC (dotted lines). Notably, there exist turning points for all the curves in the figure and may be attributed to either beyond the limitation of the Maxwell Garnett approximation or implying that 'bundled' CNTs formed in the high-concentration regime may have negative dielectric constants.[36]

Another point needed to be discussed is: due to the cooperatively-aligned nature of NLC:CNT, there should not be a scenario that is of randomly aligned CNTs in the nematic-phasic LC matrix. Besides, one scenario which can be an exception from assumption IV is that all the CNT inclusions in the isotropic NLC matrix are randomly dispersed, resulting in annihilation of the CNT's macroscopically preferred orientation, and the binary NLC:CNT mixture becomes mutually/totally isotropic. Thus, the effective permittivity of this random system should be a scalar quantity [21] as

$$\varepsilon_{\mathrm{eff\_isotropic\_random}} = \varepsilon_{\mathrm{lc}} + \frac{\frac{1}{3}f\left(\varepsilon_{\mathrm{cnt}} - \varepsilon_{\mathrm{lc}}\right)\sum_{j=x,y,z}\frac{\varepsilon_{\mathrm{lc}}}{\varepsilon_{\mathrm{lc}} + N_j\left(\varepsilon_{\mathrm{cnt}} - \varepsilon_{\mathrm{lc}}\right)}}{1 - \frac{1}{3}f\left(\varepsilon_{\mathrm{cnt}} - \varepsilon_{\mathrm{lc}}\right)\sum_{j=x,y,z}\frac{N_j}{\varepsilon_{\mathrm{lc}} + N_j\left(\varepsilon_{\mathrm{cnt}} - \varepsilon_{\mathrm{lc}}\right)}}; \tag{19}$$

and if we follow the derivative procedure described previously with Equation (19) for Equation (9), then the Debye-like MG expression for this kind of mixture becomes

$$\varepsilon_{\mathrm{eff\_isotropic\_random}} = \frac{\varepsilon_{\mathrm{lc}}}{3}\frac{\left(-fN_yN_z - fN_xN_y + 3fN_xN_yN_z - 3N_xN_yN_z - fN_xN_z\right)}{N_xN_yN_z(f-1)} \tag{20}$$

However, Equation (20) is found singular if we, as before, treat CNTs as prolonged ellipsoids which will have zeroed depolarisation factor as a denominator. Thus, the derivation described in this *paper* is not suitable for the case, since it is physically fair to imagine that the 'very long' conductive ellipsoids such as CNTs without excluded volume constraint may easily contact with one other if they are randomly dispersed in a matrix, i.e., the premise we made in the beginning of the derivation (assumption III) will be violated and the factor of percolation limit should, otherwise, be incorporated in such an analysis.

4. Conclusion and perspectives

The analytic expression based on the Maxwell Garnett approximation for the dually anisotropic mixture of NLC:CNT has been acquired in order to address the dielectric behaviour of this novel composite. The results show that the Debye parameter of the CNT dopant at optic limit seems to be the key physical cause of the enhancement of dielectric anisotropy of the NLC host. Moreover, and to the best of our knowledge, the measurement of the dielectric anisotropy of the tubular fullerene—carbon nanotube—is not a particularly easy task. Thus, this work holds promise for application to obtain the dielectric anisotropy of various types of CNTs, e.g., those of single- or multi-walled structure along with various (armchair, zigzag or helical) configurations, by measuring the effective permittivity of the NLC:CNT mixture before and after threshold voltage with known CNT conductivity and NLC parameters followed by calculation using the derived numerical expressions herein. Besides, NLC:CNT with higher concentrations, for which the Bruggeman approach (or other differential methods) that would consider the interaction between CNTs in the NLC host so that the background permittivity is no longer $\overline{\overline{\varepsilon}}_{\mathrm{lc}}$, but is $\overline{\overline{\varepsilon}}_{\mathrm{eff}}$, should come into play, and the corresponding numerical analysis is worth an independent work. Other interesting topics such as improving the MGA results of this work like using the depolarisation factor for long cylinders [37] or incorporating orientational integrals for unordered distribution of CNTs in the NLC host for this scientific duo deserve as future outlooks.

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References

[1] Lee W, Chiu CS. Observation of self-diffraction by gratings in nematic liquid crystals doped with carbon nanotubes. Opt Lett. 2001;26:521–523.
[2] Lee W, Yeh S-L. Optical amplification in nematics doped with carbon nanotubes. Appl Phys Lett. 2001;79:4488–4490.
[3] Lynch MD, Patrick DL. Organizing carbon nanotubes with liquid crystals. Nano Lett. 2002;2:1197–1201.
[4] Popa-Nita V, Kralj S. Liquid crystal–carbon nanotubes mixtures. J Chem Phys. 2010;132:024902.
[5] Dierking I, Scalia G, Morales P. Liquid crystal–carbon nanotube dispersions. J. Appl. Phys. 2005;97:044309.
[6] Lee W, Wang C-Y, Shih Y-C. Effects of carbon nanosolids on the electro-optical properties of a twisted nematic liquid-crystal host. Appl Phys Lett. 2004;85:513–515.
[7] Baik IS, Jeon SY, Lee SH, Park KA, Jeong SH, An KH, Lee YH. Electrical-field effect on carbon nanotubes in a twisted nematic liquid crystal cell. Appl Phys Lett. 2005;87:263110.
[8] Huang C-Y, Pan H-C, Hsieh C-T. Electrooptical properties of carbon-nanotube-doped twisted nematic liquid crystal cell. Jpn J Appl Phys. 2006;45:6392–6394.
[9] Dolgov L, Yaroshchuk O, Lebovka M. Effect of electro-optical memory in liquid crystals doped with carbon nanotubes. Mol Cryst Liq Cryst. 2008;496:212–229.
[10] Dolgov LA, Lebovka NI, Yaroshchuk OV. Effect of electrooptical memory in suspensions of carbon nanotubes in liquid crystals. Colloid J. 2009;71(5):603–611.
[11] Basu R, Iannacchione GS. Dielectric hysteresis, relaxation dynamics, and nonvolatile memory effect in carbon nanotube dispersed liquid crystal. J Appl Phys. 2009;106:124312.
[12] Park KA, Lee SM, Lee SH, Lee YH. Anchoring a liquid crystal molecule on a single-walled carbon nanotube. J Phys Chem C. 2007;111:1620–1624.
[13] Basu R, Iannacchione GS. Orientational coupling enhancement in a carbon nanotube dispersed liquid crystal. Phys Rev E. 2010;81:051705.
[14] Koval'chuk A, Dolgov L, Yaroshchuk O. Semicond. Dielectric studies of dispersions of carbon nanotubes in liquid crystal 5CB. Phys Quant Electron Optoelectron. 2008;11:337–341.
[15] Dolgov L, Tomylko S, Koval'chuk O, Lebovka N, Yaroshchuk O. Liquid crystal dispersions of carbon nanotubes: dielectric, electro-optical and structural peculiarities. In: Marulanda JM, editor. Carbon nanotubes [Internet]. ISBN: 978-953-307-054-4, INTECH; 2010. Chapter 24, p. 451–484. [cited 2012 Nov 15]. Available from: http://sciyo.com/books/show/title/carbon-nanotubes
[16] Jylhä L, Sihvola A. Equation for the effective permittivity of particle-filled composites for material design applications. J Phys D. 2007;40:4966–4973.
[17] Shelestiuk SM, Reshetnyak VY, Sluckin TJ. Frederiks transition in ferroelectric liquid-crystal nanosuspensions. Phys Rev E. 2011;83:041705.
[18] Landau LD, Lifshitz EM, Pitaevskii LP. Electrodynamics of continuous media. 2nd ed. New York (NY): Pergamon Press; 1984.
[19] Tanaka K, Yamabe T, Fukui K. The science and technology of carbon nanotubes. Oxford: Elsevier; 1999.
[20] Garnett JCM. Colours in metal glasses and in metallic films. R Soc London Ser B. 1904;203:385–420.
[21] Capolino F. Theory and phenomena of metamaterials. Boca Raton (FL): CRC Press; 2009.
[22] Sihvola A. On the dielectric problem of isotrophic sphere in anisotropic medium. Electromagn. 1997;17:69–74.
[23] Sihvola A. Electromagnetic mixing formulas and applications. IEEE Electromagnetic Waves Series, 47. London: IEE Publishing; 1999.
[24] Paulis FD, Nisanci MH, Koledintseva MY, Drewniak JL, Orlandi A. Homogenized permittivity

of composites with aligned cylindrical inclusions for casual electromagnetic simulations. Prog Electromagn Res B. 2012;37:205–235.
[25] Moiseev SG. Active Maxwell Garnett composite with the unit refractive index. Physica B. 2010;405:3042–3045.
[26] Sihvola A. Metamaterials and depolarization factors. Prog Electromagn Res PIER. 2005;51:65–82.
[27] Levy O, Stroud D. Maxwell Garnett theory for mixtures of anisotropic inclusions: application to conducting polymers. Phys Rev B. 1997;56:8035–8046.
[28] Cheng DK. Fundamentals of engineering electromagnetics. Reading (MA): Addison Wesley; 1993.
[29] Basu R, Iannacchione GS. Dielectric response of multiwalled carbon nanotubes as a function of applied ac-electric fields. J Appl Phys. 2008;104:114107.
[30] Van Boxtel MCW, Wübbenhorst M, Van Turnhout J, Bastiaansen CWM, Broer DJ. A dielectric study on the relaxation and switching behaviour of liquid crystals confined within a colloidal network. Liq Cryst. 2003;30:235–249.
[31] Maier W, Meier G. Eine einfache. Theorie der dielektrischen Eingenschaften homogen rientierter kristallenflussiger Phasen des nematischen Typs. Z Naturforsch A. 1961;16:262–267.
[32] Minenko SS, Lisetski LN, Goncharuk AI, Lebovka NI, Ponevchinsky VV, Soskin MS. Aggregates of multiwalled carbon nanotubes in nematic liquid crystal dispersions: experimental evidence and a physical picture. Func Mater. 2010;17:454–459.
[33] Duran H, Gazdecki B, Yamashibta A, Kyu T. Effect of carbon nanotube on phase transitions of nematic liquid crystals. Liq Cryst. 2005;32:815–822.
[34] Haller I. Thermodynamic and static properties of liquid crystals. Prog Solid State Chem. 1975;10:103–118.
[35] Kozinsky B, Marzari N. Static dielectric properties of carbon nanotubes from first principles. Phys Rev Lett. 2006;96:166801.
[36] Li Y-H, Lue J-T. Dielectric constants of single-wall carbon nano-tubes at various frequencies. J Nanosci Nanotech. 2007;7:3185–3188.
[37] Lagarkov AN, Sarychev AK. Electromagnetic properties of composites containing elongated conducting inclusions. Phys Rev B. 1996;53:6318–6336.
[38] Margulis VlA, Gaiduk EA. Dielectric function of single-wall carbon nanotubes. Chem Phys Lett. 2001;341:16–22.
[39] Benedict LX, Crespi VH, Louie SG, Cohen ML. Static conductivity and superconductivity of carbon nanotubes: relations between tubes and sheets. Phys Rev B. 1995;52:14935–14940.
[40] Huang L, Wang M, Zhang Y, Guo Z, Sun J, Gu N. Synthesis of gold nanotadpoles by a temperature-reducing seed approach and the dielectrophoretic manipulation. J Phys Chem C. 2007;111:16154–16160.
[41] Grimes CA, Mungle C, Kouzoudis D, Fang S, Eklund PC. The 500 MHz to 5.50 GHz complex permittivity spectra of single-wall carbon nanotube-loaded polymer composites. Chem Phys Lett. 2000;319:460–464.
[42] Grimes CA, Dickey EC, Mungle C, Ong KG, Qian D. Effect of purification of the electrical conductivity and complex permittivity of multiwall carbon nanotubes. J Appl Phys. 2001;90:4134.
[43] Jeon T-I, Kim K-J, Kang C, Oh S-J, Son J-H, An KH, Bae DJ, Lee YH. Terahertz conductivity of anisotropic single walled carbon nanotube films. Appl Phys Lett. 2002;80:3403.
[44] Peng ZH, Peng JC, Peng YF, Wang JY. Complex conductivity and permittivity of single wall carbon nanotubes/polymer composite at microwave frequencies: a theoretical estimation. Chin Sci Bullet. 2008;53:3497–3504.
[45] Wang Y-C, Lue J-T. Dielectric constants of multi-wall carbon nanotubes from low to microwave frequencies [master thesis]. Hsinchu: National Tsing Huang University; 2007.
[46] Nishimura H, Minami N, Shimano R. Dielectric properties of single-walled carbon nanotubes in the terahertz frequency range. Appl Phys Lett. 2007;91:011108 and communication with the corresponding author.
[47] Koledintseva MY, DuBroff RE, Schwartz RW. A Maxwell Garnett model for dielectric mixtures containing conducting particles at optical frequencies. Prog Electromagn Res PIER. 2006;63:223–242.
[48] White CT, Todorov TN. Carbon nanotubes as long ballistic conductors. Nature. 1998;393:240–242.
[49] Ebbesen TW, Lezec HJ, Hiura H, Bennett JW, Ghaemi HF, Thio T. Electrical conductivity of individual carbon nanotubes. Nature. 1996;382:54–56.

Appendix

Effective medium approximations (EMAs) are physical models that describe the macroscopic properties of a medium based on the properties and the relative fractions of its components. Since EMAs are usually regarded as phenomenological models being an adequate method of capturing experimental behaviours, the properties of the components needed in EMAs are macroscopic parameters such as permittivity ε or conductivity σ that represent the sum contributions from all relaxation/resonant or dissipative mechanisms, and the first-principle functions may not necessarily be expressed in an EMA formula.

Apparently, the fundamental expressions for ε [38] and σ [39] of CNT look much different from that of bulk metal or of graphite, but one does not need to include these *ab initial* details in EMAs for CNT as well as for the NLC matrix [31] unless explanation or more physical insight in the EMA's results is needed.

Since every complex number can be written in the form of $z = x - jy$, the permittivity of CNT can also be expressed as $\varepsilon = \varepsilon' - j\varepsilon''$. However, the problem left for the nano-scaled CNT is: Can the imaginary part still produce the same macroscopic effect as if the material had effective conductivity $\sigma = \omega\varepsilon''$ (afterwards denoted as *)? It seems like there exist cases in which the expression (*) is accepted in the nano-scaled material related researches. For example, for

gold nanotadpoles: Huang et al. [40] expressed that both of the medium and the nanoparticle obey (*) in the Clausius–Mossotti factor. For CNTs, Grimes et al. adopted (*) to predict σ of CNT by the measured ε'' and their effective medium modelling incorporating (*) was able to fit the empirical data well ([41] and [42]), implying the mathematical correctness of using the monomial expression (*) for well dispersed individual CNTs in a physical system. On the other hand, given the measured electromagnetic power absorption and index of refraction, the general relationship of (*) was adopted by Y.H. Lee et al. to determine the real conductivity of the aligned SWCNT films.[43] Based on an equivalent resistance-capacitance network in which the classical (*) is incorporated, the complex conductivity and the relative complex permittivity of SWCNTs/polymer (poly-ethyl methacrylate) composite were theoretically investigated by Peng et al. and intriguingly, the calculated complex permittivity spectra of the composite are in good agreement with the experimental data of Grimes' et al. [44]. In addition, Lue et al. also adopted (*) as a part of the mechanism of acquiring the complex permittivity of CNT with the measurement of the CNT-caused degradation of *Q*-factor of the dielectric resonator by Li et al. [36]. (Note that the detail describing the principle of the measurement can be found in Wang et al. [45].) Besides, Basu et al. [29] extracted the frequency-dependent a.c. conductivity of MWCNT by (*) from the complex dielectric spectrum of their MWCNT samples. It is also worth mentioning that using EMA including the relation (*), Shimano et al. drew out the dielectric function of SWCNT from the experimentally obtained dielectric functions of the dispersed-SWCNT/carboxymethylcellulose film, and found both of CNT's complex dielectric function and conductivity spectra in the terahertz frequency range simultaneously follow the theoretical Lorentz oscillator model. [46] Up to this point, it seems that introducing the general relation (*) for CNT into the effective medium modelling for the CNT/dielectric composites can fit not only empirical data but also the classical models.

Finally, as regarding the conductivity taking into accounts small size of nanorods comparable to the mean free path (MFP) of electrons, Koledintseva et al. kept (*) in their Maxwell Garnett model for dielectric mixtures containing conducting particles at optical frequencies, but with a correction factor for σ as $\sigma_{\text{free}} = \Lambda\sigma_{\text{i}}$, where the coefficient Λ is a function of the ratio $\Lambda = f\ (b_{\text{i}}/L_{\text{free}})$, where b_{i} is the inclusion characteristic size ($d \leq b_{\text{i}} \leq l$) along the vector of the electric field acting on the mixture, and L_{free} is the MFP for electrons in the conductor, d and l are diameter and length of nanorods, respectively.[47] Since there is no 'bulk' conductivity for CNT, and even if there was, qualitatively we do not think the correction is needed for CNT owing to its nature as a long ballistic conductor compared with its limited MFP (because with increasing length, CNT's conduction electrons ultimately become localised due to the residual disorder in the tube [48]), that smears out the small-size effect which would have caused to CNT.

Therefore, we think that at the present stage, the general relation of (*) for CNT may still be acceptable till some researches, for example, if only [49] with additional investigation in CNT's resistivity function had been carried out to prove or disprove the physical validity of (*).