Electric-field induced elastic stretching of multiwalled carbon nanotube clusters: a realistic model†

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The oscillating electric-field induced stretching phenomenon of multiwalled carbon nanotube (MWCNT) clusters in liquid crystal medium demonstrates distinct threshold behaviour under optical microscopic investigation. The optimum field required for the initiation of MWCNT cluster stretching is found to depend on their length in the field-off state. The phenomenon has been explained in light of a classical theoretical model assuming MWCNT agglomerates as a single electric dipole. The spring constant and induced charge obtained by fitting the formulated theoretical model show good agreement with previous reports, hence establish the proposed dipolar reorientation mechanism of MWCNT clusters induced by the electric field.

1. Introduction

The combination of unusual structural, mechanical and electronic properties of carbon nanotubes (CNTs) has stimulated research activities in fabrication of CNT based devices. The material has established application potential in nanotweezers,1 nanoswitches,2 bearings,3 nanotube random access memory,4,5 and gigahertz nano-oscillators.6 As a consequence, relentless theoretical and experimental research efforts have been pursued for fundamental understanding as well as large-scale industrial applications. Although tremendous progress has been made towards understanding the properties of individual CNTs,7–9 investigation of bulk anisotropic properties and utilizing them for practical application have been often hindered by the limitations of processing techniques. The nanotubes tend to agglomerate depending on operating environments and properties of the dispersion medium. Different interactive forces such as electrostatic, van der Waals, and anisotropic interfacial tension play the vital role in CNTs’ agglomeration. Previous theoretical10 and experimental11 research results established the CNT agglomerates as isotropic as well as anisotropic liquid crystal (LC) like self-assembly depending on their concentration, surface functionality, and nature of dispersion medium.

The demand of fundamental understanding has encouraged researchers to investigate mechanical properties i.e., molecular interaction12,13 and stretching14,15 phenomenon of individual biomolecules such as DNA and protein in nanoscopic order. However, microscopic scale phenomena are interesting and more realistic from the view point of applications. The duo of carbon nanotube and nematic LC16,17 remained a fascinating research topic during the last decade to the display industry from the point of view of commercialization of fast switching devices.18,19 In prior publications we have established vertical and in-plane electric field induced super-elongation phenomena of micrometre-length thin multiwalled carbon nanotube (t-MWCNT) clusters dispersed in an LC host.20,21 Although it has been mentioned that the stretching behaviour initiates at a certain electric field, i.e., threshold field ($E_{th}$), its cluster length dependence and the underlying mechanism have never been clarified. In this paper, by successive experimental efforts, we propose a realistic microscopic model to explain such a stretching behaviour which depends on the CNT cluster length. The obtained spring constant and electric field-induced charge of t-MWCNT show excellent agreement with previous reports.

2. Experimental

The t-MWCNTs have been synthesized by a catalytic chemical vapour deposition (CCVD) method using the FeMoMgo catalyst prepared by a combustion method. The details of MWCNT synthesis procedure have been reported elsewhere.22 The nanotubes are obtained in a powdered form having an outer diameter in the range of 3 to 6 nm and lengths in typically dozens of micrometres. In order to reduce the average lengths of MWCNTs, 100 mg of powder is stirred in 1 M sucrose solution for an hour and the sucrose mediated t-MWCNT is grounded in a mortar for an hour.
quality dispersion of MWCNTs in ethanol has been achieved by adding 5 mg of the ground 1-MWCNT into 30 ml of ethanol followed by ultra-sonication for 15 min. The solution with a CNT concentration of 0.167 g ml\(^{-1}\) is mixed with a nematic LC (Merck, Japan). The physical properties of the LC host are as follows: dielectric anisotropy \(\Delta \varepsilon = -4\) at 1 kHz, 20 °C, birefringence \(\Delta n = 0.077\) at \(\lambda = 589\) nm, clearing temperature of 75 °C, rotational viscosity \(\gamma_1 = 136\) mPa s. A homogeneous mixture of a superfluorinated nematic LC and MWCNTs (0.003 wt\% into LC) with a mean CNT length of 290 nm is thus finally achieved. Special care has been taken to remove the ethanol solvent using a solvent evaporator kept at 70 °C.

In order to observe field-dependent behaviour of the CNT cluster, an interdigitated electrode with transparent indium tin oxide (ITO) is fabricated on a glass plate and used as the bottom substrate. The top substrate, however, is made of a bare glass plate. For providing homogeneous alignment to the LC molecules parallel to the applied field direction, the alignment layer viz. AL16139 (Japan Synthetic Rubber Co.) is spin-coated on both the substrates followed by antiparallel rubbing. It is to be noted here that rubbing direction of the substrate is perpendicular to the direction of the in-plane field, so that the LC with negative dielectric anisotropy does not reorient under the applied field. The interdigital electrodes are 10 µm wide maintaining a 20 µm intra-electrode gap and constructed final cells have a thickness of 60 µm. The cells are filled with the CNT/LC mixture using a capillary action technique at room temperature. The textures of the test cells are observed by the optical microscope (Nikon DXM1200) while applying a 60 Hz sinusoidal field. All the experimental results shown in the present paper have been performed at room temperature (300 K) far from crystallization temperature of the LC host.

3. Results and discussion

The self-assembled MWCNT clusters in LC medium at the off-field and the threshold field induced state have been investigated under an optical microscope (OM) in order to realize the entanglement between MWCNTs. Fig. 1(a) shows the observed MWCNT cluster in LC medium under an OM in linearly polarized white light, with the direction of polarization of incident light perpendicular to the electrode direction. Changing the polarization state of incident light parallel to the electrode direction shows changes in the texture as shown in Fig. 1(b) due to occurrence of anisotropic selective light absorption of the MWCNT cluster in the visible wavelength regime, indicating local ordering of MWCNTs. Interestingly, the orientation of the MWCNT cluster is weakly affected by the LC director in our case due to weak surface anchoring of MWCNTs in the bulk LC. According to previous theoretical investigations a suspended rod-like particle in nematic LC medium orients either along or perpendicular to the nematic LC director in weak anchoring limits depending on boundary conditions. It has also been proposed in the literature that for low values of coupling strength between nematic LC and CNTs, the so-called isotropic phase of CNTs at low concentration is not only isotropic but also paranematic with some (low) nonzero degree of orientational order. However, instead of

![Fig. 1](Color online) Optical microscopic images of a CNT cluster in LC medium at field-off (a) and threshold field (d), respectively, when the polarization direction of incident light is perpendicular to the electrode direction. Figures in (b) and (d) are OM images when the polarization direction of incident light is parallel to the electrode direction. The arrow in the electrode indicates the transmission axis of the polarizer below the bottom substrate. The configuration of the CNT cluster has been illustrated schematically at field-off (c) and threshold field (f). Applied electric field direction and LC alignment direction have also been indicated by respective arrows.
anisotropic selective light absorption in MWCNTs the cluster is clearly visible in either direction of the incident polarized white light. Hence, the orientational ordering of MWCNTs is in close proximity to random with the axis of anisotropy preferably perpendicular to the LC director. The same cluster has been subjected to a sinusoidal electric field and commencement of its stretching behaviour at the threshold field \((E_{th})\) is observed through an OM in linearly polarized visible light perpendicular as well as parallel to the electrode direction as shown in Fig. 1(d) and (e) respectively. Interestingly, the same cluster almost disappears in linearly polarized visible light propagating parallel to the electrode direction while it was visible in linearly polarized visible light perpendicular to the electrode direction. The anisotropic selective absorption of visible light by the cluster clearly shows reorientation of constituent nanotubes. Finally, under sufficiently high field the elongated MWCNT cluster is clearly visible while the polarizer axis is aligned perpendicular to the electrode direction, however, it completely disappears when rotating the direction of polarization of incident light parallel to the electrode direction, which indicates electric field induced complete ordering of MWCNTs as described elsewhere.\(^{25}\)

The charge localization mechanism over CNTs by hydrogen bonding between CNT and LC molecules has been discussed in an earlier publication of our group.\(^{26}\) Following the observation under an OM it has been inferred that the t-MWCNT-doped LC filled cell under an oscillating electric field induces large dipole moment over CNTs due to their high aspect ratio and also CNTs experience the dielectrophoretic (DEP) force.\(^{27}\) The reported elongation and contraction phenomenon of CNT clusters both in the presence of vertical \(^{20}\) and in plane field\(^{21}\) has been understood in the following way. The polarisable CNT clusters are aligned and translated along the field direction by DEP torque and force, respectively. Eventually, CNTs aligned in the field direction are chained by inter CNT (dipole-dipole) interactions. Such a configuration of CNTs has been proposed earlier\(^{24}\) and appeared as an array of unidirectional electric dipoles. Analogous assumption has been successfully employed in the literature for individual single and multiwalled carbon nanotubes, representing the building blocks of nanotubes, \(i.e.\) each carbon atom as a combination of net electric charge and dipole.\(^{28-34}\) The classical theory successfully explained the electro-mechanical properties of CNTs using a computation technique and also showed good agreement with experimental results.\(^{35-36}\) Correlating previous findings with our experimental observation we have schematically illustrated the entangled MWCNTs in LC medium in electric off-field and threshold field conditions in Fig. 1(c) and (f) which appears as a unidirectional dipolar array at the threshold field. The direction of the applied electric field and the LC alignment direction have also been indicated by respective arrows. The electric field induced elongation phenomenon of MWCNT clusters is found to be unaffected with nematic LC temperature variation. The threshold field of MWCNT cluster stretching is found to be indifferent in the isotropic LC phase as well as in the nematic LC phase. Hence, we did not consider the surface anchoring energy of LC to CNTs in the Hamiltonian of the modelled system. Also the charge localization and hydrogen-bonding between CNT and LC molecules leads to the dipolar character of MWCNTs. As the dipolar character of MWCNTs has been considered in the model, the surface anchoring of LC molecules over nanotubes is not required to be considered separately. Assuming perfectly elastic interaction over the unidirectional dipolar array under a uniform applied field, the Hamiltonian can be represented as

\[
H = \sum_{i=1}^{n} \frac{p_i^2}{2m_i} + \sum_{i=1}^{n} \frac{1}{2} k(r_i - r_0)^2 - \sum_{i=1}^{n} D_i \cdot E + \sum_{i=1}^{n} \sum_{j=i+1}^{n} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} + V_{\text{VVW}}
\]

where \(p_i\) and \(m_i\) represent momentum and mass associated with charges confined at either end of the dipoles, \(r_i\) represents their respective positions under the electric field \((\vec{E})\) and \(r_0\) in the absence of the field, respectively, \(k\) represents the spring constant assumed to be equal for each individual dipole, \(\vec{D}_i\) is the electrostatic moment of induced dipoles, \(q_i\) and \(q_j\) represent charge induced over individual dipoles, \(\epsilon\) is permittivity of the medium, \(V_{\text{VVW}}\) represents the van der Waals potential of dipoles incorporating higher order terms of potential and \(\vec{r}\) is the running index. For the sake of analytical solution of the problem we have approximated the system into a single electric dipole and it is quite reasonable as classical, DFT, and molecular dynamics calculations all predict increased charge density at the end of the charged CNTs.\(^{37-39}\) The approximation is reasonable as oppositely charged nearest CNT neighbours are in close vicinity with each other in the presence of electric field and also our experimental results are bound to the limit of observations under microscope in a micrometre order. The \(V_{\text{VVW}}\) has also been treated as a constant due to similar reasons.

We have also confined the model in one dimension as the stretching phenomenon of MWCNT clusters in the nematic LC has been observed in one dimension only. Hence, the equation of motion takes the form

\[
\mu \ddot{x} + k(x - l) + \frac{q^2}{4\pi\epsilon_0 x^2} = -qE
\]

where \(\mu\) represents the effective mass of the dipole, \(q\) represents the induced charge over the dipole, \(l\) represents the length of the dipole in the absence of electric field and \(x\) is the length of the dipole in presence of electric field, treated as a dynamical variable. It is worth mentioning here that the length of the dipole has been described with reference to its centre of mass.

Substituting \(x = l + y\) in eqn (2), where \(y\) represents change of the length of the dipole, eqn (2) takes the form

\[
\mu \ddot{y} + ky + \frac{q^2}{4\pi\epsilon_0 l^2} \left(1 + \frac{y^2}{l^2}\right)^2 = -qE
\]

For the dynamical variable \(y \ll l\), eqn (3) can be approximated in eqn (4)

\[
\mu \ddot{y} + ky + \frac{q^2}{4\pi\epsilon_0 l^2} \left(1 - \frac{2y^2}{l^2}\right) = -qE
\]
Rearranging eqn (4) we get eqn (5),

\[ \mu \ddot{y} + \left( k - \frac{q^2}{2\pi \varepsilon l^3} \right) y = -\left( qE + \frac{q^2}{4\pi \varepsilon l^3} \right) \]  

(5)

By substituting \( (\omega')^2 = \left( \frac{k}{q^2} - \frac{2q}{\varepsilon \varepsilon_0} \right) \) in eqn (5),

The general solution of eqn (5) is described by eqn (6)

\[ y = A \cos(\omega' t + x) - \left( \frac{qE + \frac{q^2}{4\pi \varepsilon l^3}}{k - \frac{q^2}{2\pi \varepsilon l^3}} \right) \]  

(6)

The first term of the above expression can be realized as time dependence of stretching deformation of MWCNT clusters in LC medium. As the MWCNT cluster stretching is found to be stable under the present experimental conditions, the time dependent oscillatory cosine term is treated as a constant ‘C’.

Hence,

\[ x = l + C - \left( \frac{qE + \frac{q^2}{4\pi \varepsilon l^3}}{k - \frac{q^2}{2\pi \varepsilon l^3}} \right) \]  

(7)

We define the threshold field \( (E_{th}) \) as the field required for stretching the CNT cluster up to the resolution limit of the optical microscope, i.e., 0.2 \( \mu \)m. Hence \( E_{th} \) takes the form of eqn (8)

\[ E_{th} = A - \frac{B}{E} + \frac{D}{E^2} \]  

(8)

where

\[ A = \left( \frac{kC}{q} - \frac{0.2k}{q} \right), \quad B = \frac{q}{4\pi \varepsilon}, \quad D = \left( \frac{0.2q}{2\pi \varepsilon} - \frac{Cq}{2\pi \varepsilon} \right) \]  

(9)

Hence analyzing the stretching threshold field of a number of experimentally observed clusters and obtaining the best fitting curve with the given expression yields spring constant ‘\( k \)’ and induced charge ‘\( q \)’ in MWCNT clusters.

We have observed the MWCNT aggregates in LC medium under an optical microscope while carefully varying the applied in-plane electric field strength to pinpoint the commencement of the stretching phenomenon. Fig. 2 shows typical images showing the variation of \( E_{th} \) with varying cluster length. It is worth mentioning here that clusters of anisotropic shape have been considered for the present experimental investigations. An electric field about the threshold limits has been applied to the clusters to reorient their axis of anisotropy in the direction of the applied field. Hence, we waited for certain period of time in the field-off condition to allow the clusters to regain their self-assembled shape and the images have been captured.

Fig. 2 (Color online) Optical microscopic images of MWCNT clusters in LC medium with increasing magnitudes of their zero field lengths in respective representative cases of \( \sim 1.6 \) \( \mu \)m (a), 2.3 \( \mu \)m (b), 3.8 \( \mu \)m (c). Variation in the magnitude of the applied electric field shows increasing requirement of stretching threshold field with increasing zero field cluster length.
Thus, the cluster lengths have been measured along the direction of the applied in-plane field i.e., perpendicular to interdigital electrodes. Interestingly MWCNT clusters in the LC host have been obtained in the length range at a zero field state of ~1 μm to 4 μm. The observation assures that no bigger clusters are present in the sample; however the statement is not valid for clusters of lesser sizes due to the resolution limit of the OM. The stretching thresholds are found to be cluster length dependent, and show an increasing trend with increasing cluster length. The original morphology of the MWCNT agglomerates has been found to be restored after removal of the field, assuring that the cluster lengths are stable and are in minimum energy configuration in the absence of the field. Hence the field reversibility of cluster lengths is observed until their respective breakdown field.

The representative cases of the MWCNT cluster stretching phenomenon shown by microscopic images (Fig. 2) has been depicted in Fig. 3. The lengths of the clusters have been plotted as a function of the applied in-plane field strength for the representative cases in Fig. 3. The cluster length dependent variation of $E_{th}$ is evident from the figure. Also the CNT length is found to vary monotonously with increasing applied field strength above $E_{th}$ which is consistent with highly elastic behaviour of MWCNTs. The highly elastic behaviour of MWCNT clusters in LC medium has been established by our group in the previous reports considering time resolved microscopic images of the clusters as well.\(^{21,25}\) The threshold behaviour has been investigated over a large number of similar sized CNT clusters. By averaging a number of experimental observations of CNT cluster stretching, we have determined the magnitudes of $E_{th}$ for different cluster lengths and plotted the variation of $E_{th}$ as a function of zero field lengths of CNTs in Fig. 4. The scattered points in the figure thus represent the respective values of $E_{th}$ obtained from repeated and rigorous experimental observations and the smooth line is the best fit curve plotted following eqn (8). The theoretical curve shows good agreement with the experimental points supporting the interpretation of CNT clusters stretching in LC medium as a process of unfolding by tensile deformed compact self-assembled nanotubes. According to those reports, the MWCNT bending spring constant increases from ~1.1 $\times$ 10\(^{-3}\) N m\(^{-1}\) to 41.6 $\times$ 10\(^{-3}\) N m\(^{-1}\) with decrease in their lengths from 22.7 μm to 6.5 μm.\(^{7}\) For individual MWCNTs of lengths ~200 nm the bending spring constant rises to 0.9 N m\(^{-1}\) and by further reduction of tube length to ~50 nm the bending spring constant is found to be ~57 N m\(^{-1}\).\(^{13}\) Spring constant has also been reported for dense coiled type of carbon nanotubes. The Hook’s constant for an ~100 μm thick forest of coiled carbon nanotubes per turn has been found to be 1.2 N m\(^{-1}\) in the low strain regime.\(^{41,42}\) Again, amorphous carbon microcoil spring constant is found to be of the order of 10\(^{-4}\) N m\(^{-1}\).\(^{43}\) Hence, the dependence of the spring constant over respective MWCNT length as well as the type of entanglement is evident. In our case, the experiments have been performed over MWCNT clusters, having an anisotropic length lying between ~1 to 4 μm. Hence in the present context it is showing good agreement with earlier experimental results of bending as well as Hook’s spring constant with acceptable variation considering difference between MWCNT samples under investigation. Although we have investigated the stretching behaviour of MWCNTs in cluster form, direct observation of the phenomenon is beyond the scope of present work. However, considering the very high compatibility of the previously reported bend elastic constant of individual MWCNTs by various groups, we may interpret the phenomenon of MWCNT clusters stretching in LC medium as a process of unfolding by tensile deformed compact self-assembled nanotubes. According to a previous experimental report, the magnitude of charge induced over
individual MWCNTs is ~10–100 e µm⁻¹. In our previous investigations of electro mechanical stretching behaviour of MWCNTs, even 1000% elongation under optical microscopes has been reported. Again, an average CNT outer diameter of ~5 nm and an average length of ~290 nm result in an average volume of ~8.2 × 10⁻²⁵ m³ for a carbon nanotube. Considering cylindrical conformation of MWCNT clusters as a first approximation, the clusters of our present investigation have lengths lying between ~1 µm to 4 µm and also diameters ~2 µm to 3 µm. Hence, the huge number (~10⁷–10⁹) of self-assembled MWCNTs is anticipated which justifies the magnitude of induced charge over MWCNT clusters as obtained in present investigations. Hence, the single dipole approximated model for MWCNT clusters explains a reorientation phenomenon of MWCNTs in the applied electric field direction and additionally provides induced charge and tensile spring constant, which shows good agreement with prior reported results.

4. Conclusion

The in-plane electric field induced elongation process of CNT clusters in LC medium has been monitored under an OM. The threshold field for commencement of CNT agglomerate stretching has been found to depend on the anisotropic length of the agglomerates in the field-off state. We have developed a classical theoretical model considering an individual CNT cluster as a single electric dipole, and perfectly elastic intra CNT interaction to explain such behaviour. The comparison between previously reported bending and Hooks spring constant values for individual and coiled MWCNTs, respectively, exhibits good agreement with our result. The induced charge over individual CNT clusters has also been determined by the model which shows a rational result. Hence, MWCNT clusters stretching in LC medium might be interpreted as a process of unfolding by tensile deformed compact self-assembled nanotube bundles rather than stretching of individual nanotubes. The issue can be further addressed using currently available super resolution microscopic tools for more detailed understanding.

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