Self-assembly of Carbon Nanotubes into a Columnar Phase at Low Concentrations Revealed by Small Angle X-ray Scattering

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Abstract

Solutions of carbon nanotubes (CNTs) in chlorosulfonic acid (CSA) exhibit phase behavior consistent with the Onsager prediction for rigid rods interacting via a repulsive potential, including the appearance of an ordered liquid-crystalline phase upon increasing the concentration. However, the nature of the ordered phase, and how it depends on the properties and the average concentration
of the CNTs in the solution, is only partially understood at high concentrations. We apply small-angle X-ray scattering, paired with polarized optical microscopy, to characterize the morphology of the liquid-crystalline phases formed in CNT solutions at concentrations from 3 to 6.5 % by volume. Theoretically, for high length polydispersity of rods, such as CNTs, a direct transition is expected to occur from a nematic to a columnar phase only at high concentrations (~50 % by volume). Surprisingly, we find a hexagonal columnar phase at a relatively low concentration of about 4.3 % by volume in CNT-CSA solutions, implying a large inter-particle spacing. We attribute this early transition to undulation-enhanced electrostatic forces, which increase the effective diameter of the CNTs in solution.

**Introduction**

The entropy-driven liquid crystal phase transition in systems of anisotropic particles has been a subject of extensive theoretical and experimental research.\(^1\)-\(^4\) The key factors controlling the phase behavior of such systems are the ratio of the length to the diameter, \(L/D\) (the aspect ratio), and the ratio of the persistence length to the length, \(P/L\) (the persistence ratio), of the constitutive particles. According to Onsager theory, a solution of infinitely-long rigid rod-like particles \((L/D \rightarrow \infty, P/L \rightarrow \infty)\) should transition from a randomly oriented phase to an orientationally aligned liquid crystal phase at sufficiently high concentrations.\(^1\) Biological systems including tobacco mosaic virus (TMV), fd virus, and f-actin are example of experimental model systems that have been studied to understand the phase behavior of solutions of rod-like particles.\(^5\)-\(^12\) However, most of these systems are characterized by modest aspect ratios \(L/D \approx \mathcal{O}(\text{10}^2)\), and/or persistence length comparable to the length \((P/L \approx 1)\). Therefore, such systems are not ideal for testing the Onsager
rod-like limit. Moreover, these particles are typically charge-stabilized and the electrostatic repulsion impacts upon the phase behavior in a non-trivial fashion.\textsuperscript{13}

Carbon nanotubes (CNTs) can be synthesized with diameters as narrow as $\approx 0.7$ nm and length in excess of 1 $\mu$m, leading to aspect ratios of $L/D \approx O(10^3)$. Because of their high bending stiffness, their persistence length ranges from tens to hundreds of micrometers and scales with the cube of the CNT diameter.\textsuperscript{14} Therefore, it is possible to synthesize systems with a persistence ratio of $P/L \gg 1$, which makes them ideal models for testing the fundamental theories of rod-like particles. Superacids such as chlorosulfonic acid (CSA) are the true solvents for CNTs and can dissolve CNTs at high concentrations.\textsuperscript{15, 16} CSA charges the outer surface of the CNTs, resulting in electrostatic repulsion, which counteracts the van der Waals attraction between them.\textsuperscript{17} The dissolution mechanism is reversible, and, hence, the CNT properties are not affected by the charging process.\textsuperscript{16}

Out of the various manufacturing methods developed for macroscale CNT materials, solution-processing of CNTs in superacids yields the highest macro scale properties (mechanical strength, thermal and electrical conductivity), while also offering the best promise for scalability.\textsuperscript{15, 16, 18-22} Specifically, high-performance CNT fibers are spun out of liquid crystalline CNT solutions.\textsuperscript{18} Increasing the CNT concentration in the liquid crystal phase reduces significantly the superacid solvent use, lowering process costs and CO$_2$ footprint. Therefore, understanding the morphology of CNT liquid crystals at high concentrations is important for the implementation of these materials. Earlier studies have shown that solutions of CNTs in CSA follow the Onsager prediction for rigid rod systems and transition from an isotropic phase, characterized by randomly oriented rods, to a polydomain nematic phase, where the rods are locally aligned but exhibit no long-range
orientational order.$^{16,23,24}$ The transition concentration is inversely proportional to the aspect ratio of the CNT, following the Onsager prediction.$^{25}$

Recently, the CNT-CSA solution morphology in systems of both long ($L \approx 8.8$ µm) and short ($L \approx 0.42$ µm) CNTs were studied by small-angle neutron scattering (SANS) at concentrations up to 1.5 % by volume.$^{26}$ These studies revealed the formation of a fully nematic phase characterized by a quasi 2D “lattice” expansion for solutions of long CNTs, while short CNTs exhibit the coexistence of isotropic and nematic phases in the same range of mass concentrations.$^{26}$ Still, the highly corrosive nature of the acid, the challenging handling of superacids on account of their sensitivity to any moisture in the air, in combination with the high viscosity of the solutions at high CNT concentrations, make sample preparation extremely challenging and has so far prevented a comprehensive quantitative study of these solutions at concentrations higher than 1.5 % by volume using small angle scattering techniques. Additionally, the high scattering intensity of CSA, which contains chlorine and sulfur atoms, obscures the signal from CNTs, unless the CNT concentration is relatively high. Thus, earlier efforts on using small angle X-ray scattering (SAXS) have only been successful in the context of studying swollen CNT fibers in acids, and not in bulk solutions, that is, CNTs in their true solution environment at high concentrations.$^{27,28}$ Theory predicts that polydisperse rods such as CNTs should transition directly from nematic to columnar phase at very high volume fraction ($\approx 50\%$) rather than to a smectic-A phase (Figure 1a).$^{29,30}$ In the columnar phase, the rods are orientationally ordered (similarly to the nematic phase) while having a long-range six-fold hexagonal positional and orientational order in the radial plane.

Here we show that high-concentration CNT-CSA solutions (above $\approx 3$ % by volume) provide sufficient X-ray scattering intensity to study quantitatively their phase behavior by means of SAXS. We find that CNT-CSA solutions form a hexagonally packed columnar phase at concentrations as low as 4.3 % by volume, an order of magnitude below theoretical predictions.
Figure 1. a) Schematic representations of isotropic, nematic, and columnar phases formed in length-polydisperse system of rod-like particles. The ratio of the length to the diameter of the rods shown here differs significantly from the case of CNTs ($L/D \approx 5000$) and is only presented for illustrative purposes. b) High resolution transmission electron micrograph of the Meijo EC1.5 CNTs after purification. The yellow arrow shows a CNT of 1.95 nm in diameter. The scale bar is 20 nm.

Materials and methods

Solution preparation. CNTs were purchased from Meijo Nano Carbon Co., and purified by thermal annealing at 420 °C for 6 hours in dry air to remove residual amorphous carbon from synthesis. CNTs were then mixed with CSA (purchased from Sigma Aldrich, 99 % purity) using a speed mixer (FlackTek, Inc. DAC 150.1speedmixer) for 2.5 hours. CNT-CSA solutions were loaded into rectangular glass capillaries (VitroCom, 1 mm width, 0.1 mm path length, and 0.07 mm wall thickness were used as received) for SAXS measurements. Due to the high viscosity of the CNT-CSA solutions in the range of concentrations tested, a syringe was used to fill the capillaries. Rectangular glass capillaries are first attached to 1.5 mm round glass capillary tubes using epoxy glue. The solution was then loaded into rectangular glass capillaries by pulling up the solution using a syringe inserted into the round capillary tubes. The syringe needle was covered with Teflon tape to ensure a good sealing and prevent air from entering the capillary tube. The capillary tubes
were subsequently flame-sealed with a butane torch. In order to make the capillary ends more robust, a drop of epoxy was placed on the capillary ends and let dry.

**CNT characterization.** For TEM imaging, a drop (~3 μL) of the CNT-CSA solution was cast on a perforated carbon film supported on a copper TEM grid (lacey Formvar/carbon films on 200 mesh Cu grids, Ted Pella, Redding, CA, USA), held by tweezers in a controlled environment vitrification system (CEVS). The CEVS was inside a flexible polyethylene "glove-bag" (Sigma-Aldrich), and was kept at 25 °C, while continuously flushed with pure dry nitrogen gas, to prevent moisture penetration. A glass microfiber filter sheet was then used to blot the samples into thin films, followed by plunging them into boiling liquid nitrogen, and quenching into distilled water to coagulate the acid. The grid was then dried overnight in vacuum. The samples were examined with a FEI Talos 200C high-resolution TEM at an accelerating voltage of 200 kV at room temperature. Images were recorded digitally by a 4K×4K pixels, cooled, CMOS-detector FEI Ceta 16M camera, with the TIA software. CNTs diameter $D$ and the number of walls $N$ were estimated from a collection of micrographs obtained (Figure 1b). Additionally, we calculated the density of the CNTs, $\rho_{CNT}$, using the obtained values for the average diameter ($D = 2.04 ± 0.6$ nm) and the average number of walls ($N = 1.32$), using the expression $\rho_{CNT} = 4000 [ND - 2\delta_{vdW} \sum_{i=0}^{N-1} i] / (A_s (D + \delta_{vdW})^2)$, which leads to a $\rho_{CNT} \sim 1.3$ g/cm$^3$. Here, $A_s = 1315$ m$^2$/g is the specific area for one side of a graphene sheet, and $\delta_{vdW} = 0.34$ nm is the interlayer van der Waals distance between two CNT walls. The average aspect ratio of the CNTs was estimated using extensional rheology and found to be $L/D \cong 5000 ± 100$. The isotropic-nematic transition point was determined at 0.007 % by volume (70 ppm), using transmitted polarized light microscopy. The degree of length polydispersity $p = \sqrt{\langle L^2 \rangle / \langle L \rangle^2} - 1$ ($L$ is the length of the constitutive particles and the brackets denote averages) of the CNTs was then estimated as 0.39, using the values for
diameter, average length, and the isotropic cloud point, i.e., the concentration at which an infinitesimal amount of nematic phase forms in equilibrium with the isotropic phase.\textsuperscript{3, 25} The persistence length of the CNTs, $P$, was estimated as $280 \pm 7$ $\mu$m using $P = \pi C D^3 / (8 K_B T)$, where $C = 345$ J/m$^2$ from ab initio calculations of a tube under axial strain.\textsuperscript{14}

**SAXS measurements.** Scattering measurements on CNT-CSA solutions were performed using a Rigaku S-Max3000 SAXS machine at the University of Houston, equipped with 3 pinhole collimation and a 2-dimensional area detector with $1024 \times 1024$ pixels. The measurements were carried out in a vacuum chamber, using a 2D detector and a Cu K$\alpha$ X-rays (wavelength of $\lambda_0 = 1.54$ Å) for 24 hours. The instrument was calibrated for $q$ values using Ag behenate standard. The sample-to-detector distance was about 1.143 m. The data were calibrated with glassy carbon for intensity, and analyzed using Igor Pro 7 (WaveMetrics, Inc.) and the Irena and Nika packages (available from Argonne National Laboratory).\textsuperscript{33, 34} This was done by taking an azimuthal sector average in the direction of maximum scattering intensity, due to the anisotropic scattering pattern arising from the overall alignment of the solutions inside capillary tubes, to obtain intensity as a function of the magnitude of the scattering wave vector $q$, where $q = 4\pi \sin \theta / \lambda_0$, and $2\theta$ is the scattering angle.\textsuperscript{33, 34} The accessible range of the wave vector, $q$, is from approximately 0.0075 to 0.25 Å$^{-1}$. The signal from an empty glass capillary was first subtracted from the data prior to analysis. The data was then fitted to a hexagonal close-packed (HCP) cylinder model, using the small-angle diffraction tool in the Irena package, which considers a flat background, a power law scattering ($I(q) \propto q^4$) and four peaks.\textsuperscript{33} Each peak was modeled by a Lorentzian function – see Supplementary Material for the details.
**Solution morphology characterization.** A drop of CNT solution was sandwiched between two glass slides, and sealed with Scotch tape to limit the contact between the sample and the moisture in the environment. The samples were imaged immediately after preparation. A Zeiss AxioPlan 2 polarized light microscope equipped with a cooled charge-coupled device (CCD) camera (AxioCam Zeiss) was used to characterize the birefringent optical texture of CNT liquid crystalline solutions.

**Results and discussions**

**Polarized light microscopy.** We studied five different CNT concentrations ranging from 3 to 6.5 % by volume (See Materials and Methods section for characterizations). Figure 2 shows polarized light micrographs of the as-prepared solutions; the optical texture shows that all samples are birefringent and in the single-phase liquid-crystalline regime. Bright regions are oriented $\pm 45^\circ$ with respect to the cross polarizers of the microscope (indicated by white arrows). At high concentrations, a fan-shaped or pleated ribbon-like texture is observed for the liquid crystal phase, suggesting the formation of columnar phase at the concentrations as low as 4.3 % by volume. The pleated ribbon-like optical texture is evident in earlier studies of CNT superacid liquid crystals, in the same range of concentration; however, its origin has not been explained before.$^{16,18}$ Similar microscopic optical textures have been reported for columnar solutions of poly(c-octadecyl-l-glutamate) in octadecylamine at 60 % by weight.$^{35}$
Figure 2. Polarized light micrographs of solutions of CNTs in CSA at concentrations a) 3, b) 3.8, c) 4.3, d) 5.9, and e) 6.5 % by volume at 0 and 45 degrees with respect to the polarizers of the microscope. Images are post processed to adjust the brightness; the darkest point is set to 0 and the brightest point is set to 255. The optical texture gradually evolves from the typical Schlieren texture, indicative of a nematic phase, at low concentrations, to a pleated texture, typical of a columnar phase, at high concentrations. The crossed arrows show the orientation of the polarizer and analyzer.

Small angle X-ray scattering. Figure 2 reports the SAXS signal on these same CNT solutions. The 2D SAXS data (Figure S1) shows an anisotropic pattern due to the overall alignment of the CNT liquid-crystal solutions along the long axis of the capillary tubes. Therefore, the 2D data are sector-averaged to obtain the 1-D scattering intensity, $I$, vs. the momentum transfer, $q$, as shown in Figure 3, for the five different concentrations studied.

Upon increasing the concentration, the peaks shift to higher values of $q$, which indicates a tighter CNT packing. The lowest concentration studied (3 % by volume) yields an $I(q)$ vs. $q$ curve with a shallow second peak similar to the scattering signal of the nematic liquid crystal solutions reported on for both CNT, fd virus, and TMV solutions.\textsuperscript{26, 36, 37} Theoretical calculations show that the structure factor for a nematic system of colloidal particles interacting via hard core repulsions presents liquid-like order with multiple peaks, even at relatively low concentrations for scattering vectors along and perpendicular to the director field.\textsuperscript{38, 39} Perpendicular to the director field, the first peak is followed by a second peak, spaced at a momentum transfer of a factor of about 2.1 with respect to that of the first peak.\textsuperscript{26, 40} For higher concentrations ($\phi \geq 4.3$ % by volume), the second peak moves closer to the first peak, and is relatively spaced at a distance $\sqrt{3}$ relative to the first peak. This relative spacing characterizes the structure of a hexagonal lattice in the plane normal to the director field, i.e., the average rod axis, and is indicative of the formation of
hexagonal columnar phase, as depicted in the schematic of Figure 1a. This is in agreement with
the morphology observed by polarized light microscopy at the highest concentrations tested.

The scattering signal obtained from the CNT-CSA solutions suffers from significant noise due to
the scattering from the CSA, which masks the peaks. The higher order peaks can be distinguished
clearly only at the higher concentrations. To obtain the positions of the successive correlation
peaks, we fitted a hexagonally closed-packed cylinder model to our data (Figure 4), using the
method described in the Materials and Methods section and in the Supplementary Material.33, 34
Table S1 of the Supplementary Material shows the fitting parameters and the peak positions for
the three highest concentrations studied as presented in Table 1.

Figure 3. SAXS measurements showing the intensity, $I(q)$, vs. momentum transfer, $q$, for CNT-CSA
solutions at concentrations ranging from 3 to 6.5 % by volume. The presence of higher-order peaks
with the reciprocal spacing of $1: \sqrt{3}$ is the hallmark of a 2-D hexagonal positional ordering. The
curves are offset vertically for clarity.
Table 1. Solution concentration and the position of scattering correlation peaks for CNT-CSA solutions at volume fractions ranging from 0.043 to 0.065.

| Volume fraction φ | Mass Concentration (weight %) | $q_1$ (Å$^{-1}$) | $q_2$ (Å$^{-1}$) |
|------------------|-------------------------------|-----------------|-----------------|
| 0.043            | 3.2                           | 0.062           | 0.11            |
| 0.059            | 4.4                           | 0.071           | 0.12            |
| 0.065            | 4.8                           | 0.075           | 0.13            |

Figure 4. Fitting of a hexagonally close-packed cylinder model to the SAXS measurements of CNT-CSA solutions at concentrations ranging from 4.3 to 6.5 % by volume. The presence of successive peaks located at $q$ values in the ratio of $1: \sqrt{3}: \sqrt{4}$ are indicative of a hexagonal packing in the lateral plane. The curves are offset vertically for clarity.

The higher-order peaks shown in Figure 4 are characterized by a reciprocal spacing of $1: \sqrt{3}: \sqrt{4}$, which indicates a 2-D hexagonal positional and orientational ordering in the lateral plane in the columnar phase. The formation of more highly ordered phases than the nematic has remained elusive for CNT systems, mainly because high concentrations of CNT cannot be obtained by
typical dispersion techniques. CNTs typically have a large polydispersity in length, e.g., for CNTs used in this study $p \approx 0.39$, where we refer to Materials and Methods for details of the calculation of length polydispersity. Size polydispersity of particles can change the phase behavior of the dispersion significantly.\textsuperscript{30}

Upon increasing the concentration, a monodisperse system of rod-like particles is expected to exhibit a transition from a randomly oriented isotropic phase to an orientationally aligned nematic phase, followed by a transition to a smectic phase.\textsuperscript{29, 30, 38, 41} A smectic phase is characterized by both positional and orientation ordering in the axial direction, where rods are stacked in layers. However, for sufficiently length polydisperse systems, where there is a large distribution of the length of the particles, stacking of the rod-like particles in the form of layers becomes impossible.\textsuperscript{29, 30} In fact, in systems with length polydispersity $p > 0.18$, the smectic phase of hard rods is destabilized completely, leading to a direct nematic-columnar transition at high concentrations.\textsuperscript{30} Theoretically, the nematic-columnar phase transition is predicted to occur at volume fractions near 50 \%, and is independent of the aspect ratio of the rods.\textsuperscript{30} This prediction has been confirmed experimentally for dispersions or suspensions of rod-like particles including viruses, polypeptides, surfactant micelles, and mineral nanorods that show transitions to the columnar phase at concentrations of $\approx 10 - 50 \%$ by volume.\textsuperscript{5, 35, 42, 43} The presence of the columnar phase has also been confirmed in DNA dispersions upon evaporating the solvent and increasing the concentration of DNA molecules to $\approx 300 \text{ mg/ml}$ in solutions.\textsuperscript{44, 45} More recently, charged imogolite nanotube suspensions have been shown to display nematic-columnar transition at significantly lower concentration of 0.2 \% by volume, which was attributed to the large aspect ratio of the nanotubes and to the soft electrostatic repulsion between them.\textsuperscript{46} This electrostatic repulsion results in a large Debye screening length ($\approx 30 \text{ nm}$) that increases the nanotube’s effective diameter to $D' \approx D + 2\kappa^{-1}$, where $D'$ is the effective rod diameter, $D$ is the hard-core
rod diameter, and $\kappa^{-1}$ the Debye screening length.\textsuperscript{46} This would cause their effective volume fraction to be significantly larger than the actual one.\textsuperscript{11,46} A large inter-particle spacing has also been observed in hexagonally assembled suspensions of peptide amphiphile nanofilaments at 0.1 % by volume, where the spacing between the particles have been reported to be 11 times larger than their diameter.\textsuperscript{47} The high charge density of the nanofilaments and the resulting electrostatic repulsion between them was identified to be responsible for the large inter-particle spacing in this case as well.

The inter-particle spacing between CNTs in our system can be found using the position of the first correlation peak, $q_1^*$. According to the Bragg's law, for a crystal structure the characteristic length of the system, $a$, is related to $q_1^*$ through: $a = 2\pi / q_1^*$. This characteristic length scale is directly related to the average spacing between CNTs, $d$, assuming a hexagonal lattice, i.e., $a = d \sin 60^\circ$. For the 6.5 % by volume CNT-CSA solution, the peaks found through the fitted curve are located at $q_1^* = 0.075$, $q_2 = 0.13$, and $q_3 = 0.15 \text{ Å}^{-1}$. This reciprocal spacing translates to the center-to-center distance between neighboring rods $d$ that is about 9.6 nm. Table 2 presents the average spacing between CNTs obtained at different concentrations, assuming a hexagonal lattice for all the concentrations studied.

| Concentration (% by volume) | $q_1^*$ (Å$^{-1}$) | Average spacing $d$ (nm) |
|-----------------------------|-------------------|-------------------------|
| 3.0                         | 0.052             | 13.9                    |
| 3.8                         | 0.06              | 12.1                    |
| 4.3                         | 0.062             | 11.7                    |
| 5.9                         | 0.071             | 10.2                    |
| 6.5 | 0.075 | 9.6 |

Table 2. Concentration of CNTs in solution vs. the average spacing between neighboring particles, $d$, and the first peak position $q_L^*$ obtained through curve fitting and using the Bragg’s law.

Figure 5a shows that the center-to-center spacing between neighboring CNTs, $d$, vs. the CNT mass concentration, $c$, follows the power law $c^{-1/2}$. The power-law exponent of 1/2 suggests a two-dimensional, i.e., radial, lattice expansion of 1-D cylinders that is typical of rod-like systems in the columnar phase.\textsuperscript{12} For an aligned system of rods with $L/D \gg 1$, the rods can be assumed as 1-D cylinders, where the relative area of the rods with respect to the solution is approximated by their volume fraction.\textsuperscript{26} If the rods are packed in a hexagonal lattice, then the average center-to-center spacing between the rods, $d$, is related to the volume fraction $\phi$, through $d = (\pi D^2 / (2\sqrt{3}\phi))^{1/2}$.\textsuperscript{12, 42, 46, 48} This would allow us to obtain information on the size of our CNTs in solution using SAXS data. The average spacing, $d$ is hence plotted vs. $1/\sqrt{\phi}$, as shown in Figure 5b. The diameter, $D$, of CNTs in our system is estimated to be about 2.3 nm from the linear fitting shown in Figure 5b, which is in agreement with the TEM measurements $D = 2.04 \pm 0.6$ nm. Note that the average spacing between the CNTs (e.g., at 4.3 % by volume, $d = 11.7$ nm) is about 5 times larger than their diameter.
Figure 5. a) Center-to-center spacing, $d$, between hexagonally packed CNTs in solution vs. the CNT mass concentration, and a power-law fit with power-law exponent of -1/2. b) The variation of the spacing $d$, with the corresponding volume fraction of CNTs in solution, $\phi$. The red line represents a linear fit with the slope of 2.2.

To understand why a columnar phase arises with such large inter-particle spacing, we estimated the Debye screening length of the CNTs. In our system, CNTs are positively charged by the acid, resulting in a Debye length of $\kappa^{-1}$, where $\kappa = (e^2 I_s / \epsilon k_B T)^{1/2}$. Here, $e$ is the charge of an electron, $\epsilon$ is the dielectric permittivity, and $I_s$ is the ionic strength of the acid. The ionic strength for an electrolyte of $i$ ionic species of concentration $c_i$ and valence charge $z_i$ is $I_s = \sum_i c_i z_i^2$. For calculating the ionic strength in CNT-CSA system, we consider the ionic contribution from the
CNT protonation by the acid, as well as that of the autoprotolysis of CSA. With CSA being a Brønsted–Lowry acid protonating the sidewalls of CNTs, the protonated CNTs can be considered as positively charged colloidal particles surrounded by ClSO$_3^-$ ions. The fractional charge $\delta^+$ on CNTs in CSA, calculated using the G peak shift of the Raman spectrum (See Figure S3) and Puech’s theory is about 0.024, and is assumed to be independent of the CNT concentration. Hence, the concentration of ClSO$_3^-$ counter ions, $c_{anion}$, from CNT protonation is $c_{anion} = \phi \rho_{CNT} M_c N_A \delta^+$, where $\phi$ is the CNT concentration, $\rho_{CNT}$ the density of a CNT, $M_c$ the molecular weight of carbon, and $N_A$ Avogadro’s number. As already alluded to, CSA undergoes autoprotolysis, resulting in H$_2$ClSO$_3^+$ and ClSO$_3^-$ ions with concentrations $c_{H^+}$ and $c_{anion}$, respectively, which can be calculated using dissociation constant of the acid autoprotolysis: $K_{ap} = c_{H^+} c_{anion}$. 

Based on the two ionic contributions mentioned above, the Debye screening length, $\kappa^{-1}$, is about 2 nm for our CNT-CSA system. Here, the effective diameter $D' = D + 2\alpha \kappa^{-1} = 6$ nm, using the literature assumption of $\alpha = 1$. Therefore, the large inter-particle spacing ($d = 11.7$ nm at 4.3 % by volume) in our system cannot be explained solely by the Debye screening length, unlike the case of polyelectrolytes dispersions of peptide amphiphiles and imogolite nanotubes mentioned earlier. In fact, there are multiple terms contributing to the excluded volume between the particles, which are typically neglected. For charged colloidal nanoparticles, large counter ions result in a thick ionic cloud around the nanoparticles, renormalizing the effective volume fraction of the nanoparticles, and leading to stronger electrostatic repulsion. The size of a CSA molecule is about 0.6 nm which is comparable to the diameter of a CNT molecule (2.04 ± 0.6 nm). Most of the classical theories explaining the interaction potentials in colloidal suspensions and electrolytes, including Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, are based on the assumption that
the diameter of the colloidal particles is much larger that the solvent and ions surrounding them. In case of nanoparticles, such assumption becomes invalid. Therefore, classical colloidal theories cannot be expected to capture accurately the interaction potential between nanoparticles such as CNTs, as the contribution from the size of the screening ions should become important. Still, even if we include an additional 1.2 nm of spacing between the CNT particles in solution to account for the size of the CSA molecules, we cannot explain the large inter-particle spacing of 11.7 nm obtained from the SAXS results.

We postulate that the thermal undulations arising from the bending flexibility of CNTs affect the nematic-columnar transition point through increasing the effective diameter of the CNTs. The effect of flexibility of hard rods on the boundaries of the phase diagram in polydisperse systems has been studied extensively in the literature. The flexibility of rod-like particles can destabilize the nematic phase in favor of the columnar phase (direct isotropic-columnar transition) in the high flexibility regime \( P/D < 7.745 \), while in the low flexibility regime it does not affect the nematic-columnar transition point. Hence, for CNTs, as stiff hard rods \( P/L \gg 1 \) and \( P/D \gg O(10^3) \), their finite flexibility alone cannot explain the low nematic-columnar transition concentration. Yet, the flexibility of hard rods can drastically enhance the electrostatic repulsion between the particles beyond the Debye screening length explained above by renormalizing the electrostatic potential by a factor of \( \frac{1}{4} \exp (\kappa^2 \epsilon^2) \), where \( \epsilon \) is the mean variation of a rod away from its axis. This has been shown to be consistent with experiments on hexagonally-packed DNA-polyelectrolyte gels in the literature.

Beyond a critical concentration \( \phi^* \), where the interparticle spacing between CNTs becomes comparable to the amplitude of undulations of an unconstrained rod, the rods start to feel each
other sterically. For an unconstrained rod \((\phi < \phi^*)\), the mean value of the amplitude of undulations about an axis formed by the endpoints is \(\epsilon = \left(\frac{1}{24}(\frac{L^3}{P})\right)^{1/2}\), which is about 398 nm for CNTs of \(L = 10.2 \mu m\) and \(P = 280 \mu m\). By setting the inter-particle spacing equal to the amplitude of the undulations of an unconstrained CNT, we arrive at \(\phi^* = 0.0065 \%\) by volume (65 ppm) as the critical concentration, which is slightly lower than the cloud point of the isotropic phase. Therefore, as soon as these CNTs transition to liquid crystal, \(\phi > \phi^*\), and the CNTs are constrained by their neighboring rods, the mean amplitude of the undulations then follows the Odijk’s expression that is \(\epsilon = \left(\frac{\lambda^3}{P}\right)^{1/2}\), where \(\lambda\) is the wavelength of the thermal undulations.\(^{55}\) Such thermal undulations for CNTs as flexible hard rods then result in enhanced electrostatic forces, which increase the effective volume fraction of CNTs in solution, and explain the presence of a columnar phase at such large inter-particle spacing.

**Conclusion**

Our results of SAXS measurements, probing the structure of the liquid crystal phase in solutions of CNTs in CSA at high concentrations indicate that CNTs arrange in a hexagonal lattice configuration, indicative of the formation of a columnar phase at concentrations as low as 4.3 \% by volume. We attribute this early transition to the effect of steric forces arising from the undulation-enhanced electrostatic repulsion between CNTs. Such repulsive forces are known to increase the spacing between flexible hard rods. The increase in the effective diameter results in a higher effective volume fraction, which explains the formation of columnar phase at such low concentrations. Apart from its fundamental importance for the phase behavior of polydisperse rod-like systems, achieving positional ordering due to the formation of a hexagonal columnar phase in
CNT solutions is likely to affect processing, structure, and properties of multifunctional CNT fibers spun from high concentration solutions.\(^{18}\)

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