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Surface-charge effects on the electro-orientation of insulating boron-nitride nanotubes in aqueous suspension

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Abstract

The alignment of hexagonal boron-nitride nanotubes (BNNTs) in aqueous KCl solutions under spatially uniform electric fields was examined experimentally, using direct optical visualization to probe the orientation dynamics of individual BNNTs for different electric-field frequencies. Different from most previously studied nanowires and nanotubes, BNNTs are wide-bandgap materials which are essentially insulating at room temperature. We analyze the electro-orientation of BNNTs in the general context of polarizable cylindrical particles in liquid suspensions, whose behavior can fall into different regimes, including alignment due to Maxwell-Wagner induced dipoles at high frequencies, and alignment due to fluid motion of the electrical double layer around the particles at lower frequencies. For BNNTs, the variation of the crossover frequencies in the electro-orientation spectra was studied in electrolytes of different conductivity. The effect of BNNT surface charge on electro-orientation was further studied by changing the pH of the aqueous solution. We find that the electric-field alignment of the BNNTs in the low-frequency regime is associated with the charging and motion of the electrical double layer around the particle. However, as BNNTs are non-conducting particles, the reasons for the formation of the electrical double layer are likely to be different than that of conducting particles. We discuss two possible mechanisms for the double-layer formation and alignment of 1D dielectric particles, and make comparison to those for the more commonly studied conducting particles.

Keywords: Induced charge electroosmosis, Boron Nitride Nanotube, Surface charge, 2010 MSC: 00-01, 99-00

1. Introduction

In recent years, boron-nitride nanotubes (BNNTs) have received growing interest due to their unique properties and potential application in various fields. Exhibiting high thermal conductivity \cite{1}, pronounced oxidation resistance in extreme environments \cite{2} and remarkable mechanical properties \cite{3}, BNNTs have been considered for utilization in nano-electronics \cite{4}, polymer composite materials \cite{5}, etc. In comparison to their carbon-based structural counterparts, carbon nanotubes, BNNTs may have advantages in terms of thermal stability, and possess wide-band-gap semiconducting behavior which is not sensitive to chirality, tube diameter and the number of tube walls \cite{6}. These novel 1-D structures have engendered new possibilities for osmotic power generation \cite{7}, and observation of interlayer viscous friction within the tube walls \cite{8}, among others.

From a meso- and macroscopic standpoint, the implementation of these novel nanostructures into ordered, larger-scale architecture remains a challenging and critically important task. For this purpose, substantial effort has been devoted by numerous researchers to explore different paths for creating larger, well-organized assemblies composed of different nanostructures such as carbon nanotubes (CNTs) \cite{9} and nanowires (NWs) of ZnO, Si \cite{10-12}, etc. In most studies, chemical vapor deposition (CVD) has been employed to achieve relatively large-scale structures with aligned nanotubes and nanowires \cite{13, 14}. However, these methods may have limited scalability and cost-effectiveness. A detailed comparison of different matrix/fabrication techniques for vertically aligned CNTs (VACNTs) can be found in \cite{9}. The post-growth alignment of suspended 1D nanoparticles by electric fields is a promising method to sidestep some of the aforementioned limits of CVD synthesis of aligned nanostructures at large scale. In particular, the solution-based electro-orientation method has recently been employed to fabricate VACNT thin-film composites \cite{16}, as well as to efficiently characterize the electrical properties of semiconducting NWs in a non-contact way \cite{17, 18}. However, the electric-field alignment of BNNTs in liquid suspension has not been previously studied. Generally speaking, BNNTs are wide-bandgap materials with low electrical conductivity, and thus are different from most of the previously studied nano-
is the complex permittivity, and subscripts $p$ and $f$ refer to the particle and suspending fluid medium, respectively. The depolarization factors $L_{\parallel} = (1 - L_{\perp})/2$ and $L_{\perp} \approx \frac{1}{2} [\ln(2\beta) - 1]$ depend on particle geometry. For high-aspect-ratio nanotubes and nanowires, $a \gg b$, so that $L_{\parallel} \ll 1$ and $L_{\perp} \approx 1/2$. In this regime, Eq. 2 can be further simplified as

$$K = \left[ \frac{\xi_p - \xi_f}{3[(\xi_f + (\xi_p - \xi_f) L_{\parallel}) L_{\perp}]} \right]$$

Before further discussion of our results on electro-orientation of suspended BNNTs in AC electric fields, we first present the experimental methods.

2. Experimental method

The examination of the electric-field alignment of individual BNNTs in aqueous suspension at low concentrations was carried out using direct optical visualization under an optical microscope (Fig. 2).

Hexagonal BNNTs ($L=2-10 \mu m$, O.D.=100-200 nm) were grown by chemical vapor deposition; electron microscope images of the BNNTs are shown in Fig. 3 and a description of their synthesis is given in the Supplementary Material. Furthermore, since the goal of this study is to quantitatively explore the electromechanics of individual BNNTs under applied AC electric fields, low BNNT concentrations are employed to reduce the likelihood of particle-particle interactions. Typically, $\approx 0.1$ mg of BNNTs were mixed into 3 mL of DI water (resistivity of $\rho = 17.8$ M$\Omega$ cm) or potassium chloride (KCl) solutions of various electrical conductivities. The low concentrations also allow us to use pristine tubes without functionalization, and still avoid agglomeration.

The BNNT suspensions were bath sonicated at room temperature to individualize the tubes. To vary the solution conductivity, KCl salt (Sigma-Aldrich, ACS grade) was mixed with DI water in 500 mL glass beaker (Pyrex Vista), and a series of dilutions to the desired molarities were carried out. The electrical conductivities of the tubes and nanowires, which tend to be conducting.

Fig. 1(a) and (b) illustrates representative electric-field lines for a conducting particle, with and without charging of an electrical double layer, respectively, under an applied field. For conducting particles in a low-conductivity medium, an induced dipole is formed in the particle due to the motion of mobile charges within the particle Fig. 1(a); this mechanism is classically described by Maxwell-Wagner interfacial polarization [19, 20]. If the frequency of the applied field is lower than the frequency associated with the charging timescale of the double layer, then an electrical double layer can form in the medium and interact with the applied field to cause to induced-charge electro-osmotic flow (ICEO) around the particle Fig. 1(b). In contrast to the AC electrokinetics of conducting particles [20–23], relatively little is known (particularly experimentally) about surface-charge and double-layer-related particle motions for dielectric particles. Non-conducting particles like BNNTs do not have mobile internal charges that can freely move when subjected to an applied field. Thus, the mechanisms for double layer formation and flow around dielectric particles, if they exist, are presumably different than those for conducting particles.

For ellipsoidal particles in an electrolyte solution under an applied electric field, particle motion can result from both the electric field interacting with the induced dipole in the particle, as well as the ICEO-mediated flow around the particle. The former is described by Maxwell-Wagner theory, which expresses the electro-orientational torque as

$$\mathbf{T}_e = \mathbf{P}_e \times \mathbf{E} = \frac{\pi}{3} ab^2 \epsilon_f \text{Re} (K) E_0^2 \sin \theta$$

where $\mathbf{P}_e$ is the effective induced dipole moment of a particle with $a$ and $b$ as semi-axes ($\beta = a/b$ corresponds to aspect ratio), $\epsilon_f$ is the (real) fluid permittivity, $E$ and $E_0$ are the imposed AC electric field strength and $\text{Re} (K)$ is real part of the complex Clausius-Mossotti factor expressed as

$$K = \left[ \frac{\xi_p - \xi_f}{\xi_f + (\xi_p - \xi_f) L_{\parallel}} - \frac{\xi_p - \xi_f}{\xi_f + (\xi_p - \xi_f) L_{\perp}} \right]$$

in which $\xi$ is the complex permittivity, and subscripts $p$ and $f$ refer to the particle and suspending fluid medium, respectively. The depolarization factors $L_{\parallel} = (1 - L_{\perp})/2$ and $L_{\perp} \approx \frac{1}{2} [\ln(2\beta) - 1]$ depend on particle geometry. For high-aspect-ratio nanotubes and nanowires, $a \gg b$, so that $L_{\parallel} \ll 1$ and $L_{\perp} \approx 1/2$. In this regime, Eq. 2 can be further simplified as

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Figure 2: (a) Schematic of experimental setup used to study the electro-orientation of BNNTs in different electrical conductivity suspensions. (b) Close-up of electrodes and illustration of individual BNNT alignment. As a result of the applied AC electric field, the nanotubes orient themselves with long axis parallel to the electric-field direction.

Figure 3: Transmission electron microscope (TEM) images of BNNTs ($L=2-10$ µm, O.D.=100-200 nm, wall thicknesses $\approx 30$ nm).

aqueous solutions (without BNNTs) were measured with a conductivity-meter probe (Oakton Instruments CON6 Acorn series), calibrated each time with buffer solutions prior to measurements (Hanna Instruments HI 7033 and HI 7031). The pH of the solutions was adjusted using HCl or KOH solutions together with serial dilutions and checked with a pH meter before introducing BNNTs.

As-prepared BNNT suspensions were used immediately after sonication in the experimental set-up illustrated in Fig.2(a). Copper electrodes which were precisely cut with a digital craft-cutter were affixed to a cover slip Fig.2(b). The distance between adjacent electrode pair was established as 1200 µm. Similar to the procedure in other studies\[16, 27\], to rule out possible effect of E-field inhomogeneity within the region of interest, nanotubes were only recorded in the vicinity of the center of the electrodes. Experiments were performed with three different KCl electrolytes having conductivities of 0.35 mS/m, 1.80 mS/m, and 6.74 mS/m, which yields Debye lengths in the range of 65 to 14.5 nm. Thus, depending on molarity, the double layers are in the thin to transitional range of thicknesses as compared to the BNNT diameter. Other fluids (mineral oil, dipropylene glycol, 1,2-dichloroethane, 1,2-dichlorobenzene, and n,n-dimethylformamide) were tried but showed no evidence of BNNT electro-orientation under similar field strengths.

Images with known framing rates were recorded with a high-speed CCD camera (pco.edge CMOS, PCO AG) attached to an inverted optical microscope (Model IX71, Olympus Inc) with a 100X oil-immersion objective. A spatially uniform AC electric field was produced by a function generator (Agilent 33120A, Agilent Technologies Inc.) connected to a high-bandwidth amplifier (Trek 2100 HF, Trek Inc.). Field strengths on the order of $15 \frac{V_{rms}}{mm}$ were used. During a series of experiments, the frequency of the electric field driving nanotube alignment was changed and recorded images were analyzed with an in-house Matlab image-processing algorithm.
As described by other studies [19, 21] when a freely suspending, 1D nanoparticle is subject to an external E-field, the induced dipole is strong function of the electrical properties of both the particle and the solvent media. The particle as a result exhibits frequency-dependent alignment behavior. In the following, we first present the experimental results and discuss the underlying physical mechanisms for the electro-orientation of BNNTs.

3. Results and Discussion

In electro-orientation experiments, to interpret the rate of alignment, one can use the maximum angular velocity, \( \Omega \), (taking place at \( \theta = 45^\circ \)), in which \( \theta \) is orientation angle between the applied E-field direction and particles long axis). As reported in [16, 19] by using recorded series of images of particle rotation and fitting \( \theta \) to a form of exponential decay function, the maximum angular velocity, \( \Omega \), can be obtained as a function of frequency, solution conductivities, and other conditions.

![Figure 4](image)

**Figure 4:** (a) Measured BNNT orientation as a function of time. The maximum angular velocity for each nanotube was found using a fit of the form \( \tan(\theta) = \tan(\theta_0)e^{-2\Omega t} \), as shown by the solid line in the figure. Inset: Overlay of images showing nanotube rotating into alignment with the horizontal electric field. (b) Individual microscope images showing time series of BNNT alignment with electric field (See Supplementary Material for video).

As seen in Fig 4, these Ag-NW reference experiments used the same electrolytes as those of the BNNT electro-orientation experiments. Similar to what was reported in [19], the measured alignment behavior of Ag NWs in aqueous solution as a function of AC frequency demonstrates the combined effects of alignment of the induced dipole in the particles and also ICEO-induced rotation originating from the flow of double layer around the particle. As will be discussed in more detail later, ICEO is relevant when the time scale of the applied AC field is long enough for ions to migrate in the fluid in reaction to the induced dipole and form an electrical double layer (EDL). For the Ag NWs, the variation of alignment rate crossover with solution conductivity results from the formation of this EDL.

![Figure 5](image)

**Figure 5:** Electro-orientation spectra for Ag nanowires in different conductivity solvents \( (E = 15 \text{ V/mm}) \). The error bars show the variation for five different Ag nanowires.

As seen in Fig 5 as the solution conductivity increases, the EDL can still be formed at higher frequencies, thus shifting the crossover in alignment rate to higher frequencies. Moreover, as observed by others [19, 28, 29], when the fluid conductivity increases, the observed plateau in the alignment rate for the low-frequency regime starts to diminish due to shielding of the electric field, another sign of ICEO-influenced alignment. At higher frequencies, the EDL no longer has time to form, and alignment behavior can be classically described by the Maxwell-Wagner model of Eqs 1 – 3. Our observations for Ag NWs, in terms of the existence of two distinct regions over different frequency regimes, is consistent with prior work and validates the experimental approach.

We next switch our focus by proceeding with the electro-orientation of BNNTs which is the main topic of this study. Fig 4(a) shows the measured alignment rate of an individual BNNT as a function of orientation angle, \( \theta \), for a
constant electric-field strength, while Fig.6(b) shows the effect of field strength on the maximum alignment rate, $\Omega$. Both measurements were made at a constant frequency of $f=300$ Hz.

As seen in Fig.6(a) and (b), the alignment rates show the $\sin(2\theta)$ and $E^2$ dependence as expected from Eq.1 for classical Maxwell-Wagner behavior. Nevertheless, it is known [30, 31] that these parameters alone cannot distinguish between the underlying mechanisms (induced-dipole alignment vs ICEO flow) of electro-orientation, since the rotation of the particles have the same $\theta$- and $E$- dependence for both cases. However, the variation of the particle alignment with solution conductivity differs for the two mechanisms.

For classical induced-dipole alignment, there is a transition in the frequency response from low-frequency regime to high-frequency regime - this crossover frequency, $f_{c,MW}$, is defined as,

$$f_{c,MW} = \frac{1}{\tau_{MW}} = \frac{(1 - L_{||}) \sigma_f + \sigma_p L_{||}}{(1 - L_{||}) \epsilon_f + \epsilon_p L_{||}}$$

In this case, when the fluid properties and the aspect ratio of the particles are known, the measured crossover frequency can be used to characterize the individual nanowire’s electrical properties, as has been done for a variety of semiconducting and insulating nanowires [17, 18]. However, for BNNTs at room temperature, the expected resistance is on the order of $G\Omega$s due to their inherent wide-bandgap semiconducting behavior [6, 32]. In the limit of $\sigma_p L_{||} \ll (1 - L_{||}) \sigma_f$, the Maxwell-Wagner crossover frequency of Eq.4 can be simplified as,

$$f_{c,MW} = \frac{\sigma_f}{\epsilon_f} \frac{1}{(L_{||}^{-1} - 1)}$$

For BNNTs in low molarity KCl solutions, the expected Maxwell-Wagner crossover frequency, $f_{c,MW}$, should be greater than $10^7$ Hz. Fig.7 shows the measured orientation spectra of 15 different BNNTs, normalized by the maximum alignment rate (which occurs at low frequencies in this case) at a fixed pH of 7. As seen in the figure, the orientation spectra show a decrease in alignment rate beginning at frequencies much lower than the crossover frequency expected for Maxwell-Wagner induced-dipole alignment (starting in the kHz range rather than tens of MHz). This indicates that other mechanisms are involved in the observed BNNT alignment behavior over the studied frequency range.

As previously discussed for the control experiments with Ag nanowires, there is another important time-scale (in addition to the Maxwell-Wagner timescale) for electro-orientation that is associated with the charging of the double layer by free ions in solution. The characteristic charging time for the EDL scales as $\tau_{DL} \propto 1/\sqrt{\sigma_f}$, in which
\( \sigma_f \) represents the fluid media conductivity [16, 20, 33]. In terms of frequency, this scaling can be expressed as,

\[
f_c, EDL \propto \sqrt{\sigma_f}
\]

When the applied frequency is higher than this critical frequency, \( f > f_c, EDL \), ions no longer have enough time to migrate and the effect of EDL screening diminishes. In the frequency regime lower than this critical frequency, \( f < f_c, EDL \), the EDL forms and in turn can move under the external field, generating ICEO flow which can orient the nanotube.

To test whether the observed BNNT alignment and low-frequency crossover are related to the electrical double layer in the fluid, the conductivity of the aqueous solution was varied by adding differing amounts of KCl. Figure 4 shows that the normalized electro-orientation spectra of the BNNTs shifts towards higher frequencies when the solution conductivity is increased. This is also seen in Table 1, which shows the measured crossover frequencies, \( f_c \), obtained by fitting the electro-orientation spectrum of individual tubes to a S-shaped curve (See Fig. 4 and Supplementary Material Fig. 1).

The crossover frequency is expected to scale with fluid conductivity, and with the square root of fluid conductivity, for induced-dipole and ICEO rotation, respectively (Eqns 6 and 7). Figure 8 shows the experimentally measured crossover frequencies as a function of solution conductivity, for 15 BNNTs at each condition. As seen in the figure, the scaling of the low-frequency variation in crossover frequency is consistent with double-layer charging and flow. This is further evidence that the electroorientation of BNNTs observed here is caused by the motion of the EDL rather than classical Maxwell-Wagner alignment.

Two different mechanisms have been proposed in the literature for double-layer formation and flow around insulating particles, which do not have mobile charges that can freely move when subjected to an applied field. The first is associated with the dielectric polarization in the particle [34]. As illustrated in Fig. 9(a), the alignment of molecular dipoles by the applied field has been proposed to create positive surface charge on the side of the particle facing the negative electrode, and negative surface charge on the other side [34]. This asymmetric surface charge may then lead to the formation of an induced EDL, whose counterions migrate under the electric field to generate ICEO flow, much like the case of a conducting particle. A second mechanism for dielectric particles with surface charge is expected to scale with fluid conductivity, and with the square root of fluid conductivity, for induced-dipole and ICEO rotation, respectively (Eqns 6 and 7). Figure 8 shows the experimentally measured crossover frequencies as a function of solution conductivity, for 15 BNNTs at each condition. As seen in the figure, the scaling of the low-frequency variation in crossover frequency is consistent with double-layer charging and flow. This is further evidence that the electroorientation of BNNTs observed here is caused by the motion of the EDL rather than classical Maxwell-Wagner alignment.

Table 1: Measured electro-orientation crossover frequencies for BNNTs for different molarity KCl solutions. The crossover frequencies (\( f_c \)) were obtained by fitting the experimental data to a S-curve shape for each nanotube individually. The range represents mean ± std.dev. for 15 different BNNTs.

<table>
<thead>
<tr>
<th>( \sigma_f ) (mS/m)</th>
<th>( f_c ) (Hz)</th>
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<tbody>
<tr>
<td>6.74</td>
<td>4.11 \times 10^3 ± 7.49 \times 10^2</td>
</tr>
<tr>
<td>1.80</td>
<td>1.45 \times 10^3 ± 3.44 \times 10^2</td>
</tr>
<tr>
<td>0.35</td>
<td>6.10 \times 10^2 ± 1.06 \times 10^2</td>
</tr>
</tbody>
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Figure 8: Change in crossover frequency (\( f_c \)) with aqueous solutions of different conductivity.
Figure 9: Schematic of two potential mechanisms for EDL formation and polarization for insulating particles in a solvent. (a) Molecular dipoles in dielectric particle lead to asymmetric surface charge, which attracts counter-ions to form the electrical double layer and an effective dipole moment [34]. (b) Formation of EDL due to surface charge, and EDL polarization under ion migration [27, 30, 35].

Figure 10: Alignment rate of 15 different BNNTs as a function of applied AC frequency (E-field=15 V/mm) in various pH values, error bars represent mean ± std dev. Inset: Measured ζ-potential values of BNNTs in aqueous solutions, showing increasing surface charge with solution pH.

The alignment rate at pH 9.5 is approximately 2.5× that at pH 5.0, for the same electric field strength and solution conductivity. This is consistent with the measured ζ-potentials of these BNNTs (inset of Fig.11) which show a monotonic increase in surface charge with increasing pH. This suggests the alignment of BNNTs over the studied frequency range is surface-charge dependent, and more likely related to EDL polarization rather than dielectric polarization.

To further place these results in context, we can estimate the Dukhin number, $Du = l_{Du}/L$, to assess the relative significance of surface conductivity to bulk fluid conductivity. In the above expression, $l_{Du}$ is the Dukhin length and $L$ is the characteristic length scale of the particle. Following [30], we estimate the Dukhin length as

$$L_{Du} = \frac{K_s}{K_b} \approx \frac{|\Sigma|}{e_c}.$$  \hspace{1cm} (8)

where $K_{s,b}$ are the surface and bulk conductivities, $|\Sigma|$ is the surface charge density, and $c_s$ is the bulk salt concentration. For a surface charge density of $|\Sigma| \approx 0.1 \text{C/m}^2 = 0.9e/\text{nm}^2$ at pH 5 [27], and a salt concentration of $10^{-4}$ M (approximately corresponding to a measured electrical conductivity of $\sigma=1.80 \text{ mS/m}$), the estimated Dukhin length of $L_{Du}=10 \mu\text{m}$ greatly exceeds the diameter and is comparable to the maximum length of the BNNTs. At higher pH, when the surface charge density of BNNTs rises by an order of magnitude, the Dukhin number would be even greater. These large Dukhin numbers, which indicate the importance of surface conduction, are consistent with the idea that the observed alignment of BNNTs is likely associated with surface-charge-dependent EDL polarization.

4. Conclusion

In summary, we have experimentally demonstrated, for the first time to our knowledge, the electro-orientation of a large-bandgap non-conducting nanotube, BNNTs, in KCl electrolytes under AC electric fields. The BNNT alignment rates depend on the square of the electric field, and decrease with increasing frequency. Comparison to theory indicates that the observed frequency response is not related to the crossover for Maxwell-Wagner interfacial polarization. Instead, the cross-over frequency in the low-frequency regime scales as the square root of solution conductivity, indicating that alignment is associated with the formation and motion of an electrical double layer, much like induced-charge electro-osmosis for a conducting particle. However, the mechanism for the formation of the EDL is different for insulating particles like BNNTs as compared to conductors. By varying the surface charge of the particle by changing pH, we show that the alignment rate increases with increasing surface charge, and is likely a result of counter-ion migration and EDL polarization under the influence of applied electric field. Thus, the strong surface charge (hence large Dukhin number) of the BNNTs is believed to play a vital role in their electro-orientation in aqueous solutions.

Besides its role in demonstrating and elucidating the basic underlying mechanisms for electro-orientation of insulating 1D particles with strong surface charge, this work
may also present a path for the scalable fabrication of composites incorporating well-organized BNNTs. For this, further studies would need to explore the affinity and surface charge of BNNTs in matrices such as liquid polymers.

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