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

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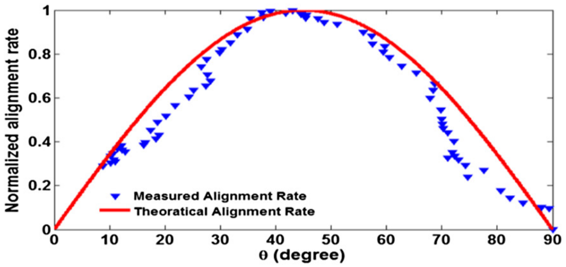
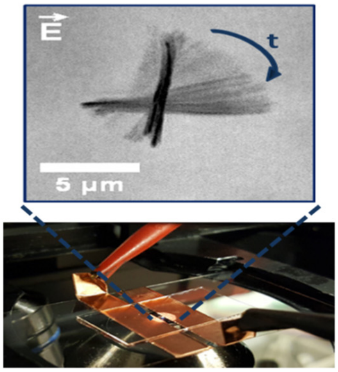
GRAPHICAL ABSTRACT





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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.

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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 [1], pronounced oxidation resistance in extreme environments [2] and remarkable mechanical properties [3], BNNTs have been considered for utilization in nanoelectronics [4], polymer composite materials [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 [6]. These novel 1-D structures have engendered new possibilities for osmotic power generation [7], and observation of interlayer viscous friction within the tube walls [8], among others.

From a meso- and macro-scopic 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) [9] and nanowires (NWs) of ZnO, and Si [10–12]. In most studies, chemical vapor deposition (CVD) has been employed to achieve relatively large-scale structures with aligned nanotubes and nanowires [13–15]. 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 [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[16], as well as to efficiently characterize the electrical properties of semiconducting NWs in a non-contact way[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 nanotubes 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 [21],

$$\vec{T}_e = \vec{\underline{P}}_e \times \vec{E} = \frac{\pi}{3} ab^2 \epsilon_f \mathbf{Re}(\underline{K}) E_0^2 \sin 2\theta \tag{1}$$

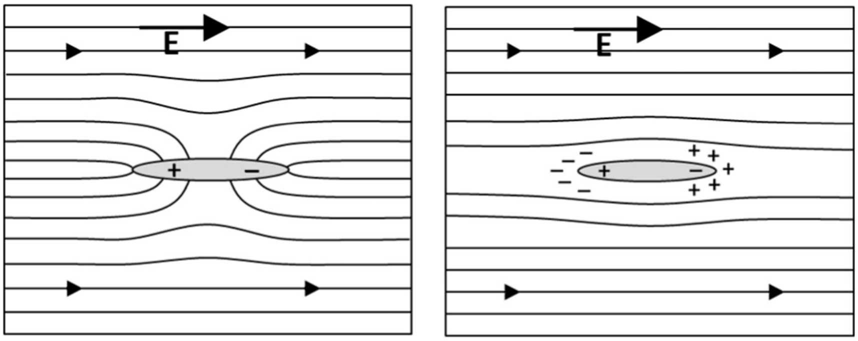
where $\vec{\underline{P}}_e$ is the effective induced dipole moment of a particle with a and b as semi-axes ($\beta = a/b$ corresponds to aspect ratio), ϵ_f is the (real) fluid permittivity, E and E_0 are the imposed AC electric field strength and $\mathbf{Re}(\underline{K})$ is real part of the complex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

$$\underline{K} = \left[\frac{\underline{\epsilon}_p - \underline{\epsilon}_f}{[\underline{\epsilon}_f + (\underline{\epsilon}_p - \underline{\epsilon}_f)L_\parallel]} - \frac{\underline{\epsilon}_p - \underline{\epsilon}_f}{[\underline{\epsilon}_f + (\underline{\epsilon}_p - \underline{\epsilon}_f)L_\perp]}\right] \tag{2}$$

in which $\underline{\epsilon}$ is the complex permittivity, and subscripts p and f refer to the particle and suspending fluid medium, respectively. The depolarization factors $L_\perp = (1 - L_\parallel)/2$ and $L_\parallel \approx \frac{1}{\beta^2}[ln(2\beta) - 1]$ 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

$$\underline{K} = \left[\frac{\underline{\epsilon}_p - \underline{\epsilon}_f}{3[(\underline{\epsilon}_f + (\underline{\epsilon}_p - \underline{\epsilon}_f))L_\parallel]}\right] \tag{3}$$

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



(a) (b)

Fig. 1. Notional electric-field lines for a conducting particle in a less-conductive medium: (a) Induced dipole when electric field is initially turned on. (b) After the formation of an electrical double layer in the fluid.