Dielectric response of multiwalled carbon nanotubes as a function of applied ac-electric fields

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The complex dielectric constant ($\varepsilon''$) is reported for multiwalled carbon nanotubes (MWCNTs) up to $10^5$ Hz as a function of ac-electric field amplitudes $E_{\text{rot}}$ (in phase and same frequency as the measurement) and $E_{\text{ac}}$ (different phase and fixed frequency with respect to the measurement). A slow relaxation process (mode 1) is observed, which shifts to higher frequency with increasing $E_{\text{rot}}$ but is independent of $E_{\text{ac}}$. A fast relaxation process (mode 2) is also observed, which is independent of $E_{\text{rot}}$ but shifts to higher frequency with increasing $E_{\text{ac}}$ (opposite to that of mode 1). An ac-conductivity analysis of MWCNT reveals insights on how $E_{\text{rot}}$ and $E_{\text{ac}}$ influence the dissipation.


I. INTRODUCTION

One-dimensional carbon nanotubes (CNTs) have been of intense research interest due to their unique atomic and electronic structures (Ref. 1). In addition to their extraordinary thermal, mechanical, and magnetic properties, their unique electrical character makes them potentially useful materials for use in nanoelectronic devices.13–17 The dielectric storage and loss properties are of special interest to researchers and engineers as these two parameters, among others, provide insight to CNTs and their suitability for electronic applications.

In recent years, a CNT dispersion in an anisotropic liquid media (such as a liquid crystal) has gained interest for inducing parallel alignment of CNTs and ac-field induced orientation manipulation for use as switches at the nanoscale level.18–20 In these kinds of applications, it is important to know the dynamic dielectric modes of CNTs as well as their behavior under an applied ac-electric field. Dielectric spectroscopy of CNTs can reveal insights on those dynamic modes of potential interests as a function of ac field intensity.

Aggregated CNTs show unique dielectric spectra, and the relaxation mechanisms are found to be distorted upon application of electric fields. However, the experimental application of an external ac-electric field can be complicated. For example, the probing field $E_{\text{rot}}(\omega)$ in an ac-capacitive measurement is in phase and at the same frequency $\omega$ as the measurement of the complex dielectric constant $\varepsilon''(\omega) = \varepsilon' - i\varepsilon''$. Thus, in the complex rotating frame of the measurement, $E_{\text{rot}}$ can be considered a “static” field. Conversely, the applied ac-electric field may be at a fixed frequency $\omega'$ with respect to the ac-capacitive measurement frequency $\omega$, i.e., $\omega' = \text{const} > \omega$. The field $E_{\text{ac}}(\omega')$ is an oscillating field in the complex rotating frame of the measurement. Figure 1 illustrates the phasor diagram of these two electric fields.

In this paper, the focus is to understand the dielectric response of CNTs with respect to applied ac-electric fields. The dielectric storage $\varepsilon'(\omega)$ and the loss $\varepsilon''(\omega)$ of a multiwalled CNT (MWCNT) sample are reported as a function of amplitude of both $E_{\text{rot}}(\omega)$ and $E_{\text{ac}}(\omega' = 203$ kHz) over the frequency range of $1 \leq \omega \leq 10^5$ Hz. The results demonstrate how $E_{\text{ac}}$ and $E_{\text{rot}}$ polarize the curved graphene layers in the MWCNT sample. The dielectric spectra reveal two relaxation modes: a slow mode below 100 Hz that is likely attributed to space-charge polarization at the electrode-nanotube interface and a fast mode in the kilohertz range that is discussed in terms of reorientation polarization of permanent and/or induced electric dipoles.

Following this introduction, a description of the ac-capacitive bridge technique, materials, and sample preparation are given in Sec. II. Dielectric spectra results as a function of applied ac-electric field amplitude are presented in Sec. III, followed by discussions and conclusions in Sec. IV, where a simple physical model is introduced to interpret the fast relaxation mode.

FIG. 1. (Color online) The ac-electric fields $E_{\text{rot}}$ and $E_{\text{ac}}$ in the complex rotating frame of the dielectric measurement. The field $E_{\text{rot}}$, along the real axis, is in phase and at the same frequency as the measurement, hence static in complex rotating frame. Being at a different frequency than the measurement, $E_{\text{ac}}$ acts as an ac field in the complex rotating frame. The field $E$ is the resultant field and, at any time, the sample experiences the real component.
II. EXPERIMENTAL PROCEDURES

A. ac-capacitance bridge technique

A homebuilt ac-capacitance bridge technique,\(^{22-24}\) operating with a probing field \(E_{\text{rot}}(\omega)\), is used to measure \(\epsilon'(\omega)\) and \(\epsilon''(\omega)\) as a function of frequency and magnitude of \(E_{\text{rot}}\) and \(E_{\text{ac}}\). The capacitive cell consists of a parallel-plate configuration, 1 cm across with a 100 \(\mu\)m gap using a Kapton spacer, housed in a temperature controlled bath. The real and imaginary parts of the complex dielectric constant are determined from the in-phase and (\(\pi/2\)) out-of-phase off-balance signals of the bridge. Comparison between the empty capacitor and sample filled capacitor allows for an absolute measurement of \(\epsilon'(\omega, E_{\text{rot}}, E_{\text{ac}})\). The probing ac-field \(E_{\text{rot}}(\omega)\) is applied across the sample through the capacitive bridge and is adjusted by increasing the probing voltage. Because of this technique, the actual magnitude of \(E_{\text{rot}}\) across the sample is not known (only the driving voltage across the bridge was controlled). However, the factor that \(E_{\text{rot}}\) increases is known if measured in units of that produced by the lowest voltage (denoted as \(E_{\text{rot}}^0\) for a 1 V amplitude applied probing voltage), this factor is labeled \(e_R = E_{\text{rot}}/E_{\text{rot}}^0\). To apply and vary the \(E_{\text{ac}}(\omega)\) field, a second signal generator, independent of the capacitance bridge, is applied directly across the parallel capacitor plates parallel to the bridge. The presence of \(E_{\text{ac}}\) can be visualized as making the measurement of \(\epsilon'(\omega)\) constant in the presence of an ac bias field that is independent of the measurement technique. The frequency of \(E_{\text{ac}}\) is a constant 203 kHz that is well above the maximum frequency range (100 kHz) of the lock-in amplifier used to detect the off-balance signal and so avoids interference. For consistency, the magnitude of \(E_{\text{ac}}\) is also labeled \(e_{\text{ac}} = E_{\text{ac}}/E_{\text{ac}}^0\), where \(E_{\text{ac}}^0\) is that produced using 1 V amplitude output. The quantities \(e_R\) and \(e_{\text{ac}}\) are the factors that the actual electric field magnitudes increase from their lowest to higher values.

B. Materials and sample preparation

The MWCNT sample, received from Sinha, was used without further processing other than drying under vacuum prior to loading into the spectrometer. The MWCNT sample used is polydisperse containing nanotubes 10–100 nm in diameter and 1–5 \(\mu\)m in length. Approximately 80 vol % of the capacitive cell was occupied by the MWCNT. The sample was filled into the capacitive cell by drop-cast evaporation; thus the orientation of the nanotubes is random between the plates. The measurements reported here are of the average complex dielectric constant \(\epsilon'(\omega) = (\epsilon_1 + 2\epsilon_\perp)/3\), where \(\epsilon_1\) and \(\epsilon_\perp\) are the complex dielectric constants parallel and perpendicular to the nanotube long axis, respectively.

III. RESULTS

The dielectric spectra of the MWCNT sample exhibit two well-distinguished dynamic modes in the frequency range studied, as shown in Fig. 2. The slow mode occurring between 20 and 100 Hz is likely due to space charge polarization at the electrode-nanotube interface (denoted mode 1), and the faster mode occurring between 1.5 and 12 kHz is likely due to orientational polarization of permanent and/or induced dipoles (denoted mode 2) either of the nanotubes themselves or within the multiple graphene layers. Mode 1 is strongly coupled to \(E_{\text{rot}}\), while mode 2 is independent of \(E_{\text{rot}}\) (see Fig. 2). The spectra reveal the opposite behavior with the application of \(E_{\text{ac}}\). Here, the relaxation frequency increases while the strength (peak height of \(\epsilon''\) for mode 2, \(\Delta\epsilon''\)) decreases for mode 2 as \(E_{\text{ac}}\) increases, while mode 1 is independent of \(E_{\text{ac}}\).

Since mode 1 is likely to originate from space charge polarization, it may involve several mechanisms of space charge accumulation at the electrode-nanotube interface. However, all such processes for powder dielectric samples generally occur at low frequency, typically below 100 Hz,\(^{25}\) and depend strongly on the surface conductivity of the sample and the cell.\(^{25}\) Note that the probing field \(E_{\text{rot}}\) is static in the rotating frame and so represents an effective dc field that couples strongly to charge conduction. This should cause the relaxation frequency of mode 1 to shift as a function of \(e_R\) but is independent of \(e_{\text{ac}}\), as observed in Fig. 2. Figure 3(a) shows the relaxation frequency of mode 1 (\(f_1\)) increasing linearly for \(0 \leq e_R < 3\). For \(e_R > 3\), \(f_1\) appears to begin saturating, reaching approximately \(f_{\text{sat}} = 75\) Hz for \(e_R > 5\). The observed behavior of \(f_1\) is consistent with conduction of finite space charges built up at the electrode-nanotube (and perhaps nanotube-nanotube) interfaces. To strengthen this interpretation, \(f_1\) extrapolates to zero as \(e_R = 0\), further indicating that mode 1 is associated with a charge conduction mechanism that vanishes as the field strength goes to zero.

It is expected that the magnitude of the probing field in an ac-capacitance bridge method \((E_{\text{rot}})\) should not affect the orientational relaxation of permanent or induced
mechanisms. Figure 4 shows the MWCNT sample ac conductivity frequency dependence and reveals the two single layer element of this analogous resistance between graphene layers. The natural frequency of a graphene layers in an MWCNT, where increasing $E_{\text{ac}}$ linearly while the strength of dispersion strength of is related to the dielectric properties by $E_{\text{ac}}$. ac-conductivity analysis was conducted. The ac conductivity of $\sigma_{\text{ac}}$ for mode 2 increases with all other factors independent of $E_{\text{ac}}$ and varying $E_{\text{dc}}$, peak magnitude of $\varepsilon''$ for mode 2 is related to the dielectric layer. Substituting gives $E_{\text{ac}}$ of MWCNT sample as a function of frequency. (a) For constant $\varepsilon_{\text{ac}}$ and varying $\varepsilon_{\text{dc}}$: star=1, diamond=2, triangle=3, circle=4, and square=5. (b) For constant $\varepsilon_{\text{ac}}$ and varying $\varepsilon_{\text{rot}}$: star=1, diamond=2, triangle=3, circle=4, and square =5.

FIG. 5. The dielectric spectrum of the MWCNT sample for $E_{\text{ac}}$ of MWCNT where $d$ is the average distance between graphene layers. The natural frequency of a single layer element of this analogous $RC$ circuit is given by $\omega_0=2\pi f_2=1/RC$. The equivalent effective capacitor $C$ for multiple graphene walls is approximately given by $C=(V/Q+V/(Q+n\cdots n\text{th layer})^{-1}=Q/(nV)$, where $n$ is the number of walls and $Q$ is the charge on the each curved graphene layer. Substituting gives $\omega_0=Vn/RQ=E_{\text{ac}}(dn/RQ)$, a linear dependence of $\omega_0$ with increasing $E_{\text{ac}}$ (once $E_{\text{ac}}$ is sufficiently above the effect of $E_{\text{rot}}$) with all other factors being constant for a given sample. This simple model appears to describe well the observed amplitude dependence of the relaxation frequency of mode 2.

To further illuminate the observed dielectric spectra, an ac-conductivity analysis was conducted. The ac conductivity is related to the dielectric properties by $\sigma_{\text{ac}}=\omega''\varepsilon_0$ (Ref. 29) and represents the sum contributions from all dissipative mechanisms. Figure 4 shows the MWCNT sample ac-conductivity frequency dependence and reveals the two modes seen in the original dielectric spectra. The slow and fast modes are observed with a $\sigma_{\text{ac}}(\omega)$ for mode 1 typical of charge conduction, while that for mode 2 reminiscent of that for induced polarization (perhaps, as discussed above, related to that between the graphene layers within a nanotube). For frequencies at or above 50 kHz, $\sigma_{\text{ac}}$ exhibits a slow increase above the plateau associated with mode 2, which may be a signature of the mode observed by Ahmad et al. 12 at $\sim 10^7$ Hz for the highest volume concentration of MWCNT in alumina.

Finally, a Debye relaxation analysis has been performed on the observed dielectric spectra. A Debye relaxation can be expressed as

$$\varepsilon^\ast = \left( \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (\omega \tau)^2} \right) - i \left( \frac{\Delta \varepsilon \omega \tau}{1 + (\omega \tau)^2} \right),$$

where $\tau$ is the relaxation time constant and $\Delta \varepsilon=\varepsilon_0-\varepsilon_\infty$ is the dielectric relaxation strength (the difference between the static and infinite frequency dielectric constants) for a single relaxation process. Figure 5 shows such a fit and indicates that mode 2 is quite consistent with this form without any additional fitting factor. This confirms that mode 2 is related to a polarization process where charge migration does not
play an important role. Clearly, mode 1 is asymmetric and not a Debye relaxation.

In summary, these results clearly reveal that this nano-scale system can be perturbed by applying ac-electric fields in two different ways: \( E_{\text{rot}} \) and \( E_{\text{ac}} \). The observed electric field dependence of the spectra reveals the polarization mechanism within the graphene layers of MWCNT. A simple theoretical model can explain the observed frequency shift of mode within the graphene layers of MWCNT. A simple theoretical model can explain the observed frequency shift of mode 2 with \( E_{\text{ac}} \): capacitor-resistor-like structure of the multiple graphene walls. This model accounts for the coupling of the polarization between multiple graphene layers in MWCNT. The extracted dielectric ac conductivity increases by four orders of magnitude for increasing frequencies up to 100 kHz and suggests a way to tune the suitable value of conductivity of a MWCNT for a given application.