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Electric birefringence of carbon nanotubes: Single- vs double-walled

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ABSTRACT

When subjected to an external electric field, carbon nanotubes in suspension are polarized and forced to rotate due to the consequent electric torque. The analysis of this electro-orientation is interesting not only at a fundamental level, but also because of the many applications that require the alignment of these particles. Moreover, the study of the interaction of the tubes with an electric field is a highly informative non-invasive technique, able to provide much information on their microscopic properties. In order to monitor the orientation of the particles, in this work we measured the macroscopic optical anisotropy of the suspension, or electric birefringence, that emerges when the tubes are oriented by the field. Two types of particle were studied: single-walled and double-walled carbon nanotubes. The electric, optical and geometrical properties of the suspended tubes were analysed via the field dependence of the electric birefringence over a wide range. Remarkably, it was found that, whilst single-walled carbon nanotubes show a positive signal, double-walled carbon nanotubes exhibit a negative birefringence caused by an anomalous optical anisotropy.

1. Introduction

Carbon nanotubes consist of rolled-up graphene sheets with a diameter in the nanoscale but a micron-sized length. Because of their extreme aspect ratio, they can be considered as the nearly one dimensional form of fullerenes. They were discovered in 1991 [1], and since then they have generated much interest both because of their unique physical properties [2–5] and their potential applications [2,4–7] in electronics, nanomaterials or nanomedicine.

Much work has been carried out on the characterization of carbon nanotubes, regarding their thermal, geometrical, mechanical, chemical or electronic properties [2,4,5,8–10]. Furthermore, many works focus on the optical properties of carbon nanotubes and other carbon-based nanoparticles, and their potential applications [8,11–14].

Special attention has been paid to the morphology of the tubes [2,3], which directly affects their microscopic properties. For instance, electronic transport is highly affected by the atomic structure, and depending on the orientation of the rolled graphene layers, the tubes can be either metallic or semiconducting [15]. Furthermore, carbon nanotubes can be made of a single graphene sheet, or by several of them structured coaxially. In the latter case, the interplay of the different layers can also play an important role in the microscopic properties of the tube [16,17].

Moreover, the current understanding of the interaction of carbon nanotubes with external electric fields is basic not only at the fundamental level, but also from the applied point of view. Thus, many applications require the controlled deposition and orientation of these particles [18–21]. For instance patterns of aligned tubes have been used as DNA or protein sensors [22,23], microscopy nanoprobes [24], structures for field emission displays [25] and photodetectors [26]. The use of electric fields has proven a simple and efficient method for the controlled orientation of these particles [18,27], but is not yet a widespread technique. Furthermore, the separation of the metallic and semiconducting nanotubes, essential for applications in nanoelectronics, may be tackled via dielectrophoresis [28,29]. Although some effort has been carried out to understand the orientation of carbon nanotubes in electric fields [27,30–33], further work is still needed for achievement of its full potential.

With this motivation, in this work we monitored the orientation of single- and double-walled carbon nanotubes in non-aqueous suspension under the application of an external electric field, via the measurement of the electric birefringence (EB) and the linear dichroism (LD). The thorough study of the birefringent phenomenology provides information about the electric, optical and

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geometrical properties of the tubes [31,34].

Non-spherical particles present anisotropic microscopic properties, in particular an anisotropic polarizability [35,36] which, for intrinsically homogeneous materials, is determined solely by the particle geometry. In the case of elongated, axially symmetric particles, this polarizability anisotropy can be written as $\Delta\alpha = \alpha_L - \alpha_d$, where L(d) refers to the major(minor) axis of the particle.

Hence, when an electric field is applied to a suspension of non-spherical particles, the dipole induced on them [35,36] is generally not parallel to the electric field, due to the electrical polarizability anisotropy at the field frequency, $\Delta\alpha^e$. This generates a torque that forces the particles to orient until the dipole is aligned with the field direction, normally with their major axis parallel to it. This phenomenon, known as electro-orientation, competes with the rotational diffusion of the particles, which tends to randomize their orientation.

The electro-orientation of the particles under the application of an electric field gives rise to an optical anisotropy of the suspension at a macroscopic level. In this work we analysed the electric birefringence Δn, and the linear dichroism ΔA.

The electric birefringence is the anisotropy induced on the refractive index of the suspension due to the electro-orientation of the particles, and it can be written as [37]

$$\Delta n = \frac{\Delta\alpha^o \phi \langle P_2(\cos\theta)\rangle}{2 n_s \varepsilon_0 V_p} \tag{1}$$

where ϕ is the volume fraction of the particles, n_s the refractive index of the suspending solution, ε_0 the vacuum permittivity and V_p the particle volume. $\Delta\alpha^o$ is the polarizability anisotropy of the particles at optical frequencies, θ the angle between the particle symmetry axis and the electric field and $\langle P_2(\cos\theta)\rangle$ the average value of the second Legendre polynomial of the orientation distribution, a measure of the degree of alignment of the particles with the external electric field. For large enough fields, when the particles are fully oriented, $\langle P_2(\cos\theta)\rangle = 1$ and the birefringence tends to the saturation value

$$\Delta n_{sat} = \frac{\Delta n(E\to\infty)}{\phi} = \frac{\Delta\alpha^o}{2 n_s \varepsilon_0 V_p} \tag{2}$$

For low fields, however, $\langle P_2(\cos\theta)\rangle$ decreases due to the effect of rotational diffusion. When expansions in power series of E_0 are usable, it can be shown that the average of the Legendre polynomial, and therefore the EB, is proportional to the second power of the field strength, a dependence known as Kerr's law. Thus, the Kerr constant, a magnitude independent of the field strength, can be defined as

$$K = \frac{\Delta n}{\lambda E_0^2 / 2} \tag{3}$$

where E_0 is the field amplitude and λ the light wavelength.

Because of this proportionality, when a sinusoidal electric field of frequency ν is applied to the suspension, the birefringence presents both a DC an AC component [35], the latter oscillating with twice the frequency of the applied field

$$\Delta n = \Delta n_{DC} + \Delta n_{AC} \sin(2\nu t) \tag{4}$$

Unless indicated otherwise, the birefringence refers to the DC component. The AC component averages to zero over time and therefore the value of Δn_{DC} can be easily obtained from the experimental signal.

In this contribution we restrict ourselves to diluted suspensions of particles with no intrinsic dipole moment. Furthermore, the viscous torque is neglected, a good approximation in the case of uncharged rods [35]. In these conditions, an explicit expression of the Kerr constant is available in the low-field range [38]

$$K = \frac{\Delta\alpha^o \Delta\alpha^e \phi}{30 n_s \varepsilon_0 k_B T V_p \lambda} \tag{5}$$

where k_B is the Boltzmann constant, T the temperature and $\Delta\alpha^e$ the electric polarizability at field frequencies.

After the application of an electric field the induced birefringence grows and reaches a stationary value in a finite time. As mentioned, the build-up process of the electric birefringence presents in general both a diffusive and an electric contribution. However, for large-enough fields, the former can be neglected.

In these conditions, it was found that the angular velocity of orientation of the particles does not depend on their size, but only on the applied field and the viscosity of the medium [31]. Hence, the polydispersity of the sample is not relevant for the build-up process, which, as a result, is in the shape of a single-exponential function

$$\Delta n(t) = \Delta n_{st}\left(1 - e^{-t/\tau_r}\right) \tag{6}$$

Here Δn_{st} is the stationary value of the birefringence and τ_r the characteristic rise time. The inverse of τ_r is expected to depend linearly on the square of the field amplitude, both in the low field [39] and high field [40] ranges, according to the expression (Θ is the rotational diffusion coefficient of the particles):

$$\left.\frac{d(\Delta n/\Delta n_{st})}{dt}\right|_{t\to 0} = \frac{1}{\tau_r} = \frac{2\Delta\alpha^e}{5 k_B T}\frac{E_0^2}{2}\Theta \tag{7}$$

Upon removal of the external electric field, rotational diffusion due to thermal agitation will randomize the orientation of the particles in a finite time. The rotational diffusion coefficient is strongly size-dependent, and, for the case of long cylinders ($\rho > 2$), can be written as [41]

$$\Theta = \frac{3 k_B T}{\pi \eta L^3}[\ln\rho + C_r] = \frac{F_\Theta}{L^3}$$
$$C_r = -0.662 + 0.917/\rho - 0.050\rho^2 \tag{8}$$

where η is the viscosity of the suspending medium and $\rho = L/d$ the aspect ratio of the particles. As a result, the decay of the birefringence is highly affected by the particle size and by the sample polydispersity. The decay of the birefringence is expected to be a superposition of individual exponential processes. Under reasonable assumptions, such superposition yields a decay in the form of a stretched exponential function [42,43]

$$\Delta n(t) = \Delta n_0 \, exp\left[-\left(\frac{t}{\tau_d}\right)^{\alpha}\right] \tag{9}$$

where Δn_0 is the initial value of the birefringence, τ_d a characteristic decay time and α a polydispersity factor. From these parameters, an average diffusion coefficient can be calculated as

$$\Theta = \frac{\alpha}{6\tau\Gamma(\alpha^{-1})} \tag{10}$$

Thus, from the analysis of the birefringence decay, the diffusion coefficient can be obtained. From it, the length of the particles can be calculated using Eq. (8). This procedure, referred to as stretched