

Dynamic Alignment of Single-Walled Carbon Nanotubes in Pulsed Magnetic Fields

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Abstract We have used linear dichroism spectroscopy to measure the dynamic alignment of single-walled carbon nanotubes (SWNT) in pulsed magnetic fields up to 55 T. We make use of the fact that SWNTs absorb light only when the electric-field vector is oriented parallel to the tube axis. SWNTs thus produce a polarization dependent change of the optical transmission, that permits precise measurements of their orientation. In order to distinguish the influence of different mechanisms governing the alignment such as the external magnetic field, Brownian motion or the tube length, we have systematically varied parameters such as the viscosity of the aqueous solution and the sample temperature.

Keywords Carbon nanotubes · Dichroism · Pulsed magnetic fields

1 Introduction

Despite characteristic differences in their magnetic properties, both semiconducting and metallic SWNTs have in common, that the susceptibility parallel to the tube axis is larger than that perpendicular to it, $\chi_{\parallel} > \chi_{\perp}$. This forces SWNTs, suspended in

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an aqueous solution, to align parallel to an external magnetic field. The degree of alignment is governed by two competing forces, the magnitude of the magnetic field constraining the tubes to align and the thermal energy which tends to randomly orient them. The equilibrium alignment thus can be characterized by [4]

$$\xi = \sqrt{B^2 N (\chi_{\parallel} - \chi_{\perp}) / k_B T} \tag{1}$$

where B is the magnetic field, N the number of carbon atoms in the SWNT and $k_B T$ the randomizing thermal energy. The application of magnetic field pulses in the milli-second range adds another dimension to this problem, as the friction experienced by a SWNT in the surrounding medium starts to delay the alignment process. The dynamic orientation of an ensemble of SWNTs thus depends on their length distribution and the viscosity of the medium. The purpose of the present paper is to investigate this phenomenon with the ultimate goal to establish a simple technique for determining the length distribution in large ensembles of SWNTs.

2 Experimental

In our experiments, we use the fact that carbon nanotubes absorb only radiation that is polarized parallel to the tube axis. We first expose our samples to light polarized parallel to the applied magnetic field. As nanotubes are tilted along the field direction their absorption of this particular polarization increases. Inversely, the absorption decreases when we use light polarized perpendicular to the field.

We consider relative changes of the transmission with respect to $B = 0$. In order to avoid the influence of intensity changes other than those caused by the alignment—e.g. the shift of optical transitions due to the Aharonov-Bohm effect—we furthermore average over the entire spectral range of detection. The time-dependent parallel (\parallel) and perpendicular (\perp) transmittances T in Fig. 1 are thus defined by

$$T_{\parallel, \perp}^{\text{av}}(t) = \frac{1}{\varepsilon_2 - \varepsilon_1} \int_{\varepsilon_1}^{\varepsilon_2} d\varepsilon \frac{T_{\parallel, \perp}(\varepsilon, t)}{T(\varepsilon, 0)} \tag{2}$$

where ε denotes the radiation photon energy and (av) indicates the spectral average. The same integration is used to determine the averages of the absorption A and the linear dichroism LD that are related to the transmittance by [2]

$$LD(\varepsilon, t) = A_{\parallel}(\varepsilon, t) - A_{\perp}(\varepsilon, t) = -\ln \frac{T_{\parallel}(\varepsilon, t)}{T(\varepsilon, 0)} + \ln \frac{T_{\perp}(\varepsilon, t)}{T(\varepsilon, 0)} = \ln \frac{T_{\perp}(\varepsilon, t)}{T_{\parallel}(\varepsilon, t)}. \tag{3}$$

In addition to the spectral averaging, we normalize the linear dichroism with respect to its maximum since we are interested in dynamic properties only. Figures 2 to 5 thus refer to the quantity

$$\overline{LD}(t) = LD^{\text{av}}(t) / LD_{\text{max}}^{\text{av}}. \tag{4}$$

3 Results and Conclusion

The results discussed in this section have been obtained with aqueous solutions of DNA-wrapped SWNTs [1]. Figure 1 shows a typical example of transmittance data obtained for our standard solution with different polarizations during a 55 T pulse. Figure 2 shows the linear dichroism derived from the same original set of data. In both figures we note at least two characteristic features altering the overall resemblance between optical properties and the magnetic field pulse. These are the smooth onset of the alignment process as opposed to the initial kink in the magnetic field and, inversely, the dealignment that lags behind towards the end of the pulse. Both features confirm the influence of a viscous drag that delays the establishment of equilibrium conditions.

Fig. 1 (Color online) Transmission spectra of light polarized perpendicular (*black*) and parallel (*red*) to the magnetic field (*blue*)

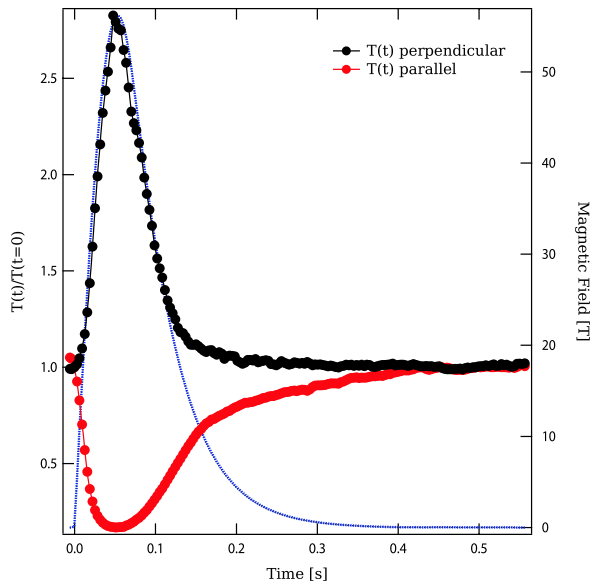


Fig. 2 $\overline{LD}(t)$ and magnetic pulse as a function of time. The normalized linear dichroism follows the magnetic pulse. The positive sign means that the tubes are aligning parallel to the magnetic field

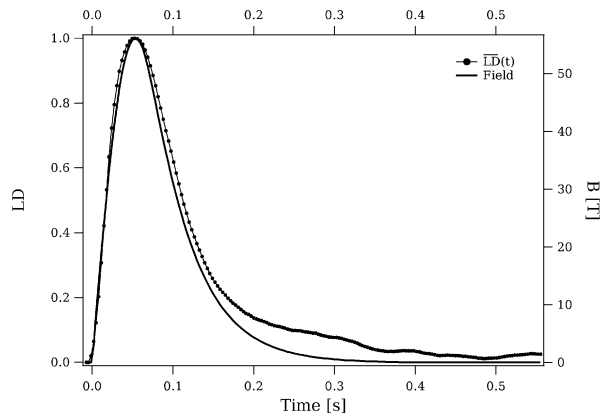


Fig. 3 (Color online) Time dependence of $\overline{LD}(t)$ for the two aqueous SWNT suspensions (sugar mixed in *black*, normal solution in *red*) at same temperature

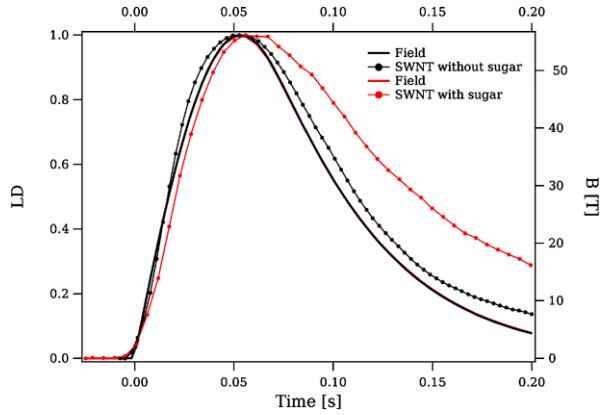
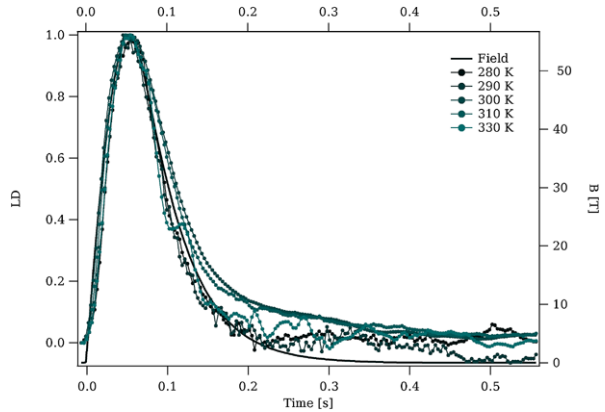


Fig. 4 (Color online) $\overline{LD}(t)$ plotted at different temperatures for the normal SWNT solution. A small broadening can be observed with decreasing temperature

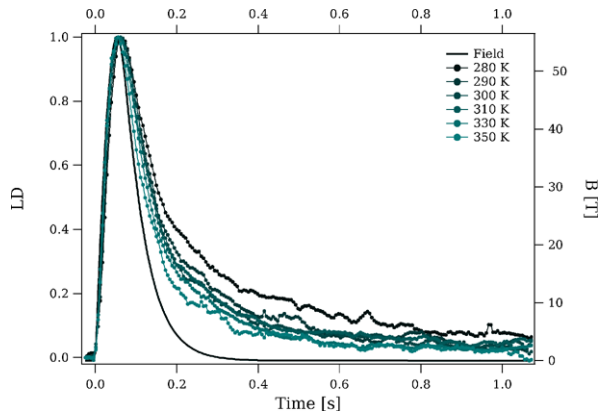


In order to investigate this effect further we have varied the viscosity and the temperature of our samples. Figure 3 shows the effect of a solution thickened with sugar compared to the behaviour of our standard sample. By inspection, the thickened solution impedes the alignment process as the magnetic field increases, and strongly delays the subsequent dealignment. However, the most prominent feature in Fig. 3 is the clear deviation between the maxima of the magnetic field and the dichroism of the thickened solution which clearly indicates an inertial movement of the SWNTs.

Figures 4 and 5 show the effect of temperature variations between 280 and 350 K on the alignment. Whereas the standard solution does not exhibit any systematic temperature dependence, the alignment in the thickened solution is clearly affected: increasing the temperature obviously decreases the viscosity of the solution, enhances the Brownian motion and thus accelerates the dealignment process. On closer inspection we also observe a slight enhancement of the alignment and a reduction of the delay between the field and alignment maxima.

From our data we conclude that, for magnetic fields with a rise time of typically 100 ms, the alignment of SWNTs in a simple aqueous solution remains close to equilibrium. The deviation towards the end of the pulse, that is most clearly visible in Fig. 2, is probably due to a fraction of tubes distinguished by their larger size. A slight

Fig. 5 (Color online) $\overline{LD}(t)$ plotted at different temperatures for the SWNT mixed with sugar solution. The alignment dynamic is slower with decreasing temperature



thickening of the solution, on the other hand, introduces a viscous drag that affects practically all SWNTs in the solution. Our aim is to investigate these phenomena quantitatively based on a model that has been developed previously [3]. These studies are underway and will be published elsewhere.

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References

1. J.A. Fagan, B.J. Landi, I. Mandelbaum et al., *J. Phys. Chem. B* **110**(47), 23801–23805 (2006)
2. A. Rodger, B. Norden, *Circular Dichroism and Linear Dichroism* (Oxford University Press, Oxford, 1997)
3. J. Shaver, A.N.G. Parra-Vasquez, S. Hansel et al., *ACS Nano* **3**, 1 (2009)
4. S. Zaric, G.N. Ostojic, J. Kono et al., *Nano Lett.* **4**, 2219 (2004)