Alignment Dynamics of Single-Walled Carbon Nanotubes in Pulsed Ultrahigh Magnetic Fields

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ABSTRACT We have measured the dynamic alignment properties of single-walled carbon nanotube (SWNT) suspensions in pulsed high magnetic fields through linear dichroism spectroscopy. Millisecond-duration pulsed high magnetic fields up to 56 T as well as microsecond-duration pulsed ultrahigh magnetic fields up to 166 T were used. Because of their anisotropic magnetic properties, SWNTs align in an applied magnetic field, and because of their anisotropic optical properties, aligned SWNTs show linear dichroism. The characteristics of their overall alignment depend on several factors, including the viscosity and temperature of the suspending solvent, the degree of anisotropy of nanotube magnetic susceptibilities, the nanotube length distribution, the degree of nanotube bundling, and the strength and duration of the applied magnetic field. To explain our data, we have developed a theoretical model based on the Smoluchowski equation for rigid rods that accurately reproduces the salient features of the experimental data.

KEYWORDS: carbon nanotubes · optical properties of carbon nanotubes · dichroism of molecules · absorption spectra of molecules · light absorption and transmission · generation of high magnetic fields

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ingle-walled carbon nanotubes (SWNTs), rolled up tubes of graphene sheets, are unique nano-objects with extreme aspect ratios, which lead to unusually anisotropic electrical, magnetic, and optical properties. They can be individually suspended in aqueous solutions with appropriate surfactants, and such suspended SWNTs behave roughly as rigid rods undergoing Brownian motion. In the absence of external fields, their orientation angles are randomly distributed. However, when placed in a perturbing field, suspended SWNTs will align parallel to the field lines owing to their anisotropic properties. The steady state alignment of SWNTs in magnetic, electric, flow, and strain fields has been characterized in many recent studies. Though mentions of dynamic alignment have been made, to date there are no comprehensive studies. Here we present the first combined experimental and theoretical study that provides fundamental insight into the hydrodynamic motion of these highly anisotropic nano-objects.

The magnetic susceptibilities of SWNTs of different diameters, chiralities, and types have been theoretically calculated using different methods. Semiconducting SWNTs are predicted to be diamagnetic (χ < 0) both parallel (||) and perpendicular (⊥) to their long axis, but the perpendicular susceptibility is predicted to have a larger magnitude (|χ⊥| > |χ||), aligning the SWNT parallel to the field. Metallic SWNTs are predicted to be paramagnetic (diamagnetic) parallel (perpendicular) to their long axes (χ|| > 0, χ⊥ < 0) and thus also align parallel to the applied field. For ~1-nm-diameter nanotubes, the values for the magnetic anisotropy, Δχ = χ⊥ − χ||, calculated by an ab initio method are between 1.2 and 1.8 × 10−5 emu/mol, depending on the tube chirality, which are similar to the values calculated by a k·p method (1.9 × 10−5 emu/mol) and by a tight-binding method (1.5 × 10−5 emu/mol). These values are consistent with recently reported experimental values, measured with steady-state optical methods.

The degree of alignment of SWNTs in a magnetic field can be conveniently characterized by the dimensionless ratio of the alignment potential energy and the thermal energy,

$$
\frac{\Delta E}{k_BT} = \sqrt{\frac{B^2N\Delta \chi}{k_BT}}
$$

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where \( B \) is the magnetic field, \( N \) is the number of carbon atoms in the SWNT, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature of the solution. A significant fraction of nanotubes in the solution will align with \( B \) when the alignment energy is greater than the randomizing energy, that is, when \( \xi > 1 \). Using \( u \) and the angle \( \Theta \) between a SWNT and the aligning magnetic field, an angular distribution function,\(^{23} P(\Theta) \), in thermal equilibrium can be calculated as\(^{23,28} \)

\[
\frac{dP(\Theta)}{d\Theta} = \frac{\exp(\xi^2 \cos^2 \Theta) \sin \Theta}{\int_{-\infty}^{\infty} \exp(\xi^2 \cos^2 \Theta) \sin \Theta \, d\Theta} \tag{2}
\]

Many experiments have studied the equilibrium alignment of SWNTs in magnetic fields.\(^{3,6,22,24} \) More recent experiments have explored the chirality dependence of SWNT alignment to extract the SWNT species specific magnetic susceptibilities.\(^{8} \)

Linear dichroism spectroscopy has a well-developed history of application to both steady state and dynamic situations, such as the flow-induced alignment of fibrils\(^{25} \) and the magnetic-field-induced alignment of polyethylene and carbon fibers.\(^{26} \) However, to date no one has studied the dynamic effects of alignment of SWNTs. Defined as the difference between the absorbance of light polarized parallel (\( A_{\parallel} \)) and perpendicular (\( A_{\perp} \)) to the orientational director of a system, \( \hat{n} \), linear dichroism (LD) is a measure of the degree of alignment of any solution of anisotropic molecules.\(^{27} \) Experimentally, the sign of LD gives qualitative information about the relative orientation of molecules, positive for alignment parallel to \( \hat{n} \) and negative for perpendicular. Reduced LD, \( LD' \), is normalized by the unpolarized, isotropic absorbance (\( A \)) of the system, and gives a quantitative measure of the alignment. The measured LD' spectrum is related to both the polarization of the transition moment being probed and the overall degree of alignment of the molecules being investigated:\(^{27} \)

\[
LD' = \frac{LD}{A} = \frac{A_{\parallel} - A_{\perp}}{A} = 3 \left( \frac{3 \cos^2 \alpha - 1}{2} \right) S \tag{3}
\]

where \( \alpha \) is the angle between the transition moment and the long axis of the molecule and \( S \) is the nematic order parameter. \( S \) is a dimensionless quantity that scales from 0 for an isotropic sample to 1 for a perfectly aligned sample and is defined as

\[
S = \frac{3\langle \cos^2 \Theta \rangle - 1}{2} \tag{4}
\]

where \( \langle \cos^2 \Theta \rangle \) is averaged over the angular probability distribution function and \( \Theta \) is the microscopic angle made between a SWNT’s long axis and the alignment director of the system.

For the case of SWNTs, optical selection rules\(^{28} \) coupled with a strong depolarization for light polarized perpendicular to the tube axis result in appreciable absorption features observed only when light is polarized parallel to the tube axis. Hence, we can simplify eq 3 using \( \alpha = 0 \), to \( LD' = 3S \), giving a direct link between the measured LD' and the orientation of the SWNTs.

In this study, the dynamic effects of SWNT alignment in pulsed high magnetic fields were investigated for the first time. We measured time-dependent transmittance through individually suspended SWNTs in aqueous solutions in the Voigt geometry (light propagation perpendicular to the applied magnetic field) in two polarization configurations, parallel and perpendicular to the applied magnetic field. From this we calculated LD as a function of time, both in millisecond (ms)-long pulsed high magnetic fields up to 56 T and microsecond (\( \mu s \))-long pulsed ultrahigh magnetic fields up to 166 T. We developed a theoretical model based on the Smoluchowski equation, which extracts the length distribution of the SWNTs in suspension based on a fit to time-dependent LD. These results pave the way to further study of SWNT dynamics in solution.

RESULTS

Measured Transmittance. All ms-pulse data was taken using a spectrally resolved, near-infrared setup. To avoid any convolution with spectral line shape broadening\(^{4,5,16} \) the data was integrated over the entire InGaAs range (~900 to 1800 nm). The benefit of removing ambiguity associated with spectral changes induced by the Aharonov–Bohm\(^{29} \) effect coupled with the large number of nanotube chiralities present in our sample outweighs the possibility for any chirality selective analysis (which has been performed at low magnetic fields\(^8 \)).

Figure 1a displays spectrally integrated, time-dependent transmittance through the sample and polarizer [in parallel (blue) and perpendicular (red) configurations] and the accompanying 56 T magnetic field trace (green). The raw transmittance data is normalized to the zero-field value as

\[
T_{\parallel,0}(t) = \frac{T_{\parallel}(t)}{T_{\parallel}(t = 0)} \tag{5}
\]

where \( T_{\parallel}(t) \) denotes the raw transmittance as a function of time with the respective polarization configuration. Starting at time zero, before the field pulse, the transmittance in both polarization configurations is equal. As the field increases, and the SWNTs start to align with the field, light polarized parallel (perpendicular) to the magnetic field decreases (increases) in overall transmittance.

Similarly, Figure 1b shows the optical response of suspended SWNTs to a \( \mu s \)-pulse magnetic field pro-
Figure 1c shows results from the Los Alamos Single Turn Generator to produce a rapidly oscillating field.

This data was collected with an Ar$^+$ ion laser at 488 nm, which is in the second sub-band region of the SWNT optical spectra, and thus the Aharonov–Bohm effect induced spectral changes are small in relation to the line width, negating the need for spectral integration. As the field rises to 140 T (~2.5 $\mu$s risetime), the nanotubes align with the magnetic field by ~2 $\mu$s. It should be noted that in this experiment the field returns to zero at ~6 $\mu$s and then increases in the negative direction, reaching a minimum ~$-50$ T at ~9 $\mu$s. However, since only the magnitude of the magnetic field ($|\vec{B}|$) is important in aligning the nanotubes, the transmittance shows a secondary peak at ~$10$ $\mu$s.

This is also clearly demonstrated by the parallel configuration data in Figure 1d where we used the Megagauss Generator to produce a rapidly oscillating field ~65 T. Figure 1c shows results from the Los Alamos Single Turn Coil Project (STP) magnet in a perpendicular configuration with a 635 nm laser and a different sample. At approximately 6 $\mu$s, when magnitude of the field was low, in part c the detector overloaded due to the arc flash from the routine disintegration of the coil; this does not affect the data collected before the coil break. This data confirms our results from the Megagauss Generator with a different magnet of similar design, different excitation wavelength, and different sample. Overall, the magnitude of the change in transmittance is less than the ms pulse experiment due to the shorter field duration. Figure 1, panels a and d are nearly the same magnitude, but the $\mu$s-pulse in 1d shows an order of magnitude smaller response than the ms-pulse in 1a. For our qualitative analysis we use ms-pulse data from Toulouse and $\mu$s-pulse data from Berlin.

**Calculated Dynamic Linear Dichroism.** The time-dependent (or dynamic) linear dichroism, LD(t), of SWNT alignment is calculated directly from the normalized transmittances. Using the relationship between transmittance ($T$) and absorbance ($A$), LD(t) can be related to the measured transmittances, $T_{||}(t)$ and $T_{\perp}(t)$, as

$$LD(t) = A_{||}(t) - A_{\perp}(t)$$

$$= -\ln \frac{T_{||}(t)}{T_0} + \ln \frac{T_{\perp}(t)}{T_0}$$

$$= \ln \frac{T_{||}(t)}{T_{\perp}(t)}$$

(6)

where the transmittance of the background medium, $T_0$, cancels out. This is of particular advantage in pulsed field experiments, where the induced change in transmittance is very straightforward to collect, but the background signal can be cumbersome. As we are studying the dynamics of SWNT alignment in pulsed fields, and not the magnitude of alignment, we can utilize LD(t) normalized to its maximum value ($LD_{max}$).

Although this procedure washes out the quantitative measure of the alignment as opposed to normalizing by isotropic absorption as in LD$^N = 3S$, it retains the dynamics of the SWNTs in response to the magnetic field pulse.

Figure 2 shows $LD(t)$ (purple) for (a) ms and (b) $\mu$s pulses calculated from the transmittances of Figure 1. The relationship of LD and LD$^N$ is such that they share the same dynamic features. The positive sign of the signal indicates that the SWNTs are aligning with the magnetic field. As the strength of the magnetic field increases, it reaches a critical value (length dependent) where the magnetic force overcomes Brownian motion. At this point, SWNTs start aligning and continue to align as long as the magnetic field remains above this critical value. However, the overall alignment of the SWNTs lags behind the applied field because of viscous drag. As the field decreases, Brownian motion becomes again more significant; beyond a critical field...
strength (corresponding to the maximum LD) the SWNTs begin to progressively lose orientation, slowed by viscous drag. At the end of the magnetic pulse, the residual SWNT alignment decays exponentially in time under the effect of Brownian motion with a characteristic time dictated by
\[ T = \frac{1}{\zeta_r} \]
where
\[ \zeta_r = \frac{\pi \eta s L^3}{3 \varepsilon f(\varepsilon)} \]
and
\[ \varepsilon = \left( \frac{\ln \frac{L}{R}}{R} \right)^{-1} \]
and
\[ f(\varepsilon) = \frac{1 + 0.64 \varepsilon - 1.5 \varepsilon^2 + 1.659 \varepsilon^3}{1 - 1.5 \varepsilon} \]
The equation for the conservation of the probability distribution \( \Psi \) then becomes
\[ \frac{\partial \Psi}{\partial t} = - \mathbf{R} \cdot (\omega \Psi) = D_I \mathbf{R} \cdot \left[ \mathbf{R} \Psi + \frac{\Psi}{k_B T} \mathbf{R} U \right] \]
where the rotational diffusion is defined as
\[ D_I = \frac{k_B T}{\zeta_r} \]
Equation 13 is known as the Smoluchowski equation for rotational diffusion.

In our system the external potential is the magnetic field’s effect on the orientation of an individual SWNT. This potential depends on the magnetic susceptibility anisotropy, \( \Delta \chi \), of the SWNT, the number of carbon at-
The energy can be expressed simply in terms of the second spherical harmonic $Y_2^0$

$$U = \Delta \chi NB^2 \cos^2 \theta = \Delta \chi NB^2 \left[ \frac{4}{3} \sqrt{\frac{\pi}{5}} |Y_2^0 + \frac{1}{3}| \right] = \kappa \left| Y_2^0 + \frac{1}{3} \right|$$ (17)

where

$$\kappa(L; t) = \frac{4}{3} \sqrt{\frac{\pi}{5}} \Delta \chi N(L) B(t)^2$$ (18)

The partial differential equations, eq 13, are then converted into a system of ordinary differential equations for $A_n^m$ using Galerkin’s method. By multiplying eq 13 by each basis function $Y_q^p$ and integrating over all orientations, the time evolution of each corresponding coefficient, $d/dt (A_n^m)$, can be determined as

$$\int \sin \theta \, d\theta \int \sin \phi \, d\phi \int \cos \psi \, d\psi \frac{d\Psi}{dt} =$$

$$= -D \kappa(q + 1) A_n^m -$$

$$\kappa \sum_{n \text{ even}} \sum_{m \text{ even}} A_n^m \int \sin \theta \, d\theta \int \sin \phi \, d\phi \int \cos \psi \, d\psi Y_q^p Y_2^0 -$$

$$\sum_{n \text{ even}} \sum_{m \text{ even}} A_n^m \int \sin \theta \, d\theta \int \sin \phi \, d\phi \int \cos \psi \, d\psi Y_q^{m-1} Y_2^1 -$$

$$\kappa \sum_{n \text{ even}} \sum_{m \text{ even}} A_n^m \int \sin \theta \, d\theta \int \sin \phi \, d\phi \int \cos \psi \, d\psi Y_q^{m+1} Y_2^{-1} \int \sin \theta \, d\theta \int \sin \phi \, d\phi \int \cos \psi \, d\psi$$ (19)

where the integrals of the multiplication of three spherical harmonics, that is, $\int \sin \theta \, d\theta \int \sin \phi \, d\phi \int \cos \psi \, d\psi Y_q^{m+1, m-1}$, are nonzero only when $m = p = 0$ or $m = -p$. The initial values of the coefficients are determined from the initial orientation of the nanotubes; a random orientation is described by $A_n^m = 0$ except for $A_0^0 = 1$. The magnetic field is turned on at $t = 0$ and varies with time. The coefficients at each time step are solved by using a numerical ordinary differential equation integration technique: third-order Runge–Kutta, available in MATLAB (ODE23). $S$ is related with the coefficients, $A_n^m(L)$, through $(\cos^2 \theta)$. 

Spherical harmonics are ideal basis functions because they are eigenfunctions of the highest derivative operator in eq 13. Note that only the even values of $n$ are used because the system is symmetric about the alignment axis. Note also that only the even values of $m$ are needed since the SWNTs have no permanent magnetic moments (they have only induced magnetic dipoles), and so $\Psi(u) = \Psi(-u)$.34

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\[
\langle \cos^2 \theta \rangle = \left( \frac{4}{3} \sqrt{\frac{\pi}{5}} Y_2^0 + \frac{1}{3} \right) \int \sin \theta \, d\theta \int d\phi \\
\left( \frac{4}{3} \sqrt{\frac{\pi}{5}} Y_2^0 + \frac{1}{3} \sum_{\text{even}} \sum_{\text{even}} A_n^m \Psi_n^m \right) = \\
\frac{4}{3} \sqrt{\frac{\pi}{5}} A_2^0 \int \sin \theta \, d\theta \int d\phi (Y_2^0) + \\
\frac{1}{3} A_0^0 \int \sin \theta \, d\theta \int d\phi = \frac{4}{3} \sqrt{\frac{\pi}{5}} A_2^0 + \frac{1}{3} \]  

(21)

By placing eq 21 into eq 4, we find \( S(L,t) \) to be

\[
S(L,t) = 2\sqrt{\frac{\pi}{5}} A_2^0(L,t) 
\]

(22)

The bulk solution’s nematic order parameter \( S(t) \) is determined by integrating \( S(L,t) \) over the distribution of lengths

\[
S(t) = 2\sqrt{\frac{\pi}{5}} \int_0^\infty A_2^0(L,t) \Omega(L) \, dL 
\]

(23)

To compare with experimental data, we assume a log-normal probability distribution,

\[
\Omega(L) = \frac{1}{L_0 \sqrt{2\pi}} \exp\left(-\frac{(\ln L - \mu)^2}{2\sigma^2}\right) 
\]

(24)

and vary the parameters \( \mu \) and \( \sigma \), the mean and standard deviation of \( \ln L \), respectively, to calculate \( \overline{LD}(t) = \max (S(t))/S(t) \), which is compared with our measured \( LD(t) \).

**DISCUSSION**

We can now use our model to calculate the dynamic response of SWNTs in time-varying magnetic fields and compare with the experimental data. Figure 4 compiles simulated \( LD \) for several lengths. Each simulated \( LD \) trace (dotted black) is offset vertically and plotted alongside its applied magnetic field (green) and experimental \( LD \) (purple). In the Smoluchowski equation, orientation is controlled by the competition between magnetic and Brownian torques; however, the overall dynamics are slowed by the viscous drag. The magnetic energy varies with \( L \) and the viscous drag varies with \( L^3 \), that is, shorter tubes do not align as much as longer ones but reach their equilibrium alignment more quickly. Thus, in the millisecond magnetic pulse (Figures 4a and 5a) the dynamics are dominated by the longer tubes as they align more significantly and need a longer time to relax, while short tubes that align quickly dominate the signal of the microsecond pulse (Figures 4b and 5b).

Because we have a sample that is polydisperse in length, as expected, no individual simulated length is able to reproduce all the features of the experimental data, as shown in Figure 4. To describe a typical SWNT length distribution, we use a log-normal form, which has been measured and confirmed by AFM and rheology measurements on similarly prepared samples.\(^{13}\) In Figure 7 the lengths indicated by symbols are those that were explicitly calculated to determine the overall \( LD \) that best fit our experiment. Figure 6 compares the experimental \( LD \) signal with that obtained from our simulation as a function of magnetic field. Our model shows a good overall match to the measured data us-
The magnetic field was generated by a two installations: the Megagauss Generator 30,36 (temperature. uid nitrogen temperature before each experiment, a cryostat using /H11011 Pulse´s in Toulouse, France. A broadband, quartz tungsten halometric setups used.

2 mm before being inserted into one of the experimental transmittance probe with an adjustable polarizer. Light transmit-
gen (QTH) lamp was used with a fiber-coupled, Voigt geometry,
standard techniques.1 It is noted that the ultracentrifugation step in
26 mm free bore reinforced copper coil cooled to liquid nitro-
thorough use. Oscillating fields were realized by preventing coil
capable of discharging ~3.8 MA on a µs time-scale through a 15 mm or 10 mm single-turn copper coil. These ex-
expansion through reinforcement. Since the duration of the field in megagauss experiments was ~10−10 that of a long-
for refinement of published values of SWNT magnetic susceptibility and chirality dependence. It is also
repeated use. Oscillating fields were realized by preventing coil
coupled sample holder, cuvette, and polarizer, with similar
measurements were done at room temperature, without the need of
Megagauss Generator and the STP magnet are single-turn coil magnets of similar design. They each utilize low inductance capacitor banks (~225 kJ in Berlin and 259 kJ in Los Alamos) capable of discharging ~3.8 MA on a µs time-scale through a 15 mm or 10 mm single-turn copper coil. These ex-
SDBS using standard techniques. It is noted that the ultracentrifugation step in

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HiPo SWNTs were suspended in aqueous surfactant solu-
tions of sodium dodecylbenzene sulfonate (SDBS) using stan-
dard techniques.1 It is noted that the ultracentrifugation step in our preparation procedure minimizes the presence of ferromag-
catalyst particles, which have been shown to have a strong
effect on SWNT alignment in low DC magnetic fields.7 Samples
were loaded into home-built cuvettes with path lengths of ~1 to 2 mm before being inserted into one of the experimental trans-
mittance setups used.

Figure 7. (color online) Histograms of log-normal length distributions used to compute the simulated linear dichro-
isim for each magnetic field pulse. The contributions from se-
lected lengths in the distribution are noted by filled circles and triangles.

ing published values5 for Δχ, the corresponding alignment potential from eq 15, and the length distribution, Ω(L) from eq 24. These results were obtained by varying average, μ, and standard deviation, σ, of the natural log of L in a log-normal distribution (Figures 5 – 7).

The comparisons in Figure 2 are fit by the length distri-
butions of Figure 7. Figure 4 gives an indication of which population of SWNTs is responsible for each part of the simulated LD. Shorter nanotubes are the pre-
dominant source of signal during the upsweep of the field and longer nanotubes for the down sweep (and lag). As the samples were not from the same batch for the different time duration pulses, a rigorous compari-
son between these effects cannot be made. Nonetheless, it is feasible to conclude that a shorter duration pulse will be moving predominantly individual nano-
tubes as our fit length distribution13 is close to pub-
lished values. The µs-pulse experiment is of too short duration to appreciably align very long SWNTs, so it is not sensitive to possible bundles in solution. The ms-pulse experiment on the other hand is long enough to move large nanotubes but shows a slight mismatch on the upsweep of the magnetic field (Figure 6). It is pos-
sible that a bimodal length distribution exists in solu-
tion, a population of shorter individualized nanotubes and one of longer bundles of nanotubes. Further ex-
periments on samples of known length distribution, measuring LD7, are needed to investigate this hypothesis.

CONCLUSION

We have measured the magnetic-field-induced dy-
amic linear dichroism of SWNT solutions. Our pre-
sented technique establishes a method for the extract-
tion of the length distribution of the SWNTs present in
solution based on the Smoluchowski equation. How-
ever, future work is needed, specifically comparison
with other techniques for determining length distribu-
tions, such as rheology and AFM measurements, allowing
for refinement of published values of SWNT magnetic
susceptibility and chirality dependence. It is also
possible from this work to design experiments that will
predominantly probe certain lengths of SWNTs in solu-
tion, and investigate the possibility of varying length
distributions with chirality.