Kinetics of Nanotube and Microfiber Scission under Sonication

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Carbon nanotubes are commonly dispersed in liquid solvents by means of sonication. This has the disadvantage, however, that it can induce the scission of the particles that are near imploding cavitation bubbles. Nanotube scission arises from the fluid friction at the surface of the nanotubes in the radial elongational flow field that forms around a cavitation bubble. An understanding of the kinetics of this phenomenon is of critical importance for controlling the length of the nanotubes in their applications yet remains elusive. We investigate this kinetics quantitatively in the present work. The strain rate of the elongational flow around a cavitation bubble is estimated experimentally using carbon microfibers of known mechanical properties. The average length \( L(t) \) of the nanotubes is measured by means of dynamic light scattering as a function of time \( t \), and we observed that \( L(t) \) scales as \( t^{-n} \), with \( n \approx 0.2 \). This scaling differs from the one predicted theoretically in the literature for the scission of flexible polymer chains. Possible origins of this difference are discussed. We believe that the reduced probability of a nanotube to be in the vicinity of a cavitation bubble if the sonication power is in some sense low and can slow down the kinetics of nanotube scission.

Introduction

Sonication is widely used to disperse nanoparticles in liquid media. Acoustic waves in liquids can induce the nucleation of gas bubbles, which grow through rectified diffusion and coalescence.\(^1,2\) After reaching a critical size, these bubbles collapse quickly, creating a strong hydrodynamic flow field in the surrounding liquid.\(^3,4\) This phenomenon, known as cavitation, explains the remarkable efficiency of sonication at disrupting nanoparticulate aggregates and even at exfoliating or cutting macromolecules\(^5-7\) and carbon nanotubes (CNTs).\(^8-10\) Understanding this process is critical because the nanotube length affects strongly the properties and applications of nanotube-based materials. For example, the rheology and phase behavior of dispersions,\(^11-13\) the electrical percolation threshold,\(^14-17\) and the stress transfer in composites all strongly depend on the nanotube length,\(^18,19\) and the performance of CNT transparent conductive films also improves with CNT length.\(^20\) Strain rates \( \frac{d\epsilon}{dt} \) of up to \( 10^9 \text{ s}^{-1} \) are theoretically predicted for the radial elongational flow around a cavitation bubble. Under these conditions, viscous forces due to fluid friction at the surface of the nanotubes can be strong enough to cut the particles. As sketched in Figure 1, this friction arises from the velocity difference between the nanotube and the surrounding liquid.

In this kind of flow field, rodlike objects are expected to ultimately align radially and in this orientation the fluid moves faster near the leading tip than the trailing end of the CNT, causing a relative velocity between CNT and fluid and hence drag forces that are balanced by mechanical tensile stresses, which are maximal near the center of the nanotube. Breakage occurs when the stress exceeds the nanotube tensile strength.\(^8-10\) The net frictional force experienced by the nanotube scales approximately as \( \mu \frac{d\epsilon}{dt} L^2 t \), where \( \mu \) is the fluid viscosity and \( L \) the length of the nanotube. The reason is that the frictional force on a tube is proportional to the frictional constant times the average relative fluid velocity along the tube, the frictional constant itself is proportional to the fluid viscosity times the nanotube length, and the average fluid velocity must be proportional to the strain rate times the length of the tubes. This scaling relation, which is independent of the nanotube diameter, is valid for rods and chains with large aspect ratio, including carbon nanotubes. Logarithmic corrections become important for small aspect ratio. However, the diameter of the particles still has a great importance because the net force needed to break a nanotube is equal to its tensile strength times its cross section.

The above scaling has another important consequence. Indeed, the cutting efficiency of the ultrasound and thereby the cutting

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rate are also expected to be proportional to $\mu \frac{d\varepsilon}{dt} L^2$ as long as the net force to break the nanotubes remains constant during sonication. The constant of proportionality should in turn be proportional to the number density of efficient cavitation bubbles that plausibly scales as the sonication power $P_{US}$ times $L^2$, where $\beta$ is an as yet unknown exponent because the larger the rods sweep out a volume and hence the larger the probability that a cavitation bubble is close to a rod. For very (in some sense) high sonication powers, one would expect $\beta = 0$, whereas for lower sonication powers it plausibly crosses over to $\beta = 3$ if the generation of sonicant bubbles becomes rate limiting. Assuming a first-order reaction for the scission kinetics of the nanotubes, one can then predict the length evolution as a function of time: \[ \frac{dN(t)}{dt} = KN \] where $K$ is the scission rate and $N$ the total number of nanotubes. Assuming a monodisperse population of nanotubes of length $L$, mass conservation implies that $N$ times $L$ is constant. If the scission rate is proportional to $L^{2+\beta}$, then $L$ is expected to decrease with the sonication time $t = T_{US}$ as $(P_{US} \times T_{US})^{-1/3\beta+2}$, that is, as $(E_{US})^{-1/3\beta+2}$, where $E_{US} = P_{US} \times T_{US}$ is the total sonication energy delivered to the sample. Of course, this relation is valid only for initial times, that is, before the rods have become so short that the frictional force acting on them has dropped so much that it cannot cut them anymore.

Experiments based on atomic force microscopy (AFM) imaging of single-wall nanotube bundles,9 ultracentrifugation characterization of single-wall nanotube bundles,22 or electron microscopy analysis of multiwall nanotubes after sonication,10 are all consistent with this expectation of a power-law decay of the mean length with sonication time. Unfortunately, accurate determination of average nanotube length, for example, by direct imaging by means of AFM or electron microscopy, is not straightforward. Sample preparation as well as limited statistics can affect the results.23 Also, as indicated by Liu et al.22 ultracentrifugation and sedimentation experiments can be used for size measurements of nanotubes. However, results of such experiments have to be carefully analyzed because ultracentrifugation depletes and precipitates larger particles, which makes the determination of the nanotube average size more delicate. Moreover, single-walled nanotubes are often assembled into the form of bundles the mean diameter of which varies with sonication power and time; the force needed to break bundles depends on bundle diameter and this complicates any quantitative analysis. Finally, and from a more quantitative point of view, one can also wonder what the effective stress is, experienced by the particles in sonicated fluids. This stress is directly related to the strain rate induced by the collapsing cavitation bubbles. Because of a lack of direct measurements, quoted estimates of these strain rates are essentially based on theoretical predictions. Actual estimates would be particularly useful because the terminal length of the particles is expected to be controlled by the strain rate of the extensional flow of the fluid in which they are embedded.

Here, we study the scission of individualized multiwalled nanotubes (MWNTs) and use dynamic light scattering to measure reliably the average nanotube length as a function of time. We also use commercial carbon fibers as model systems to estimate the stress that particles experience near cavitation bubbles. Because the tensile strength and diameter of the carbon fibers are well-known, characterization of their scission under sonication yields an estimate of the stress and strain rates induced by the flow field near collapsing cavitation bubbles. Remarkably, these values are 1 or 2 orders of magnitude higher than the values usually proposed in the literature, suggesting that carbon nanotubes could be broken into very small pieces by prolonged sonication. In situ measurements of the nanotube length by dynamic light scattering avoid potential artifacts due to drying required for direct imaging. Moreover, MWNTs do not bundle and therefore can be analyzed more straightforwardly than SWNTs. We perform experiments for up to 30 h at relatively high sonication power for deeper investigations of the scission kinetics. Under these conditions, we observe that the scission kinetics is essentially governed by the sonication energy. We also find a scaling behavior $L \sim T_{US}^{-\beta}$, with $\beta = 0.21 \pm 0.02$, which differs substantially from the one reported in previous studies.9,10,22 We discuss this finding by considering the probability of the nanotubes to be in the vicinity of collapsing cavitation bubbles, that is, a difference in the exponent $\beta$ introduced above — our measurements are consistent with a value of 3 as opposed to the value of 0 implicit in the mentioned earlier works. This effect, which was not previously considered in the literature, can explain the experimentally observed slowing down of the scission kinetics. Nevertheless, we recognize that this discussion is still speculative at this stage because other effects, such as bending of the nanotubes or polydispersity, could yield a different scaling exponent. Obviously, more work is needed, not least theoretical.

**Experimental Section**

We use two different batches of MWNTs produced by a fluidized bed chemical vapor deposition (CVD) process and provided by Arkema (Graphistrength C100 batches #6078 and #6077). As-produced materials are in the form of a light powder made of long and entangled particles. Nanotubes produced by the fluidized bed method exhibit relatively uniform diameters, but the tubes also exhibit structural defects as reflected by Raman spectra and electron microscopy observations.24 The presence of defects can alter the mechanical properties of the nanotubes.25 Nevertheless, this is not expected to change the scaling of the scission rate as a function of the length of the nanotubes. Indeed, the nanotube strength only affects prefactors of the scission rate and the terminal length of the nanotubes. The diameter $d$ of the tubes is about 10 nm for the two investigated batches. They contain catalytic iron nanoparticles supported by alumina particles. The total weight fraction of impurities is about 15 wt %. The nanotubes are purified by the following treatment: 9 wt % of MWNTs is added to a 15 wt % sulfuric acid solution. After 5 h under reflux at $T = 105\, ^\circ\text{C}$, the MWNTs are washed with deionized water, filtered, and kept in water at a weight fraction of 10 wt %. The density of acidic functions onto the nanotubes has been characterized by the Boehm’s titration method. It was found for both batches a density of $3.0 \pm 0.0$ mmol/g before and after purification. This suggests that the purification by sulfuric acid has a negligible oxidative effect. By contrast, nitric acid treatments are known to have a greater influence. Titration experiments demonstrated a substantial increase of the density of acidic functions for similar nanotubes treated by nitric acid.26 Considering the effect of nitric acid, only purification by sulfuric acid has been employed in the present work. Thermal gravimetric analyses performed with a Setaram TAG 16 instrument show that the weight fraction of iron particles drops to about 3 wt % after purification.

Figure 2 shows a scanning electron micrograph of nanotubes after gentle sonication and deposition on a substrate. A controlled amount of purified nanotubes is then added to an aqueous solution of sodium dodecyl sulfate (SDS) at 1.2 wt %. SDS is used for stabilizing the nanotubes in water. The
weight fraction of carbon nanotubes in this suspension is 0.9 wt %; 200 mL of such a dispersion is enclosed in a 50 mL vessel under gentle stirring to ensure homogenization. The dispersion circulates through a 50 mL vial in which a sonicator horn is immerged to continuously supply ultrasounds (Figure 3). The sonicator instrument is a Vibra-Cell VCX-500, equipped with a 13 mm horn and operating at 20 kHz frequency. Aliquots of 0.5 mL are taken at different times and characterized by dynamic light scattering. Determination of the average length of 0.5 mL are taken at different times and characterized by dynamic light scattering has been already reported in the literature.27,28 For these experiments, the dispersion circulates through a 50 mL vial in which a sonicator probe is located to the 500 mL reservoir. The reservoir is placed in a water bath maintained at 15 °C to avoid overheating of the dispersion. A peristaltic pump (not shown in the scheme) ensures the circulation of the dispersion.

The stretching factor \( \alpha \) is related to the sample polydispersity; \( \alpha = 1 \) for a monodisperse distribution at short but also long times. The relaxation time \( \tau \) is inversely proportional to the translational diffusion coefficient \( D_t \) of the nanotubes:

\[
\frac{1}{\tau} = 2q^2 D_t
\]

where \( q \) is the length of the scattering wave vector (the momentum transfer), \( n \) is the refractive index of the dispersion, and \( \theta \) is the scattering angle. The total scattered intensity depends on the electronic properties of the nanotubes but the fluctuations of the intensity that are considered in dynamic light scattering experiments depend only on the Brownian diffusive motion of the particles. Special care has been taken to avoid artifacts due to light absorption by the nanotubes.27 For that reason, the experiments were performed at low-power laser incident light. Broersma’s relations for rigid rods29,30 are known to approximate well the relationship between the length \( L \) and diffusivity of dilute (nonentangled) dispersions of nanotubes:31

\[
D_t = \frac{k_BT}{3\pi \eta dL} \left( \sigma - \gamma \right)
\]

\[
\sigma = \ln \left( \frac{L}{d} \right) \gamma = \frac{\gamma_{||} + \gamma_{\perp}}{2}
\]

\[
\gamma_{||} = 0.807 + \frac{0.15}{\sigma^2} + \frac{13.5}{\sigma^4} - \frac{37}{\sigma^6} + \frac{22}{\sigma^8} \gamma_{\perp} =
\]

\[
-0.193 + \frac{0.15}{\sigma^2} + \frac{8.1}{\sigma^4} - \frac{18}{\sigma^6} + \frac{9}{\sigma^8}
\]

where \( k_BT \) is the thermal energy and \( d \) the diameter of the rod. Several other analytical expressions have been proposed in the literature for the diffusion coefficient of rodlike particles.32–34 Their validity essentially depends on the aspect ratio \( L/d \) of the particles. As shown in a recent work by Mansfield and Douglas,34 discrepancies between different models become important only for small aspect ratio. In the present experiments, the aspect ratio typically varied from 20 to 50. In this range, it is generally considered that the Broersma’s expressions provide a good estimate of the diffusion coefficients. For smaller aspect ratios, it is preferable to use other expressions such as the ones proposed by Tirado et al.34–37 Although we do not expect these expressions to provide more accurate measurements in the present experiments, results deduced from their use are indicated below. A comparison with the results deduced from the Broersma’s expressions confirms that this difference in the analysis of the light scattering data does not change the main conclusions about the scission rate of the nanotubes. The same sonication cell was used to characterize the scission of carbon fibers (Toray, trade name M40, 6.5 \( \mu \)m diameter, 2.74 GPa tensile strength). Because of their large size, we simply measured their length after sonication by optical microscopy. The carbon fibers are initially cut into 1 cm long pieces and dispersed in a SDS aqueous with the same composition of that used for dispersing the carbon nanotubes.

\[
C(t) = a + b \exp \left( -\left( \frac{t}{\tau} \right)^\alpha \right)
\]

The reservoir is placed in a water bath maintained at 15 °C to avoid overheating of the dispersion. A peristaltic pump (not shown in the scheme) ensures the circulation of the dispersion.
Experimental Results

Scission of Carbon Fibers and Estimation of the Strain Rate Near Cavitation Bubbles. Figure 4 shows an optical micrograph of M40 carbon fiber fragments after 13 h of sonication at 20 W; the length of the fragments ranges from about 20 μm to about 200 μm. Of course we cannot state that the terminal length distribution of the carbon microfibers has been reached after this sonication time. Nevertheless, this experiment is sufficient to estimate lower bounds of the extensional rate produced by the implosion of cavitation bubbles.

The characteristic strain rate of this sonication flow can be estimated from the results of this simple experiment. Following the literature, it is assumed that the fibers align radially during bubble implosion, the tensile force \( F \) on a fragment of fiber is:

\[
F = \frac{\pi \mu L^2 \left(\frac{d\varepsilon}{dt}\right)}{2}
\]

Setting \( F = (\sigma_m \pi d^2)/(4) \), where \( \sigma_m \) is the tensile strength and \( d \) is the diameter of the M40 carbon fibers, and taking the conservative value of 100 μm for the length of the fragments yields an extension rate of at least \( \frac{d\varepsilon}{dt} = 6 \times 10^6 \text{ s}^{-1} \) (it would be approximately \( 2 \times 10^{11} \text{ s}^{-1} \) for 20 μm long fragments and \( 2 \times 10^9 \text{ s}^{-1} \) for 200 μm long fragments). This value, which can be viewed as a lower limit, is very large and exceeds usual literature estimates. Nevertheless, these estimates have to be taken with some caution because they are based on the assumption that the flow is laminar. It has been recently stressed by Vanapalli et al. that turbulence could affect the scission of polymers in extensional flow experiments. In the present conditions, it is unclear if turbulence has time to develop around a collapsing bubble. The collapse takes place in a few microseconds. An accurate determination of the Reynolds number \( Re \) in this nonsteady flow is not straightforward, but very rough estimates suggest that \( Re \) can be rather large. \( Re = (\rho U L_g)/(\mu) \) where \( \rho \) is the fluid density, \( U \) the fluid velocity, and \( L_g \) the characteristic largest length scale of the problem. \( U \) can be approximated to the bubble wall velocity and \( L_g \) to the size of the bubble. Considering that the velocity of the bubble wall can be on the order of several thousands m/s when the bubble size decreases down to a few micrometers, we can deduce that \( Re \) can be well above \( 10^5 \). Nevertheless, still assuming that turbulent eddies have time to develop, they are not likely to affect the scission of large fragments of carbon fibers. Indeed, the lower bound of the estimated strain rate was deduced by considering fragments that are 100 μm in length. This size is greater than the diameter of sonication bubbles that have evolved down to a few micrometers with their walls moving at very large velocity. In such conditions, turbulence is not expected to affect the scission of the microfibers. As discussed further, this probably does not hold for nanotubes, which are significantly shorter than carbon microfibers.

Scission Kinetics of Nanotubes. We investigated the influence of sonication time \( T_{US} \) and power \( P_{US} \) on the mean length of MWNTs dispersed in SDS solutions. Because smaller scattering angles are more sensitive to longer nanotubes (and vice versa), samples are characterized at seven different scattering angles (\( \theta = 30, 40, 60, 80, 90, 120, 130^\circ \)). Each corresponding temporal autocorrelation is fitted by a stretched exponential function. The factor \( \alpha \) was found to be in between 0.85 and 0.95 for all of the investigated samples, suggesting (but not proving) a low polydispersity. The inverse of the deduced characteristic time is plotted as a function of \( q^2 \). Such a multiple angle analysis was recently used by Shetty et al. to characterize the dimensions of carbon nanotubes in solution. It is appropriate for samples of low polydispersity. As expected from the relation (1), a linear fit of the data yields the translational diffusion coefficient of the nanotubes. Figures 5 and 6 show the average length of MWNTs as a function of sonication time \( T_{US} \) for various sonication powers \( P_{US} = [10 \text{ W}, 40 \text{ W}, 120 \text{ W}, 160 \text{ W}] \). Light scattering results confirm that the nanotube average length decreases with increasing sonication time and power, in agreement with previous reports related to the scission of SWNTs and MWNTs. These plots resemble earlier literature results and suggest that the length of carbon nanotubes may level off toward a terminal length as the systems are sonicated. Examination of Figures 5 and 6 also suggests that the terminal length depends on the...
with expressions derived by Tirado et al.\textsuperscript{34} the scaling exponent is
the batch other MWNT batches. An example is shown in Figure 8 with
$L$ law behavior is
same data are plotted in a log–log plot and if sonication energy
E\textsubscript{US} controls the amount of nanotubes that get disentangled and dispersed in water. The fact
that the scission kinetics is essentially driven by the sonication energy suggests that the efficiency of sonication does not depend primarily on the sonication power as long as the acoustic pressure is above the cavitation threshold.\textsuperscript{47,48} Above this threshold, the dependence of the scission kinetics of nanotubes can be understood by considering that the sonication energy controls the nucleation rate of cavitation bubbles. As proposed in the literature,\textsuperscript{8–10} the breaking of the nanotubes results from the hydrodynamic shear around the collapsing bubbles. The scission of polymer chains under sonication has been investigated for many years\textsuperscript{59} and several models have been proposed in the literature.\textsuperscript{21,50} They take into account several factors such as chain stretching and uncoiling, formation of free radicals, possible chemical recombinations, and variations of the solvent viscosity when the polymer chains are cut. These different factors make the cavitation-induced scission of polymer chains particularly complex and hence it remains a topic of highly active research. Moreover, the interplay of these different factors can lead to various forms of scission kinetics. MWNTs are somewhat simpler than polymers because they do not need to uncoil and SWNTs because they do not recombine. Moreover, in our experiments the MWNTs are so highly diluted that the dispersion viscosity does not change substantially during sonication. Such systems can therefore be useful for isolating physical phenomena and achieve a better knowledge of sonication-induced scission of particles.

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure7.png}
\caption{Average length of MWNTs #6077 as a function of the acoustic energy $E_{\text{US}}$. Symbols denote experimental data. The line is a power-law fit, $L \sim E_{\text{US}}^{-0.21}$.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure8.png}
\caption{Average length of MWNTs #6078 as a function of the acoustic energy $E_{\text{US}}$. Symbols denote experimental data. The line is a power-law fit, $L \sim E_{\text{US}}^{-0.21}$.}
\end{figure}

sonication power. However, we argue that such plots may be misleading. Indeed, different conclusions can be drawn if the same data are plotted in a log–log plot and if sonication energy $E_{\text{US}} = T_{\text{US}} \times P_{\text{US}}$ is considered. The data of Figure 5 are replotted in Figure 7; clearly, they collapse into a single master curve.

Moreover, Figure 7 shows no sign that the CNTs are reaching a terminal length. The experimental data does not follow the $L \sim E_{\text{US}}^{-1/2}$ scaling behavior predicted earlier; rather, the power-law behavior is $L \sim E_{\text{US}}^{-0.21}$. Similar results are obtained for other MWNT batches. An example is shown in Figure 8 with the batch #6078. The same collapse of data is observed and the scaling exponent is $-0.23$. Analyzing the light scattering data with expressions derived by Tirado et al.\textsuperscript{34–37} yields again the same collapse but with a slightly different scaling. For both nanotube batches it is observed that $L \sim E_{\text{US}}^{-0.18}$, a scaling exponent closer to $1/5$ than to $1/4$. This suggests that differences with previous studies are not arising from the analytical expressions chosen for analyzing the light scattering data.

\section*{Discussion}

Experiments performed with carbon fibers indicate that the strain rate in the vicinity of cavitation bubbles is of the order of $10^{10}$ $\text{s}^{-1}$. This should lead to a remarkable efficacy for cutting nanotubes into very small fragments. For example, a thin single-walled nanotube (1 nm diameter) with 30 GPa tensile strength would be cut to a terminal length of about 13 nm. This value is much smaller than that reported in previous studies related to the sonication-induced scission of single-wall nanotubes. This means that the terminal length was perhaps not yet achieved in these previous studies. Longer sonication would be needed to reach such small fragments. Nevertheless, ultrashort nanotubes obtained after sonication have been observed,\textsuperscript{44} in agreement with our expectations that the minimal length of nanotubes strongly sonicated in water can be substantially lower than 200 nm. This can also explain why the leveling off in Figure 5 is just an apparent feature resulting from the shape of the curve on a linear axis. The log–log plot of the same data (Figure 7) indicates that the terminal length is not yet achieved even after several hours of sonication. In the case of MWNTs employed in this study, a tensile strength of 10 GPa\textsuperscript{45} and a diameter of 10 nm yield a terminal length of about 75 nm. Considering the experimentally observed kinetics $L \sim 5300 E_{\text{US}}^{-0.21}$ (with $L$ in nm and $E_{\text{US}}$ in kJ), the materials should be sonicated for 47 days at 160 W. These estimations clarify why reaching the terminal length is experimentally difficult.

We also stress that the scission kinetics is essentially governed by the acoustic energy supplied to the system. A similar finding was recently reported for a different phenomenon, which is the dispersion and disentanglement of MWNTs.\textsuperscript{46} The authors have shown that the acoustic energy $E_{\text{US}}$ controls the amount of nanotubes that get disentangled and dispersed in water. The fact that the scission kinetics is essentially driven by the sonication energy suggests that the efficiency of sonication does not depend primarily on the sonication power as long as the acoustic pressure is above the cavitation threshold.\textsuperscript{47,48} Above this threshold, the dependence of the scission kinetics of nanotubes can be understood by considering that the sonication energy controls the nucleation rate of cavitation bubbles. As proposed in the literature,\textsuperscript{5–10} the breaking of the nanotubes results from the hydrodynamic shear around the collapsing bubbles. The scission of polymer chains under sonication has been investigated for many years\textsuperscript{59} and several models have been proposed in the literature.\textsuperscript{21,50} They take into account several factors such as chain stretching and uncoiling, formation of free radicals, possible chemical recombinations, and variations of the solvent viscosity when the polymer chains are cut. These different factors make the cavitation-induced scission of polymer chains particularly complex and hence it remains a topic of highly active research. Moreover, the interplay of these different factors can lead to various forms of scission kinetics. MWNTs are somewhat simpler than polymers because they do not need to uncoil and SWNTs because they do not recombine. Moreover, in our experiments the MWNTs are so highly diluted that the dispersion viscosity does not change substantially during sonication. Such systems can therefore be useful for isolating physical phenomena and achieve a better knowledge of sonication-induced scission of particles.

In this framework, Hennrich et al.\textsuperscript{3} used a model proposed by Odell et al.\textsuperscript{21} to predict the scission kinetics of nanotubes. This model considers the viscous drag force induced by the collapse of cavitation bubbles. As indicated in the introduction, assuming a first-order reaction with a kinetic constant that scales as $L^2$, $L$ is expected to scale as $t^{-1/2}$. The present experimental discrepancy means that hypothesis of the model proposed by Odell et al. for polymers cannot directly be used to the investigated nanotube dispersions. It is of course difficult to ascertain the origin of this discrepancy but our aim is to open the debate and propose possible mechanisms that could slow down the scission kinetics. A nanotube breaks when it experiences a strong shear in the vicinity of a collapsing cavitation bubble. However, nanotubes that are far from the bubbles remain unaffected. Therefore, we believe that the probability of a
nanotube to be in the vicinity of a cavitation bubble is an important factor not considered in previous models. As proposed in the Introduction, we can assume that this probability scales as the effective volume $L(t)^3$ swept by a nanotube. In such a model the kinetic constant $K$ is expected to scale as $L(t)^{18}L(t)^{-2} = L(t)^{15}$. Combining this dependence with the first-order reaction would yield $L(t) \propto t^{-\frac{1}{4}}$. Such a scaling is very close to the present experimental results $L \propto E_{US}^{-0.23}$ or $L \propto E_{US}^{-0.23}$. Of course, it is also possible that other effects come into play such as the bending of the nanotubes. Bubble collapse follows a rapid expansion, which will orient the nanotubes parallel to the bubble surface; in such starting configuration, the extensional flow during collapse will induce competing forces that could rotate the nanotube toward the radial direction (supporting the model of ref.9) or buckle it outright. Evidence of buckling has been reported in experiments showing that sonicated nanotubes can form rings and kinks.90 This is why failure modes involving buckling in addition to stretching could also be involved and lead to different kinetics of nanotube scission. Complex kinetics may also be due to length polydispersity. Although this is true in principle, polydispersity is unlikely to be a dominant factor in the anomalous scaling of our experiments because light scattering measurements show low polydispersity and minimal changes of polydispersity with sonication energy.

As stressed by Vanapalli et al.,38 turbulence can affect the scission of polymer chains in extensional steady flow experiments. The collapse of a cavitation bubble is a very brief phenomenon that yields a nonsteady flow at very small scale. However, the fluid velocity can still be very high and turbulence could also be an effect that modifies the scission kinetics of the nanotubes. In turbulent flow, the drag force would be $F \sim (\pi \mu L^2 \gamma^2 r)/(2)$, apart from an unimportant factor logarithmic in the aspect ratio of the rods, where $\gamma^2$ is now the strain rate of the velocity fluctuations.38 $\gamma^2$ decreases as a function of $r$, the length scale of the Kolmogorov cascade. The largest length scale of the present problem is plausibly set by the size of the cavitation bubble. The nanotubes are probably smaller than this size and the system would be in the so-called inertial range. In this range $\gamma^2$ scales as $r^{-2.3}$.38 The relevant length scale for the scission of the nanotubes is set by their own length. Indeed, eddies larger than the nanotube length are not expected to contribute because these act like advective flow. The effect of the much smaller ones is expected to average out. If so, we should consider velocity fluctuations at length scales on the order of $L$ and the net drag force would scale as $L^{\frac{15}{2}}$. The effect of turbulence would thus tend to accelerate the scission kinetics, in contrast to the present observations where we seek to explain a slowing down of the scission kinetics. Although any effect of turbulence cannot be ruled out, it cannot explain the observed discrepancies with the earlier work on sonication-induced scission kinetics. Lastly, it is also possible that the nanotubes could be cut layer by layer considering weak interactions between the graphene layers, as in highly crystalline graphitic materials. Nevertheless, if such a mechanism would predominantly govern the scission of the tubes, one could expect the observation of substantial diameter reductions. Such reductions are not observed in the present experiments. It is possible that structural defects increase the interactions between graphene sheets and limit thereby the possibility of layer by layer scission. Nevertheless, all of these other possibilities are still raising important questions and deserve particular attention in future work.

## Conclusions

We have experimentally determined the kinetics of scission of carbon nanotubes under sonication. We have used a simple model system made of MWNTs. The average nanotube length was measured using dynamic light scattering to minimize possible experimental artifacts. It was observed that the scission rate is governed by the supplied acoustic energy. The average length was found to scale as $L \sim (T_{US})^{-\frac{1}{2}}$ with $n = 0.21 \pm 0.02$. This scaling can be explained by considering a first-order reaction with a reaction constant that depends on the nanotube size through the probability of nanotubes to be in the vicinity of cavitation bubbles. Of course this proposal is still speculative and other mechanisms can be involved such as fracture through bending or effects of polydispersity. Nevertheless, we believe that MWNTs are an ideal system for studying sonication-induced scission because they allow the isolation of multiple effects that concur to scission in more complex systems such as polymers and SWNT bundles. We thus hope that the present findings can advance our knowledge of the effects of sonication in other systems beyond the case of multiwall nanotubes.

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