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Nematic droplets in aqueous dispersions of carbon nanotubes

Nicolas Puech,¹ Eric Grelet,¹ Philippe Poulin,¹ Christophe Blanc,² and Paul van der Schoot^{3,4}

¹Centre de Recherche Paul-Pascal, CNRS–Université Bordeaux I, 115 Avenue Schweitzer, 33600 Pessac, France

²Laboratoire des Colloïdes, Verres et Nanomatériaux, CNRS–Université Montpellier II, Place E. Bataillon, 34090 Montpellier, France

³Faculteit Technische Natuurkunde, Technische Universiteit Eindhoven, Postbus 513, 5600 MB Eindhoven, The Netherlands

⁴Instituut voor Theoretische Fysica, Universiteit Utrecht, Leuvenlaan 4, 3584 CE Utrecht, The Netherlands

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Aqueous dispersions of exfoliated, bile-salt stabilized single-wall carbon nanotubes exhibit a first order transition to a nematic liquid-crystalline phase. The nematic phase presents itself in the form of micron-sized nematic droplets also known as tactoids, freely floating in the isotropic host dispersion. The nematic droplets are spindle shaped and have an aspect ratio of about four, irrespective of their size. We attribute this to a director field that is uniform rather than bipolar, which is confirmed by polarization microscopy. It follows that the ratio of the anchoring strength and the surface tension must be about four, which is quite larger than predicted theoretically but in line with earlier observations of bipolar tactoids. From the scatter in the data we deduce that the surface tension of the coexisting isotropic and nematic phases must be extremely low, that is, of the order of nN/m.

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Carbon nanotubes or CNTs are colloidal particles with a very large aspect ratio, typically in the range from many tens to hundreds up to even thousands. Hence, it is not surprising that, provided they are properly stabilized against aggregation, fluid dispersions containing CNTs exhibit an Onsager-type isotropic-nematic transition [1–6]. This happens at concentrations in excess of a critical value that depends on the aspect ratio of the rods. The relevant concentration scale here is the volume or packing fraction because the driving force for the spontaneous alignment is the anisotropic volume exclusion between the particles. For the nematic to become stable the volume fraction of CNTs should be in excess of a few times the reciprocal of some average of their aspect ratios [7]. It follows that the nematic transition must occur at very low concentrations of, say, one per cent of CNTs. This, by and large, is in agreement with experimental observation, allowing for instance for the effects of polydispersity [1–6].

Often, before isotropic-nematic phase separation occurs on a macroscopic scale in dispersions of elongated colloidal particles, the nematic phase establishes itself in the form of droplets called tactoids. Tactoids have been observed in many dispersions, such as tobacco mosaic virus [8,9], boehmite rods [10], poly(butyl glutamate), self-assembled chromonics [11], *fd* virus [12], f-actin [13], and vanadium pentoxide [14,15]. These droplets have in common their unusual elongated, spindle-like shape. This shape can be explained by the preferential planar anchoring of the nematic director at the interface with the isotropic phase. The competition between surface tension and the elastic deformation of the bipolar director field that accommodates this preferential planar anchoring plausibly determines the optimal aspect ratio (Fig. 1). If the director field of a tactoid is indeed bipolar with field lines connecting two boojum surface defects, then its shape, as described, e.g., by the aspect ratio or the tip angle, depends on its physical dimensions because the surface and bulk elastic energies scale differently with droplet size. This seems to be the case in all systems investigated so far. Indeed, information on the ratio of (an average of) the elastic constants and the surface tension can be obtained

from the measured relation between, say, the aspect ratio and length of the droplets [13,15–18].

In this paper, we show that aqueous dispersions of surfactant-stabilized carbon nanotubes deviate from the usual picture of a bipolar director field. The tactoids that we observe in these dispersions are also quite elongated, but display a uniform director field as evidenced by polarization microscopy. This ties in with our finding that the aspect ratio of the tactoids is independent of their size, at least for the one decade range of sizes present in our samples. Theoretically, the aspect ratio of a tactoid is independent of its size if it is dictated by the surface tension anisotropy, i.e., the ratio of the anchoring strength and the surface tension [16]. This is plausible if the director field is uniform and as a result of that the anchoring conditions at the surface of the drops are sub-optimal. It is because the interfacial and anchoring free energies both scale with the area of a drop that its shape can only be a function of the ratio of the anchoring strength and the surface tension. From our observations we find that the

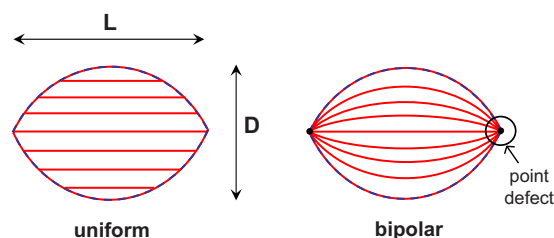


FIG. 1. (Color online) Schematic representation of the shape and director field in a uniform (left) and a bipolar (right) tactoid. The shape of the uniform tactoid is determined by the anchoring strength; the larger it is relative to the interfacial tension the more elongated the tactoid becomes. The shape of a bipolar tactoid is determined by the elastic deformation favoring an elongated shape, an effect making the director field more uniform, and by the surface tension that favors as small a surface area as possible. The crossover between the two types of director field occurs when anchoring energy of the one and elastic energy of the other are equal [16].

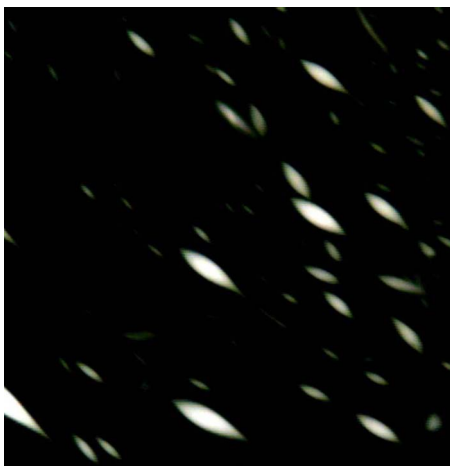


FIG. 2. (Color online) Polarization microscopic image with crossed polarizers, showing a collection of tactoids in aqueous dispersion of bile-salt stabilized single-wall carbon nanotubes. The image size is $97 \times 100 \mu\text{m}^2$.

anchoring strength is about four times larger than the bare surface tension. We put forward that the surface tension must be very small indeed, possibly as low as 1 nN/m.

We prepared our CNT tactoid dispersions from an aqueous suspension of single-wall carbon nanotubes (furnished by Elicarb batch K3778) and dispersed by bile salts, at the respective concentrations of 0.5% w/w CNTs and 0.5% w/w bile salts. To exfoliate the CNT bundles, sonication was applied to the suspension for a period of three hours. A purification process by selective centrifugation was then performed on the CNT suspensions. After removing CNT aggregates by centrifugation at low speed (30 min, 3500 rpm), the longest carbon nanotubes exhibiting some entanglements and defects were removed by ultracentrifugation (45 min, 45000 rpm). A second ultracentrifugation (180 min, 45000 rpm) was applied to the CNT suspensions to obtain the nematic liquid crystalline phase, which appeared as a black pellet on the bottom of the centrifugation tube. Finally, CNT tactoids were obtained by diluting the nematic phase up to the coexistence region with the isotropic phase. Samples of a few micron-meter thick were prepared at the isotropic-nematic phase coexistence between cover slip and glass slide. The CNT tactoids were observed by optical microscopy at different magnifications between crossed polarizers.

Figure 2 shows an image by polarization microscopy of the kind of tactoids that we find in our carbon nanotube dispersions. The background is dark because the tactoids float in the coexisting isotropic liquid phase. The tactoids are indeed quite elongated and have the typical spindlelike shape. A perfect extinction is observed when the tactoids are aligned along the polarizer or analyzer direction, demonstrating that the director field is uniform, as shown for a typical tactoid in Fig. 3. A further study under confocal Raman microspectroscopy also confirms that the director field is aligned along the tactoid long axis [19], which coincides with the main optical axis.

In Fig. 4, the aspect ratio of a large collection of tactoids is plotted against their length, which, within experimental error, is constant as advertised. Apparently, the mean aspect

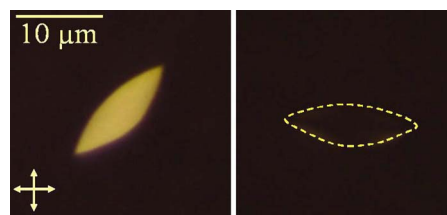


FIG. 3. (Color online) Observation by polarization microscopy of a tactoid with the main body axis at 45 degrees relative to the polarizers (left) and along one of the polarizers (right). Indicated by the dashed line is the outline of the tactoid.

ratio of the tactoids is about four for tactoids up to $36 \mu\text{m}$ in length. This result is consistent with a uniform director field in the droplets, as the aspect ratio of the drops is then dictated by the ratio of the anchoring strength and the surface tension [16]. By applying an inverse Wulff construction [20] to the shape of a typical tactoid, we have been able to probe the anisotropy of the surface free energy, σ . Shown in Fig. 5 is $\sigma(\theta)/\tau$, where τ is the bare surface tension and θ the angle between the surface tangent and the director field. We find that this angle dependence is consistent with the often-used Rapini-Papoular model for the surface free energy, i.e., $\sigma = \tau(1 + \omega \sin^2 \theta)$ with ω the ratio of the anchoring energy and the surface tension [21]. For the tactoid shown in the figure, we obtain a value for the dimensionless anchoring strength of $\omega \approx 3.4$. From the Wulff construction, we can in fact predict the aspect ratio of a nematic drop that within a Rapini-Papoular model must be equal to $2\sqrt{\omega}$ if $\omega \geq 1$ [16]. It follows from Fig. 4 that for our coexisting isotropic and nematic phases of CNTs in water, $\omega = 4 \pm 1$. This is quite larger than theoretical predictions according to which $0.5 \leq \omega \leq 1.5$, at least for cylindrical particles interacting via a harshly repulsive potential [22–25].

Additional information that we can deduce from Fig. 4 can be obtained by realizing that according to recent calcu-

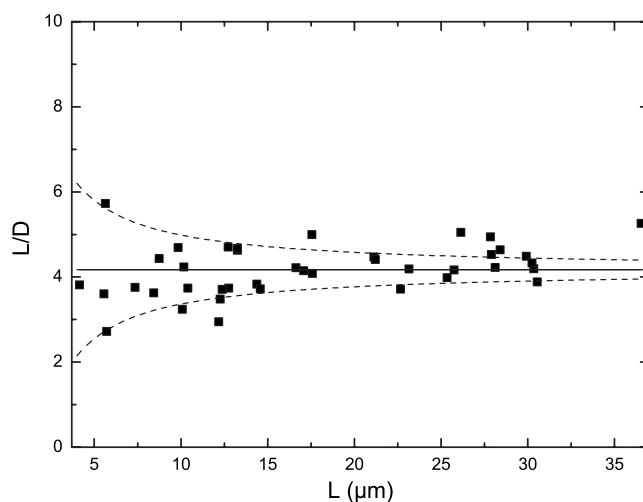


FIG. 4. Aspect ratio of the tactoids versus their length in micron-meter. Full squares: experimental data points. Drawn line: average value deduced from the experiments. Dashed lines: predicted standard deviation presuming that the surface tension is equal to 0.5 nN/m.

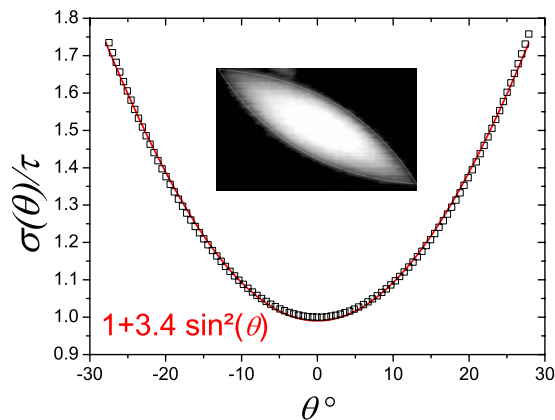


FIG. 5. (Color online) Inverse Wulff construction applied to a tactoid providing the form of surface tension anisotropy. The experimental data points (indicated by the squares) are well fitted with a Rapini-Papoular anchoring expression (drawn line).

lations [16], a tactoid changes its director field from a uniform to a bipolar one if its volume $V \approx (4\pi/3)(L/2)(D/2)^2$ is larger than $(K/\tau)^3(6.25/\omega)^{18/5}$, with K an average of the Frank elastic constants. It has to be noted that this crossover has so far only been observed in computer simulations [26]. It seems that even the largest tactoid in our samples with a length of 36 μm , has a uniform director field. This implies that a lower bound for the ratio K/τ of the nematic of CNTs must be approximately 5 μm . Interestingly, this lower bound is comparable to values found for vanadium pentoxide and *fd* virus [15–17], although that tactoids in these two systems do exhibit a bipolar field if larger than a few micron meter. It is not quite clear why single-wall CNTs behave so differently from other types of elongated particle. Indeed, CNTs exhibit a phase behavior that is in good agreement with the behavior expected for bulk suspensions of rodlike particles [3]. Nevertheless the structure of tactoids does result from a delicate interplay of bulk elastic and surface properties of the coexisting isotropic and nematic phases. These properties are known to quite sensitively depend on molecular details such as the degree of bending flexibility and the type and the strength of interactions involved in stabilizing them in suspension. Another issue is also the influence of polydispersity, which is known to be large. CNTs are polydisperse and a small fraction of very long or very short particles could affect the surface properties with a little effect on the bulk behavior. Of course, this is speculative and further work will be needed to confirm whether or not the size distribution of the CNTs confined at the isotropic-nematic interface differs from that in bulk.

Finally, the scatter in the data of Fig. 4 potentially provides physical information because in part it must be caused by thermal fluctuations of the aspect ratio of the tactoids. The Wulff construction provides only the optimal aspect ratio but does not give an indication of its variance. Using a simple scaling Ansatz based on the Rapini-Papoular surface free energy [16] and making use of the equipartition of free energy, we find that the standard deviation of the aspect ratio must approximately be equal to $(k_B T / \tau L^2)^{1/2} \omega^{3/4}$, so depend on the size of the tactoids. In Fig. 4, we have indicated around the estimated average aspect ratio the standard deviation presuming a surface tension of 0.5 nN/m. The prediction follows the magnitude and size dependence of the experimental scatter in the data reasonably well. Obviously, we should not over interpret this result because we have ignored any influence of the intrinsic error in the size measurement of the tactoids.

If we accept the very small value of the surface tension that we find at face value, then it is very much smaller than values in the range of tenths to tens of $\mu\text{N/m}$ typically found for coexisting isotropic and nematic phases in dispersions of rodlike particles [27]. Values of nN/m have been found for coexisting isotropic and nematic phases but only in dispersions of colloidal platelets [28]. Clearly, the scaling theory does not give the numerical prefactor, and this could increase the found surface tension by another factor of, say, ten. Still, this by no means takes our value within the range of the other experimentally found values. One might of course conclude from this, that the presumption that the scatter in the data is dominated by thermal fluctuations must be wrong. Indeed, some flow can occur just after sample preparation, which can induce droplet alignment and some shape distortion. The latter is clearly seen in the largest CNT tactoids, see also Fig. 2. Explicit surface tension measurements, e.g., by the capillary rise method [28] on macroscopic interfaces between coexisting isotropic and nematic phases are necessary to confirm our finding, but these are outside the scope of the present paper.

In conclusion, we find nematic tactoids of aqueous dispersions of surfactant-stabilized single-wall carbon nanotubes that have a uniform director field. Our observation accounts that the aspect ratio of about four is independent of the size of these tactoids at least for lengths up to 36 μm . The crossover to a bipolar director field must occur for sizes much larger than this value, but we have not been able to confirm this.

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