Supplementary Material:
Orientational order of carbon nanotube guests in a nematic host suspension of colloidal viral rods

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Abstract

In this Supplementary Material, theoretical results on the effects of both the CNT and fd virus dimensions on the ordering of guest CNTs in the fd virus host are first presented. Using rigid rods to describe the fd virus (i.e. $P_{fd} \to \infty$) requires the use of a much lower CNT length to find agreement with experimental results than using semiflexible rods. It is also shown that varying the diameter of the CNTs has a weak influence on their ordering, in contrast to the increase of CNT length. Furthermore, the cholesteric pitch of the fd virus host with CNTs as guest has been measured and compared with the one of pure virus suspension, confirming the validity of the dilute limit, i.e. that the CNTs do not affect the self-organization of the liquid crystalline host.

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I. EFFECT OF FD VIRUS STIFFNESS

Here the effects of fd virus stiffness on the ordering of the guest CNTs is studied by varying the persistence length P_{fd} of the host fd virus. All the calculations are based on Onsager second viral theory extended for mixtures and modified to take flexibility into account through segmentation[1–3].

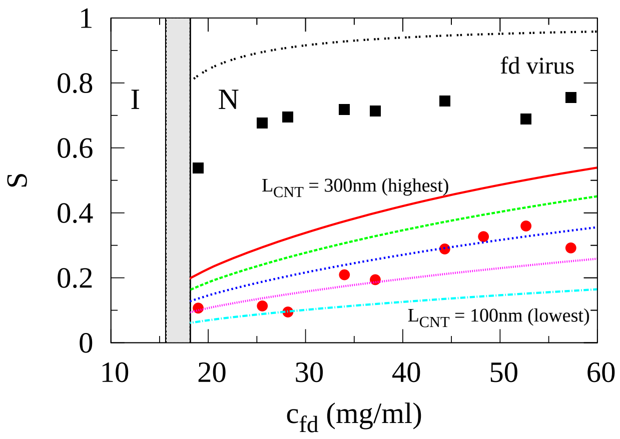

FIG. 1. Experimental orientational order parameters of the guest nematic phase of virus suspensions S_{fd} (black squares) doped with surfactant-stabilized carbon nanotubes S_{CNT} (red circles) as a function of virus concentration c_{fd}. The two vertical lines denote the isotropic liquid (I) and nematic (N) binodals. Theoretical predictions using rigid fd virus ($P_{fd} \to \infty$) and monodisperse ($\sigma = 0$) CNTs, with L_{CNT} 100nm (lowest line, light blue), 150nm (pink), 200nm (dark blue), 250nm (green) and 300nm (red) are compared. The dashed top (black) line is the calculation of S_{fd} using rigid rods ($P_{fd} \to \infty$).

Figure 1 shows the nematic order parameters of the fd virus (S_{fd}) and CNTs (S_{CNT}) for a range of CNT lengths L_{CNT} using $P_{fd} \to \infty$ (with $L_{fd} = 880$nm). The fd virus diameter is an effective one, D_{fd}^{eff}, taking into account the electrostatic repulsions between the charged viral rods: it is defined as the diameter that gives the same coexistence densities as those found experimentally. The CNT parameters are $D_{CNT} = 2$nm and a persistence length $P_{CNT} \to \infty$. For rigid fd virus, the predicted S_{fd} is found to be much higher than that found experimentally; furthermore, the values of L_{CNT} which give the best agreement between the experimental and theoretical S_{CNT} is in this case in the range of $150 - 200$nm, lower than the $200 - 250$nm predicted when using semiflexible fd virus with $P_{fd} = 2.2\mu$m and also than the experimental value of ~ 300nm. This is likely due to the much larger order parameter of the rigid fd virus, which results in a larger CNT order parameter for a given set of CNT features. Clearly, incorporating flexibility into the model system is important for a quantitative description.

II. INFLUENCE OF CNT DIAMETER

The effects of CNT diameter on the order parameter of CNTs in a host fd virus solution is now examined.

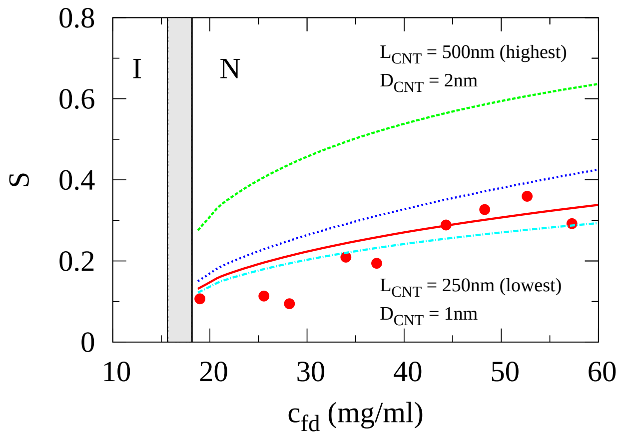

FIG. 2. Orientational order parameter of the guest carbon nanotubes S_{CNT} (red circles) in the host nematic phase of fd virus as a function of virus concentration c_{fd}. The two vertical lines mark the isotropic liquid (I) and nematic (N) binodal concentrations. Theoretical predictions for monodisperse ($\sigma = 0$) CNTs, with $L_{CNT} = 250$nm and $D_{CNT} = 1$nm (lowest line, light blue), $D_{CNT} = 2$nm (red), $D_{CNT} = 4$nm (dark blue), and with $L_{CNT} = 500$nm and $D_{CNT} = 2$nm (top line, green) are compared.

Figure 2 shows the evolution of S_{CNT} for four different cases: the first test case is performed with the following CNT features $L_{CNT} = 250$nm and $D_{CNT} = 2$nm. The three other probed cases are: one using twice the CNT length ($L_{CNT} = 500$nm and $D_{CNT} = 2$nm), one with twice the CNT diameter ($L_{CNT} = 250$nm and $D_{CNT} = 4$nm), and one using half the CNT diameter ($L_{CNT} = 250$nm and $D_{CNT} = 1$nm). For this study, the standard fd virus parameters are used, with $P_{fd} = 2.2\mu$m. As can be seen, doubling the CNT diameter for a fixed length has a much smaller effect than doubling the CNT length for a fixed diameter (which actually results in a smaller increase in the CNT volume than doubling the diameter).

Furthermore, halving the CNT diameter results in only a small decrease in the predicted order parameter. It is therefore apparent that, while there is some leeway when fixing the CNT diameter in any theoretical calculation (as a small difference will not strongly affect the results, and therefore only a rough estimate of the diameter is required), the key parameter for accurate predictions of CNT ordering is the CNT length.

III. CHIRAL NEMATIC PHASE

In order to experimentally prove the validity of the dilute limit used in this work, i.e. that the CNT guest does not disturb the physical properties of the fd virus host, the twist periodicity (or cholesteric pitch) of the chiral nematic host phase was measured, and compared with the pure fd virus suspension in absence of CNT. Indeed, it has been previously reported the high sensitivity of helical features like the cholesteric pitch with physicochemical parameters, such as the ionic strength [4–7].

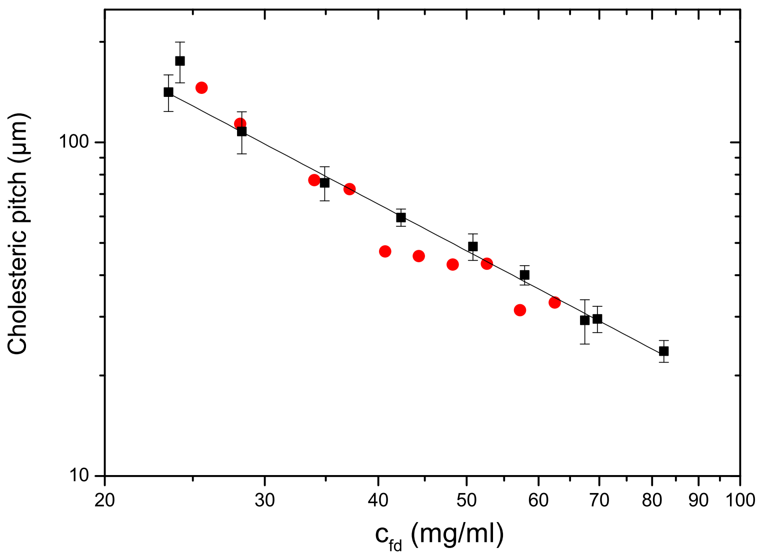

FIG. 3. Cholesteric pitch of pure virus suspension at a given ionic strength of I=30mM (black squares, fitted with a power law represented by the black line) and of a guest virus suspension (red solid circles) doped with surfactant-stabilized CNT guest.

The same samples used for measuring the orientational order parameters (See main text) have been investigated for the cholesteric pitch determination. However, the absence of magnetic field to induce a nematic monodomain allows here the winding of the nematic phase into a cholesteric one. The pitch measurements performed by polarizing microscopy [4, 5] are reported in Fig. 3, both for virus suspensions in a TRIS-HCl-NaCl buffer at 30mM and for the surfactant-stabilized CNTs dispersed in the viral liquid crystalline host. A very good agreement is found between the two systems, confirming the validity of the dilute limit used in this work, i.e. that the presence of the CNT guest with a concentration lower than 0.1% w/w does not affect the physical properties of the host mesophase of fd virus.

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