A supramolecular plot twist: chiral nematics of helical nanoparticles

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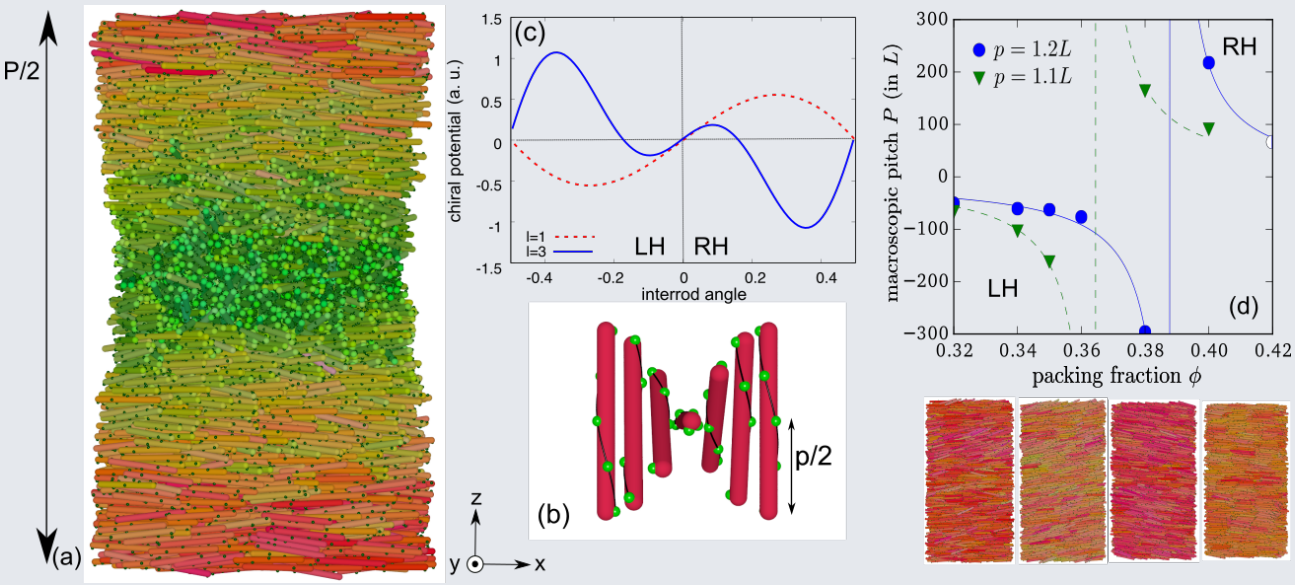
Chiral nanoparticles may self-assemble into twisted liquid crystals that find widespread use in optical applications. Simulations of assemblies of helical rods reveal that the supramolecular twist may spontaneously change handedness at fixed molecular chirality. This offers new routes towards fine-tuning the optical properties of chiral materials.
Recent theoretical studies on self-organisation of helical colloids have shed new light on the origins of supramolecular helicity and provided an important step towards resolving the question how microscopic chiral features propagate to macroscopic length scales remains a long-standing problem in the physics of liquid crystals. Large-scale simulations using a helical patchy rod model allow us to study the explicit relation between microscopic helicity and the supramolecular one (illustrated in the figure).The simulations enable us to overcome many of the approximations inherent to most theories presented to date and to test their predictions by addressing the role of multi-helix correlations, thermal fluctuationsand to elucidate the intricate torque balances that underpin the symmetry of the twisted nematic structure.

The latter is found to be rich and beguiling. The simulations unveil that both the cholesteric pitch - which sets the length-scale over which the helical director makes a full turn- and the handedness can be judiciously tuned by the particle concentration. Most surprisingly, it turns out that a twisted nematic structure of nanohelices is characterized by a compensation point where the supramolecular twist (but not the molecular chirality) vanishes and the handedness suddenly flips sign. The microscopic underpinning for this phenomenon resides in the double-minimum form of the effective potential between a pair of helical filaments. Since the two minima are located at opposite signs of the twist angle the supramolecular twist
sense imparted by the chiral potential depends critically on the degree of nematic alignment along the director field, which in turn is steered by the particle concentration.

The numerical predictions for the patchy rods are expected to be relevant to a wide range of suspensions of chiral nanoparticles including nanocrystalline cellulose, amyloid fibrils and filamentous virus rods. Their possible use in bio-inspired functional materials (e.g. silica films, mesoporous carbons, resins and hydrogels is currently being extensively investigated.



a) Simulation snapshot of chiral nematic phase of helical patchy cylinders. The vertical system dimension corresponds to half the pitch P of the helical director field (rod orientations are color coded). (b) The particles consist of a soft helical potential (indicated by the green dots) with pitch p wrapped around the surface of a cylindrical hard core (in red). (c) The mean-field chiral potential between a rod pair at fixed centre-of-mass distance depends on the interrod angle and may display a single-mimimum (l = 1) or double-minimum behavior (l = 3), depending on the sign and amplitude of the molecular pitch p. (d) The supramolecular pitch versus pack fraction exhibits a sudden inversion from left-handed (LH) to right-handed (RH) at the compensation point (vertical lines) where the global twist vanishes.

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