

Density-functional theory for cholesteric phases of realistic flexible particles

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Lyotropic cholesteric phases are commonly observed in many bio-colloidal and polymer solutions, characterised by a complex interplay between thermal fluctuations, entropic and molecular forces. The difficulty of achieving accurate microscopic descriptions of these many competing factors has led to the introduction of strongly coarse-grained theoretical models, whose microscopic underpinnings are highly non-trivial [1]. Furthermore, the wide lengthscale discrepancy between typical particle sizes and experimental pitches has largely thwarted direct numerical investigations of cholesteric self-assembly for all but the simplest model systems [2].

We here introduce a comprehensive numerical framework based on density functional theory [3] to investigate the cholesteric behaviour of generic particles in the weak chirality limit. This approach, built upon the use of highly-efficient Monte-Carlo methods for the computation of virial-type integrals, enables us to tackle arbitrarily complex mesogen models and interaction potentials. We illustrate its application to systems of near-persistence-length DNA duplexes as described by a well-documented molecular model coarse-grained at the nucleotide level [4] (Fig. 1), and investigate the relative roles of excluded volume, electrostatics and particle flexibility on phase behaviour and cholesteric pitch. We finally consider potential shortcomings of the theory in terms of symmetry assumptions and inter-particle correlations, and discuss prospective directions for future improvements.

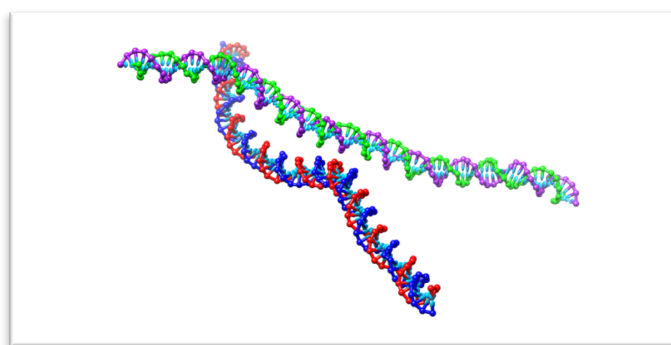


Figure 1. Model system of 146 base-pairs DNA duplexes

References

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