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Theory of wormlike polymer chains in confinement

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ABSTRACT

A semiflexible polymer chain shows characteristic local chain persistency and finite extensibility. Confinement of such a polymer introduces a confinement length scale that competes with the persistence length. This review describes the basic theoretical formalism for a single wormlike chain in an external confinement potential field and for confined wormlike chains that interact with each other through a potential energy depending on both orientational and positional variables. We present a summary of the current understanding in formulating a calculation for the free energy through a single-chain Green's function theory and multi-chain self-consistent field theory, and in specifying appropriate confinement boundary conditions. The wormlike-chain formalism has the capability to capture physical features in a length scale smaller than the persistence length and in a length scale comparable to the total chain length. It also builds the orientational dependence in the foundation of the formalism, that can be used to describe the coupled orientational and positional dependencies of many polymer problems. It has the advantage over a typical Gaussian-chain formalism for description of the physical properties where these features are the main concerns. However, the mathematical treatment of a wormlike-chain model is much more complicated than that of a Gaussian-chain model, due to the coupling between the orientational and positional degrees of freedom. It is this coupling that gives rise to physical features that are unique in semiflexible-chain systems. Example applications of the theoretical framework are also described here, on calculating the free energy and conformational properties of a confined long wormlike chain, on describing the orientational defect structures of confined liquid crystals, and on demonstrating the orientation-induced surface wetting phenomenon.

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