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SELF-CONSISTENT FIELD THEORY SIMULATIONS OF WORMLIKE CHAINS ON CYLINDRICAL SURFACE

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Abstract. Experimental investigation has shown that semiflexible polymers can wrap orderly around a cylinder. Recent Monte Carlo simulations also show that semiflexible polymers can develop linear or helical or random phase structures, depending on the rigidity or length of the polymer. Here, we use wormlike chain model and self-consistent field theory with Onsager interaction to study the micro-phase structure of polymers with local rigidity. We first give the modified diffusion equation for a wormlike chain on cylindrical surface, and then solve the equilibrium equations of the self-consistent field. A time splitting scheme is developed to solve the modified diffusion equation. However, only two kinds of nematic structures (N1 and N2) are detected in our simulation. In N1, the polymers are mainly oriented perpendicular to the axis of the cylinder; while in N2, the polymers are mainly oriented parallel to the axis of the cylinder. N1 is a metastable structure with free energy higher than N2.

Key words. wormlike chain model, modified diffusion equation, self-consistent field theory, cylindrical surface, micro-phase structure.

1. Introduction

Filaments with special chemical structure can spontaneously form a helical conformation such as some synthetic polymers [22] and biological materials like ds-DNA. And it has been shown that a filament with fully flexibility can also develop a helical conformation when it is bound to a deformable cylindrical surface [1]. For semiflexible polymers confined on the cylindrical surface, helical conformation could also be developed, for example, the arrangement of cellulose microfibrils in the plant cell wall [23]. Moreover, due to the rigidity of the polymer, this system is likely to form some liquid-crystal structures, such as nematic.

By using the Monte Carlo simulation, researchers [12, 17, 27] have studied the polymer wrapping of nanotubes. In the work of Gurevitch [12], the cylindrical surface-confinement was enforced by introducing the Lennard-Jones potential between the tube and the polymer particles. In additional to the bending potential between consecutive bonds, interactions between particles are also of Lennard-Jones type, which balances the attracting van der Waals force and the repelling force. All simulations [12, 17, 27] have maintained the existence of helical structures, which depends on the rigidity of the polymer and the radius of the tube. In these Monte carlo simulation, only one [17] or three [12] molecules are considered. That is because the computational cost depends on the number of polymers greatly. In the Monte Carlo methods, it is quite time-consuming to simulate systems of large molecule number and long contour length.

Self-consistent field theory (SCFT) is one of the common theories to study the micro-phase structure of polymers. It has achieved great success in dealing with flexible [7,11,15,20](Gaussian chain model) or semi-flexible [21,25] (wormlike chain

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model) polymers. SCFT simplifies the many-body interactions to some field interactions [9], hence is able to handle multi-chain systems. In this work, we use the SCFT models with the excluded-volume Onsager interaction to study the phase behavior of wormlike chains when confined on cylindrical surface.

In the self-consistent field model that based on the wormlike chain, a persistence length λ is used to describe the rigidity of polymers. When $\lambda = \infty$, the polymers are definitely hard; when $\lambda \ll 1$, the polymers are quite flexible. Therefore, the wormlike model is able to cover systems of different rigidity. To simulate semiflexible systems with the self-consistent field theory (SCFT), it is of great importance to write out and solve the modified diffusion equation (MDE) for the probability function of polymer chain statistics [9]. The MDEs in the cartesian coordinate system, no matter it is for the Gaussian chain model dealing with the flexible polymers or the wormlike chain model dealing with the semiflexible polymers, have both been established decades ago [9, 10]. Recently, the general MDE for the wormlike chain in curvilinear coordinate system, particularly the MDE on the surface of sphere and cylinder, has been deduced [18]. And the formulated MDE on a spherical surface has been solved to study the nematic defect states of rigid linear particles confined on a spherical surface [19]. Jeff [4] and Yang *et.al.* [26] have studied the conformations of a single long flexible polymer when confined in the cylinder or on the cylindrical surface by solving the long-polymer version of the MDE.

In the former theoretical work [18], although the MDE is given for any curvilinear coordinate, the derivative terms are still written in the Cartesian coordinates form. In this work, we first give the general self-consistent field model for wormlike chains in the Cartesian coordinates. Then in section 3, we give the specific form of the MDE, with all terms written in the curvilinear coordinate system. Two examples, MDE in the spherical polar coordinates and the circular cylinder coordinates are presented. SCFT equations for the wormlike chains confined on cylindrical surface are listed in section 4. Here we only consider the simplified situation that the functions are irrespective of the position. In section 5, details of the numerical methods are listed. The time splitting method and Fourier spectral method are used to solve the MDE, which is the most complicated equation in the SCFT model. Picard mixing and the Anderson mixing schemes are applied to the updating of the field. Section 6 deals with the numerical results. Although we expect the wormlike chains to develop a helix on the surface of the cylinder. However, only perpendicularly or parallelly oriented nematic structures (N1 and N2) are detected in our simulation. In N1 the polymers are mainly oriented perpendicular to the axis of the cylinder; while in N2 the polymers are mainly oriented parallel to the axis of the cylinder. N1 is a metastable structure with free energy higher than N2. In this section, comparison of N1 and N2 with the isotropic state are given. When the length of the polymers approximates zero, this cylindrical confined system will reduce to the two dimensional flat-plane system.

2. The general self-consistent field model for wormlike chains

The self-consistent field theory model is a mean field theory which treats the many-body interaction of the molecules as a field interaction. In the SCFT frame, finding the equilibrium state of the polymer system is to find the saddle point of the free energy, which is a functional of the field function $W(\boldsymbol{r}, \boldsymbol{u})$ and the mean segment density distribution $\rho(\boldsymbol{r}, \boldsymbol{u})$. [6,8,14] If we consider a system of n interacting semiflexible polymer chains, with each chain has a contour length L and persistence