Commun. Comput. Phys.
doi: 10.4208/cicp.OA-2017-0100

Vol. **23**, No. 5, pp. 1534-1548
May 2018

Numerical Study of the Isotropic-Nematic Phase Transition in Liquid Crystals using the String Method

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Received 3 May 2017; Accepted (in revised version) 10 July 2017

Abstract. We consider a system of liquid crystal modeled by hard spherocylinders. In certain range of the pressure, the system exhibits two metastable phases: the isotropic phase and the nematic phase. In the isotropic phase, the spherocylinders are randomly packed. In contrast, the spherocylinders are well-ordered in the nematic phase. The isotropic-nematic phase transition is a rare event because it involves the crossing of energy barrier(s). This makes direct simulations, e.g. using molecular dynamics, of the transition event infeasible. In this paper, we study the phase transition in a coarse-grained space formed by two collective variables: the order parameter of the spherocylinders and the volume of the system. We compute the free energy in the collective variable space, the minimum free energy path (MFEP) between the isotropic phase and the nematic phase, and the transition state. Our results reveal the multilayer structure of the critical nucleus. The nucleus will grow further and evolve to the nematic phase after it crosses the energy barrier.

AMS subject classifications: 65Z05, 70E55, 82D25

Key words: Phase transition, liquid crystal, order parameter, collective variables, string method.

1 Introduction

Liquid crystals formed by hard rod-like particles exhibit different metastable phases as observed in the experiments [1, 2], including the disordered isotropic phase and the aligned nematic phase. A phase diagram in the space of the concentration and the aspect ratio of the rod-like particles was constructed in Ref. [1]. In certain range of the concentration and the aspect ratio, the isotropic phase and the nematic phase coexist as metastable phases. The isotropic-nematic phase transition is a rare event since it involves the crossing of energy barrier(s). The formation of critical nucleus during the phase transition was

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investigated using computer simulations, such as biased Monte Carlo simulations [3–5]. In this work, we study the mechanism of isotropic-nematic phase transition using the string method [6–11].

A theoretical explanation for the formation of the nematic liquid crystal from the isotropic phase was provided by Onsager [12]. He explained that the isotropic-nematic phase transition could be purely entropy based. Two types of entropies compete here: the orientational entropy drives the system towards the isotropic phase in which both centers and orientations of the particles are randomly distributed, while the translational entropy drives the system towards the ordered nematic phase to minimize the excluded volume. Therefore, the ordering of the rod-like particles is closely related to the entropy of the system. This ordering can be described by an orientational order parameter [13], which measures the average alignment of the particles with respect to a common direction. In this work, we use this order parameter to distinguish the isotropic phase from the nematic phase.

Computer simulations of the particle system using hard spherocylinders play an important role in the current understanding of the liquid crystals. A mathematical model was proposed by Few & Rigby [14] and Vieillard [15], in which the rod-like particles were modeled as hard spherocylinders with radius R and a cylindrical segment of length h. The study of the system using molecular dynamics (MD) simulations was then conducted by Rebertus & Sando [16]. Afterwards, the phase diagram of the spherocylinder system in the space of concentration and aspect ratio h/R of spherocylinders was investigated [17, 18] using the MD simulations. It was shown that in certain range of concentration and aspect ratio, the isotropic phase and the nematic phase may coexist as metastable phases. The isotropic-nematic phase transition was studied using the biased Monte Carlo simulations [3–5]. These studies revealed a lamellar crystallite structure at the early stage of the nucleation. However, the subsequent thickening of the lamella is hindered by the fact that the top and bottom surfaces of the crystallite are preferentially covered by spherocylinders that align parallel to the surface. The energy barrier is too large for the simultaneous formation of multilayer nematic cluster. The lamellar crystallite can only grow laterally, leading to a single layer of nematic phase.

In this work, we use the orientational order parameter and the volume of the system as the collective variables (CVs) and study the isotropic-nematic phase transition in the CVs space. We compute the critical nucleus, the free energy barrier and the minimum free energy path (MFEP) using the string method. We identify the transition state in the CVs space. The atomistic configurations sampled from the transition state exhibit multilayer structures. This approach is similar to the study conducted by Yu *et al*. [19]. In that work, they studied the crystal polymorphism in a particle system. The Steinhardt order parameters were used to distinguish the different metastable phases such as fcc and bcc structures. The order parameters were then selected as the CVs and the mechanism of the phase transition was studied using the string method. For the recent development of the numerical methods in the study of nucleation in phase transformations, we refer to a recent review paper [20].