Orientational orders of small anisotropic molecules confined in slit pores

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We have studied phase behavior of hard gaussian overlap molecules with small anisotropic parameter confined in two plane parallel structureless hard walls. Our investigation based on standard constant-NPT Monte Carlo molecular simulation led us to some interesting findings. For small anisotropic molecules the nematic phase is instable in bulk, while, if the distance between the walls is small enough, an orientation-ordered phase can form. This result indicates that the required molecular elongation forming liquid-crystal phases is smaller in confinement than that in bulk. Considering the value of the elongation of molecules, the computed result implies that small molecule liquid crystals may exist in confinement.

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I. INTRODUCTION

There is a great number of molecular simulations in the literature on the properties of liquid crystals. Among these simulations, liquid crystal molecules are described using anisotropic models, such as the hard gaussian overlap (HGO) models [1–3], the similar hard spherocylinder [4–6] and the hard spheroidal models [7], and the wider used Gay-Berne (GB) models [8–11]. Although the detail results depend on the models used, some general conclusions have been found: for example it is generally confirmed that liquid-crystal phases can form only when the anisotropic parameters of these models are greater than some critical values. Otherwise (i.e. for molecules with small anisotropic parameters), as one increases the pressure or decreases the temperature, these systems will freeze or crystallize before forming liquid-crystal phases. Many recent works focus on the macroscopic properties and phase transitions of models with large anisotropy parameters. For example, based on molecular simulation and statistical theories, global phase diagrams of hard potential models [5,6] and GB models [8] in bulk have been developed.

On the other hand, confinement in nanometer scale is found to induce phase transitions not observed in bulk systems and shifts in phase transitions [12–14]. Recently, Gelb et al. [12] systematically reviewed research trend on confined simple fluids based on statistical physics, molecular simulations, and carried out some experimental investigations. The properties of confined liquid crystals also attracted wide interests on both sciences and technologies, such as the surface anchoring effects of liquid crystals [15]. More recently, Gruhn and Schoen [10,16] studied the microscopic structure of confined liquid crystals based on GB models. So far, these researches on the bulk and confined properties of liquid crystals only focus on systems composed of large anisotropic molecules which model the usual liquid-crystal molecules. To the best of our knowledge, properties of small anisotropic molecules have shown no interests, probably because they are believed not to form orientation-ordered phases in bulk [17].

But there is a need to address the following question: Are liquid crystal phases in confinement stable even in the small-anisotropic-molecule systems? According to the knowledge on confined simple fluids, although these systems cannot form orientation-ordered phases in bulk, confinement induce new phases when these molecules are confined in nanometer-sized pores. The answer to the above question is important not only for the sake of properties of confined fluids, but implies the possibility of existing small molecule liquid crystals.

In this paper, we study phase behavior of molecules confined between two plane parallel structureless hard walls (i.e. slit pore), we investigate orientation-ordered phases and their transitions on a few kinds of molecules with different anisotropic parameters (molecular elongation), and show that small anisotropic molecules can form stable orientation-ordered phase (nemetic phase) in confinement, though in bulk the phase does not exist. Our results indicate that the required molecular elongation which provoke stable liquid-crystal phase in HGO systems decreases with confining conditions. Therefore we suspect that small molecules might form liquid crystals in confinement. Some related discussions are presented in Sec. IV. Simulation results are shown in Sec. III. We begin, however, in Sec. II with a description of the HGO model and the presentation of our simulations.

II. POTENTIAL MODEL AND COMPUTATIONAL DETAILS

Due to a general belief that repulsive interactions are key roles to determine liquid cyrstal structures, some hard nonspherical models [1–7] are used to study properties of liquid crystals. Among them, one of the most simplest models is the HGO model [1–3,17]. In the model, interaction between a pair of molecules $i$ and $j$ is given by
\( U(\mathbf{r}_{ij}, \hat{u}_i, \hat{u}_j) = \begin{cases} \infty, & \text{if } r_{ij} \leq \sigma(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) \\ 0, & \text{if } r_{ij} > \sigma(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) \end{cases} \) \quad (1)

where, \( \hat{r}_{ij} = \mathbf{r}_{ij}/r_{ij} \) is a unit vector along the line joining the centers-of-mass of the molecules, \( \hat{u}_i \) and \( \hat{u}_j \) are unit vectors along the principal axes of the molecules, \( \sigma \) is dependent on the molecular orientation and explicitly given by

\[
\sigma(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) = \sigma_0 \left\{ 1 - \frac{X}{2} \left[ \frac{\hat{r}_{ij} \cdot \hat{u}_i + \hat{r}_{ij} \cdot \hat{u}_j}{1 + X(\hat{u}_i \cdot \hat{u}_j)} \right]^2 + \frac{(\hat{r}_{ij} \cdot \hat{u}_i - \hat{r}_{ij} \cdot \hat{u}_j)^2}{1 - X(\hat{u}_i \cdot \hat{u}_j)} \right\}^{-1/2}. \quad (2)
\]

Here, \( \sigma_0 \) is constant, which corresponds to the width of molecules, \( X \) is a measure of the nonsphericity of the molecule defined as \( X = (k^2 - 1)/(k^2 + 1) \) with \( k \) being the length-to-width ratio of the molecule.

We use the standard constant-pressure (const-NPT) Monte Carlo simulations to obtain the equation of state \( P(\rho) \) ( for hard potential, temperature \( T \) is not present explicitly ). The simulations are performed with \( N = 108 \) or 256 for the molecular elongations \( k \) being between 2.0 and 3.0. For \( k \geq 3.0 \), a great number of simulations have shown that there is isotropic-nematic phase transition in the bulk [1–3], but for \( k \leq 2.0 \), the nematic phase is unstable in bulk up to a typical high density of liquids [17]. In simulations of bulk systems, the simulating box is cubic and equally fluctuates in three directions, cubic periodic boundary conditions are used. In confinement, the distance between two walls ( \( z \) direction) is fixed, the box equally fluctuates only in the two directions ( \( x \) and \( y \) ) and uses periodic boundary conditions. The simulations are organized in MC cycles, each MC cycle consisting (on average) of \( N \) trial translational and rotational molecular displacements and one trial volume fluctuation. The maximum step length of each trial move is automatically chosen at each pressure for making the acceptable probability fall between 0.4 and 0.6. The starting configuration is a fcc lattice ( in confinement, the number of lattice in \( z \) direction may be smaller than that in other directions ), which melts at low pressure and equilibrates for 100,000 MC cycles. The system is slowly compressed in small pressure steps. For any given pressure, the system is typically equilibrated for 100,000 MC cycles and an average is taken over 100,000 additional MC cycles, then the final configuration is set as the starting configuration of the next pressure. But 300,000 MC cycles are used near the isotropic-nematic transition. After arriving at a high pressure point, in some cases, we slowly expand the system from this high pressure point to a low pressure point. In calculating average values (such as density, orientational order parameter ), we sample partial equilibrated configurations. However, the obtained results (average values and their fluctuations) are almost the same as that using all equilibrated configurations.

The orientational order parameter \( S \) is calculated in the simulations as the largest eigenvalue of the ordering \( Q_{\alpha \beta} \) tensor, defined in terms of the components of the unit vector \( u_{i\alpha} \) along the principal axis of the molecules,

\[
Q_{\alpha \beta} = \frac{1}{N} \sum_{i=1}^{N} \left( \frac{3}{2} u_{i\alpha} u_{i\beta} - \frac{1}{2} \delta_{\alpha \beta} \right) \quad (3)
\]

In the simulation of confined systems, a similar hard potential is set as the interaction between molecule and walls [10], thus

\[
U[\mathbf{z}_i^{[k]}, \hat{u}_i] = \begin{cases} \infty, & \text{if } z_i^{[k]} \leq \sigma_w(\hat{u}_i) \\ 0, & \text{if } z_i^{[k]} > \sigma_w(\hat{u}_i) \end{cases} \quad (4)
\]

where \( z_i^{[k]} \) is the distance between center-of-mass of molecule \( i \) and wall \( k \), and \( \sigma_w \) is given by

\[
\sigma_w(\hat{u}_i) = \frac{\sigma_0}{2 \sqrt{1 - \eta |\hat{u}_i \cdot \hat{z}|}}. \quad (5)
\]

Here \( \eta = (k^2 - 1)/k^2 \). We suppose the walls are at \( z = 0 \) and \( z = D \), respectively. Of course, the center-of-mass of the molecules must be between two walls.

In the remainder of this paper, \( \sigma_0 \) is set as unit of length, \( P/k_B T \) is noted as \( P \).

III. RESULTS

We first simulate the equation of state of HGO systems with \( k = 3.0 \) in bulk. For this case, isotropic-nematic (IN) phase transition had been found in previous simulations [1–3]. Based on free energy calculations of isotropic and nematic phases, the IN transition pressure was about 5 for \( k = 3.0 \). In this paper, we do not try to determine exactly IN transition point by using these free energy methods, but only estimate the transition from their \( S \sim P \) curves.

Our results are shown in Fig.(1), It is clear, the equations of state exhibit a discontinuity at \( P \sim 5 \). In Fig. (1) (b), the behavior of the orientation order parameter \( S \) shows that a spontaneous IN phase transition occurs at the discontinuous point. The result in increasing and decreasing pressure (compressing and expanding simulations) are similar to each other and in agreement with previous simulations.

To test the effects of confinement, we study the confined HGO systems with \( k = 3.0 \) in different \( D \), the obtained results are shown in Fig.(2) and Fig.(3). This leads to our first interesting result: the IN transition point shift to lower pressure (i. e. density) direction as the distance between two walls \( D \) decreases. Usually, for small anisotropic molecules, the nematic phase is unstable, the reason can be understood. The system will freeze or crystallize before forming liquid-crystal phase while increasing the pressure or decreasing the temperature. So the shift at low pressure indicates that nematic phase form in confinement easier than in bulk. Therefore, we
suspect the required smallest \( k \) forming nematic phase is smaller in confinement than that in bulk. In Fig.(4) and Fig.(5), we show the equation of state of smaller anisotropic molecules \((k = 2.0)\). Up to a typical high density of liquid (packing fraction \( y \) is about 0.5), nematic phase is not formed in bulk. Here \( y = \rho v_m \), where \( \rho \) is density of the liquid, \( v_m = \pi/6 k \sigma_0^3 \) is the volume of the molecule. The result is in agreement with previous simulations [17]. However, we do not find stable nematic phase in the system in confinement (the distance between walls is 3.5 and 4.0). Consider that \( k = 2.0 \) may be too small, we simulate another system with a little larger elongation \((k = 2.2)\) and confined in a thiner pore \((D = 2.5)\), the results are shown in Fig.(6) and Fig.(7). The system is compressed up to a typical high density \((y = 0.57)\), no phase transition is found in bulk. But for the confined system in slit pore with a part of \( D = 2.5 \), an obvious IN phase transition is found. In principle, to strictly determine the existence of liquid-crystal phase in bulk and in confinement, we should use free energy methods to calculate the global phase diagram of the system including calculations of chemical potetials in isotropic phase, orientation order phase and crystallized phase, respectively. However, in this paper, we use a rougher method used by earlier Rigby [17]: compress the system to a typical high density \((y \approx 0.5)\), if there is no nematic phase in the density zone, the nematic phase does not exist, since in higher density zone, fluids usually freeze or crystalize. The result is a rough approximation, but we still can obtain a general qualitative conclusion: confinement will decrease the required molecular elongation \( k \) to form a nematic phase. We believe that a nematic phase exists for a certain \( k \) in systems in suitable confinement, though the nematic phase of the systems is instable in bulk. Of course, it is important to obtain quantitative results on this effect, and we shall study global phase diagrams of more realistic small-anisotropic molecules in confinement.

**IV. CONCLUSION**

From the ongoing investigation, we can state that orientation ordered phase exists in bulk for some values of the molecular elongation \( k \) above a critical value \( k_c \); for smaller value of \( k \), the ordered phase becomes instable, but as these small \( k \) molecules are confined in very thin pores, the orientation ordered phase can be found. This result confirms our expectation that small-anisotropic molecules form liquid crystals in confinement.

Usually, the elongation of liquid crystal molecules is about 4–5 and \( k \) of nonspheric inorganic molecules, such as \( CO_2 \), \( CS_2 \) etc., are only about 2. Hence, the usual small molecules cannot form liquid-crystal phases in bulk. But in confinement, according to our results, the required \( k \) forming liquid crystals will decrease, so it is interesting to study whether or not some small molecules will form liquid crystal phase in special confinement. Due to the wide interests in small molecule liquid crystals, it may be important to study phase behavior of real confined small molecules. On the other hand, complicated geometrical pores may induce more complex behavior in fluids [12]. Recently, Chiccoli et al. studied the properties of liquid crystals with dispersed polymer fibrils [18], where the polymer fibrils formed networks and served as complicate pores to confine liquid crystals. Considering the required sizes of pores to induce possible liquid crystal phases in small molecules may be very small (in molecule scale), we shall study the effects of confinement in small anisotropic molecules with dispersed large anisotropic molecules. In the mixture, large anisotropic molecules may serve as complex pores to confine small molecules and induce possible orientation-ordered phases, which might induce characteristic of small-molecule liquid crystals.

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FIG. 1. Isotropic-nematic phase transition in bulk is shown. Here, the number of molecules \( N \) in our simulations is 108. The anisotropic parameter \( k = 3 \). (a) Equation of state of the system \( P(\rho) \) is shown. (b) Orientation order parameter \( S \) versus the employed pressure. Shown simulation results include that an increasing pressure and a decreasing pressure process.

FIG. 2. Equation of state \( P(\rho) \) of a HGO system in slit pores is shown. Here, \( N = 256 \), and \( k = 3 \). \( D \) is the width of the used slit pore in our Monte Carlo simulations.

FIG. 3. Orientation order parameter \( S \) versus pressure \( P \) in slit pores with different \( D \). A shift in IN transition is clearly shown. Here, \( N = 256 \) and \( k = 3 \).
FIG. 4. Equations of state $P(\rho)$ of a HGO system in bulk and in confinement are shown. Here $N = 256$ and $k = 2$. The density of the system is increased to a typical high density of liquids from zero.

FIG. 5. Equations of state $P(\rho)$ of systems are shown. Here $N = 256$ and 108. $k = 2$ and $D = 4.0$. Our result indicates no obvious sized effects in our simulations of confined systems.

FIG. 6. Equations of state $P(\rho)$ in a system in bulk and in confinement are shown, respectively. Here, $N = 108$ and $k = 2.2$. The densities of the system are increased to a typical high density from zero. In a thin slit pore ($D = 2.5$), the equation of state exhibits a discontinuity.

FIG. 7. Orientation order parameters $S$ versus pressure $P$ in a HGO system in bulk and in slit pores, where $N = 108$ and $k = 2.2$. An IN transition is found in $D = 2.5$, but the transition does not exist in bulk.