Orientational orders in binary mixtures of hard HGO molecules

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(January 12, 2022)

Based on a standard constant-NPT Monte Carlo molecular simulation, we have studied liquid crystal phases of binary mixtures of non-spherical molecules. The components of the mixtures are two kinds of hard Gaussian overlap (HGO) molecules, one kind of molecules with a small molecular-elongation parameter (small HGO molecules) cannot form stable liquid crystal phase in bulk, and other with a large elongation parameter (large HGO molecules) can form liquid crystal phase easily. In the mixtures, like the large HGO molecules, the small HGO molecules can also form an orientation-ordered phase, which is because that the large HGO molecules can form complex confining surfaces to induce the alignment of the small molecules and generate an isotropic-anisotropic phase transition in the whole binary mixtures. We also study the transition on different mixtures composed of small and large HGO molecules with different elongations and different concentrations of the large molecules. The obtained result implies that small anisotropic molecules might show liquid crystal behavior in confinement.

I. INTRODUCTION

Surface-induced ordering of liquid crystal (LC) molecules is of important technological and scientific interests \cite{1,2}. Very recently, Boamfa \cite{3} et al. experimentally observed an isotropic-nematic (IN) surface phase transition in a mixture of nematic LCs on a substrate. Usually, in confined LCs, interaction between the LC molecules and the surfaces of the confining walls gives rise to a nematic phase at the surface, though the bulk is still an isotropic phase \cite{3–5}. Based on Monte-Carlo (MC) simulation methods, Gruhn and Schoen \cite{6,7} have studied the microscopic structure of molecularly thin confined LC films. They found that the orientationally ordered thin LC films were in thermodynamically equilibrium with the isotropic bulk phase. In our recent work \cite{8}, based on MC simulations of ellipsoid-like molecules confined in slit pores, we found a similar phenomenon in confined LC molecules. Additionally, as ellipsoid molecules with a small molecular-elongation parameter are confined in very thin slit pores, the surface of the pores can induce an orientation-ordered phase which cannot be formed in bulk due to the very small elongation parameter of the studied molecules. The result implies that the surface of confining walls not only induces surface IN phase transition in LC materials, but also stabilizes the orientation-ordered phases in non-LC materials (in the bulk, non-LC materials such as small-molecular-weight fluids cannot form anisotropic phases). Since small-weight molecules can response very fast to the variation of external fields, the small-molecular-weight LCs would be of great advantage in many applications. However, in simple confined geometry, the surface-induced effects are limited to the several molecular layers neighboring the surfaces of the confining walls \cite{3,8}, but in complex confined geometry, we may expect surface-induced effects in whole fluids.

Polymer-dispersed liquids can be used to study the properties of fluids confined in complex geometry, since the dispersed polymers form complex networks. Recently, Chiccoli \textit{et al.} \textit{studied the network-induced ordering in LCs based on MC simulations} \cite{9}. In the mixture of polymers and LC molecules, the polymers are thought as “surfaces” to confine the LC molecules and the surface effect exists in the whole system. We may address the following question: Do the found properties near the confining walls in simple confined geometry globally exist in the complex confined geometry (i.e., mixtures)? However, we are interested in a particular question in this paper: Since small ellipsoid-like molecules (no orientation-order phases in bulk) can be induced an IN transition in a thin slit pore \cite{8}, can we find similar results in complex pores? For example, in mixtures of the small ellipsoid-like molecules and other molecules, can IN transition occur? We will consider a binary mixture composed of small ellipsoid molecules and usual LC molecules. These LC molecules can form complex surfaces to affect the small molecules. Can the surfaces induce ordering phases in the small (non-LC) molecules? Since there are large amount of small-weight molecules in the mixture, the systems may show some characteristics of expected small-molecule LCs.

In this paper, based on standard constant-pressure (NPT-ensemble) Monte Carlo (MC) simulations, we study binary mixtures of hard Gaussian overlap (HGO) molecules. One component of the mixtures is large HGO molecules with large molecular elongation parameter \(k\) (defined as the length-to-breadth ratio), and other is small HGO molecules with small \(k\). The large HGO molecules mimic LC molecules which can form LC phases in bulk alone, whereas the small HGO molecules, corresponding to normal small anisotropic molecules, cannot form stable LC phases in bulk. Hence each mixture is a corresponding to normal small anisotropic molecules, cannot form stable LC phases in bulk.
Here, we calculate the equation of states and orientational ordering parameter of the mixtures. Similar to our previous finding that confining walls induce an alignment of small HGO molecules in thin slit pores [8], we find, in the mixture, the large- \( k \) (LC) molecules can induce an alignment of the small- \( k \) (non-LC) molecules, hence form an orientation-ordered phase in the whole system. Our results indicate that small molecules will form LCs with the help of LC molecules in their mixtures.

The paper is organized as follows: In Sec. II, we describe a HGO model and give an explicit formula of intermolecular interaction between different- \( k \) HGO molecules, then we describe the presentation of our simulations. Simulation results are shown in Sec. III. Finally we conclude and discuss in Sec. IV.

II. POTENTIAL MODEL AND COMPUTATIONAL DETAILS

There is a great number of molecular simulations in the literature on the properties of LCs. Among these simulations, LC molecules are described using anisotropic interactive models [7,14–23]. Although the detail results depend on the models used, some general conclusions have been found: Repulsive interactions between molecules play key roles to the LC structures, so some hard nonspherical models [14–20] have been widely employed to study the properties of LCs. LC phases can form only when the anisotropic parameters of molecular interactions are greater than the critical values. Otherwise (i.e. for molecules with small anisotropic interactive parameters), as one increases the pressure or decreases the temperature, these systems will freeze or crystallize before forming LC phases [8,24]. Many recent works focus on the macroscopic properties and the phase transitions of models with large anisotropic parameters [6,7,18,19,21,25].

Among LC models, the HGO model [8,14–16,24] is widely used. The model came from the Gaussian overlap potentials developed by Berne and Pechukas [26]. It is widely used. The model came from the Gaussian overlap potentials developed by Berne and Pechukas [26]. It is supposed that the mass (or electron) density of molecules was a Gaussian function of space vector \( \mathbf{x} \),

\[
G_i(\mathbf{x}) = \exp(-\mathbf{x} \cdot \mathbf{A}_i^{-1} \cdot \mathbf{x}),
\]

\[
\mathbf{A} = (\sigma_{ij}^2 - \sigma_{ij}^2) \mathbf{u}_i \mathbf{u}_i + \sigma_{ij}^2 \mathbf{I}.
\]

Here \( \mathbf{u}_i \) is a unit vector along the principal axis of the \( i \)th molecule and \( \mathbf{I} \) is the unit matrix, \( \sigma_{ij} \) and \( \sigma_{ij} \) correspond to the size of the molecules along and perpendicular to its principal axis, respectively. The interaction between two molecules \( i \) and \( j \) is supposed to be proportional to the overlap of the two molecules,

\[
V(\mathbf{u}_i, \mathbf{u}_j, r_{ij}) \sim |\mathbf{A}_i|^{-1/2} |\mathbf{A}_j|^{-1/2} \int d\mathbf{x} G_i(\mathbf{x}) G_j(\mathbf{x} - \mathbf{r}_{ij})
\]

\[
\sim |\mathbf{A}_i + \mathbf{A}_j|^{-1/2} \exp[-r \cdot (\mathbf{A}_i + \mathbf{A}_j)^{-1} \cdot \mathbf{r}]
\]

\[
\sim \epsilon(\mathbf{u}_i, \mathbf{u}_j) \exp[-r^2/\sigma^2(\mathbf{u}_i, \mathbf{u}_j, \hat{r})],
\]

where, \( r \) and \( \hat{r} \) are the length and the unit vector of the vector \( \mathbf{r}_{ij} \), respectively. We have,

\[
\sigma^{-2}(\mathbf{u}_i, \mathbf{u}_j, \hat{r}) = \hat{r} \cdot (\mathbf{A}_i + \mathbf{A}_j)^{-1} \cdot \hat{r}.
\]

If the three eigenvalues and corresponding unit eigenvectors of \( \mathbf{A}_i + \mathbf{A}_j \) are noted as \( \lambda_k \) and \( \hat{v}_k \), \( (k = 1, 2, 3) \), respectively, we have

\[
\sigma^{-2}(\mathbf{u}_i, \mathbf{u}_j, \hat{r}) = \sum_{k=1}^{3} \frac{(\hat{r} \cdot \hat{v}_k)^2}{\lambda_k}.
\]

Actually, since a vector perpendicular to \( \mathbf{u}_i \) and \( \mathbf{u}_j \) is an eigenvector of \( \mathbf{A}_i + \mathbf{A}_j \), we only need to diagonalize a 2 \times 2 matrix. Since \( \hat{v}_k \) \( (k = 1, 2, 3) \) are unit vectors and perpendicular each other, we have \( \sum_{k=1}^{3} (\hat{r} \cdot \hat{v}_k)^2 = 1 \). Using these relationships, we easily obtain,

\[
\sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{r}) = \sigma_0 \left( 1 - \frac{X_{ij}^{2} + 2(1 + \theta)}{1 + X_{ij}^{2}(\hat{r} \cdot \hat{v}_1)^2 + 2(1 - \theta)} \right)^{-1/2}
\]

where \( \sigma_0 = \sqrt{\sigma_{ij}^{2} + \sigma_{ij}^{2}} \), and \( \theta = \frac{(\mathbf{u}_i \cdot \mathbf{u}_j)^2}{(\mathbf{u}_i \cdot \mathbf{u}_j)(1 - \alpha_{ij})} \).

\( X_{ij} \) and \( \alpha_{ij} \) are written as,

\[
X_{ij} = \frac{(\sigma_{ij}^{2} - \sigma_{ij}^{2}) + (\sigma_{ij}^{2} - \sigma_{ij}^{2}) + (\sigma_{ij}^{2} + \sigma_{ij}^{2})}{(\sigma_{ij}^{2} + \sigma_{ij}^{2}) - (\sigma_{ij}^{2} - \sigma_{ij}^{2}) - (\sigma_{ij}^{2} + \sigma_{ij}^{2})}
\]

\[
\alpha_{ij} = \frac{(\sigma_{ij}^{2} - \sigma_{ij}^{2}) - (\sigma_{ij}^{2} - \sigma_{ij}^{2}) + (\sigma_{ij}^{2} + \sigma_{ij}^{2})}{(\sigma_{ij}^{2} - \sigma_{ij}^{2}) - (\sigma_{ij}^{2} - \sigma_{ij}^{2}) + (\sigma_{ij}^{2} + \sigma_{ij}^{2})}
\]

respectively. The directions of the unit eigenvectors \( \hat{v}_1 \) and \( \hat{v}_2 \) are given as,

\[
\hat{v}_1 = \left( \theta + \alpha_{ij} \right) \mathbf{u}_i + (\mathbf{u}_i \cdot \mathbf{u}_j)(1 - \alpha_{ij}) \mathbf{u}_j,
\]

\[
\hat{v}_2 = (\mathbf{u}_i \cdot \mathbf{u}_j)(1 + \alpha_{ij}) \mathbf{u}_i - (\theta + \alpha_{ij}) \mathbf{u}_j
\]

respectively. Obviously, if the \( i \)th molecule and the \( j \)th molecule are identical, we obtain the usual formula of identical molecules [26],

\[
\sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{r}) = \sigma_0 \left( 1 - \frac{X(\hat{r} \cdot \mathbf{u}_i + \hat{r} \cdot \hat{v}_1)^2 + (\hat{r} \cdot \hat{v}_2)^2}{1 + X(\mathbf{u}_i \cdot \mathbf{u}_j)} \right)^{-1/2}
\]

where \( X(\mathbf{u}_i \cdot \mathbf{u}_j) \) is simply noted as \( X \).

The interactive potential in HGO model is simplified as,

\[
V(\mathbf{u}_i, \mathbf{u}_j, r_{ij}) = \left\{ \begin{array}{ll} \infty, & \text{if } r_{ij} \leq \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{r}_{ij}) \\ 0, & \text{if } r_{ij} > \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{r}_{ij}) \end{array} \right.
\]

where \( \sigma(\mathbf{u}_i, \mathbf{u}_j, \hat{r}_{ij}) \) is defined as Eq. (5). The HGO model is thought as an approximation for the excluded volume of hard ellipsoids of revolution [16,24]. In this paper, we study binary mixtures consisting of two kinds of HGO molecules with molecular elongation \( k_L \) and \( k_S \), respectively. Here the elongation \( k \) is defined as,
\[ k_i = \sigma_{ij}/\sigma_{i\perp}. \]  

Here \( i = L \) or \( S \), correspond to large and small HGO molecules, respectively. For simplification, we suppose \( \sigma_{L\perp} = \sigma_{S\perp} \), then \( \sigma_0 \) is a constant which is set as unit of length in our simulations, and \( X_{ij} \) can be written as

\[ X_{ij} = (k_i^2 - 1 + k_j^2 - 1)/(k_i^2 + 1 + k_j^2 + 1). \]

We use standard constant-pressure (const-NPT) MC simulations to obtain the orientational orders and the equation of state \( P(\rho) \) (where \( P \) corresponds to the real \( P\sigma_0^3/k_BT \)). The simulations are performed with \( N = 500 \) or 256 molecules which consist of \( N_L \) large-elongation molecules and \( N - N_L \) small-elongation molecules. The selected \( k_S \) is about 2.0 and \( k_L \) is between 3.0 and 6.0. According to a large number of previous simulations [8,14–16,24], the selected large-\( k \) molecules can form orientation-ordered phases in bulk alone, but the selected small-\( k \) molecules cannot form stable LC phases in bulk up to a typical high density of liquids [8,24]. In our simulations of the mixtures, the simulating box is cubic and equally fluctuates in three directions, cubic periodic boundary conditions are used. 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 trial displacements of two kinds of molecules are separately treated. The maximum step length of each trial move is automatically chosen at each pressure for making the acceptable probability fall between 0.4 and 0.5. The starting configuration is a face-center-cubic lattice which melt at low pressure and equilibrate for \( 10^5 \) MC cycles. The system is slowly compressed in small pressure steps. For any given pressure, the system is typically equilibrated for \( 10^5 \) MC cycles and an average is taken over all configurations of additional \( 10^5 \) MC cycles, then the final configuration is set as the starting configuration of the next pressure. At some higher pressure (density) zones, \( 3 \sim 5\)-times longer MC cycles are used in equilibrated and averaged processes.

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 \( u_{\alpha\beta} \) along the principal axis of the molecules,

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

Besides detecting the order parameter of all molecules, we also separately calculate the order parameter (\( S_L \) and \( S_S \)) of larger and smaller molecules by limiting the average of all molecules in Eq. (13) to single kind of molecules.

III. RESULTS

We first simulate mixtures composed of \( N_L \) large HGO molecules (\( k_L = 5 \)) and \( N_S = N - N_L \) small HGO molecules (\( k_S = 2.0 \)). The concentration of large molecules is \( x = N_L/N \). We present the equation of state and orientation order parameter \( S \) of the mixtures with different \( x \) in Fig. 1. In label of the figures, \( N_L/N \) is listed. For pure small HGO molecules (\( k = 2.0 \)), the simulations are performed with \( N = 256 \) molecules, but for other cases, we simulate systems with \( N = 500 \) molecules. In Fig. 1 (a), the equations of state exhibit a discontinuity for all larger-\( x \) systems. From Fig. 1 (b), we can clearly find the spontaneous phase transition between isotropic and anisotropic phases in the HGO system composed of small amounts of large-\( k \) molecules. However, the order parameter \( S \) of the mixture is smaller than unity, which implies that the molecules only partially align or only partial molecules align. With decreasing concentration of large molecules \( x \), the transition pressure increases and the corresponding order parameter \( S \) in the anisotropic phase decreases.

To detect the microscopic structure of two kinds of molecules in the mixtures, we calculate separately the orientation order parameter of large and small HGO molecules. In Fig. 2, we show relations between the three order parameters \( S \) and the pressure in a mixture, where \( x = 0.4 \), \( k_S = 2.2 \) and \( k_L = 5.0 \). These order parameters describe the alignment of large-\( k \) molecules, small-\( k \) molecules, and all molecules, respectively. From Fig. 2, we find a transition for both large and small molecules beginning at a same pressure \( P \sim 2.0 \) in the mixture. With increasing pressure, the large molecules almost completely align, but the small molecules only partial align. Thus the average S of all molecules is far smaller than unity. We also find the direction of the large molecules is parallel to that of the small molecules (not shown). Therefore, it can be concluded that the alignment of the small molecules is unambiguously ascribed to the alignment of of the large molecules. Additionally, the transition seems to occur at a pressure range, rather than at an exact value, which may correspond to the known I-N coexistence in LC mixtures. In Fig. 3, we show the orientation orders of large molecules and small molecules with different \( k_L \) and \( k_S \) values. The IN transition value of small molecules nematic order parameter decreases as the elongation of large molecules \( k_L \) increases. This surprising result is ascribed to the lower transition pressure as \( k_L \) is larger (see Fig. 3(d) ).

IV. CONCLUDING REMARKS

From a great number of researches of LCs, people had known that only molecules with larger anisotropic parameters can form LC phases in bulk. For example, the molecular elongation of normal LC molecules is larger than 4. In our previous work [8], we found that small anisotropic molecules may form stable LC phases as the molecules are confined in very thin pores. The result indicates that some normal inorganic small molecules
whose $k$ is about 2) may form LC phases in confined geometries (or near surfaces). In current widely studied polymer-dispersed LC systems, the polymers can be thought as complex surfaces confining LC molecules, so we guess that small anisotropic molecules may also show LC phases due to the existing large (LC or polymer) molecules in the mixtures.

In this paper, we present results from standard NPT-ensemble simulations of mixtures of small and large HGO molecules. Among the two components, the small HGO molecules cannot form LC phases alone in bulk, but large HGO molecules can. We detect possible isotropic-anisotropic phase transition in the mixtures. The results presented here give clear evidence of spontaneous formation of orientation-order phases in the mixtures. We find that the spontaneous ordering of the large and small molecules occur at the same pressure. It implies that the ordering of the small molecules is ascribed to the induction of the large molecules. We also study the induced phase transition behaviour for different large-molecule concentrations and different molecular elongations of the large and small molecules.

The confinement-induced LC phases in mixtures present here may be useful. In the mixtures, the viscosity should be smaller than large-molecule systems (usual LCs), so we think that both the large and the small molecules may faster align in external field, which implies that the mixtures may show the characteristics of expected small-molecule LCs, such as short response time. However, it is necessary to study the confined effects based on more reliable molecular models.

X. Z is financially supported by the Grants-in-Aid for Scientific Research of JSPS; H. Chen is supported by the Singapore Millennium Scholarship.

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FIG. 1. (a) The Equation of state (pressure versus density) of binary mixtures with two kinds of HGO molecules. Their molecular elongation $k$ are 5.0 and 2.0, respectively. The data in label correspond to $N_L/N$ of each curves. For $N_L = 0$, we select $N = 256$. (b) The Orientation order parameter $S$ versus pressure of the mixtures. All parameters and symbols are same as that in Fig. 1. It is clearly shown an Isotropic-nematic phase transition except in small $x$ cases. However, except a trivial case ($x = 500/500 = 1.0$), in nematic phase, the order parameter $S$ of the mixture does not arrive at unit.

FIG. 2. Orientation order parameters of large, small and all molecules versus pressure $P$ in a mixtures. Where $x = 200/500$, $k_S = 2.2$ and $k_L = 5.0$.

FIG. 3. Orientation order parameters of large and small molecules versus pressure in mixtures with different $k_S/k_L$ for detecting the elongational dependence of the ordering parameters. For systems with $k_L = 3.0$, $N_L/N = 101/256$; for other systems, $N_L/N = 200/500$. The symbols of (b) are same as that of (a) and the symbols of (c) are same as that of (d). (a) Orientational order parameter $S_L$ of large molecules in mixtures versus $P$ (only near transition zone); (b) Orientational order parameter $S_S$ of small molecules in mixtures versus $P$; (c) $S_L$ versus $P$; (d) $S_S$ versus $P$. In (c) and (d), for the case of $k_S/k_L = 2.0/5.0$, we only show data in lower pressure range (triangle).
Fig. 3 X, Zhou et al. x=0.4