

Phase Behavior of Amphiphiles at Liquid Crystals/Water Interface: A Coarse-grained Molecular Dynamics Study^{*}

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Abstract We present a coarse-grained molecular dynamics simulation study of phase behavior of amphiphilic monolayers at the liquid crystal (LC)/water interface. The results revealed that LCs at interface can influence the lateral ordering of amphiphiles. Particularly, the amphiphile tails along with perpendicularly penetrated LCs between tails undergo a two-dimension phase transition from liquid-expanded into a liquid-condensed phase as their area density at interface reaches 0.93. While, the liquid-condensed phase of the monolayer never appears at oil/water interface with isotropic shape oil particles. These findings reveal the penetration of anisotropic LC can promote ordered lateral organization of amphiphiles. Moreover, we find the phase transition point is shifted to lower surface coverage of amphiphiles when the LCs have larger affinity to the amphiphile tails.

Keywords: Phase behavior; Amphiphilic monolayer; Lateral ordering; Molecular simulation; Liquid crystal.

INTRODUCTION

The phase behavior and interfacial properties of a ternary mixture containing amphiphilic molecules and immiscible binary components have attracted considerable attention for their importance in basic research and in technological applications^[1–3]. For example, diblock copolymers are often added to the immiscible polymers mixtures as polymeric surfactants, by self-assembling along the interface between two homopolymer phases and extending their different blocks into the appropriate phases they can lower the interfacial tension, stabilize the dispersed phase, and improve the interfacial mechanical strength of polymer blends^[4]. In such a case understanding and controlling the interfacial assembly state of these amphiphilic molecules is certainly curial for tailoring the material properties for applications in nanotechnology, composition materials, and emulsions. Furthermore, experimental works have shown that as an excellent model system for studying novel ordering phenomena in low dimensions, amphiphile monolayers at interface can undergo a two-dimensional (2D) phase transition as the area per molecule decreases or the lateral pressure increases, *i.e.*, from a fluid-like “liquid expanded” phase with high molecular mobility and no translational order to a “liquid condensed” phase with higher viscosity and ordered in-plane structure^[5, 6]. This lateral ordering transition is in some sense equivalent of the main transition in bilayers and is interesting from a biological view of point^[7]. Consequently, studying the phase transition in amphiphile monolayers is not only fundamental in life science, but also important for theoretical and practical researches.

Nowadays, a special focus in research is placed on exploring the phase behavior of amphiphile monolayers

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at the interface of heterogeneous systems composed of an anisotropic liquid crystal (LC) phase and an immiscible liquid, not only due to the pure academic interest but also due to the considerable promising applications. On the one hand, a liquid crystal, when placed into contact with an immiscible liquid, exhibits an orientational ordering in ways that reflect interactions defined by the chemistry and geometry of the interfacial region. This phenomenon is often referred to as the anchoring of liquid crystals by interfaces^[8]. Moreover, the self-assembling of amphiphiles such as polymers^[9], lipids^[10] and surfactants^[11] at such interface can strongly influence the orientations of the LC molecules, the homeotropic alignment can be realized from the penetration of some LCs into an orientating amphiphile monolayer. Accordingly, the adsorption and organization of amphiphiles at interfaces can be detected through the use of anchoring transitions in LCs, thereby providing the basis for the development of fast and inexpensive biological and medical sensors^[12, 13]. On the other hand, LC phase possesses long-range orientational order, which is expected to play an important role in directing the interfacial organization of molecular assemblies^[14–16]. In a technological context, this realization will offer unique opportunities to design interfaces at which the amphiphile assembly can be placed under active control. As a result, the interface between an aqueous phase and a nematic liquid-crystal phase has been experimentally employed for studying the coupling between the anchoring transition of LCs and the interfacial organization of amphiphiles^[17]. Although these experimental studies provide some insight into the dependence of the anchoring of LCs on the structure and organization of the amphiphile monolayer, our understanding of how the orientational ordering of the liquid crystals affects the lateral ordering of amphiphiles at aqueous-nematic LC interfaces is far from complete. For example, Price *et al.*^[18, 19] suggested that the interactions between monolayers and bulk nematic phases may not only shift the phase behavior of monolayers at the LC-water from that at the air-water interfaces, but also induce the appearance of new phases. However, due to the buried and deformable nature of the LC-water interface, it is rather difficult for these experimental studies to provide information on the structure present at this interface. Therefore, the knowledge of the molecular-level organization of amphiphiles at aqueous-nematic LC interfaces and the molecular-level mechanisms by which the orientational ordering of the liquid crystals affects the lateral ordering of amphiphiles remains rather limited.

With the rapid development in computational power, molecular-level simulations play a more important role in the study of the microscopic origin of experimental phenomena. However, as far as we know, there have been few simulations dealing with such particularly complex amphiphile-coated nematic LC-water system^[20]. In the case of its great fundamental and practical interests, it is important to systematically study the interfacial organization of amphiphiles and its relation with orientations of LCs. Additionally, to elucidate the basic mechanism of lateral phase transitions as well as the nature of the coupling between LCs and amphiphiles, a MD simulation with a reduced or coarse-grained model is expected to provide useful information at a reasonable computational cost. Therefore, in the present work, we employ coarse-grained MD (CGMD) simulations to study the phase behavior of amphiphiles at LC/water interface, as well as the coupling between LC order and interfacial structure. Interestingly, we not only successfully find a phase transition from liquid expanded to liquid condensed in the mixed monolayer composed by amphiphiles along with inserted LCs but also discover that the LCs with a stronger affinity to the tail chains of amphiphilic molecules can induce the formation of a condensed monolayer phase at lower amphiphile coverage. These finds revealed the important role of LCs penetration in dictating the lateral organization of amphiphiles. The remainder of this paper is organized as follows. First, we describe the simulation model and method. After that, we present and discuss our results. Finally, we summarize the prime results of this paper.

MODEL AND METHOD

We employ coarse-grained (CG) models, wherein each particle represents a group of real atoms or a single molecule. As schematically illustrated in Fig. 1(a), in this study we have three kinds of molecular species including water molecules, LC molecules, and amphiphilic molecules, and four types of CG particles: W, M, H, and T for water particle, LC particle, amphiphile-head monomer, and amphiphile-tail monomer. To capture the essential physics of real molecules, in our model LC particles are represented by ellipsoids while other three

types of particles are represented by spheres, which interact with each another through Gay-Berne (GB) or Lennard-Jones (LJ) potentials^[21, 22].

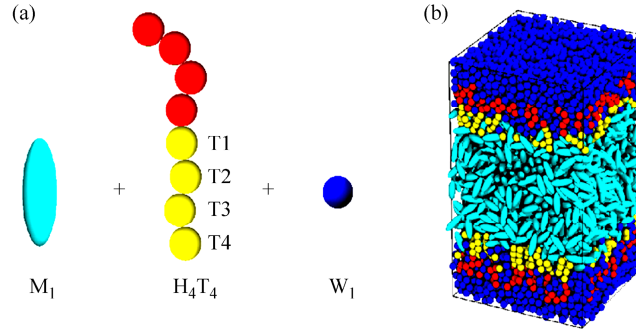


Fig. 1 Schematic representation of (a) the molecular structures of LC (M_1), amphiphile (H_4T_4) and water (W_1), the tail particles are labeled from T1 to T4 and (b) the initial configuration of simulation system

Note that each GB ellipsoid is specified by the position of its center of mass r_i and the unit vector $\hat{u}_i$ along its principal axis, the Gay-Berne potential between two ellipsoids i and j is thus given by^[23]

$$U_{ij} = 4e_{ij}\epsilon(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) \left[\left(\frac{\sigma_0}{r_{ij} - \sigma(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) + \sigma_0} \right)^{12} - \left(\frac{\sigma_0}{r_{ij} - \sigma(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) + \sigma_0} \right)^6 \right] \quad (1)$$

Here, σ_0 is the contact distance for the cross configuration ($\hat{u}_i \cdot \hat{u}_j = \hat{u}_i \cdot \hat{r}_{ij} = \hat{u}_j \cdot \hat{r}_{ij} = 0$), r_{ij} is the distance between the centers of mass of particles i and j , $\hat{r}_{ij}$ is a unit vector along the inter-particle separation vector. e_{ij} is a coupling parameter for rescaling potential energy amplitude while keeping the distance dependence unaltered. In this study we choose $e_{ij} = 1$ for the interaction between two M particles. The shape parameter σ denotes an orientation-dependent diameter, and is defined as the distance (for a given molecular orientation) at which the inter-particle potential vanishes

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

where χ depends on the shape anisotropy parameter κ and $\chi = \frac{\kappa^2 - 1}{\kappa^2 + 1}$. κ is also denoted as the aspect ratio of the particle and $\kappa = \frac{\sigma_{ee}}{\sigma_{ss}}$ with σ_{ee} being the molecular length along the principal axis and σ_{ss} the cross-sectional diameter of the particle and $\sigma_{ss} = \sigma_0$. The energy parameter $\epsilon(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j)$ denotes an orientation-dependent interaction strength and is given by

$$\epsilon(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) = \epsilon_0 [\epsilon_1(\hat{u}_i, \hat{u}_j)]^\nu \times [\epsilon_2(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j)]^\mu, \quad (3)$$

with

$$\epsilon_1(\hat{u}_i, \hat{u}_j) = [1 - \chi^2(\hat{u}_i \cdot \hat{u}_j)^2]^{-1/2}, \quad (4)$$

and

$$\epsilon_2(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) = 1 - \frac{\chi'}{2} \left[\frac{(\hat{r}_{ij} \cdot \hat{u}_i + \hat{r}_{ij} \cdot \hat{u}_j)^2}{1 + \chi'(\hat{u}_i \cdot \hat{u}_j)} + \frac{(\hat{r}_{ij} \cdot \hat{u}_i - \hat{r}_{ij} \cdot \hat{u}_j)^2}{1 - \chi'(\hat{u}_i \cdot \hat{u}_j)} \right]. \quad (5)$$

Here, ϵ_0 is the well depth for the cross configuration. χ' denotes the anisotropy of the well-depth and is a function

of the energy anisotropy parameter κ' with $\chi' = \frac{1 - \kappa'^{1/\mu}}{1 + \kappa'^{1/\mu}}$. Here $\kappa' = \frac{\epsilon_{ee}}{\epsilon_{ss}}$, ϵ_{ee} and ϵ_{ss} are the depths of the minima

of potential for a pair of particles aligned parallel in end-to-end and side-by-side configurations, respectively. The exponents μ and ν are adjustable and influence the GB potential in more subtle way, and they are often set as $\mu = 2$ and $\nu = 1$. Since the phase behavior of GB model with parameters ($\kappa = 3$; $\kappa' = 5$, $\mu = 2$, $\nu = 1$) has been well studied^[24] and these parameters are often used as the general parameter set for modeling real mesogenic molecules, in this paper, GB (3, 5, 2, 1) model is selected for our computational investigation of the phase behavior of amphiphiles at the LC/water interface.

For two sphere particles i and j of the same type or compatible types, their interaction is given by

$$U_{ij}(r_{ij}) = 4e_{ij}\epsilon_0 \left(\left(\frac{\sigma_0}{r_{ij}} \right)^{12} - \left(\frac{\sigma_0}{r_{ij}} \right)^6 \right) \quad (6)$$

While, if the particles i and j are of unlike or incompatible types, *i.e.* H and T, a shift, repulsive Lennard-Jones potential is used in order to induce phase separation between immiscible species,

$$U_{ij}^{\text{Repulsive}} = \begin{cases} 4\epsilon_0 \left(\left(\frac{\sigma_0}{r_{ij}} \right)^{12} - \left(\frac{\sigma_0}{r_{ij}} \right)^6 + \frac{1}{4} \right), & r_{ij} < 2^{1/6} \sigma_0, \\ 0, & r_{ij} \geq 2^{1/6} \sigma_0, \end{cases} \quad (7)$$

In the case of ellipsoids and spheres, we follow the work of Cleaver *et al.*^[25] and use the generalized Gay-Berne potential to describe the ellipsoid-sphere interaction. By assuming that particle i is a LJ sphere and particle j is a GB ellipsoid and the sphere diameter is equal to the ellipsoid cross-sectional diameter, the basic form of Eq. (1) is adopted if particles i and j have favorable interactions, but the shape parameter and the energy parameter in Eq. (1) are modified as below:

$$\sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_j) = \sigma_0 [1 - \chi(\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_j)^2]^{-1/2}, \quad (8)$$

and

$$\epsilon(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_j) = \epsilon_0 \left[1 - \left(1 - \left(\frac{\epsilon_E}{\epsilon_S} \right)^{1/\mu} \right) (\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_j)^2 \right]^\mu. \quad (9)$$

Here the ratio ϵ_E/ϵ_S controls the end-to-side well-depth anisotropy of the interaction. In this paper, we chose $\epsilon_E/\epsilon_S = 0.2$ so that the spheres prefer to locate on the sides of the ellipsoids rather than the ends^[26]. Also, if the particles i and j are unfavorable to each other, for example, W and M, a shift repulsive GB potential is used:

$$U_{ij}^{\text{Repulsive}} = \begin{cases} 4\epsilon(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_j) \left(\left(\frac{\sigma_0}{R_{ij}} \right)^{12} - \left(\frac{\sigma_0}{R_{ij}} \right)^6 \right) - U_c, & R_{ij} < 2^{1/6} \sigma_0, \\ 0, & R_{ij} \geq 2^{1/6} \sigma_0, \end{cases} \quad (10)$$

where the energy parameter $\epsilon(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_j)$ is given in Eq. (9) and $R_{ij} = r_{ij} - \sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_j) + \sigma_0$ with the shape parameter $\sigma(\hat{\mathbf{r}}_{ij}, \hat{\mathbf{u}}_j)$ given in Eq.(8). U_c is a GB energy value determined by Eq. (1) at $R_{ij} = 2^{1/6} \sigma_0$, which is included to avoid the discontinuities in the potential energy.

In this work, we assume that all particles have the same mass, energy, and length scales: $m = 1$, $\sigma_0 = 1$, and $\epsilon_0 = 1$. All quantities in the following are reported in terms of the reduced units: ϵ_0 for energy, σ_0 for length, m for mass, and ϵ_0/k_B for temperature, where k_B is Boltzmann's constant. As a consequence, $\sqrt{m\sigma_0^2/\epsilon_0}$ is the unit

of time, and the number density, ρ , is measured in units of σ_0^{-3} .

Like most diblock copolymer simulations^[27–29], the amphiphilic molecule is a linear chain composed of a block of head monomers connected to another block of tail monomers, denoted by H_nT_n . Therefore, in addition to the LJ potentials, a spring force needs to be introduced to link the adjacent particles along the chain. Similar to most CG models of amphiphilic molecules and polymers^[27–30], monomers in each chain are held together by a finitely extensible nonlinear elastic (FENE) spring with spring constant $k = 30 \epsilon_0 / \sigma_0^2$ and maximum extension $R_0 = 1.5\sigma_0$:

$$U^{\text{FENE}}(r_{ij}) = \begin{cases} -\frac{1}{2}kR_0^2 \ln \left[1 - \left(\frac{r_{ij}}{R_0} \right)^2 \right], & r_{ij} < R_0, \\ \infty, & r_{ij} \geq R_0, \end{cases} \quad (11)$$

Additionally, following past simulation studies of amphiphiles^[30], a bending potential is also applied to the tail chain, which takes the form:

$$U^{\text{Angle}}(r_{i-1,i}, r_{i,i+1}) = k_{\text{angle}} \left(1 - \frac{r_{i-1,i} \cdot r_{i,i+1}}{|r_{i-1,i}| |r_{i,i+1}|} \right) \equiv k_{\text{angle}} (1 - \cos \phi_i) \quad (12)$$

where k_{angle} is a stiffness constant and ϕ_i is the angle formed by the adjacent bonds. In view of the fact that semi-flexible tails with a higher stiffness are expected to exhibit a higher orientational order at the interface than the flexible tails of conventional amphiphiles, which could facilitates the formation of ordered 2D phase^[31], the parameter k_{angle} is chosen to be $40\epsilon_0$, which makes the averaged bond angle around 165° – 168° as surface coverage of amphiphiles increases from 0.05 to 0.65 in this study.

For simplicity, we choose to simulate the molecules of water and LC by simple monomeric spheres and ellipsoids and choose the block length of each amphiphile molecule n to be 4, larger than the principal axis length of our selected GB mesogens. Hence we will only concentrate on the model system of $W_1 + M_1 + H_4T_4$. Additionally, with this set of interaction potentials given above, our studied model system is characterized by ten interaction coupling parameters e_{ij} , which describe the mutual incompatibility of M, W, H and T particles. In order to systematically study the phase behavior of amphiphile tails as a function of the amphiphile interfacial coverage, these e_{ij} values need to be preset. Following CG simulations of amphiphiles at water/oil interfaces^[32], we assume that almost all identical particle pairs have the same e_{ij} , that is $e_{H-H} = e_{W-W} = e_{M-M} = 1$. Since tails are often extended into the LC phase and in direct contact with LC particles, we choose $e_{T-T} = 0.4$ in this study in order to ensure that the LJ interaction potential between two tail chains approaches the GB interaction potential between two M particles, especially in the side-by-side configuration. This is because the tails in most situations interact with each other in a side-by-side configuration when the tails are extended to the LC phase. Note, to preserve the known experimental features that amphiphiles are most likely at the interfaces between LC and water regions with their head and tail blocks extending into the water phase and the LC phase, for the particle pairs of unlike or immiscible species *i.e.*, W and M, W and T, H and M, H and T we used the shift repulsive potentials of Eqs. (7) and (10), which corresponds to set e_{W-M} , e_{W-T} , e_{H-M} and e_{H-T} to 0. For further simplification, we treat one head monomer identical to the water particle by setting $e_{H-W} = e_{H-H} = e_{W-W} = 1$, which also means that a head interacts with the water in exactly the same way as with another head. As for the interaction coupling parameter between M and T particles, e_{M-T} , previous studies^[12, 20] indicated that the LC and tail interaction is the most important contribution when considering the LC anchoring and the tail orientations, in particular the attractive interaction can promote LCs to perpendicularly penetrate into the tail layer and induce the homeotropic anchoring. However, due to the shape dissimilarity between M and T particles, to model the experimentally observed perpendicular penetration of LCs between the tail chains, the M–T interaction

potential should be carefully parameterized so that the anisotropy of LC-tail interaction can be identical to that of LC-LC. We note that the interaction between the last (or outmost) tail particle T4 and a M particle is the most important contribution when considering the tail-LC interaction in Tee-shape configurations, while at the side-by-side configuration the T4-M interaction makes little contribution to the tail-LC interaction. Therefore a simple way for causing the side-to-tee anisotropy of LC-tail potential close to that of LC-LC one is to tune the T4-M interaction. For this, we set two different coupling parameters e_{M-T}^{T4} and $e_{M-T}^{T1 \text{ to } T3}$ for the last (or outmost) tail particle T4 and other three T particles in tail chains and relate them by a scaling parameter k^{T4}

$$e_{M-T}^{T4} = k^{T4} \cdot e_{M-T}^{T1 \text{ to } T3} \quad (13)$$

For convenience, $e_{M-T}^{T1 \text{ to } T3}$ is denoted as e_{M-T} thereafter. Additionally, since the end-to-Tee well-depth ratio of tail-LC potential is closely related to the end-to-side well-depth ratio of T4-M potential, in order to tune the end-to-tee anisotropy of LC-tail potential close to that of LC-LC potential, we set $\varepsilon_E / \varepsilon_S^{T4}$ to be 1.0 when T4 particles are interacting with M particles so that T4 and M particles have no preference to side-by-side or end-to-end configurations. We see that by adjusting these two parameters $\varepsilon_E / \varepsilon_S^{T4}$ and k^{T4} to 1.0 and 0.382 when the T4 particle is interacting with M particles the anisotropy of tail-LC interaction potential, that is, the side-to-tee and end-to-tee ratios of tail-LC potential, becomes similar to that of LC-LC interaction potential. In this study, to explore the phase behavior of amphiphiles in LC/water interface and understand the influence of the interaction strength of LCs and tails on the interfacial ordering, e_{M-T} is varied from 1.1 to 1.5 wherein $e_{M-T} = 1.1$ corresponds to the case that LCs have small affinity to the tails, while $e_{M-T} = 1.5$ correspond to the fact that LCs have larger affinity to tails. We should stress that the anisotropy of tail-LC potentials stays the same regardless the choice of e_{M-T} value because e_{M-T}^{T4} is scaling with e_{M-T} as defined in Eq. (13). Additionally, under these e_{M-T} values the experimentally observed homeotropic anchoring phenomena are well reproduced. All the basic coupling parameters we used are listed in Table. 1.

Table 1. Interaction coupling parameters used in our simulations

e_{ij}	M	W	H	T
M	1	0	0	1.1, 1.3 and 1.5
W	0	1	1	0
H	0	1	1	0
T	1.1, 1.3 and 1.5	0	0	0.4

The simulation method is molecular dynamics (MD) with a Nosé-Hoover thermostat. We ran all simulations on the model system of $W_1 + M_1 + H_4T_4$ at the same temperature of $T = 1.0\varepsilon_0/k_B$ and at the same overall particle density $\rho = 0.65\sigma_0^{-3}$, corresponding to 2100 GB particles and 6500 LJ spheres in a rectangular simulation box of $L_x = L_y = 20\sigma_0$ and $L_z = 33.08\sigma_0$. Note that in this instance the number density of GB particles in the LC-rich region is about $\rho_{LC} = 0.33\sigma_0^{-3}$ corresponding to a nematic state in the bulk LC system^[24]. For the simulation with isotropic LCs, $L_z = 35.83\sigma_0$, which makes $\rho = 0.6\sigma_0^{-3}$ and $\rho_{LC} = 0.3\sigma_0^{-3}$ so that LCs are in isotropic phase. For the additional simulations of amphiphiles at oil/water interface, the oil molecules are represented by T particles and the system contains 12800 LJ spheres in a rectangular simulation box of $L_x = L_y = 20\sigma_0$ and $L_z = 33.08\sigma_0$. For the integration of the equations of motion, we employed the velocity Verlet algorithm with a timestep $\Delta t = 0.002 \sqrt{m\sigma_0^2 / \varepsilon_0}$. Following most work on GB potential^[23–26], to speed up the calculations, the potential cutoff radius of Eq. (1) is chosen as $R_C = 4.0\sigma_0$. In this study, the use of periodic boundary conditions in three dimensions results in the formation of two separate interfaces perpendicular to the z-axis upon the phase separation of mesogens and waters into two rich-phase regions. However, L_z is long enough such that the two interfaces are not interfering with each other. To access a rich ordering behavior, we carried out a systematic study on the $W_1 + M_1 + H_4T_4$ system for a wide range of amphiphile interfacial coverage $\rho_s \in [0, 0.65]$ at a finer resolution, wherein ρ_s is defined as

$$\rho_s = \frac{N_{\text{surf}}}{2L_x L_y}. \quad (14)$$

Here, N_{surf} is the number of amphiphile molecules at the LC-water interfaces.

To avoid metastable states due to insufficient kinetics in the formation process as well as to minimize equilibration time, we started our simulations from a pre-assembled system consisting of two neighboring slabs of water and LCs with amphiphile monolayers at two water-LC interfaces, which is similar to the Langmuir-Schaefer transfer^[9]. Additionally, amphiphiles are equally segregated at both interfaces in random positions with all head-groups and tail chains in contact with the water and the LC phases, respectively. The orientation of GB particles in the initial state is set to be random in order to eliminate influence of the preset orientation, as schematically illustrated in Fig. 1(b). Then, all simulated systems are evolved at least 1×10^7 time steps until the thermodynamic properties (the total energy and the pressure), the order parameter of the LCs and tails remain generally stable, which to some extent proves that all samples we used to investigate the phase transitions were equilibrated. To further justify all the simulated systems were well equilibrated and not trapping in metastable states, for each studied ρ_s we repeated simulations by initially placing LCs in planar and homeotropic orientations, which give essentially identical results and confirm that our simulation time is long enough to reach equilibrium state.

The average tilt angle $\langle\theta\rangle$ and the relative order parameter S of amphiphile tails and of LCs are used to monitor the phase behavior of system. The $\langle\theta\rangle$ is defined as the average angle between the principle axis of GB particles or end-to-end vector of tail chains and the interface normal. The relative order parameter, which quantifies the degree of the orientational ordering relative to a given director and usually takes the form of

$$S = \frac{1}{2} \langle 3 \cos^2 \psi - 1 \rangle$$

to describe their organization at the interfaces, ψ is measured from the principle axis of GB particles or end-to-end vector of tail chains to the interface normal (z axis of systems). S has a value of 1, 0 and -0.5 if the orientation of the GB particles or tail chains is parallel, random and perpendicular to the interface normal, respectively.

In order to understand the orientation coupling between amphiphile tails and interfacial LCs, we measure above mentioned orientational order parameter for LCs located in the amphiphile tail-layer. The criteria for selecting the LCs within the amphiphile tail-layer are as follows.

$$\begin{aligned} \langle r_z^{\text{upper}} \rangle &> r_z^{\text{LC}} > \langle r_z^{\text{upper}} \rangle - \langle l_z \rangle \\ \langle r_z^{\text{down}} \rangle &< r_z^{\text{LC}} < \langle r_z^{\text{down}} \rangle + \langle l_z \rangle \end{aligned} \quad (16)$$

Here, as we place the center of simulation box at $z = 0$, the headnotes “upper” and “down” denote the monolayers locating at position with positive and negative z axis values respectively. $\langle r_z^{\text{upper}} \rangle$ and $\langle r_z^{\text{down}} \rangle$ are the averaged z -axis coordinators of the first (or the innermost) tail particles in each individual amphiphile molecules within upper and lower tail-layer region respectively, which also denote the position of tail-layer/water interfaces. $\langle l_z \rangle$ is the average length of amphiphile tail projected on the z axis, as schematically illustrated in Fig. 2.

To characterize the lateral organization of amphiphiles, besides the two-dimensional radial distribution function ($g_{\perp}(r_{\perp})$), the lateral diffusion coefficient (D_{lat}) of amphiphiles is measured as below:

$$D_{\text{lat}} = \lim_{t \rightarrow \infty} \frac{1}{4N_{\text{tail}}t} \left\langle \sum_{i=1}^{N_{\text{tail}}} [r_{i,xy}(t) - r_{i,xy}(0)]^2 \right\rangle, \quad (18)$$

where t is time interval between two measured samplers, N_{tail} is number of tails and $\mathbf{r}_{i,xy}$ is the xy coordinator components of the centers of mass of amphiphile i .

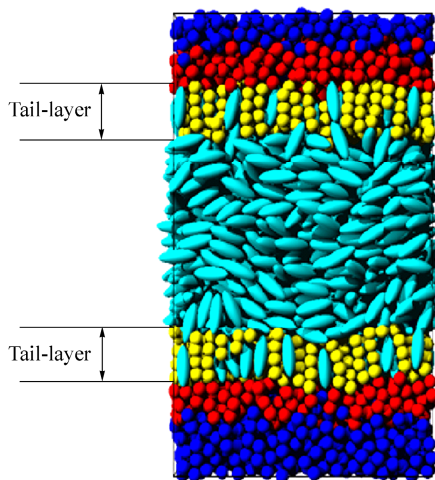


Fig. 2 Schematic illustration of the criteria for selecting the LCs in tail-layer

RESULTS AND DISCUSSION

First, we study phase behavior of the amphiphile monolayer by varying the surface coverage of amphiphiles from 0 to 0.65 at LCs/water interface in the case of a large affinity between LCs and tails, *i.e.* $e_{M-T} = 1.5$. We note that in addition to hexagonal packing and low lateral mobility the liquid-condensed phase is often characterized by an increased orientational ordering of tail chains. We therefore firstly measured the relative order parameter S_t and tilt angle $\langle\theta_t\rangle$ of amphiphile tails, to learn the coupling between LC orientation and lateral organization we also measured the relative order parameter S_m as well as tilt angle $\langle\theta_m\rangle$ for the LCs penetrated in the tail-layer, and plotted them in Fig. 3.

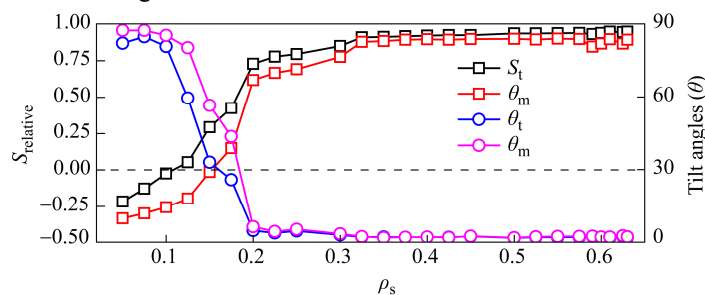


Fig. 3 The variation of relative order parameters of amphiphile tails (S_t) and of LCs in tail-layer (S_m) and average tilt angles of amphiphile tails ($\langle\theta_t\rangle$) and LCs in tail-layer ($\langle\theta_m\rangle$) with ρ_s . $S_{\text{relative}} = 0$ are marked by a dash line for reference

We see at low amphiphile coverages, *i.e.*, $\rho_s \leq 0.1$, both amphiphile tails and interfacial LCs adopt planar orientation as their tilt angles $\langle\theta_t\rangle$ and $\langle\theta_m\rangle$ remain close to 90° with S_t and S_m ranging from $[-0.21, 0]$ and $[-0.37, -0.35]$, respectively. On the one hand, the planar orientation of interfacial LCs at low surface coverage of amphiphiles is in line with past experiment works^[11], the physical origin of which is that at low coverage there is more free space between amphiphile tails so that LCs can easily penetrate into the tail layer and lie down at the LC/water interface. On the other hand, the planar orientation of amphiphile tails, which is in contrast to the often-observed orientational disorder at air/water or oil/water interface at low amphiphile coverage^[5], is likely driven by the planar alignment of the LCs. We note that to maximize the favorable interactions between LCs and

tails at interface, LCs and nearby tails prefer to contact in a side-by-side configuration. Therefore the planar alignment of the LCs, which stems from a large penetration of the nematogens into a loosely packed amphiphile layer, can drive a planar orientation of adjacent amphiphile tails. To justify this, we run a similar simulation with the exception of the LCs in an isotropic phase. It appears that the amphiphile tails stay normal to the interface between the isotropic LC and the aqueous phases as ρ_s increases, *i.e.* from 0.05 even up to the value at which the amphiphile monolayers collapse, supporting the importance of parallel ordering of nematogens at aqueous interfaces on aligning of amphiphile tails. Additionally, the increase of the density of amphiphiles at the interface would decrease the density of the LCs that can penetrate into the tail layer and lie parallel at the interface, and such a lesser extent of penetration of the parallel-oriented LCs could reduce their parallel aligning effect on the adjacent amphiphile tails. Meanwhile, to accommodate a higher area density of amphiphiles at the interface, amphiphile tails might have a small preference to align perpendicular to the interface, thus disrupting the preferred planar alignment. Therefore, as shown in Fig. 3, although the $\langle\theta_t\rangle$ remains close to 90° , S_t gradually increases from -0.21 to 0 as ρ_s increases in this region. When $\rho_s > 0.1$, to accommodate a higher area density of amphiphiles at the interface, amphiphile tails turns their orientation towards interface normal, we see $\langle\theta_t\rangle$ begins to decrease and S_t becomes positive and grows monotonously with ρ_s , as indicated in Fig. 3. Additionally, S_m and $\langle\theta_m\rangle$ of LCs follows the changes in S_t and $\langle\theta_t\rangle$, in a manner that the relative order parameter of LCs is always smaller than that of tails but the difference between them is decreasing as ρ_s increases. When ρ_s reaches 0.2 , both amphiphile tails and penetrated LCs align approximately along the interface normal as the average tilt angles of tails and LCs reduce to near-zero in Fig. 3. In agreement with experiments^[11] a critical coverage is required for LCs to perpendicularly penetrate into the tail layer, which then induces the homeotropic anchoring. With a further increase of ρ_s , both tails and inserted LCs remain oriented along the interface normal, S_t and S_m continue to grow with ρ_s but with a slower increase rate. Interestingly, a kink is observed in the curve of S_t and S_m around $\rho_s = 0.325$, where S_t and S_m reach the values of 0.9 and 0.87 respectively. Such high orientational ordering suggests that the amphiphile tails together with inserted LCs may form an ordered lateral structure at interface at $\rho_s = 0.325$. As ρ_s further increases, we see that both amphiphile tails together with inserted LCs still maintain such high orientational order. Finally, at $\rho_s \geq 0.65$, the interface becomes saturated with amphiphiles as indicated by the undulation in the monolayer, therefore the phase behavior at coverage above 0.65 is not explored here.

To further probe 2D phase transition as well as the interfacial organization, we calculated the two-dimensional radial distribution function ($g_\perp(r_\perp)$), where $r_\perp$ is the distance between the center of mass of any two particles including either amphiphile tails or penetrated LCs projected onto the interface, and the lateral diffusion coefficient of amphiphiles. The typical results are presented in Fig. 4.

We see that $g_\perp(r_\perp)$ at $\rho_s = 0.25$ exhibits no long-range ordered molecular organization at the amphiphile-LCs interface. While at $\rho_s = 0.325$, $g_\perp(r_\perp)$ has a well-defined oscillatory form with the peak position ratio of $1:\sqrt{3}:2$, indicating a long-ranged translational ordering of amphiphiles and LCs at the interface, which corresponds directly to the hexagonal packing. Besides, we find that D_{lat} first gradually decreases with increasing ρ_s , decreases by one orders of magnitude from $\rho_s = 0.3$ to 0.325 , and it levels off at larger ρ_s values. Note that the coverage for a steep fall in D_{lat} is precisely that for a leap in order parameter curve of amphiphile tails in Fig. 3, which can be inferred as the location of 2D phase transition. Therefore, relatively low orientational order and relatively high lateral diffusion coefficient, together with no ordered lateral structure at interface, indicate that monolayers composed of amphiphiles and penetrated LCs adopt the liquid-expanded phase at $\rho_s < 0.325$. Similarly, low amphiphile lateral mobility, hexagonal packing and increased orientational ordering suggest that for $0.325 < \rho_s < 0.65$ the above mixed monolayer forms a liquid-condensed phase. Although the interpenetration of LCs is weakened as ρ_s further increases, the presence of more amphiphiles at the interface makes them more densely packed and significantly stretched, therefore the hexagonal correlation increases strongly and the mixed monolayers exhibit more ordered 2D arrangements. Based on these results, we confirm that the 2D phase

transition from liquid-expanded to liquid-condensed at an amphiphile-laden aqueous-nematic LC interface takes place at intermediate amphiphile coverage, then the liquid-condensed phase is retained until increasing ρ_s to the collapse point. This is in line with past experimental works^[18, 19, 33] where they claimed the liquid-condensed phase is formed at amphiphile monolayer. However these studies do not provide molecular information on the monolayer structure, therefore the important role that the LC penetration plays in directing the 2D packing of the monolayer phases is not revealed.

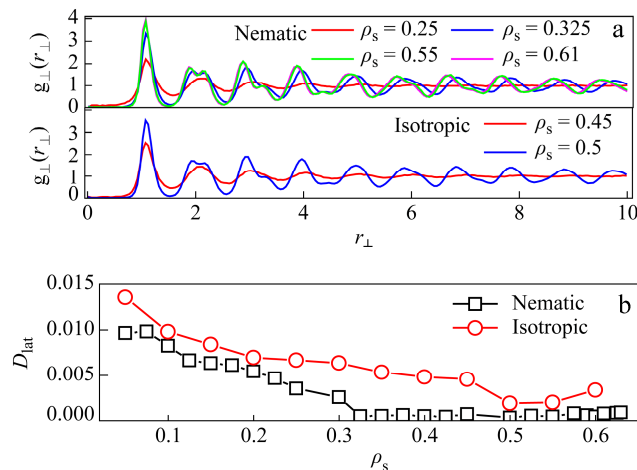


Fig. 4 (a) The 2D radial distribution function for both tails of amphiphile and LCs in the mixture monolayer at $\rho_s = 0.25, 0.325, 0.55$ and 0.61 for nematic system and $\rho_s = 0.45$ and 0.5 for isotropic system; (b) Lateral diffusion coefficient D_{lat} as functions of amphiphiles interfacial density ρ_s for both nematic and isotropic system

To further understand how the penetration of the LCs affects the lateral ordering transition in monolayer, we performed additional simulations on a similar system except that the bulk LC phase is in an isotropic state. For this system, direct inspection of D_{lat} , $g_{\perp}(r_{\perp})$ given in Fig. 4 suggests that amphiphile monolayers at the aqueous-isotropic LC interface pass directly from a liquid-expanded state to a liquid-condensed state at $\rho_s = 0.5$, larger than the ordering transition location of $\rho_s = 0.325$ at the aqueous-nematic LC interface. By examining the amount of LCs inserted in the tail-layer, as shown in Fig. 5 as a function of amphiphile coverage, we see a large penetration of the nematic LCs, suggesting that the higher the number of LCs in the tail-layer the lower the interfacial coverage of amphiphiles has to be in order to induce an ordering transition at interfaces.

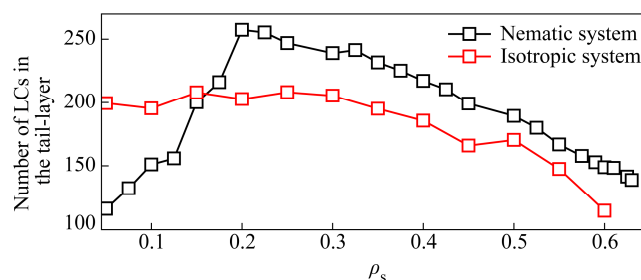


Fig. 5 Number of LCs which insert in amphiphile tail-layer as function of surface coverages of amphiphiles ρ_s in both nematic system and isotropic system

As expected, the diverse abilities of isotropic and nematic LCs to penetrate into the amphiphile layer give rise the different lateral ordering transition locations. It is well known that LCs penetrating into the tails can lead to a large gain of attractive energy from interactions between the tails and LCs as well as the translational entropy gain. However, the loss of rotational entropy of the isotropic LCs associated with confining them

between tails where they cannot maintain random orientations is high and the penetration of an isotropic LC molecule is more costly in terms of free energy. Therefore it is more favorable for nematic LCs to penetrate into the tail layer. Since LC molecules are more rigid compared to tails of amphiphile, the penetration of LCs into monolayer can enhance the order of amphiphile tails^[34] so that promote the formation of more orderly lateral structure in the monolayer. To further justify the important role of LC orientation in influencing the phase transition of monolayers, we compare the phase behavior of amphiphiles at LC/water interface in current system with that in a similar system except that nematic LC molecules are substituted by isotropic oil particles. Interestingly, we find no liquid-condensed phase is formed in the monolayer up to the largest accessible surface coverage of amphiphiles at oil/water interface. Apparently, the findings presented here provide valuable new insights into the coupling between the amphiphiles and LCs at the aqueous-LC interface, which can induce the formation of a condensed monolayer phase.

To illustrate the importance of LC-tail interactions in controlling the phase behavior of amphiphiles, we run additional simulations with a smaller e_{M-T} , *i.e.*, $e_{M-T} = 1.1$ and 1.3. Similarly, 2D phase-transition in amphiphile monolayers is monitored by relative order parameter, tilt angle, $g_{\perp}(r_{\perp})$, and D_{lat} .

As typically shown by D_{lat} and RDF in Fig. 6, the expanded-to-condensed phase transition is shift to $\rho_s = 0.45$ in system with $e_{M-T} = 1.3$, while in the system with $e_{M-T} = 1.1$, there is no sign of the formation of liquid-condensed phase at the interface even up to the largest ρ_s before the monolayer collapses. This finding can be rationalized by the fact that, in the system with LCs having stronger affinity to the tails, the stronger LC-tails interaction leads to a stronger orientation coupling between LCs and tails. More importantly, as the LCs penetrating into the tails can lead to a larger gain of enthalpy, the number of inserted LCs is larger in the system with larger value of e_{M-T} . As a result, a larger density enhancement of molecules at the interface promotes an ordered lateral organization of amphiphiles and inserted LCs at the interface, and shifts the expand-to-condensed 2D phase transition to lower ρ_s . While in a system with $e_{M-T} = 1.1$, the weaker LC-tail interaction leads to smaller amount of inserted LCs. Hence the total number of particles at interface fails to reach the value needed for the dense packing or the formation of a liquid-condensed phase even at largest accessible ρ_s . As clearly shown in Fig. 7, in both systems with $e_{M-T} = 1.3$ and 1.5, the total number of particles at interface both reaches a value around 372, corresponding to an area density of 0.93 as soon as the liquid-condensed phase appears at interface. While for the system with $e_{M-T} = 1.1$, the number of particles at interface keeps raising as ρ_s increases but fails to reach the value of 372 before the monolayer collapses. These results indicate the larger affinity between LCs and amphiphiles can promote the formation of an ordered phase in the mixture monolayer at the LC/water interface.

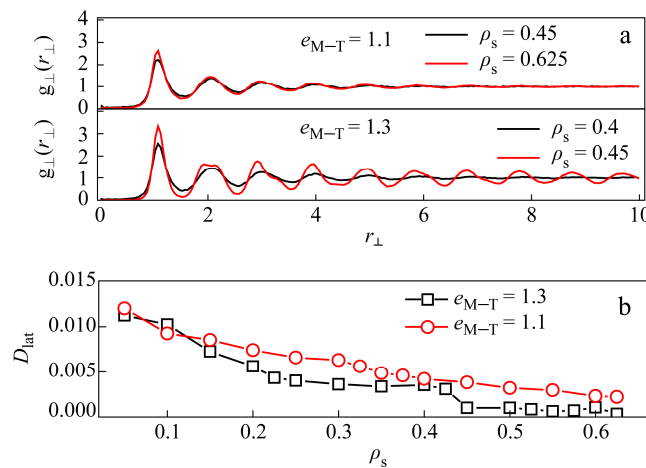


Fig. 6 (a) The 2D radial distribution function for both tails of amphiphile and LCs in the mixture monolayer at $\rho_s = 0.45, 0.625$ for system with $e_{M-T} = 1.1$ and $\rho_s = 0.4$ and 0.45 for system with $e_{M-T} = 1.3$; (b) Lateral diffusion coefficient D_{lat} as functions of amphiphiles interfacial density ρ_s for systems with $e_{M-T} = 1.1$ and 1.3

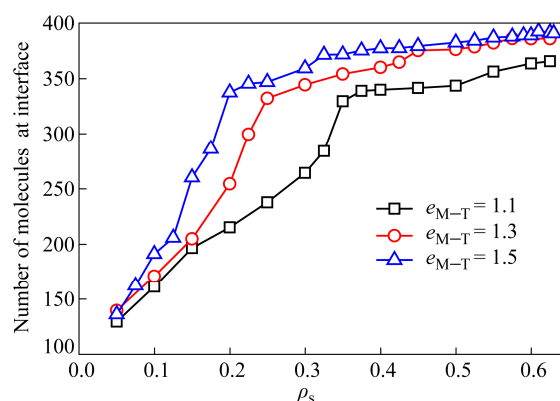


Fig. 7 Total number of both amphiphiles and inserted LCs at LC/water interface in systems with $e_{M-T} = 1.1, 1.3$ and 1.5

CONCLUSIONS

In conclusion, we have applied coarse-grained MD simulation using GB model and LJ chains to study the phase behavior of amphiphiles at LC/water interface. Our results reveal that the presence of LCs can influence the lateral organization of amphiphiles at LC/water interface. At low surface coverage of amphiphiles, the LCs can drive a planar orientation of amphiphile tails. With increases of amphiphiles at interface, the perpendicular penetration of LCs in monolayer as well as stronger coupling between LCs and amphiphile tails, promote the 2D ordering transition from liquid-expanded to liquid-condensed phase of the resulting mixed monolayer. Additionally, by comparing the systems with different e_{M-T} , we find the larger affinity between LCs and tails, which facilitates the penetration of LCs into the monolayer, can shift the 2D ordering transition to lower surface coverage. These findings revealed the penetration of anisotropic LCs into the monolayer at LC/water interface, can greatly promote the formation of ordered lateral organization of amphiphiles.

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