



Theory of biomolecular interactions at phospholipid-decorated surfaces of liquid crystals



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ABSTRACT

To discuss the biomolecular interactions at phospholipid-decorated surfaces of liquid crystals, we propose a Ginzburg–Landau free energy, which is functional of three kinds of order parameters. The mean-field treatment of the Ginzburg–Landau free energy expansion shows the existence of assembly of phospholipid monolayer at planar interfaces between thermotropic liquid crystals and aqueous phases. Several structure functions characterizing the assembly of phospholipid at the interfaces are calculated. The model qualitatively explains some aspect of the experimental observations on the physical behavior of phospholipid monolayer formed at the above described interfaces.

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1. Introduction

Phospholipids are amphiphilic molecules with a hydrophilic head group and one or more hydrophobic hydrocarbon chains. When lipid molecules are dissolved in water at sufficient concentration, they assemble into bilayer membranes in which their oily tails are shielded from contact with the surrounding water. Monolayers of lipids on a water surface have attracted much interest as models of biological membranes, but also as precursors of multilayer systems promising many technical applications. They exhibit very interesting physico-chemical properties as two-dimensional and interfacial systems [1]. It was established that most biomolecular interactions at biological membranes are accompanied by a reorganization of the proteins, lipids, and other species that constitute the membranes [2–8]. The most phospholipid monolayers are in metastable states [9]. In many cases the monolayers are not in thermodynamic equilibrium with the environment, but often nucleation of the more stable phases is very slow or even unmeasurable during times of days. Thermotropic liquid crystal (TLC) can be used as responsive support for phospholipid monolayers. Brake et al. [10] combined the phospholipid monolayers with a thermotropic liquid crystal [4'-pentyl-4-cyanobiphenyl (5CB)] to create a device that can rapidly detect incoming analytes. They observed that the spontaneous assembly of phospholipid monolayers at planar interfaces between thermotropic liquid crystals and aqueous phases gives rise to patterned orientations of the liquid crystals that reflect the spatial and temporal organization of phospholipids. In this publication these authors

demonstrate that assays based on liquid crystals can easily be used to detect ligand–receptor interactions. In a separate publication Cremer [11] discussed this technique in quite details. These results provide the development of new approaches for studying interface processes and for detecting the presence of specific biological species in aqueous environments. The mechanism by which the liquid crystal detection scheme operates is still not completely clear.

The purpose of the present paper is to present a simple, qualitative model to explain the biomolecular interactions at phospholipid-decorated surfaces of TLC. In this paper we introduce a Ginzburg–Landau model for phospholipid assemblies formed at interfaces between TLC and aqueous phases. We discuss how this model explains some aspect of the experimental results. The theory discussed here is closely related to the oil–water–surfactant system and amphiphilic film studied by several authors [13–17].

2. Theory and discussion

We consider three scalar order parameters $\phi(\mathbf{r})$, $\psi(\mathbf{r})$ and $S(\mathbf{r})$, respectively. The local density difference between water and lipid is described by the scalar order parameter field $\phi(\mathbf{r})$. The order parameter of the phospholipid monolayer of the i -th CH_2 group is defined as the thermodynamic average $\psi_i = \langle (\frac{3}{2} \cos^2 \theta_i - \frac{1}{2}) \rangle$. Here θ_i is the angle between the normal n_i to the plane formed by the i -th CH_2 group and the z -axis normal to the plane monolayers (Fig. 1). The order parameter for the whole chain ψ is an average over the ψ_i i.e. $\psi = \langle \psi_i \rangle$. The nematic order parameter proposed by de Gennes [12] is a symmetric, traceless tensor described by $Q_{ij} = \frac{5}{2}(3n_i n_j - \delta_{ij})$. The quantity $S = \langle (\frac{3}{2} \cos^2 \theta - \frac{1}{2}) \rangle$ defines the strength of the nematic ordering, where θ is the angle between the director and the long

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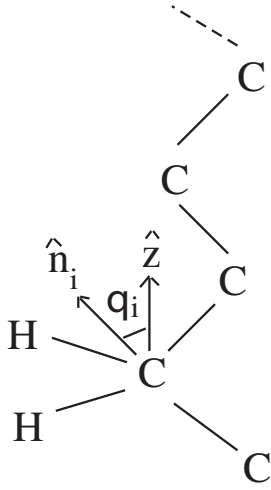


Fig. 1. Schematic representation of the configuration state of the chain at the liquid crystal-aqueous interface.

molecular axis. Having defined two scalar order parameters $\phi(\mathbf{r})$ and $\psi(\mathbf{r})$ and one tensor order parameter $Q_{ij}(\mathbf{r})$, the Ginzburg–Landau free energy functional can be written as

$$\begin{aligned}
 F = \int d^3r & \left[\frac{1}{3} a Q_{ij}(\mathbf{r}) Q_{ij}(\mathbf{r}) - \frac{4}{9} b Q_{ij}(\mathbf{r}) Q_{jk}(\mathbf{r}) Q_{ki}(\mathbf{r}) + \frac{1}{9} c_1 (Q_{ij}(\mathbf{r}) Q_{ij}(\mathbf{r}))^2 \right. \\
 & + \frac{1}{9} c_2 Q_{ij}(\mathbf{r}) Q_{jk}(\mathbf{r}) Q_{kl}(\mathbf{r}) Q_{li}(\mathbf{r}) + \frac{1}{2} u \phi^2(\mathbf{r}) - \frac{1}{3} w \phi^3(\mathbf{r}) + \frac{1}{4} v \phi^4(\mathbf{r}) \\
 & + \frac{1}{2} p \psi^2(\mathbf{r}) - \frac{1}{3} r \psi^3(\mathbf{r}) + \frac{1}{4} q_1 \psi^4(\mathbf{r}) + \frac{1}{3} \gamma \phi(\mathbf{r}) Q_{ij}(\mathbf{r}) Q_{ij}(\mathbf{r}) \\
 & + \frac{1}{3} \delta \psi(\mathbf{r}) Q_{ij}(\mathbf{r}) Q_{ij}(\mathbf{r}) + \frac{1}{3} G_1 \psi^2(\mathbf{r}) Q_{ij}(\mathbf{r}) Q_{ij}(\mathbf{r}) + \frac{1}{3} G_2 \phi^2(\mathbf{r}) Q_{ij}(\mathbf{r}) Q_{ij}(\mathbf{r}) \\
 & + \lambda \psi(\mathbf{r}) \phi(\mathbf{r}) + \frac{1}{2} \eta \phi^2(\mathbf{r}) \psi^2(\mathbf{r}) + \frac{1}{2} D_1 (\nabla \phi(\mathbf{r}))^2 + \frac{1}{2} D_2 (\nabla \psi(\mathbf{r}))^2 \\
 & + \frac{1}{3} D_3 \nabla_i Q_{jk}(\mathbf{r}) \nabla_i Q_{jk}(\mathbf{r}) + L_{ijkl} (\nabla_i \psi(\mathbf{r})) (\nabla_j Q_{kl}(\mathbf{r})) \\
 & + M_{ijkl} (\nabla_i \phi(\mathbf{r})) (\nabla_j Q_{kl}(\mathbf{r})) + N (\nabla \psi(\mathbf{r})) (\nabla \phi(\mathbf{r})) + \frac{1}{2} H_1 (\nabla^2 \psi(\mathbf{r}))^2 \\
 & + \frac{1}{2} H_2 (\nabla^2 \phi(\mathbf{r}))^2 + \frac{1}{2} H_3 (\nabla_i \nabla_j Q_{ij}(\mathbf{r}))^2 + \alpha \psi(\mathbf{r}) (\nabla_i \nabla_j Q_{ij}(\mathbf{r})) \\
 & + \beta \psi(\mathbf{r}) (\nabla^2 \phi(\mathbf{r})) - \frac{1}{3} E_1 \psi(\mathbf{r}) \nabla_i Q_{jk}(\mathbf{r}) \nabla_i Q_{jk}(\mathbf{r}) - \frac{1}{2} E_2 \psi(\mathbf{r}) (\nabla \phi(\mathbf{r}))^2 \\
 & \left. - \frac{1}{3} E_3 \phi(\mathbf{r}) \nabla_i Q_{jk}(\mathbf{r}) \nabla_i Q_{jk}(\mathbf{r}) \right] \quad (2.1)
 \end{aligned}$$

where $a, b, c_1, c_2, u, v, p, q_1, w, r, \alpha, \beta, \lambda, G_i, L, M, N, D_i, E_i$ and H_i are the phenomenological coefficients. The coefficients $c_1, c_2, q, w, r, v, \gamma, \delta, \eta$, and H_i are assumed to be positive. The gradient terms $D_1 > 0, D_2 > 0$ and $D_3 > 0$ disfavor the spatially varying order parameter configurations. For $D_2 < 0$, the amphiphilic molecules try to put their heads or their tails together. The terms $\lambda \phi \psi, \eta \phi^2 \psi^2, \gamma \phi Q_{ij} Q_{ij}$ and $G_2 \phi^2 Q_{ij} Q_{ij}$ act like a chemical potential. The coupling terms $\delta \psi Q_{ij} Q_{ij}$ and $G_1 \psi^2 Q_{ij} Q_{ij}$ describe the interactions of phospholipids to orientational transitions of liquid crystal films. $H_1 > 0, H_2 > 0$ and $H_3 > 0$ ensure thermodynamic stability. The coupling terms E_1 and E_2 favor the phospholipid monolayers to sit at aqueous and liquid crystal (LC) interfaces. The coupling term E_3 favors the aqueous phase sit at the LC films before the formation of phospholipid monolayers. The coupling terms λ, L, M, N, α and β are the lowest order linear terms in $(\psi, S), (\phi, S)$ and (ψ, ϕ) , respectively. L_{ijkl} and M_{ijkl} are of the form $L_{ijkl} = \frac{1}{2} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})$.

The substitution the value of $Q_{ij}(\mathbf{r})$ in Eq. (2.1) leads to the free energy

$$\begin{aligned}
 F = \int d^3r & \left[\frac{1}{2} a S^2(\mathbf{r}) - \frac{1}{3} b S^3(\mathbf{r}) + \frac{1}{4} c S^4(\mathbf{r}) + \frac{1}{2} u \phi^2(\mathbf{r}) - \frac{1}{3} w \phi^3(\mathbf{r}) \right. \\
 & + \frac{1}{4} v \phi^4(\mathbf{r}) + \frac{1}{2} p \psi^2(\mathbf{r}) - \frac{1}{3} r \psi^3(\mathbf{r}) + \frac{1}{4} q_1 \psi^4(\mathbf{r}) + \frac{1}{2} \gamma \phi(\mathbf{r}) S^2(\mathbf{r}) \\
 & + \frac{1}{2} \delta \psi(\mathbf{r}) S^2(\mathbf{r}) + \frac{1}{2} G_1 \psi^2(\mathbf{r}) S^2(\mathbf{r}) + \frac{1}{2} G_2 \phi^2(\mathbf{r}) S^2(\mathbf{r}) + \lambda \psi(\mathbf{r}) \phi(\mathbf{r}) \\
 & + \frac{1}{2} \eta \phi^2(\mathbf{r}) \psi^2(\mathbf{r}) + \frac{1}{2} D_1 (\nabla \phi(\mathbf{r}))^2 + \frac{1}{2} D_2 (\nabla \psi(\mathbf{r}))^2 + \frac{1}{2} D_3 (\nabla S(\mathbf{r}))^2 \\
 & + L (\nabla \psi(\mathbf{r})) (\nabla S(\mathbf{r})) + M (\nabla \phi(\mathbf{r})) (\nabla S(\mathbf{r})) + N (\nabla \psi(\mathbf{r})) (\nabla \phi(\mathbf{r})) \\
 & + \frac{1}{2} H_1 (\nabla^2 \psi(\mathbf{r}))^2 + \frac{1}{2} H_2 (\nabla^2 \phi(\mathbf{r}))^2 + \frac{1}{2} H_3 (\nabla^2 S(\mathbf{r}))^2 \\
 & + \alpha \psi(\mathbf{r}) (\nabla^2 S(\mathbf{r})) + \beta \psi(\mathbf{r}) (\nabla^2 \phi(\mathbf{r})) - \frac{1}{2} E_1 \psi(\mathbf{r}) (\nabla S(\mathbf{r}))^2 \\
 & \left. - \frac{1}{2} E_2 \psi(\mathbf{r}) (\nabla \phi(\mathbf{r}))^2 - \frac{1}{2} E_3 \phi(\mathbf{r}) (\nabla S(\mathbf{r}))^2 \right] \quad (2.2)
 \end{aligned}$$

where $c = c_1 + c_2/2$.

The effective free energy functional (2.2) can be written in the momentum space as

$$\begin{aligned}
 F = \int d^3q & \left[\frac{1}{2} (a + D_3 q^2 + H_3 q^4) S_q S_{-q} + \frac{1}{2} (u + D_1 q^2 + H_2 q^4) \phi_q \phi_{-q} \right. \\
 & + \frac{1}{2} (p + D_2 q^2 + H_1 q^4) \psi_q \psi_{-q} - \frac{1}{3} b \sum_{q_1 q_2} S_{q_1} S_{q_2} S_{-q_1 - q_2} + \frac{1}{4} c (S_q S_{-q})^2 \\
 & - \frac{1}{3} w \sum_{q_1 q_2} \phi_{q_1} \phi_{q_2} \phi_{-q_1 - q_2} + \frac{1}{4} v (\phi_q \phi_{-q})^2 \\
 & - \frac{1}{3} r \sum_{q_1 q_2} \psi_{q_1} \psi_{q_2} \psi_{-q_1 - q_2} + \frac{1}{4} q (\psi_q \psi_{-q})^2 + (\alpha + L) q^2 \psi_q S_{-q} \\
 & + M q^2 \phi_q S_{-q} + (\lambda + \beta q^2 + N q^2) \psi_q \phi_{-q} \\
 & + \frac{1}{2} \sum_{q_1 q_2} (\delta - E_1 q^2) \psi_{q_1} S_{q_2} S_{-q_1 - q_2} + \frac{1}{2} \sum_{q_1 q_2} (\eta - E_2 q^2) \psi_{q_1} \phi_{q_2} \phi_{-q_1 - q_2} \\
 & + \frac{1}{2} \sum_{q_1 q_2} (\gamma - E_3 q^2) \phi_{q_1} S_{q_2} S_{-q_1 - q_2} + \frac{1}{2} G_1 \psi_q \psi_{-q} S_q S_{-q} \\
 & \left. + \frac{1}{2} G_2 \phi_q \phi_{-q} S_q S_{-q} \right] \quad (2.3)
 \end{aligned}$$

where S_q, ϕ_q and ψ_q are the Fourier space

$$S(\mathbf{r}) = \sum_{\mathbf{q}} S(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}),$$

$$\phi(\mathbf{r}) = \sum_{\mathbf{q}} \phi(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}),$$

$$\psi(\mathbf{r}) = \sum_{\mathbf{q}} \psi(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}).$$

The free energy functional (2.3) can be rewritten as

$$F = \frac{1}{2} \int d^3q (S_q \phi_q \psi_q) P(q) \begin{pmatrix} S_{-q} \\ \phi_{-q} \\ \psi_{-q} \end{pmatrix} + \int d^3q F_{NG}(S_q, \phi_q, \psi_q) \quad (2.4)$$

where

$$P(q) = \begin{pmatrix} A_1 & 2Mq^2 & A_3 \\ 0 & B_2 & B_3 \\ 0 & 0 & C_3 \end{pmatrix} \quad (2.5)$$

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