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The interacting electrostatic charge model on the shape formation of monolayer domains at the air–water interface comprised of tilted dipoles with orientational deformation

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Abstract

The electrostatic energy in a dipolar monolayer domain with orientational deformation has been analyzed for the study of monolayer shapes. It is demonstrated that a monolayer domain is viewed as a system of interacting induced electric charges distributed at the inside and boundary of a domain. Since induced charge distribution is determined by orientational deformation and domain shape, the electrostatic energy is represented in the form of Frank splay elastic energy with spontaneous splay and curvature elastic energy with spontaneous curvature.

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1. Introduction

The physicochemical properties of amphiphilic monolayers at the air–water interface have attracted much attention since the preparation technique was discovered by Langmuir [1]. On account of the symmetry breaking at the air–water interface, monolayers form non-centrosymmetric orientational structures. During the monolayer compression, monolayers experience a variety of phases and phase transitions [2]. The structures of monolayers are determined by the positional order of hydrophilic molecular heads on the water surface and orientational order of hydrophobic molecular tails pointing towards the air. The crystallographic structures of monolayers comprised of rod-shaped molecules, e.g. fatty acids, have been studied by X-ray diffraction methods [2]. The orientational order parameters $S_n \equiv \langle P_n(\cos\theta)\rangle$ have been introduced to represent the orientational structure of monolayers as an extention of orientational order parameters of nematic liquid crystals S_2 [3], where $P_n(\cos\theta)$ is the Legendre polynomials of n-th rank. The non-centrosymmetric orientational structures of monolayers are expressed by the orientational order parameters of odd-number-th rank, e.g. $S_1 \neq 0$ and $S_3 \neq 0$. From the viewpoint of dielectric physics of monolayers, the dielectric polarizations generated from monolayers are functions of orientational order parameters S_n [4]. The spontaneous and second order non-linear polarizations are functions of S_1 and S_3, and linear polarization is a function of S_2. We have developed Maxwell displacement current (MDC), Brewster angle reflectometry (BAR), and optical second harmonic generation (SHG) techniques to detect the spontaneous, linear, and second order non-linear polarizations, and have measured S_1, S_2, and S_3 of monolayers comprised of rod-shaped molecules, e.g. alkyl-cyanobiphenyl homologues [5,6]. It is important to establish the physics of monolayers in terms of the orientational order parameters S_1, S_2, and S_3.

In two-phase coexistent states, monolayers form domain structures. Characteristic domain shapes have been observed by Brewster angle microscopy (BAM) [6–9] and fluorescence microscopy [10–12]. For 3D liquid materials ($S_1 = 0$), the surface tension plays a dominant role in the formation of material shapes. On the other hand, since monolayers form non-centrosymmetric structures ($S_1 = 0$), the electrostatic energy is stored due to the dipole–dipole interactions of constituent polar molecules, and makes an important contribution to the formation of domain shapes. McConnell et al. have proposed a model [13] that monolayer domain shapes are determined by

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competition between the line tension λ and the dipole–dipole interaction. The equilibrium domain shapes are calculated by the minimization of the shape free energy

$$F = \lambda \oint \mathrm{d}s + F_{\perp} + F_{\|} \cdot \tag{1}$$

where $F_{\perp}$ and $F_{\|}$ are the electrostatic energy due to the interaction of dipole moments normal and parallel to the water surface, respectively. s is the length of the domain boundary. In the early studies, the domain shapes in gaseous–liquid coexistent states ($F_{\|}=0$), have been studied intensively [11–13]. The line tension contributes to make the domain shape circular, whereas $F_{\perp}$ contributes to elongating the domain shape to long rectangular. However, these approaches have been applied only to some simple domain shapes, e.g. circles and rectangules due to the mathematical difficulty in generally treating $F_{\perp}$. In order to overcome this difficulty, we have reformulated the McConnell's model in terms of differential geometry [14]. $F_{\perp}$ has been approximately represented as the sum of the negative line tension and curvature elastic energy (see Eq. (5)), where it is analogous to the shape free energy of lipid vesicle [15]. The shape equation of monolayer domains has been derived on the analogy of the shape equation of lipid vesicles. The experiments, which support these approaches, have demonstrated the importance of the electrostatic energy and non-zero S_1 in the formation of monolayer domain shapes [11,12].

The in-plane orientational order is established in condensed phase domains ($F_{\|}\neq 0$), and $F_{\|}$ is an origin of the variety of observed condensed phase domain shapes. $F_{\|}$ is dependent on the orientational structure of the in-plane dipole moments. The non-uniform spatial distribution, i.e. the orientational deformation, of average orientational direction (**c**-director) has been observed by means of polarized fluorescence microscopy (PFM) and BAM from condensed phase domains of fatty acid [16] and phospholipid [10] monolayers, etc. Thus, it is important to clarify the contribution of orientational deformation of **c**-director to F and to domain shapes for the further understanding of the formation mechanism of condensed phase domain shapes. However, only domain shapes with uniform in-plane dipolar orientation have been analyzed in this approach [13,17]. In PFM and BAM experiments on fatty acid monolayers, it has been observed that orientational deformation of **c**-director develops a cusp in the domain shapes, and the importance of orientational deformation on the formation of domain shapes has been recognized. Phenomenological models, analogous to Frank elastic energy, have been used to investigate the contribution of the orientational deformation of **c**-director to the domain shapes [18,19]. In the phenomenological theories, the spontaneous splay, i.e. the linear term of splay deformation in free energy density, has been taken into account due to the non-centrosymmetry of monolayer domains ($S_1\neq 0$). The spontaneous splay also contributes to deforming the domain shape so that the boundary becomes normal to **c**-director at the domain boundary (anisotropic line tension) [19]. It has been concluded that the cusped shape of fatty acid domains originates from the anisotropic line tension due to the orientation at the cusped part. However, origins of the spontaneous splay and anisotropic line tension have not been discussed from the viewpoint of electrostatic energy.

The orientational deformation of **c**-director accompanies inhomogeneous orientational distribution of in-plane dipole moments. It is analogous to the inhomogeneous distribution of polarization in inhomogeneous dielectric materials in a uniform external electric field. In a uniform electric field, electric charges are induced not only at the boundary but also at the internal part of an in-homogeneous dielectric material ($\rho = -\nabla\cdot\mathbf{P}(\mathbf{R})$), whereas electric charges are induced only at the boundary of a homogeneous dielectric material. This argument indicates that the electric charges are induced at the internal part of a domain in the orientational deformation of **c**-director, and that the electrostatic energy is expressed as the interaction between the induced charges. In the present study, we demonstrated that the electrostatic energy due to the interaction between in-plane dipoles is expressed as the electrostatic energy due to the interaction between induced electric charges for the study of monolayer domain shapes. We then discuss the geometrical energies, e.g. anisotropic line tension and spontaneous splay, in the context of the electrostatic energy for the analysis of the contribution of orientational deformation. In Section 2, we represent the electrostatic energy in terms of the in-plane spontaneous polarization by the coarse graining of constituent dipoles. The electrostatic energy is further expressed as the interaction of induced charge at the internal part ($\rho_{\mathrm{induced}}=-\nabla\cdot\mathbf{P}_0(\mathbf{R})$) and boundary ($\sigma_{\mathrm{induced}}=\mathbf{P}_0(\mathbf{r}(s))\cdot\mathbf{m}(s)$) of monolayer domains. In other words, a monolayer domain is viewed as a system of interacting induced electric charges. In Section 3, we reformulate the electrostatic energy in terms of differential geometry to clarify the relationship between the electrostatic interaction and domain shape geometry. In the limit of uniform charge distribution and small boundary curvature, the electrostatic energy is represented as the Frank elastic energy with spontaneous splay and curvature energy with spontaneous curvature. In Section 4, we discuss the usefulness of the present approach for the domain shape studies. We conclude our paper in Section 5.

2. Electric charge model of monolayer domain shape

In this section, we analyze the contribution of orientational deformation to the electrostatic energy F_{e} ($\equiv F_{\perp}+F_{\|}$) due to the dipole–dipole interaction, and show it is possible to regard a monolayer domain as a system of interacting induced charges distributed at the internal part and boundary of the domain. The electrostatic energy due to the dipole–dipole interaction is written as $F_{\mathrm{e}}=1/2\sum_{i\neq j}(\mu_i\cdot\mu_j/|\mathbf{x}_i-\mathbf{x}_j|^3-3\,\mu_i\cdot(\mathbf{x}_i-\mathbf{x}_j)\mu_j\cdot(\mathbf{x}_i-\mathbf{x}_j)/|\mathbf{x}_i-\mathbf{x}_j|^5)$, where $\mathbf{x}_i$ is the position of a constituent dipole μ_i. The spontaneous polarization $\mathbf{P}_0(\mathbf{R})$ is the average of dipoles in the area ΔS larger than the order of intermolecular distance h centered at $\mathbf{R}$, i.e. $\mathbf{P}_0(\mathbf{R})=1/\Delta S\sum_{\mathrm{k}\in\Delta S}\mu_{\mathrm{k}}$. When the averaging area ΔS is sufficiently large, the in-plane component of spontaneous polarization $\mathbf{P}_{0\|}(\mathbf{R})$ is dependent on **c**-director of the position $\mathbf{R}$. For example, monolayer domains comprised of dipoles parallel to molecular long axis generate the in-plane spontaneous polarization $\mathbf{P}_{0\|}$ parallel to **c**-director [20]. In other words, the