

Quantized Symmetry of Liquid Monolayer Domains

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Theoretical arguments have been developed that the shapes of lipid domains at the air-water interface can be understood in terms of a competition between line tension and long-range electrostatic forces. These electrostatic forces can be approximated by effective dipoles, that is, the differences in dipole densities μ in coexisting phases. Recent experimental work has given quantitative confirmation that the long-range electrostatic forces can be expressed in terms of these dipoles. The present work further tests the theory of domain shapes involving competition between line tension and dipolar forces by observations of transitions of circular domains to domains of lower symmetry. These transitions occur when the electrostatic repulsive forces exceed the forces of line tension λ . Transitions of circular domains to domains with shapes of lower symmetry are functions of domain radius and the dimensionless parameter λ/μ^2 ; the experimental results are in accord with theory to within the experimental error.

Introduction

Fluorescence microscopy has been used to show that certain binary mixtures of lipids give rise to immiscible liquid phases at the air-water interface.¹⁻⁴ The immiscibility of the two liquid phases results in a monolayer with domains of one liquid interspersed in a two-dimensional sea of the other. The domain shapes and sizes in these lipid mixtures have been interpreted phenomenologically in terms of a competition between line tension at the domain boundary and dipole-dipole electrostatic repulsion between molecules within and between domains.⁵⁻¹² Line tension acts to minimize the length of the interface between the two liquid phases and thus favors compact domain shapes. The electrostatic repulsive force tends to maximize the distance between molecules within a domain and thus favors noncircular domain shapes.

Based on this line tension-equivalent dipole picture, a number of theoretical studies have been carried out to model shape transitions of lipid monolayer domains at the air-water interface.⁷⁻¹³ Earlier work gives a thermodynamic equilibrium size for a circular lipid domain.⁸ As the domain size increases beyond this equilibrium value, a point is reached when it becomes unstable with respect to distortion to a shape with 2-fold symmetry.^{7,8} As the size further increases, the domain becomes unstable with respect to higher harmonic distortions.⁹ For a very large domain, the domain boundary appears straight to short-wavelength harmonic distortions. A dynamical stability analysis has recently been performed for the straight edge of a large domain.¹² There have been a number of experimental studies of shape instabilities and shape relaxation dynamics of domains in Langmuir films at the air-water interface.^{3,13,14} However, there still lacks experimental results that thoroughly test the theoretical model for lipid monolayer domain shape transitions.

The present work involves both theoretical and experimental aspects of shape transitions of domains. On the theoretical side, we extend the shape transition analysis of circular domains to higher-order harmonic distortions.⁹ Comparison is made with the straight edge instability analysis;¹² both give identical results in the limit of high harmonics. The shapes of lipid domains bear a strong resemblance to those found in quasi-two-dimensional domains of ferrofluids in transverse magnetic fields.^{15,16} Recently, Langer *et al.* examined the dynamics of labyrinthine pattern formation in these systems by developing a formalism for the description of the dissipative motion of closed curves while

conserving area.¹⁷ A comparison between our calculations and those of Langer *et al.* is given in the Appendix.

The motivation behind this experimental work has been to test the validity of the theoretical model, by examining how well it accounts for observed shape transitions. We have accordingly employed a binary mixture of dihydrocholesterol (DChol) and dimyristoylphosphatidylcholine (DMPC) that forms two immiscible liquid phases at certain temperatures and pressures; one phase is rich in DChol, and the other phase is rich in DMPC.¹⁸ This system is ideal for testing the model for shape transitions since (i) all molecular dipoles are on average perpendicular to the monolayer surface and (ii) the lipid-phase composition, and thus the line tension, can be changed by altering the monolayer surface pressure. However, one difficulty for such experimental studies is that the domains spontaneously formed at the air-water interface upon spreading are typically a few microns in size. We circumvent this by utilizing a special technique yielding lipid domains of large size. Our experiments use these large domains to study the shape transitions. Comparisons of the experimental findings and the theoretical model are then possible.

Background Theories

Consider an isolated, circular lipid domain of radius R_c in the xy plane. As in previous work, it is assumed that the molecular dipoles within as well as outside the domain are vertically oriented in the z direction.⁹ This approximation is most accurate for liquid domains surrounded by a second liquid. The shape-dependent energy of this domain is a sum of an electrostatic energy F_{el} and a line tension energy F_λ .^{7,8}

$$F = F_{el} + F_\lambda \quad (1)$$

The two energies are

$$F_{el} = -\frac{\mu^2}{2} \oint \oint \frac{d\vec{R} \cdot d\vec{R}'}{r} \quad (2)$$

$$F_\lambda = \oint \lambda dR \quad (3)$$

Here, μ is the difference in dipole densities between the two phases, and λ is the effective line tension given by

$$\lambda = \lambda_0 - \mu^2 \quad (4)$$

with λ_0 a hypothetical line tension in the absence of dipolar forces.¹⁹ For a circular domain of fixed area $A = \pi R_c^2$, the total energy

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