Closed Form Results for Shape Transitions in Lipid Monolayer Domains

José A. Miranda[†]

Laboratório de Física Teórica e Computacional, Departamento de Física, Universidade Federal de Pernambuco, Recife, Pernambuco CEP. 50670-901, Brazil

Received: October 8, 1998

Isolated domains in lipid monolayers exhibit shape transitions as a consequence of the competing effects of line tension and long-range dipolar interactions. Nontrivial integrals ultimately arise in stability analysis calculations of these domains. In this work we present a closed form evaluation of such integrals in terms of associated Legendre functions. Our approach is motivated by and extends the work of J. M. Deutch and F. E. Low (*J. Phys. Chem.* **1992**, *96*, 7097−7101). Our closed form solutions lead to simpler analytic expressions for stability thresholds, which are easier to evaluate explicitly. Relevant asymptotic behavior is calculated in various limits of interest. For the case of Coulomb interactions, a general closed form expression is obtained for the critical domain radii.

1. Introduction

In the past few years the study of shape transitions in lipid monolayer domains at the air−water interface has received considerable attention from the physical−chemical community.[1] The great interest toward this subject is in part due to the diversity of domain shapes, which range from simple circular structures to complex labyrinthine patterns. Theoretical investigations study this variety of shapes by a model in which an array of molecular dipoles is arranged normal to the two-dimensional domain. The basic mechanism behind the formation of such structures arises from the competition between interfacial tension and long-range electrostatic interactions. Line tension acts to minimize the domain perimeter and favors compact domain shapes. In contrast, repulsive electrostatic dipole−dipole interaction tends to maximize the distance between dipoles and favors extended domain shapes. In this context, the total area of the domain is not changed.

In previous work McConnell,[2] Deutch and Low,[3] and Goldstein and Jackson[4] have studied the shape transitions of initially circular (radius R) lipid monolayer domains in a lowest order (quadratic) stability analysis. In all these theoretical studies many relevant quantities are calculated exactly, but due to their complexity, some of the computed expressions are not evaluated in closed form. For example, the formulas for stability thresholds found in refs 2−4 are usually expressed in terms of nontrivial integrals. Related integrals arise in stability investigations of other systems, also presenting polarized domains, such as planar-confined ferrofluids in magnetic fields[5] and thin ferromagnetic films forming magnetic bubble patterns.[6]

A considerable difficulty to perform stability analysis of lipid monolayer domains is the evaluation of the electrostatic dipole−dipole energies for various domain shapes. These calculations involve the manipulation of double line integrals, which are obtained by an ingenious application of Green's theorem.[7] The subtleties concerning the validity of Green's theorem under such circumstances are connected to the necessity of introducing a cutoff distance required to prevent divergence at zero separation between dipoles.[8] As shown by Deutch and Low,[3] the subtle

application of Green's theorem can be avoided by calculating the electrostatic energy directly through area integrals.

The purpose of the present work is to evaluate in closed form the integrals and pertinent stability conditions obtained in ref 3. Even though the nontrivial integrals that appear in refs 2−4 basically belong to the same general family, we focus on Deutch and Low's paper,[3] since their work precisely illustrates the utility of our closed form expressions. Our calculations are performed in the same spirit as those by Miranda and Widom,[9] who recently carried out a related closed form study focused on ferrofluids. We evaluate the integrals in terms of associated Legendre functions. Asymptotic behavior in interesting limits such as small cutoff or high spatial frequency is rigorously calculated. Finally, we address the case that considers repulsive Coulombic interactions within a charged domain. Comparison between our results and those derived in ref 3 is consistently made throughout the text. We obtain simpler and compact expressions that facilitate the explicit evaluation of many important quantities derived in previous studies of shape transitions in lipid monolayers.[2−4]

2. Stability Analysis of Lipid Monolayer Domains. Closed Form Results

2.1. Integrals $B_n(\hat{\alpha})$. Following Deutch and Low,[3] the perturbed domain shape is described by the Fourier expansion

$$r(\theta) = R + \sum_{n \neq 0} \zeta_n \exp(in\theta) \tag{1}$$

where θ is the polar angle, n (an integer) denotes the discrete azimuthal wave number, and ζ_n represents the perturbation amplitudes (Figure 1). In (1) ζ_0 is expressed in terms of the amplitudes ζ_n ($n \neq 0$) in order to satisfy the condition that the total area $\mathcal{A} = (1/2)\int_0^{2\pi} r(\theta)^2 \, d\theta$ of the domain remains constant and independent of the perturbation, i.e., $\mathcal{A} = \pi R^2$. The perturbation mode with $|n| = 1$ corresponds to a global off-center shift (rigid translation) of the unperturbed initial shape. It is a spurious, shape-preserving mode that does not contribute to domain energy changes.

The total energy of the domain described by $r(\theta)$ can be calculated by considering electrostatic and line-tension contribu-
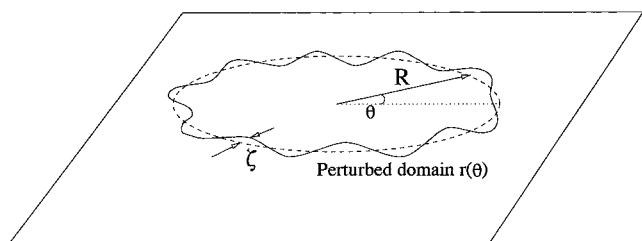

[†] E-mail: jme@lftc.ufpe.br.

Figure 1. Schematic configuration of a two-dimensional lipid domain. The dashed line represents an initially circular domain of radius R, and the solid undulated curve depicts its perturbed shape $r(\theta) = R + \zeta$. The perturbation $\zeta = \sum_{n \neq 0} \zeta_n \exp(in\theta)$, where n denotes the azimuthal wave number and θ gives the angular location of the points on the boundary. The domain area enclosed by the curve $r(\theta)$ remains constant and equals πR^2.

tions. The bulk (dipole−dipole) electrostatic energy of a distribution of molecular dipoles oriented in a direction normal to the two-dimensional domain is given by the double surface integral

$$W[r(\theta)] = \frac{\mu^2}{2} \int d^2 r \int d^2 r' \frac{1}{[|\vec{r} - \vec{r}'|^2 + \alpha^2]^{3/2}} \qquad (2)$$

where μ is the dipole density of the surface and α is a cutoff distance of closest approach of neighboring dipoles. On the other hand, the line-tension energy, given by the product of line tension λ by the domain perimeter, is

$$F_\lambda[r(\theta)] = \lambda \int_0^{2\pi} d\theta \left[r(\theta)^2 + \left(\frac{dr(\theta)}{d\theta} \right)^2 \right]^{1/2} \qquad (3)$$

By using (1)−(3), Deutch and Low[3] showed that the total energy $F[r(\theta)] = W[r(\theta)] + F_\lambda[r(\theta)]$, accurate to order $O(\zeta_n^2)$, can be expressed in the form

$$F = F_0 + \frac{2\pi}{R} \sum_{n>0} \Omega_n |\zeta_n|^2 \qquad (4)$$

where F_0 is the energy of the unperturbed circle and

$$\Omega_n = \lambda(n^2 - 1) - 2\mu^2 [B_1(\hat{\alpha}) - B_n(\hat{\alpha})] \qquad (5)$$

where

$$B_n(\hat{\alpha}) = \frac{1}{2^{3/2}} \int_0^\pi \frac{\cos n\theta}{\left[\left(1 + \frac{\hat{\alpha}^2}{2} \right) - \cos \theta \right]^{3/2}} d\theta \qquad (6)$$

and $\hat{\alpha} = \alpha/R$. We can examine the stability of the circle simply by looking at the sign of Ω_n: instability occurs when $\Omega_n < 0$. Similar results have been obtained in refs 2 and 4, despite subtleties regarding their implementation of the cutoff. Even though expression 5 is exact (to second order), it is written in terms of the integrals $B_n(\hat{\alpha})$ and has not been explicitly evaluated. Consequently, relevant physical quantities like the critical radii R_n (radii beyond which a circular domain becomes unstable with respect to n-fold harmonic perturbations) are often written in an indirect fashion, which involves complicated sums and integrals or requires the use of recursion relations.[10] The lack of closed form results makes difficult the precise and explicit evaluation of R_n for arbitrary n. Therefore, it is of practical interest to find closed form solutions for the integrals $B_n(\hat{\alpha})$.

The closed form expression for the integrals $B_n(\hat{\alpha})$ can be found with the help of the integral representation for the
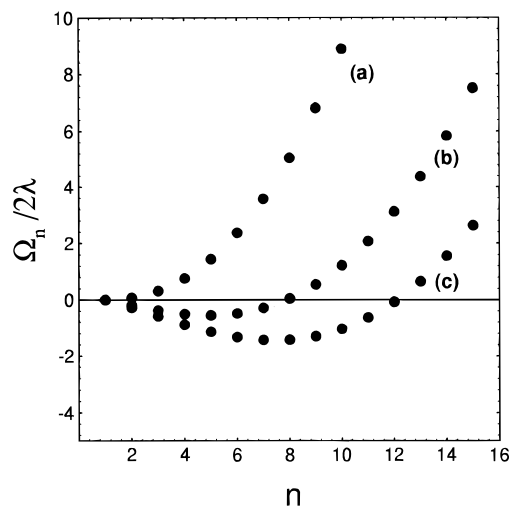

Figure 2. Ratio $\Omega_n/2\lambda$ as a function of mode number n, for three distinct values of μ^2/λ: (a) 0.090; (b) 0.107; (c) 0.112. The critical dimensionless parameter $D_{Cr}(2) \approx 0.095$ and $\hat{\alpha} = 2 \times 10^{-5}$. All points were found exactly using our closed form equation (9).

associated Legendre function of the second kind[11]

$$Q_\nu^m(z) = \frac{\exp(m\pi i)}{(2\pi)^{1/2}} \Gamma\left(m + \frac{1}{2} \right) (z^2 - 1)^{m/2} \times$$
$$\left\{ \int_0^\pi \frac{\cos\left(\nu + \frac{1}{2} \right) t}{[z - \cos t]^{m+1/2}} dt - \cos(\nu\pi) \int_0^\infty \frac{\exp\left[-\left(\nu + \frac{1}{2} \right) t \right]}{[z + \cosh t]^{m+1/2}} dt \right\} \qquad (7)$$

with $\mathrm{Re}(m) > -1/2$, $\mathrm{Re}(\nu + m) > -1$, and $|\arg(z \pm 1)| < \pi$. Γ denotes the gamma function. Set $\nu = n - 1/2$ and $m = 1$ in (7) and compare the resulting expression with (6) to get

$$B_n(\hat{\alpha}) = - \frac{Q_{n-1/2}^1\left(1 + \frac{\hat{\alpha}^2}{2} \right)}{\hat{\alpha}\left(1 + \frac{\hat{\alpha}^2}{4} \right)^{1/2}} \qquad (8)$$

This way, (5) can be rewritten as

$$\Omega_n = \lambda(n^2 - 1) - 2\mu^2 \left[\frac{Q_{n-1/2}^1\left(1 + \frac{\hat{\alpha}^2}{2} \right) - Q_{1/2}^1\left(1 + \frac{\hat{\alpha}^2}{2} \right)}{\hat{\alpha}\left(1 + \frac{\hat{\alpha}^2}{4} \right)^{1/2}} \right] \qquad (9)$$

We stress that Ω_n is now written in a closed form fashion, which explicitly expresses its precise functional dependence on n, $\hat{\alpha}$, λ, and μ. The fact that Ω_n is written in terms of the associated Legendre functions is very convenient, since their fundamental properties and basic functional behavior are quite well-known.[11] The usefulness of (9) becomes specially evident in the calculation of asymptotic expressions in important limiting situations such as small cutoff ($\alpha \rightarrow 0$) and long wavelengths ($n \rightarrow \infty$, $\alpha \rightarrow 0$, with $\hat{\alpha}$ kept finite and small). In such relevant limits our closed solution leads to simple and elegant expressions, which are easier to evaluate than those derived in ref 3.

In order to gain insight about the role of Ω_n in the domain instability, we plot in Figure 2 the ratio $\Omega_n/2\lambda$ as a function of mode number n. We assume that $\hat{\alpha} = 2 \times 10^{-5}$ and take three different values of the dimensionless parameter μ^2/λ, a quantity that characterizes the relative importance of dipolar and surface energies. All points are obtained exactly, using our eq 9. The

Shape Transitions in Lipid Monolayers

J. Phys. Chem. B, Vol. 103, No. 8, 1999 **1305**

domain boundary remains stable to nth mode distortions up to a critical value $D_{Cr}(n)$ of μ^2/λ, defined by setting $\Omega_n = 0$ in (9). In (a) $\mu^2/\lambda < D_{Cr}(2)$, so $\Omega_n \geq 0$, and the domain is stable. For larger values of μ^2/λ (see (b) and (c)) Ω_n can be negative and the domain deforms.

2.2. Stability Condition and Critical Radii R_n. For amphiphilic systems the ratio between the microscopic cutoff α and the radius R of the circular domain is a small quantity. In this section, we take advantage of our closed form expression (9) to evaluate the stability condition and critical radii R_n in the limit of small $\hat{\alpha}$.

From our discussion in the previous section the stability condition $\Omega_n \geq 0$ for circular lipid monolayer domains can be written as

$$\frac{\lambda}{\mu^2} \geq \frac{2}{(n^2-1)}\left[\frac{Q^1_{n-1/2}\left(1+\frac{\hat{\alpha}^2}{2}\right) - Q^1_{1/2}\left(1+\frac{\hat{\alpha}^2}{2}\right)}{\hat{\alpha}\left(1+\frac{\hat{\alpha}^2}{4}\right)^{1/2}}\right] \quad (10)$$

In order to evaluate (10) in the limit of small $\hat{\alpha}$, we use the following property of the associated Legendre functions[11]

$$Q^m_\nu(z) = (z^2-1)^{m/2}\frac{d^m Q_\nu(z)}{dz^m} \quad (11)$$

to rewrite (10) as

$$\frac{\lambda}{\mu^2} \geq \frac{\dfrac{d}{dx}[Q_{n-1/2}(1+2x) - Q_{1/2}(1+2x)]}{(n^2-1)} \quad (12)$$

where $x = \hat{\alpha}^2/4$.

To get a closed form expression for the stability condition (12) we need to evaluate $Q_{n-1/2}(1+2x)$ for small values of x. To succeed in doing this, we use ref 12 to expand $Q_{n-1/2}(1+2x)$ near $x = 0$, to first order in x

$$Q_{n-1/2}(1+2x) \approx \left[-C - \frac{1}{2}\ln\left(\frac{x}{x+1}\right) - \psi\left(n+\frac{1}{2}\right)\right] + \left[(1-C) - \frac{1}{2}\ln\left(\frac{x}{x+1}\right) - \psi\left(n+\frac{1}{2}\right)\right]\left(\frac{4n^2-1}{4}\right)x + \mathcal{O}(x^2\ln x, x^2) \quad (13)$$

where Euler's psi function ψ is the logarithmic derivative of the gamma function[11] and C is Euler's constant.

Using (12) and (13), we obtain the closed form stability condition, accurate to order α,

$$\frac{\lambda}{\mu^2} \geq \ln\left(\frac{8R}{\alpha e}\right) - \left\{\frac{1}{4}\left(\frac{4n^2-1}{n^2-1}\right)\left[\psi\left(n+\frac{1}{2}\right) - \psi\left(\frac{3}{2}\right)\right] + \frac{1}{2}\right\} \quad (14)$$

At this point, we compare our expression (14) with an equivalent result obtained by Deutch and Low[3] (eq 36 in their work). In ref 3 the part corresponding to the term between curly brackets on the right hand side of (14) is written as complicated definite integrals involving Chebyshev polynomials. The authors in ref 3 do not solve such integrals explicitly. In contrast, our derivation, based on the well-known properties of the associated Legendre functions, naturally provides a closed form stability condition. Obviously, our solutions are useful only if they lead to easier manipulation of the obtained results. This is exactly the case: the right hand side of our stability condition (14) is much easier to be evaluated explicitly than the equivalent piece
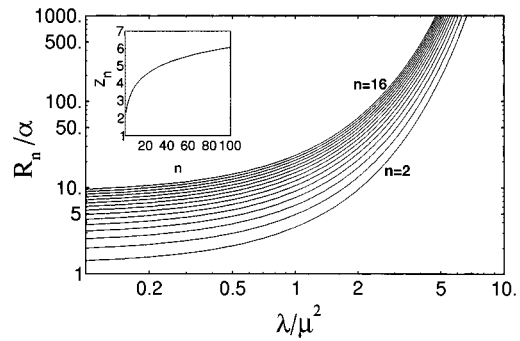

Figure 3. Dimensionless critical radius R_n/α as a function of λ/μ^2. Closed form equations (16) and (17) were used to plot the various curves $2 \leq n \leq 16$. Inset: behavior of the critical parameter Z_n with respect to n.

that appears in ref 3. Notice that analytic evaluation of (14) can be promptly performed, for specific n, by means of a simple property relating ψ functions[11]

$$\psi\left(n+\frac{1}{2}\right) - \psi\left(n-\frac{1}{2}\right) = \frac{2}{2n-1} \quad (15)$$

Another important quantity that can be immediately obtained from (14) refers to the critical radii at which the circular domain becomes unstable with respect to a given Fourier mode n

$$R_n = \frac{\alpha}{8}\exp\left(\frac{\lambda}{\mu^2}\right)\exp(Z_n) \quad (16)$$

where the critical parameter for transition is given by

$$Z_n = \frac{3}{2} + \frac{1}{4}\left(\frac{4n^2-1}{n^2-1}\right)\left[\psi\left(n+\frac{1}{2}\right) - \psi\left(\frac{3}{2}\right)\right] \quad (17)$$

The values calculated for Z_n directly using our eq 17 agree precisely with those computed in eq 39 of ref 3. Again, the major difference between our results resides on the fact that in ref 3, to get a particular value of Z_n, it is necessary to appeal to an indirect approach that requires solving several different integrals involving Chebyshev polynomials, for each n to be considered. Our eq 17 offers a simpler, direct, and more convenient way to evaluate the various Z_n.

Figure 3 depicts the dimensionless critical radius R_n/α plotted against the ratio λ/μ^2. All curves are computed analytically from our eqs 16 and 17. This figure illustrates important physical behavior captured by lowest order stability analysis. Mode $n = 2$ is always the first to become unstable (elliptical instability), establishing a stability boundary. At a fixed value of λ/μ^2, higher modes ($n \geq 3$) become unstable at larger R_n/α. As R_n/α increases, each mode becomes dominant for a range of radii, and hence there is a cascade to higher modes. For a given critical radius, smaller values of λ/μ^2 lead to stronger mode competition, meaning more intricate domain boundaries. Related stability diagrams have been numerically obtained in refs 5 and 13. The critical parameter Z_n is plotted as a function of mode number n in the inset of Figure 3.

2.3. Relevant Asymptotic Behavior and the Coulomb Interaction Case. We begin this section by calculating further asymptotic expansions by taking advantage of our closed form expression (10). First, consider the large n and small α limit, assuming that the product $n\hat{\alpha}$ is kept fixed. This is the limit of interest in many practical situations.[2–4] Considering the large n limit, use the asymptotic expression[11]

$$\lim_{n \to \infty} \frac{Q^m_{n-1/2}\left[\cosh\left(\frac{\tau}{n}\right)\right]}{n^m \exp(i\pi m)} = K_m(\tau) \tag{18}$$

where $K_m(\tau)$ is the modified Bessel function of order m, and set

$$\tau = n \cosh^{-1}\left(1 + \frac{\hat{\alpha}^2}{2}\right) \approx n\hat{\alpha} + \mathcal{O}(n\hat{\alpha}^3) \tag{19}$$

to rewrite stabzility condition (10) as

$$\frac{\lambda}{\mu^2} \geq \frac{2}{n^2}\left[\frac{K_1(\hat{\alpha}) - nK_1(n\hat{\alpha})}{\hat{\alpha}\left(1 + \frac{\hat{\alpha}^2}{4}\right)^{1/2}}\right] \tag{20}$$

In addition, take into account the fact that $\hat{\alpha}$ is small, keeping $n\hat{\alpha}$ fixed, to obtain

$$\frac{\lambda}{\mu^2} \geq 2\left[\frac{1}{(n\hat{\alpha})^2} - \frac{1}{n\hat{\alpha}}K_1(n\hat{\alpha})\right] \tag{21}$$

where we have used the small argument expansion

$$K_1(y) \approx \frac{1}{y} + \frac{1}{2}\left[\left(C - \frac{1}{2}\right) + \ln\left(\frac{y}{2}\right)\right]y + \mathcal{O}(y^3 \ln y, y^3) \tag{22}$$

and a power series expansion of the denominator in (20). Equation 21 is quite general, being valid for large values of n and small values of α, provided $n\hat{\alpha}$ is kept finite. We would like to point out that our result (21) differs from the equivalent one obtained in ref 3 (see eq 46 in their work). Because of a mistake in their calculation, Deutch and Low have written their eq 46 in terms of the modified Bessel function of order zero $K_0(n\hat{\alpha})$ (there is also a sign error), which is not the correct result. This minor mistake would be of no consequence if the authors in ref 3 would have not derived an important subsequent result, using their incorrect expression (46) as a starting point. This fact generates some confusion. Further comments on this issue are given in the next paragraph.

We take advantage of our eq 21 to discuss the so-called straight edge limit.[3,14] This is the situation in which the domain interface is flat with a small perturbation of wave number k. To get this limit from our circular geometry, we take radius $R \to \infty$ at fixed α. Fixed wave number $k \equiv n/R$ implies $n \to \infty$ and $\hat{\alpha} \to 0$, with fixed $n\hat{\alpha}$ as in our asymptotic expansion equation (21). Taking the limit of (21) for large wavelengths compared to the cutoff ($k\alpha \ll 1$), we use the small argument expansion (22) to get the critical spatial frequency

$$k_c = \left[\frac{\alpha}{2}\exp\left(\frac{\lambda}{\mu^2} + C - \frac{1}{2}\right)\right]^{-1} \tag{23}$$

The straight edge of the domain is unstable for all spatial frequencies $k < k_c$. This result agrees with eq 13 in McConnell's work[14] since the line tension considered in his derivation contains an additional electrostatic contribution given by $-\mu^2$.[15] Our result (23) also agrees with the quantity $R_M(n) \equiv n/k_c$ derived by Deutch and Low (eq 48). In principle, we should not expect agreement since $R_M(n)$ in ref 3 is obtained using their incorrect intermediate expressions (46) and (47), as pointed out in the previous paragraph. It is worth mentioning that the critical spatial frequency (23) could have been calculated by taking the large n limit of our earlier results (16) and (17).

We conclude by extending our analysis to the case of Coulomb interactions in charged domains.[16] As indicated in ref

3, for a Coulomb interaction between two particles (charge q) of the form $u(\rho) = (q^2/\rho)$, with $\rho = [r^2 + r'^2 - 2rr' \cos\theta]^{1/2}$, the domain stability condition can be written as

$$\lambda(n^2 - 1) \geq 2^{1/2}q^2R^2[\mathcal{B}_1(\theta) - \mathcal{B}_n(\theta)] \tag{24}$$

where

$$\mathcal{B}_n(\theta) = \int_0^\pi \frac{\cos n\theta}{[1 - \cos\theta]^{1/2}}\,d\theta \tag{25}$$

As in the case of the dipolar interaction potential, the integrals $\mathcal{B}_n(\theta)$ are not evaluated in ref 3. Using (7) with $\nu = n - 1/2$, $m = 0$, and $z \to 1$, plus expansion 13, we find closed form expressions for the integrals $\mathcal{B}_n(\theta)$ and, consequently, for the stability condition (24). With the help of these results, we calculate the critical radii for a given n mode distortion

$$R_c(n) = \left\{\frac{\lambda(n^2 - 1)}{2q^2\left[\psi\left(n + \frac{1}{2}\right) - \psi\left(\frac{3}{2}\right)\right]}\right\}^{1/2} \tag{26}$$

Keller et al.[16] studied the specific case of elliptical deformations in charged domains. Our result is identical to theirs if we set $n = 2$ in (26). Equation 26 generalizes previous results found for $R_c(n)$,[3,16] providing a closed form expression, valid for arbitrary n.

3. Concluding Remarks

Lipid monolayers form two-dimensional domains as a result of the competition between line-tension and long-range repulsive interactions. Stability analysis of these domains depends on a family of nontrivial integrals. For repulsive electrostatic dipole–dipole interaction, we present a closed form evaluation of these integrals as a combination of associated Legendre functions. Asymptotic behavior in several interesting limits is evaluated. A general closed form result is also obtained for the case in which the repulsive interaction is of Coulombic nature. Our theoretical results should be viewed as complementary to the work of Deutch and Low,[3] leading to exact, simpler, and explicit formulas that commonly appear in the study of shape transitions in lipid monolayer domains.

We hope our results will be helpful for future work on the subject of shape instabilities in amphiphilic monolayers. While the present work has addressed transitions associated with a slightly deformed circle, we anticipate that the analytical treatment of more complicated domain shapes may benefit from our closed form results. In higher order perturbative calculations, the various harmonic modes couple and cannot be studied separately. In order to cope with larger distortions, a mode coupling theory is required. We point out that a weakly nonlinear analysis of such a situation can be carried out analytically, following a related recent work on viscous fingering instability.[17] Once applied to monolayers, this approach would also lead to nontrivial integrals, which could be explicitly evaluated by employing the methodology and results we presented here.

References and Notes

(1) For a nice review on this fascinating topic, see: McConnell, H. M. *Annu. Rev. Phys. Chem.* **1991**, *42*, 171.

Shape Transitions in Lipid Monolayers

J. Phys. Chem. B, Vol. 103, No. 8, 1999 **1307**

(2) McConnell, H. M. *J. Phys. Chem.* **1990**, *94*, 4728.

(3) Deutch, J. M.; Low, F. E. *J. Phys. Chem.* **1992**, *96*, 7097.

(4) Goldstein, R. E.; Jackson, D. P. *J. Phys. Chem.* **1994**, *98*, 9626.

(5) Langer, S. A.; Goldstein, R. E.; Jackson, D. P. *Phys. Rev. A* **1992**, *46*, 4894.

(6) Thiele, A. A. *Bell Syst. Technol.* **1969**, *48*, 3287.

(7) McConnell, H. M.; de Koker, R. *J. Phys. Chem.* **1992**, *96*, 7101.

(8) In theoretical models for ferrofluids and magnetic bubbles it is not necessary to introduce an *ad hoc* cutoff. In contrast to the strictly two-dimensional approach for monolayers, these systems are described as three-dimensional, presenting a finite thickness that prevents the integrals from diverging.

(9) Miranda, J. A.; Widom, M. *Phys. Rev. E* **1997**, *55*, 3758.

(10) See, for instance, the expressions calculated for R_n in ref 2 (eq 30) and 3 (eq 38).

(11) Magnus, W.; Oberhettinger, F.; Soni, R. P. *Formulas and Theorems for the Special Functions of Mathematical Physics*; Springer-Verlag: New York, 1966. Gradshteyn, I. S.; Ryzhik, I. M. *Table of Integrals, Series, and Products*; Academic Press: New York, 1994.

(12) Robin, L. *Fonctions Sphériques de Legendre et Fonctions Sphéroidales*; Gauthier-Villars: Paris, 1959; Tome II and III.

(13) Lee, K. Y. C.; McConnell, H. M. *J. Phys. Chem.* **1993**, *97*, 9532.

(14) McConnell, H. M. *J. Phys. Chem.* **1992**, 96, 3167.

(15) The reason for introducing such an additional term into the line tension has its origin in the discussion of the applicability of Green's theorem to the calculation of the dipolar electrostatic energies of lipid domains. This issue is discussed in detail in ref 7.

(16) Keller, D. J.; Korb, J. P.; McConnell, H. M. *J. Phys. Chem.* **1987**, *91,* 6417.

(17) Miranda, J. A.; Widom, M. *Physica D* **1998**, *120*, 315.