Theory of Shape Transitions of Two-Dimensional Domains

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A theory is presented to describe the instability in the circular shape of a two-dimensional domain of particles that experience repulsive and surface tension forces. The treatment is motivated by and extends the work of H. M. McConnell (*J. Phys. Chem.* **1990**, *94*, 4728-4731). We present exact results for the case where the repulsion arises from electrostatic dipole-dipole interaction. We show how to determine the critical radius R_n at which the circular domain becomes unstable to harmonic perturbations in shape of order n. An analysis is given of the case of general repulsive interactions.

I. Introduction

McConnell and collaborators have presented a number of theoretical studies of the shape transition of finite lipid monolayer domains located at the air-water interface.[1-12] Recently, McConnell has reviewed the subject.[13] These lipid domains exhibit surprisingly rich phase behavior that can be observed with fluorescence microscopy.[14] The theoretical analysis of the phase transition in these systems is based on a model of molecular dipoles oriented vertically to the two-dimensional domain. The phase transition arises from a competition between the repulsive dipole-dipole interaction that tends to spread the dipoles and the surface tension force that tends to minimize the perimeter.

In a recent paper,[15] McConnell analyzed the stability of a circular two-dimensional domain to harmonic perturbations in its shape. In arriving at the limits to stability of the circular region, McConnell introduced several approximations. Our purpose here is to present an exact solution to the stability problem posed by McConnell. Moreover, the method we develop permits the treatment of a wide range of surface stability problems.

II. Method and Analysis

We assume that the two-dimensional dipolar region is defined by a boundary $R(\theta)$. The free energy of the domain $F[R(\theta)]$ is composed of two contributions. The first contribution is the bulk energy $W[R(\theta)]$

$$W[R(\vartheta)] = \frac{\mu^2}{2}\int_A d\mathbf{r}\int_A d\mathbf{r}'\{|\mathbf{r}-\mathbf{r}'|^2+\alpha^2\}^{-3/2} \quad (1)$$

where μ is the dipole density of the surface, α is a cutoff distance of closest approach of the two molecules, and A is the domain area enclosed by the closed curve $R(\theta)$

$$A[R(\vartheta)] = \frac{1}{2}\int_0^{2\pi} d\vartheta\, R(\vartheta)^2 \quad (2)$$

The second contribution is the line energy which is proportional to the perimeter times the line tension λ

$$F_\lambda[R(\vartheta)] = \lambda\int_0^{2\pi} d\vartheta \left\{R(\vartheta)^2+\left(\frac{dR(\vartheta)}{d\vartheta}\right)^2\right\}^{1/2} \quad (3)$$

Our problem is to minimize the total free energy $F[R]$

$$F[R(\vartheta)] = W[R(\vartheta)] + F_\lambda[R(\vartheta)] \quad (4)$$

subject to maintaining the area A constant.

We consider a perturbation $\delta R(\theta)$ about a reference shape R. The reference shape we select is a circle, although the method we introduce is appropriate for more complex reference shapes. For the circle, of radius R, perturbations in shape lead to perturbations in area according to

$$\delta A = A[R+\delta R(\vartheta)] - A[R] = R\int_0^{2\pi} d\vartheta\left[\delta R(\vartheta)+\frac{\delta R(\vartheta)^2}{2R}\right] \quad (5)$$

We consider successive orders of shape perturbation according to

$$\delta R(\vartheta) = \delta R_0(\vartheta) + \delta R_1(\vartheta) + \ldots \quad (6)$$

so that

$$\delta A = R\int_0^{2\pi} d\vartheta\,\delta R_0(\vartheta) + R\int_0^{2\pi} d\vartheta\left[\delta R_1(\vartheta)+\frac{\delta R_0(\vartheta)^2}{2R}\right] \quad (7)$$

For the lowest perturbation we choose

$$\int_0^{2\pi} d\vartheta\,\delta R_0(\vartheta) = 0 \quad (8)$$

Then, in order for δA to equal zero, the first-order perturbation must locally satisfy[16]

$$\delta R_1(\vartheta) = -\frac{[\delta R_0(\vartheta)]^2}{2R} \quad (9)$$

A. Evaluation of Line Tension Contribution. For the circle

$$\delta R_\lambda = F_\lambda[R+\delta R] - F_\lambda[R] = \lambda\int_0^{2\pi} d\vartheta\,\delta R(\vartheta) + \frac{\lambda}{2R}\int_0^{2\pi} d\vartheta\left(\frac{d\delta R(\vartheta)}{d\vartheta}\right)^2 \quad (10)$$

which reduces to

$$\delta F_\lambda = \frac{\lambda}{2R}\int_0^{2\pi} d\vartheta\left\{\left(\frac{d\delta R_0(\vartheta)}{d\vartheta}\right)^2 - \delta R_0(\vartheta)^2\right\} \quad (11)$$

with use of eqs 8 and 9.

We adopt a harmonic form for the shape perturbation

$$\delta R_0(\vartheta) = \sum_{n\neq 0} r_n \exp(in\vartheta) \quad (12)$$

which satisfies the lowest order condition in eq 8. Substitution of eq 12 into eq 11 leads to the same result as obtained by McConnell[17]

$$\delta F_\lambda = \frac{2\pi\lambda}{2R}\sum_{n\neq 0}|r_n|^2(n^2-1) \quad (13)$$

In eqs 12 and 13 the sum is over all positive and negative n except $n = 0$. The term $n = 1$ does not contribute because it corresponds to a degenerate rotation of the reference circle.

B. Evaluation of the Bulk Energy Contribution. To second order the variation in the bulk energy about a circular shape is

$$\frac{\delta W}{\mu^2/2} = \delta W^{(1)} + \delta W^{(2)} \quad (14)$$

The linear term is

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$$\delta W^{(1)} = R\int_0^{2\pi} d\vartheta \int_0^{2\pi} d\vartheta' \left\{\int_0^R r\, dr\, B(r,R,\omega)\delta R(\vartheta') + \int_0^R r'\, dr'\, B(R,r',\omega)\delta R(\vartheta)\right\} \quad (15)$$

where

$$B(r,r',\omega) = [r^2 + r'^2 - 2rr'\cos(\vartheta - \vartheta') + \alpha^2]^{-3/2} \quad (16)$$

and $\omega = \theta - \theta'$. The quadradic term is

$$\delta W^{(2)} = \int_0^{2\pi} d\vartheta \int_0^{2\pi} d\vartheta' \left\{\frac{1}{2}\int_0^R r\, dr \times \left(\frac{\partial r' B(r,r',\omega)}{\partial r'}\right)_{r'=R} \delta R(\vartheta')^2 + \frac{1}{2}\int_0^R r'\, dr' \times \left(\frac{\partial r B(r,r',\omega)}{\partial r}\right)_{r=R} \delta R(\vartheta)^2 + \delta R(\vartheta)\delta R(\vartheta')R^2 B(R,R)\right\} \quad (17)$$

We evaluate the linear term $\delta W^{(1)}$ eq 15 by introducing eq 6 for δR. Use of eqs 8 and 9 yields a contribution quadradic in δR_0. When this term is combined with eq 17 for $\delta W^{(2)}$, one obtains the following expression for the variation in the bulk energy:

$$\delta W = \frac{\mu^2}{2}(G_1 + G_2) \quad (18)$$

The first term on the right-hand side of eq 18 is easily evaluated

$$G_1 = \int_0^{2\pi} d\vartheta \int_0^{2\pi} d\vartheta'\, \delta R_0(\vartheta)\delta R_0(\vartheta')R^2 B(R,R,\omega) = \frac{4\pi}{R}\sum_n |r_n|^2 B_n \quad (19)$$

when the lowest order variation δR_0, eq 12 is introduced. Here B_n is the integral defined by

$$B_n = \int_0^{\pi} d\vartheta \cos(n\vartheta)\frac{1}{[2 - 2\cos\vartheta + (\alpha/R)^2]^{3/2}} \quad (20)$$

The second term on the right-hand side of eq 18 can be written as

$$G_2 = \int_0^{2\pi} d\vartheta \int_0^{2\pi} d\vartheta'\, \delta R_0(\vartheta')^2 R^2 \int_0^R r\, dr \left[\frac{\partial B(r,r',\omega)}{\partial r'}\right]_{r'=R} \quad (21)$$

In Appendix A, we show that G_2 can be transformed to

$$G_2 = -\int_0^{2\pi} d\vartheta'\, \delta R_0(\vartheta')^2 R^2 \int_0^{2\pi} d\vartheta \frac{1}{[2R^2(1 - \cos\vartheta) + \alpha^2]^{3/2}} \quad (22)$$

and this expression is easily evaluated with use of eq 12

$$G_2 = -\frac{4\pi B_1}{R}\sum_{n\neq 0} |r_n|^2 \quad (23)$$

Combining these results leads to the following expression for the bulk energy variation:

$$\delta W = \frac{2\pi\mu^2}{R}\sum_{n\neq 0} |r_n|^2 (B_n - B_1) \quad (24)$$

This result should be compared with the expansion obtained by McConnell.[17]

III. Results and Discussion

A. The Unperturbed Free Energy. We begin by evaluating the zeroth-order free energy

$$F^{(0)} = F_\lambda^{(0)} + W^{(0)} \quad (25)$$

where the quantities are to be evaluated for the circle. One finds immediately

$$F_\lambda^{(0)} = 2\pi R\lambda \quad (26)$$

The evaluation of the bulk dipolar energy term

$$W[R(\vartheta)] = \frac{\mu^2}{2}\int_A d\mathbf{r} \int_A d\mathbf{r}' \{|\mathbf{r} - \mathbf{r}'|^2 + \alpha^2\}^{-3/2} \quad (27)$$

over the area $A = \pi R^2$ is complicated. Unlike McConnell, we attack the integral directly and obtain, in the limit of small α, the result

$$W^{(0)}(R) = (\pi R^2)\left(\frac{\pi\mu^2}{\alpha}\right) - 2\pi R\mu^2 \ln\left(\frac{8R}{\alpha e}\right) + \text{terms of order } R^0 \quad (28)$$

The procedure we follow to evaluate $W^{(0)}$ is described in the Appendix B.

McConnell employs a different approach to evaluate $W^{(0)}$ that leads to the value $(4R/\alpha e^2)$ for the argument of the logarithm. The difference that arises from this procedure employed by McConnell means that we cannot expect numerical agreement between our results when the cutoff appears. However, McConnell has recently demonstrated[18] that when corrections are included, identical results to those given here are obtained.

B. The Second-Order Free Energy and Stability Condition. The entire second-order term for the free energy is obtained from eqs 4, 13, and 24

$$\delta F = \frac{2\pi}{2R}\sum_{n\neq 0} |r_n|^2 [\lambda(n^2 - 1) + 2\mu^2(B_n - B_1)] \quad (29)$$

where B_n is given by eq 20.

Stability requires that δF be positive. Therefore, the point of instability arises when the inequality

$$\lambda(n^2 - 1) - 2\mu^2(B_1 - B_n) \geq 0 \quad (30)$$

is violated. The key quantity that must be evaluated is

$$2\mu^2[B_1 - B_n] = 2\mu^2\int_0^{\pi} d\vartheta \frac{\cos\vartheta - C_n(\cos\vartheta)}{[2(1 - \cos\vartheta) + \hat{\alpha}^2]^{3/2}} \quad (31)$$

where $\hat{\alpha} = (\alpha/R)$ and $C_n(\cos\theta) = \cos(n\theta)$ is the Chebyshev polynomial of order n. It is convenient to rewrite eq 31 in terms of the variable $y = \sin(\theta/2)$

$$2\mu^2[B_1 - B_n] = 4\mu^2\int_0^1 dy \frac{1}{(1 - y^2)^{1/2}} \frac{1 - 2y^2 - T_n(y)}{[4y^2 + \hat{\alpha}^2]^{3/2}} \quad (32)$$

Here $T_n(y) = C_n(1 - 2y^2)$.

This integral has unpleasant behavior near $y = 0$. Accordingly, it is helpful to split off the small y asymptotic behavior of $T_n(y)$

$$T_n^0(y) = 1 - 2n^2y^2 \quad (33)$$

that permits eq 32 to be written as

$$2\mu^2[B_1 - B_n] = 8\mu^2(n^2 - 1)\int_0^1 dy \frac{1}{(1 - y^2)^{1/2}} \frac{y^2}{[4y^2 + \hat{\alpha}^2]^{3/2}} - 4\mu^2\int_0^1 dy \frac{1}{(1 - y^2)^{1/2}} \frac{T_n(y) - T_n^0(y)}{[4y^2 + \hat{\alpha}^2]^{3/2}} \quad (34)$$

So far the expression is exact for the dipolar case and the unpleasant behavior at small y has been segregated in the first integral on the right-hand side of eq 34.

We wish to evaluate these integrals in the limit of small α. For small α, the major contribution to the first integral occurs for small y. Accordingly, the expression can be approximated, to order α, by

$$2\mu^2[B_1 - B_n] = 8\mu^2(n^2 - 1)\int_0^1 dy \frac{y^2}{[4y^2 + \hat{\alpha}^2]^{3/2}} + \mu^2(n^2 - 1)\int_0^1 dy \times \frac{1}{y}\left[\frac{1}{(1 - y^2)^{1/2}} - 1\right] - \frac{\mu^2}{2}\int_0^1 dy \frac{1}{(1 - y^2)^{1/2}} \frac{T_n(y) - T_n^0(y)}{y^3} \quad (35)$$

The first two integrals on the right-hand side of eq 35 can easily be evaluated so one obtains for the stability condition stated in eq 30

$$\frac{\lambda}{\mu^2} \geq \ln\left(\frac{8R}{\alpha e}\right) - \frac{1}{2(n^2-1)}\int_0^1 dy\, \frac{1}{(1-y^2)^{1/2}}\,\frac{T_n(y) - T_n^0(y)}{y^3} \tag{36}$$

This stability condition can be put in the suggestive form

$$0 \geq \ln\left(\frac{R}{R_n}\right) \tag{37}$$

where R_n is the critical radius for distortion into harmonic shape n. This critical radius can be expressed as

$$R_n = \frac{\alpha}{8}\exp(\lambda/\mu^2)\exp(Z_n) \tag{38}$$

where the critical parameter for transition is defined by

$$Z_n = 1 + \frac{1}{2(n^2-1)}\int_0^1 dy\, \frac{1}{y^3}\,\frac{1}{(1-y^2)^{1/2}}[T_n(y) - T_n^0(y)] \tag{39}$$

The critical radii R_n are increasing functions of n. Thus if the physical size R of a circular lipid domain exceeds the critical radius for a particular mode n_0, all modes with $n > n_0$ will be unstable.

The procedure for computing the Z_n is straightforward. First, one computes the Chebyshev polynomials $C_n(\cos\theta)$ according to the recursion relation

$$C_{n+1} = 2\cos\theta\, C_n - C_{n-1} \tag{40}$$

$$\text{with } C_0 = 1 \text{ and } C_1 = \cos\theta$$

One then forms $T_n(y) = C_n(1-2y^2)$ and with use of eq 33 performs the indicated integration. One finds: $Z_2 = 7/3$, $Z_3 = 8/3$, $Z_4 = 73/25$, etc.

C. Comparison with McConnell's Results. How do these results compare to those of McConnell?[15] We do not expect precise numerical agreement because of the difference in the treatment of the cutoff.[18] However we should expect agreement for physical quantities that do not depend on the cutoff parameter. Accordingly, we investigate the ratio of the critical radii R_n: to the equilibrium radius R_{eq} defined by McConnell as the radius that minimizes the total free energy, F_{tot} when the number and radius of unperturbed circular domains is permitted to vary at constant overall area, A_{tot}

$$F_{tot} = (A_{tot}/\pi R^2)F^{(0)}(R) \tag{41}$$

Minimization of F_{tot} with use of eqs 25 and 28 leads immediately to the result

$$R_{eq} = \frac{\alpha e^2}{8}\exp(\lambda/\mu^2) \tag{42}$$

If we form the ratio R_n/R_{eq}, dependence on the cutoff disappears and thus we expect that the result $(Z_n - 2)$ will agree precisely with the ratio determined by McConnell. As expected we find agreement

$$\ln\left(\frac{R_2}{R_{eq}}\right) = \frac{1}{3}\ln\left(\frac{R_3}{R_{eq}}\right) = \frac{2}{3}\ln\left(\frac{R_4}{R_{eq}}\right) = \frac{23}{25} \tag{43}$$

As McConnell has pointed out, the numerical values for Z_n are in good agreement with the computer calculations of Vanderlick and Mohwald.[19]

D. Stability at Short Wavelengths. It is tempting to look for a limit for the critical radius R_n as $n \to \infty$. However, this limit is complicated because we do not expect the model to remain valid when the length scale of the boundary variation is comparable to the cutoff. Thus, our treatment will break down when $\beta = n(\alpha/R)$ becomes large.

It is possible to seek a limit for short wavelength $n \to \infty$, small cutoff $\alpha \to 0$, and β finite and small. This limiting procedure assures that all wavelengths considered will be large compared to the cutoff.

In order to examine this limit, we consider the stability condition in its original form in eqs 30 and 31 with the change of variable $x = \theta/n$. In the limit of large n, one has

$$\frac{\lambda}{\mu^2} \geq 2\int_0^{n\pi} dx\, \frac{\cos(x/n) - \cos x}{[2n^2(1-\cos(x/n)) + \beta^2]^{3/2}} \tag{44}$$

One can show that in the limit of large n this integral is approximated by

$$\frac{\lambda}{\mu^2} \geq 2\int_0^{\infty} dx\, \frac{1-\cos x}{[x^2+\beta^2]^{3/2}} \tag{45}$$

that can be evaluated to yield

$$\frac{\lambda}{\mu^2} \geq 2\left[\frac{1}{\beta^2} + \frac{1}{\beta}K_0(\beta)\right] \tag{46}$$

Here, $K_0(\beta)$ is the modified Bessel function that has an expansion for small β

$$K_0(\beta) = -[\ln(\beta/2) - \gamma][1 + (\beta/2)^2] + (1/4)\beta^2 + o[\beta^4 \ln\beta, \beta^4] \tag{47}$$

In this expression γ is Euler's constant. Carrying out the indicated operations in eq 46 leads to the following stability condition in the limit of small β and large n

$$0 \geq \ln\left(\frac{R}{R_M(n)}\right)$$

$$\text{where} \qquad R_M(n) = \frac{\alpha n}{2}\exp[\gamma - (1/2) + (\lambda/\mu^2)] \tag{48}$$

This condition determines a wavelength n_M, for fixed R and a, from the condition $R_M(n_M) = R$. All wavelengths above this value of n_M are inadmissable.

IV. More General Interactions

The method we have developed can easily be extended to any interaction of the form $(1/2)u(\rho)$ where $\rho = \mathbf{r} - \mathbf{r}'$. The result one obtains is exactly of the same form as eq 26

$$\frac{\lambda}{R}(n^2-1) - 2R^2[B_1(\vartheta) - B_n(\vartheta)] \geq 0 \tag{49}$$

with B_n of the form

$$B_n(\vartheta) = \int_0^{\pi} d\vartheta\, u[R(1-\cos\vartheta)]\cos(n\vartheta) \tag{50}$$

The limits of stability from the reference circular shape can be investigated for any particular repulsive interaction. Here we present two examples.

A. Coulomb Interactions. For a Coulomb interaction between the particles on the surface $u(\rho) = (q^2/\rho)$ with $\rho = [r^2 + r'^2 - 2rr'\cos(\theta)]^{1/2}$. For this interaction a cutoff does not need to be introduced.

One finds from eq 50 that

$$2R^3[B_1(\vartheta) - B_n(\vartheta)] = 2^{1/2}q^2R^2\int_0^{\pi} d\vartheta\, \frac{\cos\vartheta - \cos(n\vartheta)}{(1-\cos\vartheta)^{1/2}} \tag{51}$$

The substitution $x = \cos\theta$ leads to the result

$$\lambda(n^2-1) \geq 2^{1/2}q^2R^2\int_{-1}^{1} dx\, \frac{x - T_n(x)}{(1-x)(1+x)^{1/2}} \tag{52}$$

For the particular case of distortion to ellipsoidal shape $n = 2$, $T_2(x) = (2x^2 - 1)$, and eq (52) takes the simple form

$$\lambda 3 \geq 2^{1/2}q^2R^2\int_{-1}^{1} dx\, \frac{2x+1}{(1+x)^{1/2}} \tag{53}$$

This leads to the following result for the critical radius

$$\pi R_c^2 = \frac{9\pi\lambda}{4q^2} \tag{54}$$

which is identical to the result of Keller, Korb, and McConnell[20] for Coulomb interactions. No discrepency is found in numerical values because a cutoff is not needed.

B. Exponential Interactions. For the case of exponential interactions between the particles on the surface, one has $u(\rho) = g\exp[-\rho/\delta]$

$$\lambda(n^2-1) \geq 2R^3 g\int_0^{\pi} d\vartheta \exp\left[-\frac{R}{\delta}(2(1-\cos\vartheta))^{1/2}\right][\cos\vartheta - \cos(n\vartheta)] \tag{55}$$

Since $(R/\delta) \gg 1$, the principal contribution from this integral occurs for small θ. Therefore, the right-hand side of eq 55 can be approximated as

$$\lambda(n^2-1) \geq (n^2-1)R^3 g\int_0^{\pi} d\vartheta \exp\left[-\frac{R}{\delta}\vartheta\right]\vartheta^2 \tag{56}$$

which is easily evaluated to be

$$\lambda(n^2-1) \geq (n^2-1)\delta^3 g\int_0^{\infty} dx \exp[-x]x^2 = (n^2-1)\delta^3\, 2g \tag{57}$$

In this case the stability condition is independent of the harmonic order n. This is a general result for all interactions u that are of short range. For these interactions the line energy contribution is local and can be included as a contribution to λ.

V. Concluding Remark

We have given an exact analysis of the stability in shape fluctuations of a circular dipolar region where the dipoles are oriented perpendicular to the surface. Our method is easily generalized to more general reference shapes and dipole orientations. We demonstrate how the method applies to different interactions.

Future work will be directed to three-dimensional drops, bubbles, and bilayers. Our method should also prove useful for the analysis of fluctuations in the elastic energy of vesicles which involves volume and surface area constraints.[21-23]

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Appendix A: Proof of Equation 22

Equation 21 for G_2 can be written as

$$G_2 = \int_0^{2\pi} d\vartheta'\, \delta R_0(\vartheta')^2 R^2 g(\vartheta')$$

$$g(\vartheta') = \int_0^{2\pi} d\vartheta \int_0^R r\, dr \left[\frac{\partial B(r,r',\omega)}{\partial r'}\right]_{r'=R} \tag{A.1}$$

The integral $g(\theta')$ is

$$g(\vartheta') = \int_0^{2\pi} d\vartheta \int_0^R r\, dr \left[\frac{(-3)(R - r\cos\vartheta)}{\{[R^2 + r^2 - 2rR\cos(\vartheta-\vartheta')] + \alpha^2\}^{5/2}}\right] \tag{A.2}$$

If we assume r' is along the x axis and switch from polar coordinates to Cartesian coordinates in eq A.2 one finds

$$g(\vartheta') = -\int_{-R}^{+R} dy \int (R^2 - y^2)^{1/2}\, dx\, \frac{\partial}{\partial x}\frac{1}{[(R-x)^2 + y^2 + \alpha^2]^{3/2}} \tag{A.3}$$

This expression when re-expressed in polar coordinates after integration with respect to x, becomes

$$g(\vartheta') = -R\int_{-\pi/2}^{\pi/2} d\vartheta\, \{V[2R(1-\cos\vartheta)] - V[2R(1+\cos\vartheta)]\} \tag{A.4}$$

with

$$V[2R(1-\cos\vartheta)] = \frac{1}{[2R(1-\cos\vartheta) + \alpha^2]^{3/2}} \tag{A.5}$$

Equation A.4 can be simplified to

$$g(\vartheta') = -R\int_0^{2\pi} d\vartheta\, V[2R(1-\cos\vartheta)] \tag{A.6}$$

which when placed into eq A.1 leads to the expression for G_2 stated in eq 22.

Appendix B: Evaluation of the Integral $W^{(0)}$

We wish to evaluate the integral $W^{(0)}(R)$, eq 27, in the limit of small α. It is most convenient to begin by examining the derivative $dW^{(0)}(R)/dR$

$$dW^{(0)}(R)/dR = 2\pi\mu^2 R\int_0^{2\pi} d\vartheta \int_0^R dr\, \frac{r}{[r^2 - 2rR\cos\vartheta + (R^2+\alpha^2)]^{3/2}} \tag{B.1}$$

This integral is elementary and one obtains

$$dW^{(0)}(R)/dR = 8\pi\mu^2 H(R) \tag{B.2}$$

where the integral $H(R)$ is

$$H(R) = \frac{1}{2}\int_0^{\pi} d\vartheta\, \frac{1}{\sin^2\vartheta + \hat{\alpha}^2}\left[(1+\hat{\alpha}^2)^{1/2} - \frac{(1-\cos\vartheta) + \hat{\alpha}^2}{(2(1-\cos\vartheta) + \hat{\alpha}^2)^{1/2}}\right] \tag{B.3}$$

or in terms of the variable $y = \sin(\theta/2)$

$$H(R) = \int_0^1 dy\, \frac{1}{(1-y^2)^{1/2}}\left\{\frac{1}{4y^2(1-y^2) + \hat{\alpha}^2}\right\} \times \left[(1+\hat{\alpha}^2)^{1/2} - \frac{2y^2 + \hat{\alpha}^2}{(4y^2 + \hat{\alpha}^2)^{1/2}}\right] \tag{B.4}$$

Here $\hat{\alpha} = (\alpha/R)$.

We divide the integral into two parts, $H = H_1 + H_2$, in order to isolate the small α behavior of the integral into H_1. The integral H_1 is

$$H_1(R) = \int_0^1 dy \left\{\frac{1}{4y^2 + \hat{A}^2}\right\}\left[(1+\hat{\alpha}^2)^{1/2} - \frac{2y^2 + \hat{\alpha}^2}{(4y^2 + \hat{\alpha}^2)^{1/2}}\right] \tag{B.5}$$

which can be evaluated to yield

$$H_1(R) = \frac{(1+\hat{\alpha}^2)^{1/2}}{2\hat{\alpha}}\tan^{-1}\left(\frac{2}{\hat{\alpha}}\right) - \frac{1}{4}\ln\left(\frac{4e}{\hat{\alpha}}\right) \tag{B.6}$$

The integral H_2 is

$$H_2(R) = \int_0^1 dy\, \frac{1}{(1-y^2)^{1/2}}\left\{\frac{1}{4y^2(1-y^2) + \hat{\alpha}^2} - \frac{(1-y^2)^{1/2}}{4y^2 + \hat{\alpha}^2}\right\} \times [(1+\hat{\alpha}^2)^{1/2} - \frac{2y^2 + \hat{\alpha}^2}{(4y^2 + \hat{\alpha}^2)^{1/2}} \tag{B.7}$$

This integral is well behaved in the limit that $\hat{\alpha}$ tends to zero. Since we only require the small $\hat{\alpha}$ behavior, we evaluate the integral $H_2(R)$ in this limit. One finds

$$H_2(R) = \int_0^1 dy\, \frac{1}{(1-y^2)^{1/2}}\left\{\frac{1}{4y^2} - \frac{(1-y^2)^{1/2}}{4y^2}\right\}(1-y) \tag{B.8}$$

that yields the result

$$H_2(R) = \frac{1}{4}[2 - \ln 2] \qquad (B.9)$$

Thus, in the limit of small $\hat{\alpha}$, we have

$$H(R) = \frac{\pi R}{4\alpha} - \frac{1}{4} - \frac{1}{4}\ln\left(\frac{8R}{\alpha e}\right) \qquad (B.10)$$

$$dW^{(0)}(R)/dR = 2\pi\mu^2\left[\frac{\pi R}{\alpha} - 1 - \ln\left(\frac{8R}{e\alpha}\right)\right] \qquad (B.11)$$

This expression when integrated with respect to R is identical to eq 28.

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(18) McConnell's approach is based on a clever use of Green's theorem that replaces the double surface integral in $W^{(0)}$ with a double line integral. The approach is clearly described in ref 9. However, it is not free of objection since the identity desired from use of Green's theorem (eq 7, ref 9) is not exact in the presence of the cutoff required to prevent divergence at zero separation. This difficulty is avoided by including correction terms to Green's theorem formula as employed by McConnell as is described in the paper by McConnell, H. M.; De Koker, R. *J. Phys. Chem.*, following paper in this issue.
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Note on the Theory of the Sizes and Shapes of Lipid Domains in Monolayers

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A detailed analysis is given for the application of Green's theorem to the calculation of the dipolar electrostatic energies of lipid domains at the air–water interface. This theorem enables an area integration of a r^{-3} dipole–dipole interaction to be represented by a double line integral involving r^{-1}, substantially simplifying the calculation of the electrostatic energy. When a cutoff Δ is introduced in the expression for the dipole–dipole interaction so as to avoid the divergence at $r = 0$, a multipole correction term needs to be included in the Green's theorem formulation of the electrostatic energy. The present work provides an exact expression for this correction term and shows that it scales like a line tension energy, independent of Δ when Δ is small compared to the dimensions of the domain. For two liquid phases this electrostatic contribution to the line tension is simply $-\mu^2$, where μ is the difference in the dipole density in two adjoining phases.

Introduction

A number of experimental and theoretical studies have been made of the sizes and shapes of lipid domains observed at the air–water interface using fluorescence microscopy.[1-3] The theoretical picture involves a competition between line tension and electrostatic dipole–dipole interactions. Large line tension favors large domains with compact shapes, whereas large dipole–dipole repulsion forces favor small domains and/or domains with extended shapes. The equilibrium shapes are then determined theoretically by variational calculations, allowing domain shapes and sizes to change in finding a free energy minimum. The largest obstacle to such calculations is the evaluation of the electrostatic dipole–dipole energy for various domain shapes. To simplify these calculations, we have in previous work employed Green's theorem to convert area integrals of dipolar energies to line integrals around domain perimeters.[4] In such calculations it is necessary to introduce a cutoff Δ to avoid the divergence in the r^{-3} dipole–dipole energy. As has been noted recently by Deutch and Low, the validity of this application of Green's theorem is not obvious; in a recent study of harmonic distortions of circular domains, they have circumvented this issue by a direct attack on the area integrals.[5]

The purpose of the present note is to show that Green's theorem can be applied rigorously to these problems and to show that our previous results concerning domain sizes and shapes are strictly correct providing the line tension includes an electrostatic contribution. In this case the published formulas for domain sizes and shapes require no modification.

Analysis

As in previous work, the electrostatic dipole–dipole free energy of an isolated lipid domain of area A is given by the expression

$$F_e = A\epsilon - 1/2\ \mu^2 \int\int |\vec{r} - \vec{r}'|^{-3}\, dA\, dA' \qquad (1)$$

where ϵ is the electrostatic energy per unit area for a domain of infinite size with dipole density μ and the area integral gives the dipole repulsion between all dipoles within the area A and all virtual dipoles exterior to it in area A'. If the domain of area A is surrounded by a second lipid region A' with different dipole density, then μ is the difference in dipole densities in regions A and A'. Thus, the area integral in eq 1 gives the *shape dependence* of the dipolar energy of the domain of area A. See Figure 1. This simple expression for the electrostatic energy of course applies only to dipoles oriented perpendicular to the plane of the mono-

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