Surface charge relaxation and the pearling instability of charged surfactant tubes

T. T. Nguyen,* A. Gopal,† K. Y. C. Lee, and T. A. Witten

The James Frank Institute, The University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois 60637
(Received 18 September 2004; revised manuscript received 28 July 2005; published 30 November 2005)

The pearling instability of bilayer surfactant tubes was recently observed during the collapse of fluid monolayers of binary mixtures of Dimyristoylphosphocholine (DMPC): Palmitoyloleoylphosphoglycerol (POPG) and Dipalmitoylphosphocholine (DPPC):POPG surfactants. It can be explained by a Rayleigh-like instability under the action of the bilayer surface tension. The magnitude of surface tension is dictated by the electrostatic interaction between charged surfactants. Relaxation of charged molecules is proposed here as an additional mechanism driving the instability. We find the functional dependence of the electrostatic surface tension and relaxation energies on the screening length κ^{-1} explicitly. Relaxation lowers the cost of bending a tube into pearls making the cylindrical tube even more unstable. It is known that for the weak screening case in which the tube radius is smaller than the screening length of the solution, this effect is important. However, for the case of strong screening it is negligible. For the experiments mentioned, the situation is marginal. In this case, we show that the effect of relaxation remains small. It contributes about 20% to the total electrostatic energy.

I. INTRODUCTION

The formation of surfactant tubes and budding of spheroidal structures are of significant interest in biological processes. In particular, such structures constitute intermediates that are responsible for critical cellular processes such as material trafficking from the Golgi complex [1], and fusion and fission of membranes [2]. As seen during cell locomotion and the formation of Golgi structures, natural surfactant tubes are prone to transform to a structure resembling a string of pearls [1].

Pearling has been induced in tubular phospholipid membranes by adsorption of oil [3] or polymer [4], on one side of the membranes. These phenomena were interpreted in terms of the creation of membrane spontaneous curvature due to those external stimuli.

We have recently observed pearling in tubular structures formed during the collapse (two- to three-dimensional transition) of fluid monolayers of mixed phospholipids [5]. Collapse in binary monolayers containing [6] 70% DPPC and 30% POPG, and 70% DMPC and 30% POPG, lead to the formation of cylindrical tubes [7]. These tubes, which are still attached to the monolayer, can be tens of micrometers in length, with diameters of about 1 μm. A few of these are wide enough to resolve by fluorescence microscopy. As seen in Fig. 1, such tubes show instability towards pearling without the introduction of any external gradients that may affect or induce the spontaneous curvature. Furthermore, the tubes, being microscopic and submerged in water are likely to be composed of surfactant bilayers, which are in the liquid

phase at the temperature measured. This suggests that the tube surface does not have intrinsic spontaneous curvature itself. Thus, the abovementioned mechanisms of pearling are questionable for the present case.

The pearling instability can be explained by a simpler mechanism arising from the surface tension energy of the surfactant bilayer. As shown by Nelson *et al.* [8], this is very similar to the well-known Rayleigh instability of a cylinder of fluid [9]. In systems with charged surfactants (POPG in the above case), a significant part of surface tension arises from electrostatic interactions. In other words, the surface tension can be written as a sum of two contributions:

$$\alpha = \alpha_e + \alpha_0. \tag{1}$$

Here, α_e is the contribution from the electrostatic interaction between charged surfactants and α_0 is the contribution from other interactions such as the van der Waals attraction between lipid molecules or their hydrophobicity. The magnitude of the surface tension can be estimated assuming α, α_0, and α_e are of the same order. The magnitude of the last is $\pi\sigma_0^2/\kappa D$, where σ_0 is the surface charge density of the bilayer, κ is the inverse screening radius of the solution, and $D = 80$ is the dielectric constant of water. Using relevant experimental parameters, this electrostatic energy is estimated to be about 10^{-3} mN/m. On the other hand, the bending
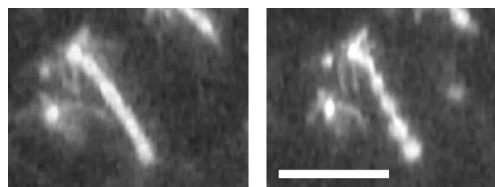

FIG. 1. Two fluorescence micrographs taken within a few seconds of each other, showing a surfactant tube undergoing a pearling instability. The top end of the tube is attached to the 7DMPC:3POPG monolayer from which it grew. The scale bar corresponds to 20 μm.

*New address: Department of Physics and Astronomy, University of California at Los Angeles, 475 Portola Plaza, Los Angeles, California 90095.

†New address: Department of Chemistry and Biochemistry, University of California at Los Angeles, 607 Young Drive East, Los Angeles, California 90095.

energy of a surfactant phospholipid bilayer is known [15] to be about $\gamma \simeq 30 k_B T$ (here, k_B is the Boltzmann constant and T is the temperature of the solution). For a tube with radius R_0 of 1 μm, this translates into an elastic (bending) energy of about $\gamma / R_0^2 \simeq 10^{-4}$ mN/m per unit area. Thus, the elastic energy is more or less negligible in comparison to surface tension energy. In other words, an instability similar to the Rayleigh instability of a liquid cylinder must be present for micrometers-sized tubes. For the case of a liquid cylinder, this instability leads to the breaking up of the cylinder into small droplets. However, for a surfactant tube, the breaking process is improbable because all surface tension energies involved are far below the rupture tensile stress (about 1 mN/m) of the lipid bilayer. The pearled structure is obviously the most likely candidate for the final structure of this instability.

In the current work, we propose an additional electrostatic mechanism of pearling, namely, charge relaxation. This is an extra degree of freedom in binary mixtures. This relaxation is similar to that observed in another well known electrostatics-induced pearling instability, namely, the pearls-on-string structure of polyelectrolyte in poor solvent or of polyampholytes [10]. The physics underlying these instabilities are however different. Even though both are induced by electrostatics, in surface tension induced pearling, the characteristic size of pearls is determined kinetically. On the other hand, the pearl size and period of polyelectrolytes is determined thermodynamically by the balance between electrostatic force and nonelectrostatic force (entropic or solvent-monomers interactions). This force balance leads to the strong redistribution of charged molecules (strong charge relaxation) in the system to lower its overall free energy, which is obviously not needed in the case of Rayleigh instability. One expects charge relaxation to be the driving force of pearling when screening is weak such that the Debye screening length (κ^{-1}) is larger than the pearl size. On the other hand, when the screening is strong $(\kappa^{-1}$ is smaller than the pearl size), electrostatic interactions become short range and the instability therefore of the dynamical Rayleigh type.

In the experimental system of Fig. 1, deionized water is used. In this case, the screening radius of the system is comparable to the tube radius (about 1 μm). Thus, the situation is marginal, and it is not clear whether or not the relaxation of charged surfactants still plays a significant role in the pearling instability. We address this question by calculating explicitly the gain in the electrostatic energy of the system when the charged molecules of the bilayer redistribute themselves during the pearling transition. We show that in this marginal case in which the screening radius is equal to or smaller than the tube radius, the charge relaxation remains small. The energy gain due to this effect contributes roughly 20% to the total electrostatic energy. For smaller screening radius, the ratio between these two energies decreases very quickly (as fourth power in the ratio between the screening length and the pearl size).

This paper is organized as follows. In Sec. II, using linear analysis, we briefly calculate changes in the surface tension and bending energies when a cylinder deforms into a string of pearls. In Sec. III, we calculate the change in the electrostatic energy under this deformation and separate the contri-

bution due to the relaxation of charged molecules. The latter is always negative. This gives an additional gain in the energy of deformation, making the tube even more unstable. In Sec. IV, we discuss the relative importance of charge relaxation effect as well as various approximations involved.

II. ELASTIC ENERGY

Even though the elastic (surface tension and bending) energy changes when a cylinder undergoes pearling deformation has been calculated [11,12] before, we briefly repeat the calculation here in order to introduce the notations and to simplify their comparison with electrostatic energy in later sections.

Let us start with a model elastic free energy describing the cylindrical tubes. Denoting the bilayer tube length L, area S, and volume V, our starting free energy is the sum of the surface tension energy, the bending energy, and an osmotic pressure energy:

$$E = E_s + E_b + E_o = \alpha \int dS + \int dS [2\gamma H^2 + \bar{\gamma} K] + \delta p \int dV, \tag{2}$$

where γ and $\bar{\gamma}$ are the bending rigidity and the Gaussian bending rigidity of the bilayer, respectively, H and K are the mean and Gaussian curvature of the tube surface, respectively, and δp is an osmotic pressure difference between the inner and outer regions of the tube. In the above model, the osmotic pressure term is somewhat artificial. This term is needed to make the cylindrical shape the minimum of the energy for certain range of the parameters α, γ, and δp (because the growth of the tubes is slow in experiments, we consider the tubes are in (quasi-)equilibrium and their shapes are determined by the minimum of the free energy). Without this term, a spherical vesicle will always be the shape that minimizes the free energy [Eq. (2)]. This osmotic pressure term was also used by the authors of Ref. [12] to study instability of cylindrical vesicles. A second choice for the model energy is to replace the osmotic pressure term in Eq. (2) by a line tension term, which has been used by the authors of Ref. [11] to study coiling instability in multilamellar tubes. Each of these models incorporate different physics in stabilizing the cylindrical tube. The choice of one model over the other is not important in this paper because we do not allow either the volume or the length of the cylinder to change in our subsequent analysis of the cylinder instability. In the free energy [Eq. (2)], the surface tension and the osmotic pressure are actually Lagrangian multipliers that enforce the restrictions of area and volume conservation of the surfactant tube.

Within linear analysis, to investigate the change in the energy of a tube undergoing a pearling instability, let us slightly deform the cylinder radially with a relative amplitude, $\varepsilon \ll 1$, and a wave vector k (see Fig. 2). As a result, the radius of the new tube varies along its axis according to

$$R(z) = \bar{R}[1 + \varepsilon \cos(kz)]. \tag{3}$$

Due to the small permeability of water through the bilayer surface, in our model, we require that the tube volume does
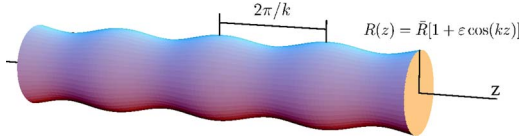
FIG. 2. (Color online) A cylindrical tube is deformed radially with wave vector k.

not change under deformation. This makes the average radius $\bar{R}$ of the new tube different from the original radius R_0. This new radius can be easily calculated. The volume per unit length of the new tube is

$$V = \frac{k}{2\pi} \int_{-\pi/k}^{\pi/k} dz \int_0^{R(z)} 2\pi r \, dr = \pi \bar{R}^2 (1 + \varepsilon^2/2). \quad (4)$$

The condition of volume conservation then leads to the simple relation

$$\bar{R} = R_0/\sqrt{1 + \varepsilon^2/2} \simeq R_0(1 - \varepsilon^2/4). \quad (5)$$

Let us calculate the change in the surface tension energy of the tube. The element of the area of the new tube is

$$dS(z,\phi) = dz \, d\phi \, R(z)\sqrt{1 + R'(z)^2}$$
$$= dz \, d\phi \, \bar{R}[1 + \varepsilon \cos(kz)]$$
$$\times \sqrt{1 + [\varepsilon k \bar{R} \sin(kz)]^2}, \quad (6)$$

where $R'(z) \equiv dR/dz$. The area of the deformed tube per unit length is then

$$A = \frac{k}{2\pi} \int_{-\pi/k}^{\pi/k} \int_0^{2\pi} dS(z,\phi)$$
$$= 2\pi R_0 \frac{E[-(kR_0)^2 \varepsilon^2/(1 + \varepsilon^2/2)]}{(\pi/2)\sqrt{1 + \varepsilon^2/2}}$$
$$\simeq 2\pi R_0 \left[1 - \frac{1 - (kR_0)^2}{4} \varepsilon^2 \right], \text{ for } \varepsilon \ll 1, \quad (7)$$

where E is the complete elliptic integral of the second kind. The change in surface tension energy per unit length is easily calculated to be

$$\Delta E_s = \alpha(A - 2\pi R_0) \simeq \frac{\pi \alpha R_0}{2}[(kR_0)^2 - 1]\varepsilon^2. \quad (8)$$

Let us next calculate the change in the bending energy. Because the Gaussian curvature energy $\bar{\gamma} \int dA K$ is a topological invariant and we do not change the topology of the tube, this energy does not change. For the mean curvature, standard geometry consideration [13] of the tube surface gives

$$H = \frac{1 + R'(z)^2 - R(z)R''(z)}{2R(z)[1 + R'(z)^2]^{3/2}}. \quad (9)$$

Substituting Eq. (9) into the expression for bending energy [the second term in Eq. (2)], and keeping terms up to second order in ε, one obtains for the bending energy change

$$\Delta E_b \simeq \varepsilon^2 \frac{\pi\gamma}{4R_0}[3 + 2(kR_0)^4 - (kR_0)^2]. \quad (10)$$

III. ELECTROSTATIC ENERGY AND RELAXATION OF CHARGED SURFACTANTS

Let us now proceed to calculate the electrostatic energy change in the system under pearling deformation. We use the standard Debye-Hückel (DH) approximation to describe interactions between the charged surfactant molecules. In this approximation, the only role of free ions in solution is to screen the Coulomb potential of a charged surfactant. In other words, the electrostatic potential due to a charged surfactant molecule at a distance r from it is

$$V^{\mathrm{DH}}(r) = e \exp(-\kappa r)/Dr, \quad (11)$$

where e is the charge of one surfactant molecule (without loss of generality, we assume the charge of the surfactant is positive, $D = 80$ is the dielectric constant of water), and κ is the inverse Debye-Hückel screening radius. If the concentration of monovalent ions in water solution is c_0, κ is given by

$$\kappa = \sqrt{8\pi c_0 e^2/Dk_B T}. \quad (12)$$

The deformation of the tube also leads to the redistribution of charged molecules (or charge relaxation). The degree of charge relaxation depends on the specific system. In this section, for simplicity we assume the relaxation of charged surfactant happens instantly and the distribution of surface charge is the equilibrium distribution with respect to a given shape of the tube. We return to this assumption in detail in the next section.

To find the equilibrium charge distribution $\sigma(z)$, which in turn enables us to calculate the change in the electrostatic energy, one needs to solve the DH equation for the electrostatic potential $V(\mathbf{r})$ in the system

$$\nabla^2 V(\mathbf{r}) = \kappa^2 V(\mathbf{r}) \quad (13)$$

self-consistently with the boundary condition that the electric field at the tube surface is $2\pi\sigma(z)$ and the surface charge is at a constant potential. In this paper, we use a simpler approach. Namely, we use a variational approach to calculate the electrostatic energy. Assuming the following ansatz for the charge distribution of the deformed tube,

$$\sigma(z) = \bar{\sigma}[1 + x \cos(kz)], \quad (14)$$

we optimize the electrostatic energy of the tube with respect to the variational parameter x. As we shall see later, x is proportional to ε. This, coupled with the fact that for small deformation the response of the system is linear, the charge distribution obtained using variational approach is actually the true charge density of the system up to the second order in ε.

The conservation of the total charge of the tube,

$$\sigma_0 2\pi R_0 = \frac{k}{2\pi} \int_{-\pi/k}^{\pi/k} \int_0^{2\pi} dS(z,\phi)\sigma(z), \quad (15)$$

immediately gives for the average charge density $\bar{\sigma}$:

$$\bar{\sigma} \simeq \sigma_0 \left[1 + \frac{1 - (kR_0)^2}{4}\varepsilon^2 - \frac{x\varepsilon}{2} \right]. \qquad (16)$$

The electrostatic energy of the tube with surface charge density [Eq. (14)] is

$$E_e = \frac{1}{2} \int dS(z_1, \phi_1) dS(z_2, \phi_2) \sigma(z_1) \sigma(z_2)$$
$$\times V^{\mathrm{DH}}[d(z_1, z_2, \phi_1, \phi_2)], \qquad (17)$$

where the distance $d(z_1, z_2, \phi_1, \phi_2)$ between the two points (z_1, ϕ_1) and (z_2, ϕ_2) on the tube surface is

$$d^2(z_1, z_2, \phi_1, \phi_2) = (z_1 - z_2)^2 + R^2(z_1) + R^2(z_2)$$
$$- 2R(z_1)R(z_2)\cos(\phi_1 - \phi_2). \qquad (18)$$

Substituting Eqs. (6), (11), (14), (16), and (18) into Eq. (17), and expanding the integrand to second order in ε (x and ε are of the same order of smallness), one obtains the following expression for the electrostatic energy per unit length of the tube after integration:

$$E_e \simeq \frac{2\pi\sigma_0^2 R_0^2}{D}(a_0 + \varepsilon^2 a + \varepsilon b x + c x^2), \qquad (19)$$

where the coefficients a_0, a, b, and c are

$$a_0 = 2\pi I_0(\kappa R_0) K_0(\kappa R_0),$$

$$c = \pi I_0(\sqrt{\kappa^2 + k^2}R_0) K_0(\sqrt{\kappa^2 + k^2}R_0),$$

$$a = c + \left(\frac{R_0^2}{4}\frac{\partial^2}{\partial R_0^2} + \frac{3R_0}{4}\frac{\partial}{\partial R_0} \right)\left(\frac{a_0}{2} + c \right)$$

$$+ \frac{\sqrt{\pi}\kappa R_0}{4} G_{13}^{21}\left(\kappa^2 R_0^2 \left|\begin{array}{c} 1 \\ \frac{1}{2}, \frac{1}{2}, \frac{-1}{2} \end{array}\right. \right)$$

$$- \frac{\sqrt{\pi(k^2 + \kappa^2)}R_0}{4} G_{13}^{21}\left[(k^2 + \kappa^2) R_0^2 \left|\begin{array}{c} 1 \\ \frac{1}{2}, \frac{1}{2}, \frac{-1}{2} \end{array}\right. \right]$$

$$+ \frac{\sqrt{\pi}\kappa R_0}{2} G_{13}^{21}\left(\kappa^2 R_0^2 \left|\begin{array}{c} 0 \\ \frac{-1}{2}, \frac{1}{2}, \frac{-1}{2} \end{array}\right. \right)$$

$$- \frac{\sqrt{\pi(k^2 + \kappa^2)}R_0}{2} G_{13}^{21}\left[(k^2 + \kappa^2) R_0^2 \left|\begin{array}{c} 0 \\ \frac{-1}{2}, \frac{1}{2}, \frac{-1}{2} \end{array}\right. \right]$$

$$b = 2c + R_0 \frac{\partial}{\partial R_0}\left(\frac{a_0}{2} + c \right), \qquad (20)$$

I_0 and K_0 are the modified Bessel functions of zeroth order, and

$$G_{pq}^{mn}\left(x \left|\begin{array}{c} a_r \\ b_s \end{array}\right. \right)$$

is the Meijer's G-function [14].

Minimizing the electrostatic energy [Eq. (19)] with respect to x, one gets for x and the electrostatic energy change per unit length:

$$x = -\varepsilon b/2c.$$

$$\Delta E_e = E_e - \frac{2\pi\sigma_0^2 R_0^2}{D}a_0 = \varepsilon^2 \frac{2\pi\sigma_0^2 R_0^2}{D}\left[a - \frac{b^2}{4c} \right]. \qquad (21)$$

As expected, x is of the same order of smallness as ε. This is consistent with the starting assumption we use in the expansion [Eq. (19)].

If the charged surfactant molecules do not relax to equilibrium surface distribution, their density remains constant under the deformation, $x=0$. From Eq. (19), the change in the electrostatic energy in this case is given by

$$\Delta E_e^{\mathrm{norel}} = \varepsilon^2 \frac{2\pi\sigma_0^2 R_0^2}{D}a. \qquad (22)$$

Correspondingly, the energy change due to the relaxation of charged surfactants comes from the two x-dependent terms in Eq. (19):

$$\Delta E_e^{\mathrm{rel}} = -\varepsilon^2 \frac{2\pi\sigma_0^2 R_0^2}{D}\frac{b^2}{4c}. \qquad (23)$$

As one sees from Eq. (20), c is a positive coefficient. Thus, the relaxation energy is negative as expected: electrostatic relaxations lower the cost of deforming a tube into pearls.

IV. DISCUSSION

In this section, we comment on the relative importance of various energies in the system starting with the electrostatic energy and the contribution coming from the relaxation of charged molecules given by Eqs. (21) and (23). To gain a better physical insight into these equations, it is instructive to consider the strong screening case, $\kappa \gg k$ and $\kappa R_0 \gg 1$ and expand the energies in powers of $1/\kappa R_0$. For $\Delta E_e^{\mathrm{norel}}$, the zeroth order term of the expansion is

$$\Delta E_e^{\mathrm{norel}(0)} \simeq -\frac{\pi^2 \sigma_0^2 \kappa^{-1} R_0}{2D}[(kR_0)^2 - 1]\varepsilon^2. \qquad (24)$$

It is easy to see that this energy behaves in the same way as the surface tension energy [Eq. (8)]. One, therefore, identifies the electrostatic contribution to the surface tension of the surfactant tube:

$$\alpha_e = -\pi\sigma_0^2 \kappa^{-1}/D. \qquad (25)$$

It is not surprising to see that, in the absolute value, this "electrostatic" surface tension is simply the electrostatic energy per unit area of a flat bilayer at the same charge density. The negative sign in this expression reflects the fact that electrostatic repulsions between charged surfactants prefer to increase the area of the surfactant bilayer. The total surface tension of the layer, of course, remains positive because of the nonelectrostatic interaction between surfactant molecules counterbalance this negative electrostatic contribution.

The next nonzero term of the expansion of $\Delta E_e^{\mathrm{norel}}$ is of second order in $1/\kappa R_0$:

$$\Delta E_e^{\mathrm{norel}(1)} \simeq \varepsilon^2 \frac{\pi^2 \sigma_0^2 \kappa^{-1} R_0}{16D} \frac{1}{(\kappa R_0)^2} \times \{[2 - 2(kR_0)^2]$$
$$+ [3 + 2(kR_0)^4 - (kR_0)^2]\}. \tag{26}$$

The first square bracket term simply adds a small correction, $\alpha_e/4(\kappa R_0)^2$, to the electrostatic surface tension energy. Comparing the second square bracket term with the bending energy change [Eq. (10)], one immediately identifies this term as the "electrostatic" bending energy change with the corresponding "electrostatic" bending rigidity given by

$$\gamma_e = \pi \sigma_0^2 \kappa^{-3}/4D. \tag{27}$$

This is positive and, within a constant numerical factor, agrees with the well-known expression [16] for γ_e calculated using other methods. Thus expanding the electrostatic energy with respect to the tube curvature $(1/\kappa R_0)$ in this near flat limit, one recovers all standard formulae for the "electrostatic" contributions to the elastic parameters (surface tension and bending rigidity) of the bilayer surface.

Also in this limit, the relaxation energy becomes, to the lowest order in $1/\kappa R_0$,

$$\Delta E_e^{\mathrm{rel}} \simeq -\varepsilon^2 \frac{\pi \alpha_e R_0}{16} \frac{(kR_0)^4}{(\kappa R_0)^4}. \tag{28}$$

Thus, the relaxation of charged molecules belongs to the fourth order or higher in the expansion with respect to the tube curvature. Since the electrostatic surface tension and the electrostatic bending energy are, correspondingly, the zeroth- and second-order terms in this expansion (the first-order term in the expansion vanishes because of the symmetry of the reference flat surface), charge relaxation energy gain is parametrically small compared to the electrostatic surface tension and bending energy in this limit and can be ignored. In other words, in this strong screening limit, the charge density of the surfactant bilayer can be considered uniform during the deformation of the tube.

In the opposite limit of very weak screening $(\kappa R_0 \ll 1)$, generally speaking, the electrostatic interaction is long range and is so large that linear analysis becomes invalid in a very short time after the instability develops and nonlinear terms must be included in describing the development of instability. This is, however, a very complicated task. This is why in literature one usually assumes the final (pearl-on-a-string) structure of instability as given and variationally minimizes its total energy to find its parameters (size, period). Nevertheless, for the discussion of the role of charge relaxation energy, one can still use the result of a linear analysis given by exact expression [Eq. (21)], which is valid at a very early time of instability.

Expanding the energies in powers of κR_0, for $k \geqslant \kappa$, to the lowest order in κR_0, we get

$$\Delta E_e^{\mathrm{rel}} = \varepsilon^2 \frac{2\pi^2 \sigma_0^2 R_0^2}{D} \frac{I_0(kR_0)[K_0(kR_0) - kR_0 K_1(kR_0)]^2}{K_0(kR_0)},$$

$$\Delta E_e = \varepsilon^2 \frac{2\pi^2 \sigma_0^2 R_0^2}{D} \left\{ \frac{(kR_0)^2}{2} \left[I_0(kR_0)K_0(kR_0) - I_1(kR_0)K_1(kR_0) \right. \right.$$
$$\left. - \frac{1}{2} \right] + \frac{I_0(kR_0)}{K_0(kR_0)} kR_0 K_1(kR_0)$$
$$\left. \times [K_0(kR_0) - kR_0 K_1(kR_0)] \right\}. \tag{29}$$

Since $k \geqslant \kappa$, all length scales are smaller than the screening radius and electrostatic interactions are not screened. Correspondingly, the energies are independent of κ, as shown by Eqs. (29).

For $k \ll \kappa$, we get to the second lowest order in κR_0 and k/κ:

$$\Delta E_e^{\mathrm{rel}} = \varepsilon^2 \frac{2\pi^2 \sigma_0^2 R_0^2}{D} \left\{ \ln \frac{\kappa R_0}{2} + (2 + \gamma_E) + \frac{1}{2}\frac{k^2}{\kappa^2} \right.$$
$$\left. - \frac{k^2}{\kappa^2} \frac{\gamma_E}{\ln(\kappa R_0/2)} \right\}$$

$$\Delta E_e = \varepsilon^2 \frac{2\pi^2 \sigma_0^2 R_0^2}{D} \left[1 - \frac{k^2}{\kappa^2} \frac{\gamma_E}{\ln(\kappa R_0/2)} \right]. \tag{30}$$

Here, $\gamma_E = 0.5772$ is the Euler's constant. For the latter case, we see that the relaxation energy is larger than the total electrostatic energy by a large logarithmic term, $\ln(\kappa R_0/2)$. This is because, the first expansion term which logarithmically diverges with $\kappa R_0 \to 0$ in the relaxation energy is exactly equal in magnitude and opposite in sign to the the first expansion term for the nonrelaxation energy. As a result, the total electrostatic energy, contains only the second- and higher-order expansion terms. Thus, it is parametrically smaller than either of these components. Obviously, within linear analysis, the inclusion of the relaxation energy is important in this limit to get the correct behavior of the electrostatic energy.

For the experimental situation of Fig. 1 and Ref. [5], where the screening radius, the tube radius, and the pearl size are comparable to each other, the screening is marginal. Therefore, one might ask whether or not charge relaxation still plays a significant role. To answer this question, we numerically evaluate the exact (within linear analysis) expressions Eqs. (22) and (23) for the $\Delta E_e^{\mathrm{norel}}$ and $\Delta E_e^{\mathrm{rel}}$, respectively.

In Fig. 3, we plot the ratio between the energy gained due to the relaxation of charged molecules and the total electrostatic energy change for different values of κR_0. The divergence of this ratio observed at about $kR_0 \simeq 1$ is because the total electrostatic energy change goes through zero at this wave vector. As one can see from this figure, for strong screening $\kappa R_0 > 1$, the relaxation energy contributes a small part of the total electrostatic energy, while for weak screening $\kappa R_0 < 1$, it contributes significantly to the total energy. However, for the marginal case $\kappa R_0 = 1$, which is more relevant to the experiments, the numerical result shows that the relaxation of charged molecules contributes about 20%, which is a small fraction. For smaller screening radius, the exponent of 4 in Eq. (28) quickly reduces the relaxation en-
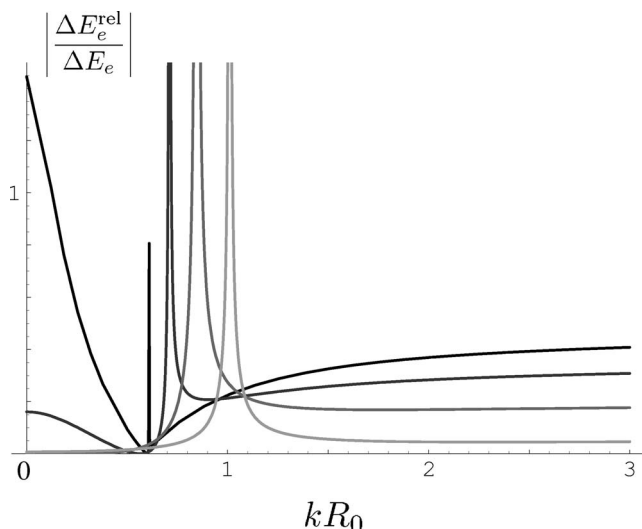
FIG. 3. The absolute value of the ratio between the electrostatic energy gain due to the relaxation of charged molecules to the total electrostatic energy when a tube deforms into a pearling structure as a function of the wave vector of deformation, kR_0 for $\kappa R_0 = 1$. Four different values of $\kappa R_0 = 0.1, 0.5, 1.0$, and 2.0, are used. Lighter curve corresponds to higher κR_0. The divergencies observed near $kR_0 \sim 1$ arise due to the vanishing of ΔE_e owing to Rayleigh instability.

ergy to an irrelevant contribution in the total energy. Thus, we conclude that in our experimental situation, electrostatic relaxation is a small effect and pearling of tubes is dominantly due to the surface tension induced Rayleigh instability.

In reference to the Rayleigh instability, we note that electrostatic surface tension (α_e) is a negative quantity (repulsions between charged molecules prefer to expand, not to reduce, the surface area of the tube). However, for the tube to be stable, the total surface tension (α) must be positive. This means the nonelectrostatic surface tension (α_0) has to be positive and greater than the electrostatic one (α_e) in magnitude. Thus, $|\alpha_e|$ is a good measure for estimating the relative importance of relaxation.

In our experiment, tubes are not observed to pearl in the presence of monovalent salt. The effect of monovalent salt is to reduce the magnitude of α_e. Based on our assumption that all surface tensions are of the same order of magnitude, α is also reduced, leading to the disappearance of pearling. (Quantitative calculation of the balance between various surface tensions requires detail understanding of the transition region that connects the tube to the collapsed lipid monolayer, which is beyond the scope of this paper.) In this context, we suggest that surface tension induced pearling is electrostatic in origin.

Before concluding, let us come back to the assumption made in the previous section that the surface charge is always in equilibrium with a given shape of the tube. To show that this is a reasonable assumption, let us estimate the charge relaxation of the surfactant bilayer. This can be done by viewing the tube as an RC circuit. For one typical wavelength $k^{-1} \simeq R_0$, the conductance of the circuit is the same as the conductivity: $\mathcal{R}^{-1} \simeq \sigma_0 e \mu$ with $\mu \simeq 10^9 \mathrm{m/sN}$ the mobility of the surfactant. Because all charges are screened at the distance κ^{-1}, the capacitance of this circuit is of the order $\mathcal{C} \simeq R^2 \kappa$. Thus, the relaxation time of this circuit (or of our surfactant tube) is of the order $(\mathcal{RC})^{-1} \simeq \sigma_0 e \mu / R^2 \kappa$, which is about 0.1 ms using experimental parameters. This is much smaller than the growth rate of the pearling instability (in seconds). Thus, the surfactant charges, to a good approximation, can be considered always in equilibrium.

V. CONCLUSION

We have considered the relaxation of charged surfactant as an additional factor in the pearling instability of surfactant tubes. It results from an extra degree of freedom available to binary mixtures. We have calculated this contribution exactly and compared it to the electrostatic surface tension. This gives a measure of the relative importance of relaxation and total surface tension in driving pearling.

For weak screening ($\kappa R_0 \ll 1$), the relaxation energy is larger than the total electrostatic energy by a logarithmic factor $\ln(\kappa R_0 / 2)$. For intermediate screening ($\kappa R_0 \approx 1$), it is about 20% of the total electrostatic energy. For strong screening ($\kappa R_0 \gg 1$), it decreases as the fourth power of $1/\kappa R_0$.

For biological systems such as surfactant tubes, relaxation can be a relevant factor for submicron length scales and can rapidly diminished by the addition of monovalent salt. In the domain of flowing microemulsions, where the tube diameters can get much smaller, relaxation may well play a more important role. These are interesting questions for the future.

[1] T. Shemesh, A. Luini, V. Malhotra, K. N. J. Burger, and M. M. Kozlov, Biophys. J. **85**, 3813 (2003).

[2] P. F. Devaux, Biochimie **82**, 497 (2000).

[3] S. Chaieb and S. Rica, Phys. Rev. E **58**, 7733 (1998).

[4] I. Tsafrir, D. Sagi, T. Arzi, M.-A. Guedeau-Boudeville, V. Frette, D. Kandel, and J. Stavans, Phys. Rev. Lett. **86**, 1138 (2001).

[5] A. Gopal, Ph.D. thesis, University of Chicago, 2004 (unpublished); A. Gopal, D. Wilson, T. T. Nguyen, and K. Y. C. Lee (unpublished).

[6] DPPC=Dipalmitoylphosphocholine, DMPC =Dimyristoylphosphocholine, and POPG =Palmitoyloleoylphosphoglycerol.

[7] It should be mentioned here that the observed tube structures can actually be ribbons of bilayer surfactant. However, there are no known examples of a ribbon structure undergoing pearling instability. This paper deals with pearling structures only. For these structures, we believe the original structures are cylindrical tubes.

[8] P. Nelson, T. Powers, and U. Seifert, Phys. Rev. Lett. **74**, 3384 (1995).

[9] L. Rayleigh, Proc. R. Soc. London **29**, 71 (1879); extension to viscous fluids: S. Tomotika, *ibid.* **150**, 322 (1935).

[10] A. V. Dobrynin, M. Rubinstein, and S. P. Obukhov, Macromolecules **29**, 2974 (1996); H. Schiessel and P. Pincus, Macromolecules **31**, 7953 (1998); A. V. Dobrynin and M. Rubinstein, *ibid.* **32**, 5673 (1999); C. E. Williams, in *Electrostatic Effects in Soft Matter and Biophysics*, edited by C. Holm, R. Kekicheff, and R. Podgornik (Kluwer Academic, Dordrecht, 2000).

[11] C. D. Santangelo and P. Pincus, Phys. Rev. E **66**, 061501 (2002).

[12] Ou-Yang Zhong-can and W. Helfrich, Phys. Rev. A **39**, 5280 (1989).

[13] See e.g., S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces, and Membranes* (Addison-Wesley, Reading, MA, 1994).

[14] For definition, see, e.g., I. S. Gradsteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products*, 5th ed. (Academic, New York, 1994).

[15] W. Häckl, U. Seifert, and E. Sackmann, J. Phys. II **7**, 1141 (1997).

[16] M. Winterhalter and W. Helfrich, J. Phys. Chem. **92**, 6865 (1988); H. N. W. Lekkerkerker, Physica A **159A**, 319 (1989); B. Duplantier, R. E. Goldstein, V. Romero-Rochin, and A. I. Pesci, Phys. Rev. Lett. **65**, 508 (1990); P. Pincus, J. F. Joanny, and D. Andelman, Europhys. Lett. **11**, 763 (1990).