Surface charge relaxation and the pearling instability of charged surfactant tubes

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The pearling instability of bilayer surfactant tubes was recently observed during the collapse of fluid monolayers of binary mixtures of DMPC–POPG and DPPC–POPG surfactants. We suggested it has the same physics as the well-known Raleigh instability under the action of the bilayer surface tension whose magnitude is dictated by the electrostatic interaction between charged surfactants. In this paper, we calculate the relaxation of charge molecules during the deformation of the tubes into pearling structure. We find the functional dependence of the relaxation energy on the screening length $\kappa^{-1}$ explicitly. Relaxation effect lowers the cost of bending a tube into pearls making the cylindrical tube even more unstable. It is known that for weak screening case where the tube radius is smaller than the screening length of the solution, this relaxation 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 this relaxation effect remains small. It gives less than 20% contribution to the total electrostatic energy.

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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 like material trafficking from the Golgi complex, and fusion and fission of membranes. 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.

Pearling has been induced in tubular phospholipid membranes by adsorption of oil or polymer, on the 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 (2D-3D transition) of fluid monolayers of mixed phospholipids. Collapse in binary monolayers of 7DPPC:3POPG and 7DMPC:3POPG lead to the formation of cylindrical tubes. These tubes can be 10s of microns in length, with diameters close to 1µm (limit of resolution). A few of these are wide enough to resolve detailed features. 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 above mentioned mechanisms of pearling instability is questionable for the present case.

In the same paper, we proposed that the pearling instability observed is due to a simpler mechanism. Namely, the instability is caused by the surface tension energy of the surfactant bilayer. This is very similar to the well-known Raleigh instability of cylinder of fluid. Indeed, because one type of surfactants used in experiments are POPG surfactant, a charged molecule, the surface tension of the bilayer should be, at least, of the same order of magnitude as the electrostatic energy per unit area of the tube. The latter is $\pi \sigma_0^2/\kappa D$ where $\sigma_0$ is the surface charge density of the bilayer, $\kappa$ 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 energy of a surfactant phospholipid bilayer is known 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 micron, 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 Raleigh instability of a fluid cylinder must be present for micron size tubes. For the case of a fluid 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 1mN/m) of the lipid bilayer.
pearled structure is obviously the most likely candidate for the final structure of this instability.

We note that electrostatic surface tension energy is a negative quantity (repulsions between charged molecules prefer to expand, not to reduce, the surface area of the tube). Therefore, it cannot be the driving force of instability. However, because the total surface tension of the bilayer must be positive, the presence of the negative surface tension forces the non-electrostatic surface tension to be positive and greater than the electrostatic one in magnitude. Quantitative calculation of the non-electrostatic surface tension from the balance between these energies requires the knowledge of the lateral compressibility of the bilayer and is presented in details in Ref. 5. It is shown that this non-electrostatic surface tension is of the same order of magnitude as the the electrostatic one, and thus, is much bigger than the bending energy. It is this non-electrostatic surface tension whose magnitude is dictated by the electrostatic counterpart which drives the tube towards pearling instability.

This explanation of pearling instability as a Raleigh instability due to electrostatic effect is supported further by the experimental observation that adding monovalent salt to the solution diminishes electrostatic energy and remove the instability of the cylinder. It is also observed that cylinders with smaller radius are more stable against pearling. This can be explained simply by the rapid increase of the elastic energy when the tube radius decreases.

There is another well known electrostatics-induced pearling instability in literature, namely, the pearls-on-string structure of polyelectrolyte in poor solvent or of polyampholytes. The physics behind these instabilities is different from that described above. Even though both instabilities are induced by electrostatic effects, 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 electrostatics energy and non-electrostatic energy (entropic or solvent-monomers interactions). This leads to the strong redistribution of the charge molecules (strong charge relaxation) in the system to lower its overall free energy, which is obviously not needed in the case of Raleigh instability. One expects charge relaxation is the driving force of pearling instability when screening of the solution is weak such that the Debye screening length is much larger than the pearl size. On the other hand when the screening is strong, the Debye screening length is much smaller than the pearl size, electrostatics is a short range interaction and the instability is of the dynamical Raleigh type.

In the experimental system of Ref. pure water is used. In this case, the screening radius of the system is comparable to the tube radius (about one micron). Thus, the situation is marginal, and it is not clear whether or not the relaxation of charge surfactants still plays a significant role in the pearling instability. In this paper, we would like to 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.

Even though the elastic (surface tension and bending) energy changes when a cylinder undergoes pearling deformation has been calculated 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:

$$E = E_s + E_b + E_o = \alpha \int dS +$$

$$+ \int dS[2\gamma H^2 + \bar{\gamma} K] + \delta p \int dV$$  \hspace{1cm} (1)

where $\gamma$ and $\bar{\gamma}$ are the bending rigidity and the Gaussian bending rigidity of the bilayer, $H$ and $K$ are the mean and Gaussian curvature of the tube surface, $\delta p$ is an osmotic pressure difference between the inner and outer region 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 $\alpha$, $\gamma$ and $\delta p$ (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 which minimizes the free energy, Eq. (1). This osmotic pressure term was also used by the authors of Ref. to

\[\text{II. ELASTIC ENERGY}\]

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study instability of cylindrical vesicles. A second choice for the model energy is to replace the osmotic pressure term in Eq. 11 by a line tension term, which has been used by the authors of Ref. 9 to study coiling instability in multilamellar tubes. Each of these models incorporates 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. 11, the surface tension and the osmotic pressure are actually Lagrangian multipliers which 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:

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

(2)

![FIG. 2: A cylindrical tube is deformed radially with wavevector \( k \).](image)

Due to the small permeability of water through the bilayer surface, in our model, we require that the tube volume does 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:

\[
V = \frac{k}{2\pi} \pi \int_{-\pi/k}^{\pi/k} dz \int_0^{R(z)} 2\pi r dr = \pi \bar{R}^2 (1 + \varepsilon^2/2)
\]  

(3)

The condition of volume conservation then leads to the simple relation:

\[
\bar{R} = R_0/\sqrt{1+\varepsilon^2/2} \simeq R_0 (1 - \varepsilon^2/4)
\]  

(4)

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

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

(5)

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

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

(6)

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:

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

(7)

Let us next calculate the change in the bending energy. Because the Gaussian curvature energy \( \gamma \int dAK \) is a topological invariant quantity and we do not change the topology of the tube, this energy does not change. For the mean curvature, standard geometry consideration of the tube surface gives:

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

(8)

Substituting Eq. 9 into the expression for bending energy (the second term in Eq. 11), and keeping terms up to second order in \( \varepsilon \), one obtains for the bending energy change:

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

(9)

### 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

\[
V^{DH}(r) = \frac{e}{\kappa r} / Dr,
\]  

(10)

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 \( \kappa \) is the inverse Debye-Hückel screening radius. If the concentration of monovalent ions is water solution is \( c_0 \), \( \kappa \) is given by:

\[
\kappa = \sqrt{8\pi c_0 e^2 / Dk_B T}
\]  

(11)
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, $V(r)$, in the system

$$\nabla^2 V(r) = \kappa^2 V(r)$$

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:

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

we optimize the electrostatic energy of the tube with respect to the variational parameter $x$. As we shall see later, $x$ is proportional to $\varepsilon$. 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 $\varepsilon$.

The conservation of the total charge of the tube:

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

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

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

The electrostatic energy of the tube with surface charge density, Eq. (13), is:

$$\begin{align*}
E_e &= \frac{1}{2} \int dS(z_1, \phi_1) dS(z_2, \phi_2) \sigma(z_1) \sigma(z_2) \times V^{DH}[d(z_1, z_2, \phi_1, \phi_2)] \\
&= \frac{2\pi \sigma_0^2 R_0^2}{D} (a_0 + \varepsilon^2 a + \varepsilon b x + c x^2)
\end{align*}$$

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

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

Substituting Eq. (16) and (17) into Eq. (15), and expanding the integrand to second order in $\varepsilon$ ($x$ and $\varepsilon$ are of the same order of smallness), one obtains the following expression for the electrostatic energy per unit length of the tube after integration:

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

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

$$\begin{align*}
a_0 &= 2\pi I_0(\kappa R_0)K_0(\kappa R_0), \\
b &= 2c + R_0 \frac{\partial}{\partial R_0} \left( \frac{a_0}{2} + c \right), \\
c &= \pi I_0 \left( \sqrt{\kappa^2 + k^2 R_0} \right) K_0 \left( \sqrt{\kappa^2 + k^2 R_0} \right), \\
a &= c + \left( \frac{R_0^2}{4} \frac{\partial^2}{\partial R_0^2} + \frac{3R_0}{4} \frac{\partial}{\partial R_0} \right) \left( \frac{a_0}{2} + c \right) + \\
&\quad + \frac{\sqrt{\pi} \kappa R_0}{4} G_{13}^{21} \left( \kappa^2 R_0^2 \left[ \frac{1}{2}, \frac{1}{2}, \frac{-1}{2} \right] \right) \\
&\quad - \frac{\sqrt{\pi} (k^2 + \kappa^2) R_0}{4} G_{13}^{21} \left( (k^2 + \kappa^2) R_0^2 \left[ \frac{1}{2}, \frac{1}{2}, \frac{-1}{2} \right] \right) \\
&\quad + \frac{\sqrt{\pi} \kappa R_0}{2} G_{13}^{21} \left( \kappa^2 R_0^2 \left[ 0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right] \right) \\
&\quad - \frac{\sqrt{\pi} (k^2 + \kappa^2) R_0}{2} G_{13}^{21} \left( (k^2 + \kappa^2) R_0^2 \left[ 0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right] \right)
\end{align*}$$

$I_0$ and $K_0$ are the modified Bessel functions of zeroth order and $G_{pq}^{mn}$ is the Meijer’s G function.

Minimizing the electrostatic energy, Eq. (18), with respect to $x$, one gets for $x$ and the electrostatic energy change per unit length:

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

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

As expected, $x$ is of the same order of smallness as $\varepsilon$. This is consistent with the starting assumption we use in the expansion, Eq. (15).

If the charged surfactant molecules do not relax to equilibrium surface distribution, their density remains constant under the deformation, $x = 0$. From Eq. (18), the change in the electrostatic energy in this case is given by:

$$\Delta E_{enrel} = \varepsilon^2 \frac{2\pi \sigma_0^2 R_0^2}{D} a$$

Correspondingly, the energy change due to the relaxation of charged surfactants comes from the two $x$-dependent terms in Eq. (18):

$$\Delta E_{erel} = -\varepsilon^2 \frac{2\pi \sigma_0^2 R_0^2}{D} \frac{b^2}{4c}$$

As one sees from Eq. (15), $c$ 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 electrostatics energy and the contribution coming from the relaxation of charge molecules given by Eq. (20) and Eq. (22). 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 \( \Delta E_{c}^{\text{rel}} \), the zeroth order term of the expansion is

\[
\Delta E_{c}^{\text{rel}} (0) \simeq -\frac{\pi^2 \sigma_0^2 \kappa^{-1} R_0}{2D} \left[(kR_0)^{2} - 1\right] \varepsilon^2,
\]

(23)

It is easy to see that this energy behaves in the same way as the surface tension energy, Eq. (7). One, therefore, identifies the electrostatic contribution to the surface tension of the surfactant tube:

\[
\alpha_c = -\pi \sigma_0^2 \kappa^{-1}/D.
\]

(24)

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 non-electrostatic interaction between surfactant molecules counter-balance this negative electrostatic contribution.

The next non-zero term of the expansion of \( \Delta E_{c}^{\text{rel}} \) is of second order in \( 1/\kappa R_0 \):

\[
\Delta E_{c}^{\text{rel}} (1) \simeq \varepsilon^2 \frac{\pi^2 \sigma_0^2 \kappa^{-1} R_0}{16D} \frac{1}{(kR_0)^2} \times \left\{ \left[2 - 2(kR_0)^2\right] + \left[3 + 2(kR_0)^4 - (kR_0)^2\right] \right\}.
\]

(25)

The first square bracket term simply adds a small correction, \( \alpha_c/4(\kappa R_0)^2 \), to the electrostatic surface tension energy. Comparing the second square bracket term with the bending energy change, Eq. (9), one immediately identifies this term as the "electrostatic" bending energy change with the corresponding "electrostatic" bending rigidity given by

\[
\gamma_{e} = \pi \sigma_0^2 \kappa^{-3}/4D.
\]

(26)

It is positive and, within a constant numerical factor, agrees with the well-known expression for \( \gamma_{e} \) 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 \( 1/\kappa R_0 \):

\[
\Delta E_{c}^{\text{rel}} \simeq -\varepsilon^2 \frac{\pi \alpha_c R_0}{16} \frac{(kR_0)^4}{(kR_0)^4}.
\]

(27)

Thus, the relaxation of charged molecules belong 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 is given and variationally minimized 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 a linear analysis given by exact expression, Eq. (20), which is valid at a very early time of instability.

Expanding the energies in powers of \( \kappa R_0 \), for \( k \geq \kappa \), we get to the lowest order in \( \kappa R_0 \):

\[
\Delta E_{c}^{\text{rel}} = \varepsilon^2 \frac{2\pi^2 \sigma_0^2 R_0^2}{D} \frac{I_0(kR_0)}{K_0(kR_0)} \left[ K_0(kR_0) - kR_0 K_1(kR_0) \right]^2
\]

\[
\Delta E_{c} = \varepsilon^2 \frac{2\pi^2 \sigma_0^2 R_0^2}{D} \left\{ \frac{(kR_0)^2}{2} \left[ \frac{I_0(kR_0) K_0(kR_0) - I_1(kR_0) K_1(kR_0)}{K_0(kR_0) - kR_0 K_1(kR_0)} \right] - \left[ K_0(kR_0) - kR_0 K_1(kR_0) \right] \right\}.
\]

(28)

Since for \( k \geq \kappa \), all length scales are smaller than the screening radius and electrostatic interactions are not screened. Correspondingly, the energies are independent of \( \kappa \) as shown by the above equation (28).

For \( k \ll \kappa \), we get to the second lowest order in \( \kappa R_0 \) and \( k/\kappa \):

\[
\Delta E_{c}^{\text{rel}} = \varepsilon^2 \frac{2\pi^2 \sigma_0^2 R_0^2}{D} \left\{ \ln \frac{kR_0}{2} + (2 + \gamma_E) + \frac{1}{2} \frac{k^2}{\kappa^2} \frac{\ln(\kappa R_0/2)}{\gamma_E} \right\}
\]

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

(29)

Here \( \gamma_E = 0.5772 \) is the Euler’s constant. For the later 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 first expansion term for the non-relaxation 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 behaviour of the electrostatic energy.

For the experimental situation of Ref. 5 where the screening radius, the tube radius and the pearl size are comparable to each other, the situation is marginal. Therefore, one might ask whether or not the charge relaxation still plays a significant role. To answer this question, we numerically evaluate the exact (within linear analysis) expressions, Eqs. (21) and (22), for the $\Delta E^\text{nonrel}$ and $\Delta E^\text{rel}$, 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 $\kappa R_0$. The divergence of this ratio observed at about $kR_0 \sim 1$ is due to the vanishing of $\Delta E^\text{rel}$ owing to Raleigh instability.

We have considered the relaxation of charged surfactant in the pearling instability for surfactant tubes observed in the experiments of Ref. 3. This effect is known to be the main driving force for pearling instability of polyelectrolytes in poor solvent for which screening is very weak. Using linear analysis, we showed that for the marginal situation of Ref. 3, the effect is small and the pearling instability is mainly due the Raleigh stability caused by the surface tension of the bilayer.

Charge relaxation becomes important only for weak screening such that $\kappa R_0 \ll 1$. In this limit, in our linear analysis, the relaxation energy is larger than the total electrostatic energy by a logarithmic factor, $\ln(\kappa R_0/2)$. For very weak screening condition, its inclusion is a must if one wants to obtain the correct behaviour of electrostatic energy. Thus, although charge relaxation plays small role in the biological phenomena of Ref. 3, it might well play a role in the domain of flowing microemulsions, where the tube diameters are much smaller.

V. CONCLUSION

We have considered the relaxation of charged surfactant in the pearling instability for surfactant tubes observed in the experiments of Ref. 3. This effect is known to be the main driving force for pearling instability of polyelectrolytes in poor solvent for which screening is very weak. Using linear analysis, we showed that for the marginal situation of Ref. 3, the effect is small and the pearling instability is mainly due the Raleigh instability caused by the surface tension of the bilayer.

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![Figure 3](image_url)
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