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# Electrohydrodynamic instability of a charged membrane

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The stability of shape fluctuations of a flat charged membrane immersed in a fluid is analyzed using a linear stability analysis. A displacement of the membrane surface causes a fluctuation in the conterion density at the surface. This in turn causes an additional contribution to the force density in the momentum equation for the fluid, which results in a normal stress at the surface which is opposite in direction to the stress caused by surface tension. This electrohydrodynamic effect destabilizes fluctuations when the surface potential exceeds a critical value.

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## I. INTRODUCTION

Two of the salient features of surfaces encountered in biological systems, such as cell membranes and organelles, are that they are soft and they can undergo shape changes, and they have adsorbed charges. It is well known [1] that significant variations in the charge distribution and the transmembrane potential of membranes coincide with shape changes. There has also been experimental evidence to indicate that the variation in charge densities could be important in influencing the shapes of vesicles made of lipid bilayers. Vesicles are usually made under nonequilibrium conditions, because the bending energy for the formation of a vesicle of micron size is large compared to the thermal energy. However, some interesting experimental results [2] have revealed that stable vesicles could be made at equilibrium if a mixture of lipids with surface charges of opposite signs are used.

Previous studies have examined the shape changes of biological membranes due to forces exerted by ion transport in proteins, due to the asymmetry of inclusions in the membrane and their phase separation on the surface, and due to other nonequilibrium processes [3]. Though most of the studies on biological membranes have examined fluctuations at thermal equilibrium [4], it has recently been realized that the forces generated on membranes by inclusions could play a crucial role in the structure and dynamics of membranes. These could be in the form of proteins with head-tail asymmetry, which induce a spontaneous growth of fluctuations in the membrane [5]. In addition, phase separation of the components of a membrane could also alter the shape [6,7]. However, it is expected that effects like head-tail asymmetry would lead to structures with characteristic lengths of the same magnitude as the domains on the surface, whereas typical sizes of vesicles could be two to three orders of magnitude larger than the membrane thickness. Since shape changes in biological membranes are accompanied by changes in the transmembrane potential, it is useful to examine whether shape changes of flexible charged surfaces could be caused by changes in the surface potential. As a first step, the present study examines the stability of fluctuations on a charged surface as a function of the surface potential.

Ion transport processes in cells are fairly complicated, but simple models of these processes [8–10] have shown that there is an electro-osmotic instability. However, this requires the active transport of ions by ion pumps such as proteins in order to generate an ion current. The transport of ions across the cell membrane also exerts a force on the fluid, the results of which could destabilize fluctuations if the ion pumps are permitted to diffuse on the surface [5]. A redistribution of charges occurs on charged vesicles under externally applied fields [11], and this surface redistribution has a significant effect on the mobility of the vesicles, and could even cause it to change sign. In addition, a spatial variation of charges on a surface could result in a net force in the presence of an electric field [12]. There has also been recent work on the interaction between macroscopically neutral surfaces due to charge fluctuations [13], though these do not incorporate the fluid velocity field or the deformability of the membrane. The interfacial instability between two immiscible fluids due to an electric field has also been studied [14].

The effect of charges on the elasticity of membranes has been studied by many authors. The early studies of Winterhalter and Helfrich [15] and Lekkerkerker [16], as well as the subsequent studies [17,18], found that there is an increase in the elasticity due to adsorbed charges. These studies show that there is a change in the modulus for the mean curvature and the Gaussian curvature due to adsorbed charges, and the change in the Gaussian curvature could favor the spontaneous formation of vesicles. In these studies the change in the electrostatic energy due to the curvature of the membrane is determined, and the corrections to the elasticity moduli are calculated from the free energy change. The corrections to the elastic moduli are manifested as additional contributions to the curvature energy when a net curvature is imposed on the membrane. In the present analysis, we are interested in the dynamical stability of the flat state of the membrane, and the perturbations are in the form of Fourier modes. The effect of the electrostatic stress on the perturbations in the membrane surface is determined. The connection between the two approaches was demonstrated in Winterhalter and Helfrich [15], where the Gaussian curvature was related to the second moment of the stress profile in a flat membrane. It was shown that within the Debye-Huckel approximation, the two approaches provide the same result for the Gaussian curvature. In the present analysis also, we verify that the same result for the Gaussian curvature is obtained in the Debye-Huckel approximation to show consistency with previous results.

It has been shown [19] that a difference in the charge densities in the two lipid layers forming a bilayer could stabilize a vesicle, because there is a reduction in electrostatic energy when the higher charge density is on the outside of the vesicle. This could compensate for the increase in the curvature energy. The effect of charge density-curvature coupling on the dynamics of fluctuations on a charged surface were analyzed [20]. The analysis showed that when the charges are permitted to move on the membrane surface, there is an instability of the flat state of the membrane due to a correlated variation in the charge density and the curvature. However, this analysis assumed that the thickness of the counterion layer at the surface is small compared to the wavelength of the perturbations, and variations in the counterion density parallel to the surface were neglected.

It is important to note that the wavelength of perturbations in this case is of the same magnitude as the thickness of the counterion layer near the surface. The counterion layer thickness under physiological conditions is about 1 nm [10], which is small compared to the length scale of structures such as vesicles. The present analysis predicts that the most unstable mode for a flat membrane has zero wave number, indicating that the most unstable mode for a system of finite size is likely to be the size of the system itself. However, the selection of the most unstable mode is likely to depend very sensitively on the surface potential when the size of the structure is large compared to the thickness of the couterion layer. There are other situations where the thickness of the counterion layer could increase to 1 $\mu$m when the salt concentration is decreased, and the results of the present analysis would be directly applicable in those cases.

In the present analysis, the variation in the counterion density parallel to the surface is incorporated by solving the diffusion equation for the counterions. A linear stability analysis is used, where the parameter values for the transition from stable to unstable modes is determined. The linear stability analysis only provides the transition from damped to growing modes, and does not provide information about the nonlinear stabilization of the growing modes. First, the limit of zero Peclet number and zero Reynolds number is considered, where the diffusion of counterions is fast compared to convective transport, and the inertial terms in the momentum conservation equation are neglected. However, it is subsequently shown that the analysis is valid even at finite Reynolds and Peclet numbers, because the inertial and convective terms in the equations for the charge density and fluid momentum are zero for the unstable modes. The limit of low Reynolds number is appropriate for micron scale structures in biological systems. The validity of the zero Peclet number limit can be estimated as follows. The diffusion of a small molecule in a liquid is $O(10^{-9}\ \mathrm{m}^2/\mathrm{s})$, and the Peclet number $(UL/D)$ is small for structures of micron scales $L \sim 10^{-6}$ m if the velocity scale is smaller than $10^{-3}$ m/s. For membranes with surface tension and in the absence of fluid inertia, a characteristic velocity scale can be estimated as $(\Gamma/\mu)$, where $\Gamma$ is the surface tension and $\mu$ is the viscosity. The viscosity of water is $O(10^{-3}\ \mathrm{kg/m/s})$, and therefore the velocity is small compared to $10^{-3}$ m/s for $\Gamma < 10^{-6}\ \mathrm{kg/m/s}^2$. This is about three orders of magnitude less than the surface tension of an air-water interface, and therefore the present analysis is likely to be applicable only for membranes with very low tension.

In the analysis, we assume that the charge densities on the two sides of the membrane are decoupled. This is valid when the dielectric constant of the hydrophobic tails in the lipid layer is small compared to the dielectric constant of the surrounding water. In practical situations, the ratio is about $(1/40)$, so the approximation is valid for distances about 40 times the bilayer thickness [15]. Though this is not strictly true in cases where the dielectric constants are comparable, we use this as a first approximation to make the problem analytically tractable.

## II. BASE STATE CHARGE DISTRIBUTION

In the following analysis, dimensional variables are denoted with a superscript *, while dimensionless variables are written without the superscript in order to simplify the notation. The potential and charge distribution in the base state are determined by solving the conservation equation for the two charged species with number densities $n^*_+$ and $n^*_-$,

$$d_t n^*_+ + \mathbf{v}^* \cdot \nabla^* n^*_+ = \nabla^* \cdot D\left[\nabla^* n^*_+ + \frac{zen^*_+}{T}\nabla^*\psi^*\right], \quad (1)$$

$$d_t n^*_- + \mathbf{v}^* \cdot \nabla^* n^*_- = \nabla^* \cdot D\left[\nabla^* n^*_- - \frac{zen^*_-}{T}\nabla^*\psi^*\right], \quad (2)$$

where the potential $\psi^*$ is given by

$$\nabla^{*2}\psi^* = -\left(\frac{zen^*_+}{\epsilon} - \frac{zen^*_-}{\epsilon}\right), \quad (3)$$

where $\nabla^*$ is the dimensional gradient operator, $e$ is the charge on an electron, and $\epsilon$ is the dielectric constant. The equations are simplified by defining the nondimensional variables $n_+ = (n^*_+/N^*_\infty)$, $n_- = (n^*_-/N^*_\infty)$, $\psi = (ze\psi^*/T)$, and $\mathbf{x} = \kappa\mathbf{x}^*$. Here, $N^*_\infty$ is the concentration of the electrolyte at a large distance from the surface, and the inverse of the Debye screening length $\kappa$ is $(2N^*_\infty z^2 e^2/\epsilon T)^{1/2}$. With these scalings, the equations reduce to

$$Pe(d_t n_+ + \mathbf{v}\cdot\nabla n_+) = \nabla\cdot[\nabla n_+ + n_+\nabla\psi], \quad (4)$$

$$Pe(d_t n_- + \mathbf{v}\cdot\nabla n_-) = \nabla\cdot[\nabla n_- - n_-\nabla\psi] \quad (5)$$

and the potential $\psi$ is given by

$$\nabla^2\psi = -\left(\frac{n_+ - n_-}{2}\right). \quad (6)$$

In the above equations, the velocity has been scaled by a characteristic velocity scale $\mathbf{v} = (\mathbf{v}^*/V)$, and the Peclet number is given by $Pe = (V/\kappa D)$. In the present analysis, we consider the limit $Pe \ll 1$, and neglect the terms on the left-hand side of Eqs. (4) and (5). The extension to the finite

Peclet number case is briefly discussed at the end. With this assumption, the dimensionless equations for the charge concentrations become

$$\nabla \cdot [\nabla n_{+} + n_{+} \nabla \psi] = 0, \tag{7}$$

$$\nabla \cdot [\nabla n_{-} - n_{-} \nabla \psi] = 0, \tag{8}$$

$$\nabla^2 \psi = -\left( \frac{n_{+} - n_{-}}{2} \right). \tag{9}$$

In the base state, there are concentration and potential variations only in the $y$ direction perpendicular to the surface of the membrane. The equations for the charge concentration and potential in the base state, $N_{+}$, $N_{-}$, and $\Psi$, are

$$d_y N_{+} + N_{+} d_y \Psi = 0, \tag{10}$$

$$d_y N_{-} - N_{-} d_y \Psi = 0, \tag{11}$$

$$d_y^2 \Psi = -\left( \frac{N_{+} - N_{-}}{2} \right). \tag{12}$$

The above equations can be easily simplified to provide the Poisson-Boltzmann equation for the potential

$$d_y^2 \Psi = -\frac{\exp(-\Psi) - \exp(\Psi)}{2}. \tag{13}$$

It is difficult to obtain an analytical solution for this equation, but a series solution of the following form can be easily obtained:

$$\Psi = \sum_{i=0}^{\infty} \Psi_i \exp(-iy), \tag{14}$$

where the coefficients $\Psi_i$ are determined by inserting the above expansion into the Poisson-Boltzmann equation (14) and evaluating the coefficients for each value of $i$. The coefficient $\Psi_0$ can be set equal to zero without loss of generality, since the charge dynamics is affected only by the gradients of the potential. With this, it is easily verified that $\Psi_i = 0$ for all even values of $i$. In the Debye-Huckel approximation, only the first term (corresponding to $i = 1$) is retained in the above expansion (14). In the present analysis, higher-order terms are also retained in the expansion, typically up to $i = 5$. There is a difference of about 2% when $i$ is increased from 1 to 5 for $\Psi_s = 1$, and a difference of about 15% at $\Psi_s = 2$, where $\Psi_s$ is the scaled surface potential.

The charge densities are easily determined from Eqs. (10) and (11) once the potential is known. It is convenient to represent the charge densities in terms of $R = (N_{+} + N_{-})/2$ and $Q = (N_{+} - N_{-})/2$, where $Q$ is determined from the Poisson-Boltzmann equation

$$Q = \sum_{i=0}^{\infty} Q_i \exp(-iy), \tag{15}$$

where

$$Q_i = -i^2 \Psi_i. \tag{16}$$

It can easily be verified that all coefficients $Q_i$ for even values of $i$ are zero, since $\Psi_i = 0$ for even values of $i$. The total charge is determined from the relation

$$d_y R + Q d_y \Psi = 0. \tag{17}$$

Using Eq. (13) for $\Psi$ and Eq. (16) for $Q$, the equation for the total charge is

$$R = R_\infty + \sum_i R_i \exp(-iy), \tag{18}$$

where $R_\infty$, the scaled ion concentration at a large distance from the surface, is 1, $R_0 = R_1 = 0$, and

$$R_i = -\sum_{j=0}^{i} \frac{(i-j) Q_j \Psi_{i-j}}{i} \tag{19}$$

for $i \geq 2$. In the Debye-Huckel approximation, where the right side of Eq. (13) is linearized in the potential $\Psi$, the solutions for the scaled charge densities and potential are

$$\Psi = \Psi_s \exp(-y),$$
$$Q = -\Psi_s \exp(-y), \tag{20}$$
$$R = 1,$$

where $\Psi_s$ is the potential at the surface of the membrane.

At this point, it is useful to compare the present results with those of Winterhalter and Helfrich [15] for the Debye-Huckel approximation. Expressions (20) are identical to those obtained by Winterhalter and Helfrich for the Debye approximation. The normal pressure due to electrical effects can be determined from the static momentum balance equation for the liquid

$$-d_y P - Q d_y \Psi = 0, \tag{21}$$

where $P$ is the mean pressure. The above equation is easily solved to get

$$P = \tfrac{1}{2} \Psi^2 \tag{22}$$

for the Debye-Huckel approximation, which is the scaled form of Eq. (18) of Winterhalter and Helfrich for the osmotic pressure at the surface. This can be used to recover the Gaussian curvature obtained by Winterhalter and Helfrich.

## III. CHARGE FLUCTUATIONS

In the linear analysis, small perturbations are placed on the concentration and potential fields

$$n_{+} = N_{+} + \tilde{n}_{+}(y) \exp(\imath k x + s t),$$
$$n_{-} = N_{-} + \tilde{n}_{-}(y) \exp(\imath k x + s t), \tag{23}$$
$$\psi = \Psi + \tilde{\psi}(y) \exp(\imath k x + s t),$$

where $s$ is the growth rate and $k$ is the wave number of the perturbations. These are inserted into Eqs. (7), (8), and (9), and linearized in order to obtain the following equations for the perturbations to the concentration and potential fields:

$$(d_y^2-k^2)\tilde{r}-2\tilde{q}Q+(d_yQ)(d_y\tilde{\psi})+(d_y\tilde{q})(d_y\Psi)=0, \tag{24}$$

$$(d_y^2-k^2)\tilde{q}-\tilde{r}Q-\tilde{q}R+(d_yR)(d_y\tilde{\psi})+(d_y\tilde{r})(d_y\Psi)=0, \tag{25}$$

$$(d_y^2-k^2)\tilde{\psi}=-\tilde{q}, \tag{26}$$

where $\tilde{r}=(\tilde{n}_+ + \tilde{n}_-)/2$ and $\tilde{q}=(\tilde{n}_+ - \tilde{n}_-)/2$. Equations (24), (25), and (26) are the governing equations for the perturbation fields $\tilde{r}$, $\tilde{q}$ and $\tilde{\psi}$.

Solutions for Eqs. (24), (25), and (26) are difficult to obtain analytically, but it is possible to obtain series solutions similar to Eqs. (14), (15), and (18),

$$\tilde{\psi}=\sum_{i=0}^{\infty}\tilde{\psi}_i^{(1)}\exp(-(k+i)y]+\sum_{i=0}^{\infty}\tilde{\psi}_i^{(2)}\exp[-(l+i)y],$$

$$\tilde{\psi}_0^{(1)}=\tilde{\psi}_0,$$

$$\tilde{\psi}_0^{(2)}=-\tilde{q}_0,$$

$$\tilde{r}=\tilde{r}_0\exp(-ky)+\sum_{i=1}^{\infty}\tilde{r}_i^{(1)}\exp[-(k+i)y] \tag{27}$$

$$+\sum_{i=1}^{\infty}\tilde{r}_i^{(2)}\exp[-(l+i)y],$$

$$\tilde{q}=\tilde{q}_0\exp(-ly)+\sum_{i=1}^{\infty}\tilde{q}_i^{(1)}\exp[-(k+i)y]$$

$$+\sum_{i=1}^{\infty}\tilde{q}_i^{(2)}\exp[-(l+i)y],$$

where $l=(k^2+1)^{1/2}$. The coefficients $\tilde{\psi}_0$, $\tilde{r}_0$, and $\tilde{q}_0$ are determined using the boundary conditions, while the other coefficients are determined using Eqs. (24), (25), and (26). The coefficients in the equations for $\tilde{\psi}$ and $\tilde{q}$ are easily related from Eq. (26),

$$\begin{aligned}\tilde{\psi}_i^{(1)}&=-\frac{\tilde{q}_i^{(1)}}{(k+i)^2-k^2},\\ \tilde{\psi}_i^{(2)}&=-\frac{\tilde{q}_i^{(2)}}{(l+i)^2-k^2}.\end{aligned} \tag{28}$$

The relations for the coefficients in the relations for $\tilde{q}$ and $\tilde{r}$ are obtained by inserting the expansions into Eqs. (24) and (25),

$$\begin{aligned}\tilde{q}_i^{(1)}&=\frac{1}{(i+k)^2-l^2}\Bigg[\sum_{j=0}^{i}[\tilde{r}_j^{(1)}Q_{i-j}+\tilde{q}_j^{(1)}R_{i-j}-(j+k)(i-j)\\ &\quad\times(\tilde{r}_j^{(1)}\Psi_{i-j}+\tilde{\psi}_j^{(1)}R_{i-j})]\Bigg],\\ \tilde{q}_i^{(2)}&=\frac{1}{(i+l)^2-l^2}\Bigg[\sum_{j=0}^{i}[\tilde{r}_j^{(2)}Q_{i-j}+\tilde{q}_j^{(2)}R_{i-j}-(j+l)(i-j)\\ &\quad\times(\tilde{r}_j^{(2)}\Psi_{i-j}+\tilde{\psi}_j^{(2)}R_{i-j})]\Bigg],\end{aligned} \tag{29}$$

$$\begin{aligned}\tilde{r}_i^{(1)}&=\frac{1}{(i+k)^2-k^2}\Bigg[\sum_{j=0}^{i}[2\tilde{q}_j^{(1)}Q_{i-j}-(j+k)(i-j)(\tilde{q}_j^{(1)}\Psi_{i-j}\\ &\quad+\tilde{\psi}_j^{(1)}Q_{i-j})]\Bigg],\\ \tilde{r}_i^{(2)}&=\frac{1}{(i+l)^2-k^2}\Bigg[\sum_{j=0}^{i}[2\tilde{q}_j^{(2)}Q_{i-j}-(j+l)(i-j)(\tilde{q}_j^{(2)}\Psi_{i-j}\\ &\quad+\tilde{\psi}_j^{(2)}Q_{i-j})]\Bigg].\end{aligned}$$

The recurrence relations can be solved to obtain the coefficients $\tilde{r}_i^{(1)}$, $\tilde{r}_i^{(2)}$, $\tilde{q}_i^{(1)}$, and $\tilde{q}_i^{(2)}$ as linear functions of the coefficients $\tilde{\psi}_0$, $\tilde{q}_0$, and $\tilde{r}_0$. These coefficients are fixed by the boundary conditions as discussed below.

The boundary conditions at the membrane surface for the ion concentration fields are the zero flux conditions for the two ionic species at the perturbed interface $y=u_y$, where $u_y$ is the vertical displacement of the membrane

$$\begin{aligned}[d_yn_+ + n_+d_y\psi]|_{y=u_y}&=0,\\ [d_yn_- - n_-d_y\psi]|_{y=u_y}&=0.\end{aligned} \tag{30}$$

In the linear approximation, the boundary conditions at the perturbed interface are expanded in a Taylor series about their values at the unperturbed interface $y=0$. The base state concentration and potential fields satisfy the zero flux condition at the unperturbed interface $y=0$. The correction to the boundary conditions due to fluctuations are determined by retaining terms correct to linear order in the perturbation quantities $\tilde{n}_+$, $\tilde{n}_-$, and $\tilde{u}_y$,

$$\begin{aligned}&\tilde{u}_y[d_y(d_yN_+ + N_+d_y\Psi)]|_{y=0}+[d_y\tilde{n}_+ + \tilde{n}_+d_y\Psi\\ &\quad+N_+d_y\tilde{\psi}]|_{y=0}=0,\\ &\tilde{u}_y[d_y(d_yN_- - N_-d_y\Psi)]|_{y=0}+[d_y\tilde{n}_- - \tilde{n}_-d_y\Psi\\ &\quad-N_-d_y\tilde{\psi}]|_{y=0}=0,\end{aligned} \tag{31}$$

where $\tilde{u}_y$ is defined by the relation $u_y = \tilde{u}_y \exp(ikx+st)$. The first term on the left sides of the boundary conditions (31) are proportional to the variations in the $y$ direction of the flux in the base state. Since the base state concentration and potential fields satisfy the zero flux conditions (10) and (11) throughout the domain, these derivatives are zero, and the boundary conditions reduce to

$$\begin{aligned}&[d_y\tilde{r}+\tilde{q}d_y\Psi+Qd_y\tilde{\psi}]|_{y=0}=0,\\&[d_y\tilde{q}+\tilde{r}d_y\Psi+Rd_y\tilde{\psi}]|_{y=0}=0.\end{aligned}\tag{32}$$

This can be used to determine two of the three constants, $\tilde{r}_0$, $\tilde{q}_0$, and $\tilde{\psi}_0$. It turns out that the coefficient of the constant $\tilde{q}_0$ in the above equations is zero, and therefore the above equations are satisfied only if $\tilde{r}_0=0$ and $\tilde{\psi}_0=0$. The third constant $\tilde{q}_0$ is determined from the boundary condition for the potential at the interface.

The boundary condition for the potential at the interface is determined by the dynamics of the charges on the surface. If the potential at the surface is maintained at the same value as that at the unperturbed surface, then the potential boundary condition reduces to

$$[\Psi+\tilde{\psi}\exp(ikx+st)]|_{y=u_y}=(\Psi)|_{y=0}.\tag{33}$$

Expanding the above equation in a Taylor series about the unperturbed surface, and retaining terms correct to linear order in the perturbation variables $\tilde{\psi}$ and $\tilde{u}_y$, we get

$$(\tilde{u}_y d_y\Psi+\tilde{\psi})|_{y=0}=0.\tag{34}$$

Alternatively, the charge at the perturbed surface could be maintained as a constant. In this case, it is necessary to infer a relationship between the surface potential and the surface charge by examining the change in the counterion density profile at a curved surface. For a surface with curvature $(1/R)$, the dimensional surface charge is related to the dimensional surface potential by

$$\sigma=\left[-\psi\left(1-\frac{c}{2R}\right)\right]\Bigg|_{y=u_y}.\tag{35}$$

The above expression is correct to $O(\kappa R)^{-1}$ in the limit $(\kappa R)\ll 1$. This limit is consistent with the present analysis because it is assumed that the surface is flat in the base state, and the perturbations are small compared to the inverse of the Debye length. If the surface charge density $\sigma$ is maintained as a constant, the interface condition is

$$\left[\psi\left(1-\frac{c}{2R}\right)\right]\Bigg|_{y=u_y}=\Psi|_{y=0}.\tag{36}$$

Using an expansion in the perturbations to the surface position and the potential, and retaining terms correct to linear order in the perturbation quantities, the above relation reduces to

$$\tilde{u}_y d_y\Psi-(c/2)\Psi k^2\tilde{u}_y+\tilde{\psi}|_{y=0}=0,\tag{37}$$

where the curvature $(1/R)$ is given by $d_x^2 u_y$ up to linear order in the displacement $u_y$.

It should be noted that the membrane displacement affects the charge distribution only due to the boundary conditions (34) and (37). This is because in the base state, there is an exponential decay of the potential from the membrane surface. When the membrane is displaced upwards, the mean potential at the displaced position is lower than that in the flat state. However, the boundary condition requires that the potential (or charge) at the membrane surface should be a constant even when the membrane is displaced. This requires a fluctuation component which augments the potential at the displaced position, and a simultaneous perturbation in the charge density at the surface.

If the series solutions (27) are cut off at $i=1$ (the Debye-Huckel approximation), the solutions for the charge density and potential fluctuations as a function of the constant $\tilde{q}_0$ are

$$\begin{aligned}&\tilde{q}=\tilde{q}_0\exp(-ly),\\&\tilde{\psi}=-\tilde{q}_0\exp(-ly).\end{aligned}\tag{38}$$

The boundary condition (34), in the Debye-Huckel approximation, provides the following relationship between the constant $\tilde{q}_0$ and the surface potential:

$$\tilde{q}_0=-\Psi_s\tilde{u}_y,\tag{39}$$

while for the boundary condition (37), the relation between the constants $\tilde{q}_0$ and $\Psi_s$ is

$$\tilde{q}_0=-\Psi_s\tilde{u}_y(1-ck^2/2).\tag{40}$$

## IV. VELOCITY FLUCTUATIONS

The effect of charge density fluctuations on the dynamics of a charged membrane is considered in the present section. The membrane consists of two surfaces, the upper surface (represented with superscript $u$) and the lower surface (represented with superscript $l$). First, the calculations for the velocity and stress fields are carried out for the upper surface with a surface potential $\Psi_{su}$, and symmetry arguments are used to determine the velocity and stress fields on the lower surface. The boundary conditions are then applied to determine the growth rate of the perturbations.

The perturbations to the velocity fields are calculated from the Stokes equations in the absence of fluid inertia. The dimensional equations are

$$\boldsymbol{\nabla}^*\cdot\mathbf{v}^*=0,\tag{41}$$

$$-\boldsymbol{\nabla}^*p^*+\mu\boldsymbol{\nabla}^*2\mathbf{v}^*-(n_+^*-n_-^*)ze\boldsymbol{\nabla}^*\psi^*=0,\tag{42}$$

where $\mu$ is the fluid viscosity. The lengths in the above problem are scaled by the screening length $\kappa^{-1}$ as before, since we are interested in perturbations of the scale of the screening length. For the velocity field, it is convenient to use the velocity scale $(2N_\infty^* T/\mu\kappa)$, and the pressure is scaled by $(2N_\infty^* T)$. With these, the equation for the velocity field becomes

$$-\nabla p+\nabla^2\mathbf{v}-q\nabla\psi=0. \tag{43}$$

Since the total charge and the potential are related by $q=-\nabla^2\psi$, the momentum equation can be recast as

$$-\nabla p+\nabla^2\mathbf{v}+\nabla\cdot\boldsymbol{\sigma}_\mathbf{e}=0, \tag{44}$$

where the additional stress due to the Debye layer, which is a second-order tensor, is given by

$$\boldsymbol{\sigma}_e=(\nabla\psi)(\nabla\psi)-(1/2)\mathbf{I}(\nabla\psi)\cdot(\nabla\psi), \tag{45}$$

where $\mathbf{I}$ is the second-order isotropic tensor. Taking the divergence of the above equation, it is easily seen that the pressure field is related to the charge density and potential by

$$-\nabla^2 p-\nabla\cdot(q\nabla\psi)=0. \tag{46}$$

The fluid velocity is zero in the base state, but there is a net pressure gradient due to the charge density in the Debye layer given by (21). This equation is easily solved to provide the mean pressure $P^u$ above the membrane surface is

$$P^u=\sum_{i=1}^{\infty} P_i^u \exp(-iy), \tag{47}$$

where

$$P_i^u=-\frac{1}{i}\sum_{j=0}^{i} j\Psi_j Q_{i-j}. \tag{48}$$

The velocity and pressure fluctuations are expressed in the form of Fourier modes

$$v_x^u=\tilde{v}_x^u(y)\exp(\imath kx+st),$$

$$v_y^u=\tilde{v}_y^u(y)\exp(\imath kx+st), \tag{49}$$

$$p^u=\tilde{p}^u\exp(\imath kx+st).$$

These are inserted into the conservation equations (41) and (42), and simplified to obtain an equation for the velocity field

$$(d_y^2-k^2)(d_y^2-k^2)\tilde{v}_y^u+k^2(\tilde{q}d_y\Psi-\tilde{\psi}d_yQ)=0. \tag{50}$$

It can easily be verified that the second term on the left side of the above equation is identically zero if $\tilde{r}_0=\tilde{\psi}_0=0$ in Eq. (27), and with this simplification the velocity and pressure fields reduce to

$$\tilde{v}_y^u=A_1^u\exp(-ky)+A_2^u ky\exp(-ky),$$

$$\tilde{v}_x^u=-\imath A_1^u\exp(-ky)+\imath A_2^u(1-ky)\exp(-ky), \tag{51}$$

$$\tilde{p}^u=2A_2^u k\exp(-ky)+\sum_{i=0}^{\infty}(\tilde{p}_i^{(1)u}\exp[-(i+k)y] + \tilde{p}_i^{(2)u}\exp[-(i+l)y],$$

where

$$\tilde{p}_i^{(1)u}=-\sum_{j=1}^{i} Q_j^u\tilde{\psi}_{i-j}^{(1)u},$$

$$\tilde{p}_i^{(2)u}=-\sum_{j=1}^{i} Q_j^u\tilde{\psi}_{i-j}^{(2)u}. \tag{52}$$

Similar relations can be derived for the velocity and stress fields at the lower surface of the membrane

$$v_x^l=\tilde{v}_x^l(y)\exp(\imath kx+st),$$

$$v_y^l=\tilde{v}_y^l(y)\exp(\imath kx+st), \tag{53}$$

$$p^l=\tilde{p}^l\exp(\imath kx+st),$$

$$\tilde{v}_y^l=A_1^l\exp(ky)+A_2^l ky\exp(ky),$$

$$\tilde{v}_x^l=-\imath A_1^l\exp(ky)+\imath A_2^l(1-ky)\exp(ky), \tag{54}$$

$$\tilde{p}^l=2A_2^l k\exp(ky)+\sum_{i=0}^{\infty}\tilde{p}_i^{(1)l}\exp[(i+k)y]+\tilde{p}_i^{(2)l}\exp[(i+l)y],$$

where

$$\tilde{p}_i^{(1)l}=-\sum_{j=1}^{i} Q_j^l\tilde{\psi}_{i-j}^{(1)l},$$

$$\tilde{p}_i^{(2)}=-\sum_{j=1}^{i} Q_j^l\tilde{\psi}_{i-j}^{(2)l}, \tag{55}$$

where the coefficients $Q_i^l$, $\tilde{\psi}_i^{(1)l}$, and $\tilde{\psi}_i^{(2)l}$ are calculated in a manner similar to $Q_i^u$, $\tilde{\psi}_i^{(1)u}$, and $\tilde{\psi}_i^{(2)u}$.

The dispersion relation is obtained using the boundary conditions at the membrane surface. When the amplitude of fluctuations is large compared to the thickness of the membrane, it is appropriate to set the tangential velocity $v_x$ equal to zero at the surface. With this, the boundary conditions for the linearized problem are

$$\tilde{v}_x^u=0,$$

$$\tilde{v}_x^l=0, \tag{56}$$

$$\tilde{v}_y^l=\tilde{v}_y^u=s\tilde{u}_y\,,$$

$$\tilde{\tau}_{yy}^u-\tilde{\tau}_{yy}^l=\Gamma k^2\tilde{u}_y\,,$$

where the normal stresses $\tilde{\tau}_{yy}^u$ at the surface are given by

$$\tilde{\tau}_{yy}^u=-p^u+2d_y\tilde{v}_y^u+d_y\tilde{\psi}^u d_y\Psi^u-\tilde{u}_y d_y[P^u-(1/2)(d_y\Psi^u)^2], \tag{57}$$

$$\tilde{\tau}_{yy}^l=-p^l+2d_y\tilde{v}_y^l+d_y\tilde{\psi}^l d_y\Psi^l-\tilde{u}_y d_y[P^l-(1/2)(d_y\Psi^l)^2], \tag{58}$$

and the scaled surface tension $\Gamma=(\Gamma^*\kappa/2N_\infty T)$, where $\Gamma^*$ is the dimensional surface tension. In Eqs. (57) and (58), the last term on the right accounts for the variation in the mean pressure and electrical stress due to membrane displacement. However, it is easily seen that the sum $[P^u+1/2(d_y\Psi^u)^2]$ is identically zero, and so the variation in the mean stress does not enter into the normal stress balance at the interface. The above equations are solved to provide an expression for the growth rate of fluctuations of the form

$$s=-k\left(\Gamma-\sum_{i=1}^{\infty}(\Psi_{su}^{2i}+\Psi_{sl}^{2i})F_i(k)\right), \tag{59}$$

where the functions $F_i(k)$ are functions of the scaled wave vector.

It is useful to first study the stability characteristics of the system using the Debye-Huckel approximation, which corresponds to retaining just the first term in the series on the right side of Eq. (59). The first function in the series $F_1(k)=[(1+k^2)^{1/2}-1]/k^2$ for a surface with constant surface potential, and the expression for the growth rate reduces to

$$s=-k[\Gamma-(\Psi_{su}^2+\Psi_{sl}^2)(\sqrt{1+k^2}-1)/k^2]. \tag{60}$$

From the above, it is clear that the stresses exerted by the charge distribution at the surface tends to destabilize the perturbations, and long-wavelength perturbations are unstable for $(\Psi_{su}^2+\Psi_{sl}^2)>2\Gamma$, and long-wavelength perturbations with $k<k_c$ are unstable, where $k_c=(1-2\alpha)/\alpha^2$, and $\alpha=(\Psi_{su}^2+\Psi_{sl}^2)/\Gamma$. For a system with constant charge density on the surface, the first function in the series is $F_1(k)=(1-ck^2/2)[(1+k^2)^{1/2}-1]/k^2$ and the expression for the growth rate is

$$s=-k[\Gamma-(\Psi_{su}^2+\Psi_{sl}^2)(1-ck^2/2)(\sqrt{1+k^2}-1)/k^2]. \tag{61}$$

From the above, it is clear that the fixed charge boundary condition does not affect the stability of the long-wavelength perturbation, but increases the potential required for destabilizing finite wavelength perturbations.

The above result can be systematically corrected to include higher-order terms in Eq. (59). Attention is restricted to the case where $\Psi_{sl}=0$, so that only one surface of the membrane is charged, and the surface potential is fixed, though the results could be easily extended to other cases. The parameter $(\Psi_{su}^2/\Gamma)$ at which the perturbations become unstable is plotted as a function of the wave vector $k$ for different values of the potential $\Psi_{su}$ in Fig. 1. The solid line shows the result for the Debye-Huckel approximation where only one term in the series is retained. It is observed that the neutral stability curve tends to a finite value on the limit $k\rightarrow 0$, and increases proportional to $k$ in the limit $k\gg 1$. The broken lines show the results obtained by retaining five terms in the series (59) for $\Psi_{su}=1$ and $\Psi_{su}=2$. It is observed that the Debye-Huckel approximation overestimates the surface potential for neutrally stable modes.

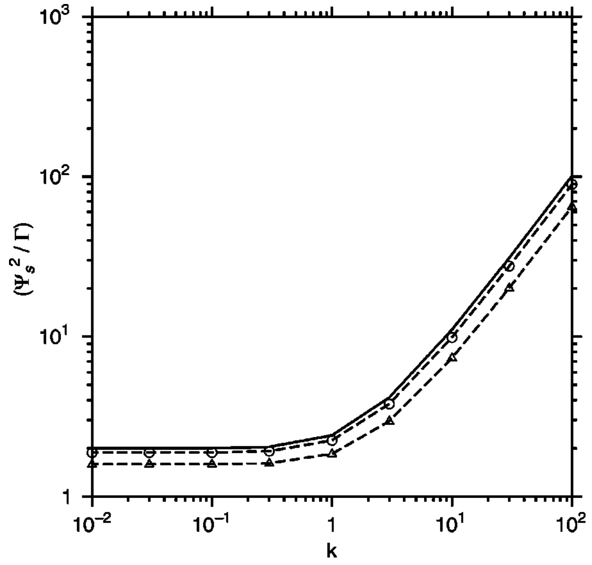

FIG. 1. Transition values for $(\Psi_{su}^2/\Gamma)$ as a function of wave number $k$. The solid line shows the result from the Debye-Huckel approximation; the broken line with circles and triangles shows the results of the series solution with five terms for $\Psi_{su}=1$ and $\Psi_{su}=2$, respectively.

Finally, it can be shown that even though the above expressions were derived for zero Peclet and Reynolds number, they are valid for nonzero Reynolds and Peclet numbers as well. As can be seen from the above expressions, the real and imaginary parts of the growth rate are simultaneously equal to zero for the neutral modes. Since the velocity is the time derivative of the normal displacement at the surface, the normal velocity is also zero for the neutral modes. Consequently, the inertial and convective terms in the ion conservation and momentum equations are zero, and the above neutral stability curves are valid even for nonzero Reynolds and Peclet numbers.

## V. CONCLUSIONS

The stability of surface fluctuations of a charged membrane immersed in a fluid were considered using a linear stability analysis. The wavelength of the perturbations is considered to be of the same order of magnitude as the Debye screening length. In previous calculations where the variation to the counterion density parallel to the surface is neglected, the surface fluctuations were found to be stable if the charge or potential at the surface is fixed. The present analysis differs from previous studies because the variation in the counterion density due to surface perturbations is explicitly taken into consideration by solving the diffusion equation for the counterions. The results of the present analysis are qualitatively different, and indicate that a coupling between the shape fluctuations and the concentration fluctuations of the counterion density is necessary for the instability. This mechanism could be of importance in generating shape changes in biological systems, such as cell membranes and organelles, since it has been observed that there are significant changes in the surface potentials of membranes when a shape change occurs.

The physical reason for the instability is as follows. There is an exponential decay of the potential as a function of distance from the surface in the base state. When the membrane is displaced upwards, the mean potential at the displaced position is lower than that at the original position. However, to maintain the constant potential condition at the interface, the perturbation to the potential has to be positive. This requires a depletion of the charges. There are two contributions to the normal stress at the surface, one due to the additional pressure in Eqs. (52) and (55), and the other due to the electrical stress in Eqs. (57) and (58). The pressure contribution tends to exert a downward force on a membrane curved upwards, while the electrical contribution to the normal stress exerts a larger upward force. When tangential variations in the charge density are neglected, the two are equal in magnitude and opposite in direction and provide no net force. When the tangential variations are included, there is a net upward force which tends to destabilize fluctuations when the potential is increased beyond a critical value.

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