Static and dynamic correlations in a charged membrane

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We study static and dynamic correlations of two fluctuations, the charge density fluctuation and height fluctuation (undulation), on a fluid membrane with a finite excess charge in a viscous fluid. For a planar and symmetrical membrane, we consider a model Hamiltonian inclusive of the fluctuations at the Gaussian level, and construct their equations of motion. Within the model, there exists no coupling, either static or dynamic, between the two fluctuations. The correlation function of the charge density has a short-range damped oscillation over the size of lipid heads due to Coulomb attraction between unlike-charged lipids. Its dynamic correlation function is shown to decay much faster in time than that in simple diffusion. The correlation function of height undulation, on the other hand, has a long-range damped oscillation (bud) over the membrane size, due to Coulomb repulsion among the excess charges. As the excess charge density increases to a critical value, a bending instability sets in, where a minute perturbation on the membrane can cause a large bud to form. Due to the excess charge, the dynamic correlation of the undulation decays slowly in time; at the critical density of the instability, the decay becomes infinitely slow.

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I. INTRODUCTION

The biomembrane constitutes an essential feature of a living cell, by forming and modulating interfaces of the cell and its various internal compartments [1]. The membranes are highly flexible and dynamical so that they perform a variety of self-organizations necessary to biological functions. The membranes are self-assembled bilayers mostly of lipid molecules which are composed of hydrophilic heads and hydrophobic tails. The lipids of a fluid membrane can diffuse laterally within the bilayer so that they freely arrange themselves to adopt at equilibrium the conformation corresponding to the free energy minimum. Over a mesoscopic length scale which is longer than the lipid size, a membrane can be regarded as a quasi-two-dimensional structure immersed in the three dimensional solution. The low dimensionality and fluidity of the membrane endow it with a variety of shapes and shape transitions, which have been a great interest to physicists for over a decade [2].

Usually lipids can have electrically charged head groups. In addition, biological membranes are dissolved in electrolyte solutions containing counterions and coions. The electrostatic interaction therefore plays a fundamental role in determining structural properties such as intermembrane interaction, stability, and rigidity, etc. [3,4]. According to the mean-field theory using the Poisson-Boltzmann equation, the electrostatic interaction between like charges in a body appears to enhance the bending rigidity, leading to a stretched conformation [4]. Counterions can bind on the membrane surface due to electrostatic attraction, and can unbind to gain entropy. This, along with the lateral diffusion of charged lipids, gives rise to ceaselessly varying surface charge density. The charge fluctuations, which are not captured by mean-field theories, play an important role in many biological phenomena ranging from DNA condensation [5,6] to cell adhesion [7]. For instance, a charged membrane becomes more flexible [8,9] and two like-charged membranes can attract each other [10,11] as a result of correlated charge fluctuations. The influence of this charge correlation is believed to be more prominent in the presence of multivalent ions [12,13], and much effort is devoted to investigating the effects of electrostatic interaction beyond the mean-field theory. Furthermore, as suggested in the recent work [13], the collective coupling between the charge fluctuation and the shape fluctuation can be a key component in the structural stability and dynamics of membranes. It is therefore worth studying in a quantitative way the correlation functions of fluctuating membranes which are charged by lipids and condensed counterions as well.

In this paper we study the static and dynamic correlation functions of undulation and charge fluctuation in a planar charged membrane immersed in a viscous fluid. Although these correlation functions are essential attributes of membranes, representative two-dimensional soft condensed matter, few theoretical investigations have been made and only for neutral membranes, to the best of our knowledge [14]. While the correlation functions of lipid density or related quantities such as structure factors and mean square undulations are probed by scattering and spectroscopy measurements, the correlation functions mentioned above are more directly related to simple thought experiments. Suppose that a small force is applied to a point of the membrane, giving rise to a perturbation in either shape or charge density. The average undulation and average charge density incurred at a distance away from the point are given by the static correlation functions of undulation and charge density, respectively, via linear response theory. If the applied force is removed at a certain time, the average undulation and charge density at later times are given by their dynamical, time-dependent correlation functions.

Here we consider a planar lipid membrane, which is symmetric in the sense that both lipid layers are situated in the

same electrical environment so as to have a single charge distribution. In our case, the membrane has a nonvanishing excess charge. Nevertheless, net charge neutrality for the entire system is maintained by the ionic background fluid. In real situations, the ionic screening of electrostatic interaction might be important. However, as we want to focus on the fundamental effects of the electrostatics on the membrane, we neglect the screening in this study. The present analysis will be valid for very dilute ionic solutions where the Debye screening length is longer than the average distance between the charged lipids. In Sec. II, we consider a model Hamiltonian of a charged, planar membrane in terms of charge fluctuation and height undulation. Within the Gaussian approximation, the static correlations of the two variables are obtained and analyzed. In Sec. III, we construct two stochastic equations of motion from the Hamiltonian, the generalized diffusion equation for charge fluctuation and the equation for undulation in a viscous hydrodynamic medium. From these equations we obtain the dynamic correlation functions of the variables and analyze their characteristic time-dependent behaviors. In Sec. IV, a summary and concluding remarks are given.

II. THE EFFECTIVE HAMILTONIAN AND STATIC CORRELATION FUNCTIONS

Let us consider a mesoscopic level description to incorporate the salient features of collective excitations of membrane. The Helfrich Hamiltonian [15] has been successful in describing the membrane shape and its fluctuation in terms of the curvature. For a planar fluid membrane, the Helfrich Hamiltonian is given by the bending energy

$$\mathcal{H}_b = \frac{\kappa}{2}\int d^2\mathbf{x}[\nabla_{\mathbf{x}}^2 h(\mathbf{x})]^2, \tag{1}$$

where $h(\mathbf{x})$ is the local undulation relative to a reference plane represented by the two-dimensional coordinate $\mathbf{x}=(x,y)$, and κ is an elastic constant, called the bending rigidity, ranging from tens to hundreds of k_BT.

Now consider an undulating planar membrane composed of a dilute mixture of cationic and anionic lipids. Because of the fluidity of the membrane, the charged lipids are laterally diffusive so that surface charge density is no longer uniform. The energy cost of the density fluctuation and the Coulomb interaction constitute two additional terms in the total Hamiltonian $\mathcal{H}$ as [9]

$$\beta\mathcal{H} = \frac{\chi}{2}\int d^2\mathbf{x}[\delta\sigma(\mathbf{x})]^2 + \frac{\ell_B}{2}\int d^2\mathbf{x}\, d^2\mathbf{x}'\frac{\sigma(\mathbf{x})\sigma(\mathbf{x}')}{|\mathbf{r}-\mathbf{r}'|} + \frac{\beta\kappa}{2}\int d^2\mathbf{x}[\nabla_{\mathbf{x}}^2 h(\mathbf{x})]^2. \tag{2}$$

Here $\beta=1/k_BT$ and $\sigma(\mathbf{x})$ is the excess surface charge density: $\sigma(\mathbf{x})=q_+n_+(\mathbf{x})-q_-n_-(\mathbf{x})$, where $n_{+(-)}$ and $q_{+(-)}$ are the cationic (anionic) number density and charge. Here we consider the case $q_+=q_-=e$ for simplicity. $\delta\sigma(\mathbf{x})=\sigma(\mathbf{x})-\langle\sigma\rangle$ denotes the fluctuations around the average density $\langle\sigma\rangle$. The first term in Eq. (2) accounts for the entropy cost for density fluctuations: considering the ideal gas entropy expression for the charged lipids, a measure of the charge fluctuation is obtained as the compressibility $\chi^{-1}=n_t$, where $n_t=\langle n_+\rangle+\langle n_-\rangle$ is the total number density of all charged lipids and e is put to unity [8]. The second term in Eq. (2) is the sum of the Coulomb interaction between two charges located at three-dimensional positions $\mathbf{r}=(\mathbf{x},h(\mathbf{x}))$ and $\mathbf{r}'=(\mathbf{x}',h(\mathbf{x}'))$ on the undulating surface. Here $\ell_B=e^2/\epsilon k_BT$ is the Bjerrum length at which the electrostatic interaction energy is comparable to the thermal energy in a medium of dielectric constant ϵ. It should be noted here that our surface density $\sigma(\mathbf{x})$ is measured over a fixed reference plane, so that it differs from the one defined over the undulating surface by the factor $\sqrt{1+[\nabla_{\mathbf{x}}h(\mathbf{x})]^2}$ [9].

A Hamiltonian of the type above is also applicable to a charged membrane (for example, composed of anionic and neutral lipids) in the presence of counterions. The counterions in the solution tend to condense within a thin layer on a negatively charged surface. Within our coarse-grained model, the condensed counterions are treated so as to modify the surface charge density of the membrane, as there is no explicit distinction between charged lipids and condensed counterions. The adsorption and subsequent desorption of counterions, along with the lateral diffusion of the charged lipids, lead to the fluctuations of surface charge density. On the other hand, the noncondensed, free ions in the bulk contribute to screening the Coulomb interaction among the surface charges so that the bare Coulomb interaction in Eq. (2) is replaced by the screened one, $\exp(-|\mathbf{r}-\mathbf{r}'|/\lambda_D)/|\mathbf{r}-\mathbf{r}'|$, where λ_D is the (three-dimensional) Debye screening length [9]. This study is therefore applicable to very weak electrolytes where the screening length λ_D is much longer than the average spacing between charged lipids.

Assuming small undulations, the above Hamiltonian can be handled analytically by expanding the Coulomb interaction terms with respect to the undulations. First, define the Fourier modes for $\delta\sigma(\mathbf{q})$ and $h(\mathbf{q})$ as

$$\delta\sigma(\mathbf{x}) = \frac{1}{L}\sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{x}}\delta\sigma(\mathbf{q}), \tag{3}$$

$$h(\mathbf{x}) = \frac{1}{L}\sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot\mathbf{x}}h(\mathbf{q}), \tag{4}$$

where L is the membrane size and $a=L/N$ is a microscopic length about the diameter of lipid heads. Here each component of $\mathbf{q}$, q_x and q_y takes N discrete values $2n\pi/L$ where the integer n runs from $-N/2$ to $N/2$. The Hamiltonian in terms of the fluctuation modes to the second order is

$$\mathcal{H} = \frac{1}{2}\sum_{\mathbf{q}}[X(q)|\delta\sigma(\mathbf{q})|^2 + M(q)|h(\mathbf{q})|^2], \tag{5}$$

where

$$X(q) = \chi + \frac{2\pi\ell_B}{q} = \chi\left(1+\frac{1}{\lambda q}\right), \tag{6}$$

$$M(q) = \beta\kappa q^4 - 2\pi\ell_B\langle\sigma\rangle^2 q, \tag{7}$$

and $\lambda = \chi/2\pi\ell_B$ is akin to the two-dimensional screening length. Note that the charge density fluctuation and height undulation are decoupled within the Gaussian approximation we take. Also it is shown below that the density fluctuation is independent of the net surface charge $\langle\sigma\rangle$ while the height undulation is independent of the compressibility χ. These are consequences of membrane symmetry within the Gaussian approximation. If one either goes beyond the Gaussian approximation or considers an asymmetrically charged bilayer membrane [16], the coupling will be apparent. According to the equipartition theorem, $k_BT/2$ is allocated to the average energy of each Fourier mode, leading to

$$\langle|\delta\sigma(\mathbf{q})|^2\rangle = \frac{1}{X(q)}, \tag{8}$$

$$\langle|h(\mathbf{q})|^2\rangle = \frac{1}{M(q)}, \tag{9}$$

where $\langle\ \rangle$ means the statistical average over the equilibrium ensemble of the system. From the above equation we can immediately assess the electrostatic effects on the fluctuations. First, as implied in Eq. (6), the inverse compressibility $X(q)$ for two-dimensional charged lipids is positively renormalized by the Coulomb interaction by a factor of $(\lambda q)^{-1}$, meaning that the long-range Coulomb interaction suppresses the density fluctuation. On the other hand, Eq. (7) indicates that the Coulomb repulsion between like charges softens the membrane and enhances the height undulation.

One can also see from Eq. (7) that the $M(q)$ for height undulation can be negative, depending upon the excess charge density $\langle\sigma\rangle$: for $q<q_c$ with $q_c=(2\pi\ell_B\langle\sigma\rangle^2/\beta\kappa)^{1/3}$, $M(q)<0$, indicating that the membrane becomes unstable with respect to undulations with that wavelength. Since the lower bound of q is $q_m=\pi/L$, the instability condition $q_m<q_c$ can be written as

$$L > L_c = \left(\frac{\beta\kappa\pi^2}{2\pi\ell_B\langle\sigma\rangle^2}\right)^{1/3} \tag{10}$$

for fixed $\langle\sigma\rangle$, or

$$\langle\sigma\rangle > \langle\sigma\rangle_c = \left(\frac{\beta\kappa\pi^2}{2\ell_B L^3}\right)^{1/2} \tag{11}$$

for fixed L. Equation (11) implies that, due to the Coulomb repulsion of like charges, the membrane tends to be very soft and unstable with respect to spontaneous bending when the excess surface charge gets sufficiently high, as already investigated earlier [9]. Seemingly this instability is incompatible with the previous mean-field theory results where the charge tends to stiffen the matter [4,17]. Most of these theories, unlike our case, assume constant charge density over the undulating surface. We instead use the charge density defined on the planar reference plane with the total excess charges over the whole undulating surface kept constant. Therefore, on a curved surface, the distance between excess charges increases and the electrostatic energy decreases to induce instability above a critical excess density. Also, this mechanism is apparently different in origin from the charge-fluctuation-induced bending softening studied by Lau and Pincus [8]. (See Ref. [9] for comparisons.) Our definition for the charge density is expected to be more appropriate for the fluid membrane with an effectively vanishing tension, which has no energy cost associated with changing the area. We will investigate in more detail the instability phenomena in the context of static and dynamic correlation functions of the undulation in the following.

The static correlation functions $\langle\delta\sigma(\mathbf{x})\delta\sigma(\mathbf{x}')\rangle$ and $\langle h(\mathbf{x})h(\mathbf{x}')\rangle$

The static correlation functions can be obtained by the inverse-Fourier transform of Eqs. (8) and (9). In order to understand the operational meaning of the correlation behavior, consider a thought experiment as follows. A small constant potential U and charge δq are applied on a infinitesimal area s around a point $\mathbf{x}'$ of a membrane which initially has the uniform charge density $\langle\sigma\rangle$. The perturbing Hamiltonian can be written as

$$\mathcal{H}' = -U\delta q(\mathbf{x}') = -\delta\sigma(\mathbf{x}')sU. \tag{12}$$

The change of average charge density incurred at another point $\mathbf{x}$ in the presence of the perturbing potential is given by

$$\langle\delta\sigma(\mathbf{x})\rangle_U = \frac{\mathrm{Tr}[\delta\sigma(\mathbf{x})e^{-\beta(\mathcal{H}+\mathcal{H}')}]}{\mathrm{Tr}(e^{-\beta(\mathcal{H}+\mathcal{H}')})} \approx \beta sU\langle\delta\sigma(\mathbf{x})\delta\sigma(\mathbf{x}')\rangle, \tag{13}$$

where Tr denotes integration over all realizations of the surface charge distribution. This is an example of the well-known linear response theory that tells us that response of the system to an external perturbation is proportional to correlation of the conjugate variable at equilibrium in the absence of the perturbation [18]. The theory can be extended to a variety of external perturbations and their conjugate variables. Also it can be extended to the time-dependent case where the perturbation is removed at a certain time, say, $t=0$, and then relaxation of the conjugate variable is proportional to its time correlation [18]. Using the linear response theory in a similar way we can relate the average height undulation at $\mathbf{x}$ induced by a force $\mathbf{f}$ localized at $\mathbf{x}'$ with the correlation of the undulation at equilibrium,

$$\langle h(\mathbf{x})\rangle_{\mathbf{f}} \sim \langle h(\mathbf{x})h(\mathbf{x}')\rangle. \tag{14}$$

The density correlation function is given as

$$\begin{aligned}\langle\delta\sigma(\mathbf{x})\delta\sigma(\mathbf{x}')\rangle &= \frac{1}{L^2}\sum_{\mathbf{q}} e^{-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')}\langle|\delta\sigma(\mathbf{q})|^2\rangle \\ &= \frac{1}{(2\pi)^2}\int d^2\mathbf{q}\, e^{-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')}\langle|\delta\sigma(\mathbf{q})|^2\rangle \\ &= \frac{1}{(2\pi)^2}\int d^2\mathbf{q}\, e^{-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')}\frac{1}{X(q)} \\ &= \frac{1}{2\pi}\int dq\, W_\sigma(q)J_0(q|\mathbf{x}-\mathbf{x}'|),\end{aligned} \tag{15}$$

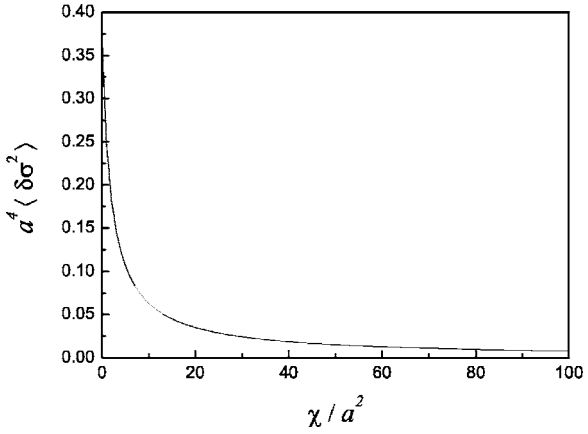

FIG. 1. $\langle\delta\sigma^2\rangle$ versus χ/a^2. The linear size of the membrane is taken as $L=100a$.

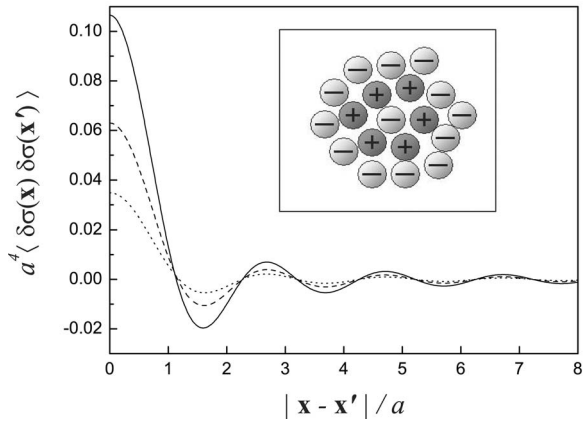

FIG. 2. The static correlation function of charge density fluctuations $\langle\delta\sigma(\mathbf{x})\delta\sigma(\mathbf{x}')\rangle$ for different value of χ: $\chi/a^2=5$ (solid line), 10 (dashed line), and 20 (dotted line). Inset is a schematic picture of charge oscillation (coordination) around a central charge.

where the integration over q ranges from $q_m=\pi/L$ to $q_M=\pi/a$, $W_\sigma(q)=q/\chi(1+1/\lambda q)$, and $J_0(qr)=\int d\theta\, e^{-iqr\cos\theta}/2\pi$ is the zeroth-order Bessel function of the first kind. On the other hand, the variance of the density fluctuation is given as

$$\begin{aligned}\langle\delta\sigma^2\rangle &= \frac{1}{2\pi}\int dq\, W_\sigma(q)\\ &= \frac{1}{2\pi\chi}\left[\frac{1}{2}\left(\frac{\pi}{a}\right)^2\left(1-\frac{4\ell_B a}{\chi}\right)\right.\\ &\quad\left.+\left(\frac{2\pi\ell_B}{\chi}\right)^2\ln\left(1+\frac{\chi}{2\ell_B a}\right)\right]\\ &= \frac{\pi}{4\chi a^2}\left[1-\frac{2a}{\pi\lambda}+2\left(\frac{a}{\pi\lambda}\right)^2\ln\left(1+\frac{\pi\lambda}{a}\right)\right]. \quad (16)\end{aligned}$$

Figure 1 depicts $\langle\delta\sigma^2\rangle$ as a function of λ/a. As λ/a or χ/a^2 decreases, i.e., the electrostatic interaction increases, $\langle\delta\sigma^2\rangle$ is shown to monotonically increase.

The normalized correlation function is then given by

$$C_\sigma(|\mathbf{x}-\mathbf{x}'|)=\frac{\langle\delta\sigma(\mathbf{x})\,\delta\sigma(\mathbf{x}')\rangle}{\langle\delta\sigma^2\rangle}=\frac{\int dq\, W_\sigma(q)J_0(q|\mathbf{x}-\mathbf{x}'|)}{\int dq\, W_\sigma(q)}. \quad (17)$$

Equation (17) indicates that the normalized correlation function is the average of $J_0(q|\mathbf{x}-\mathbf{x}'|)$ over the distribution weighted by the function $W_\sigma(q)$. Since $W_\sigma(q)$ increases monotonically with q over the whole range, the correlation function is approximated as

$$C_\sigma(|\mathbf{x}-\mathbf{x}'|)\cong J_0(q_\sigma|\mathbf{x}-\mathbf{x}'|), \quad (18)$$

where q_σ is of the order of the allowed maximum wave vector $q_M=\pi/a$, meaning that the correlation is characterized by the microscopic length scale, i.e., the size of the charged lipid head a. Throughout this paper, we adopt values of χ in the range $5<\chi/a^2<20$, which represents moderate to dilute charged lipid density regimes. The microscopic and macroscopic lengths are chosen as $a=1$ nm and $L=100$ nm, respectively. We also consider room temperature as $T=300$ K, at which the Bjerrum length ℓ_B is about 7 Å. Figure 2 depicts the static charge density correlation functions for several values of χ. The correlation is shown to have an oscillatory behavior that decays over the characteristic length a, in good agreement with Eq. (18) with $q_\sigma\approx 1.4q_M$. For the range of χ values considered, the periodicity or q_σ is nearly independent of χ, but the amplitude of the oscillation, given by Eq. (16), is smaller for larger χ, i.e., for smaller charge fluctuation, as it should be. The amplitude is proportional to the total number density of charged lipids (within the ideal gas approximation for χ), but independent of excess charge density of lipids. This feature of charge oscillation is in accord with the microscopic theory of Lee and Fisher [19] for a three-dimensional ionic fluid with net charge neutrality. The charge oscillation in our mesoscopic theory is implemented in part by the microscopic cutoff length a. Without the cutoff the integrals of Eqs. (15) and (16) diverge to infinity. The microscopic length, which can self-consistently be determined by relating the observed value of $\langle\delta\sigma^2\rangle$ with Eq. (16), can not only regularize the infinity, but also incorporate the hard-core effects of lipids on the oscillation independent of the density of the charged lipids. Following the linear response theory, we can attribute the oscillatory behavior of the charge density correlation to an alternation in sign of the net charge carried by successive coordination shells in response to a central charge positioned at a certain position (inset of Fig. 2), which arises from competition between their Coulomb attraction and hard-core repulsion. The layer size of the shell is of the order of a, that is, the spacing between the adjacent lipids.

The correlation function of height undulation is the Fourier inverse of the Eq. (9), written as

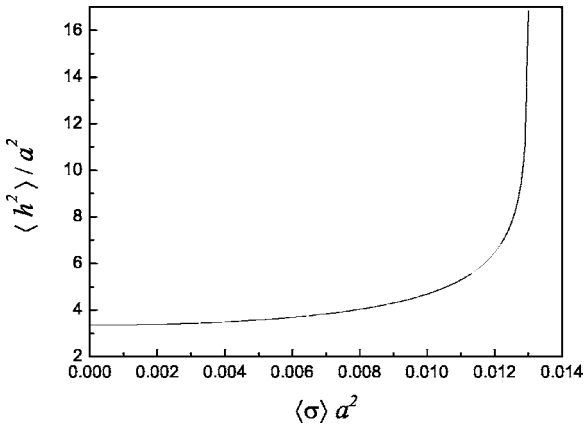

FIG. 3. $\langle h^2 \rangle$ vs $\langle \sigma \rangle a^2$. Here parameters are given as $\kappa = 24 k_B T$ and $L/a = 100$.

$$\langle h(\mathbf{x}) h(\mathbf{x}') \rangle = \frac{1}{(2\pi)^2} \int d^2\mathbf{q}\, e^{-i\mathbf{q}\cdot(\mathbf{x}-\mathbf{x}')} \langle |h(q)|^2 \rangle = \frac{1}{2\pi} \int dq\, W_h(q) J_0(q|\mathbf{x}-\mathbf{x}'|), \tag{19}$$

where $W_h(q) = q/(\beta\kappa q^4 - 2\pi \ell_B \langle \sigma \rangle^2 q)$. The variance of the height undulation is

$$\langle h^2 \rangle = \frac{1}{2\pi} \int dq\, W_h(q) = \frac{1}{12\pi\beta\kappa q_c^2} \left[\ln\left(\frac{q_c^2 L^2 + \pi q_c L + \pi^2}{q_c^2 a^2 + \pi q_c a + \pi^2} \right) + 2 \ln\left(\frac{q_c a - \pi}{q_c L - \pi} \right) + 2\sqrt{3} \tan^{-1}\left(\frac{q_c + 2\pi/L}{\sqrt{3} q_c} \right) - 2\sqrt{3} \tan^{-1}\left(\frac{q_c + 2\pi/a}{\sqrt{3} q_c} \right) \right], \tag{20}$$

where q_c is the critical wave vector of bending instability defined earlier. Figure 3 depicts $\langle h^2 \rangle$ as a function of the excess charge of the values $\langle \sigma \rangle a^2$. $\langle h^2 \rangle$ is shown to increase from the well-known value of the neutral membrane, $\langle h^2 \rangle_0 = k_B T L^2 / 4\pi^3 \kappa$, to infinity as the charge density increases from zero to $\langle \sigma \rangle_c$. Here we take $\kappa = 24 k_B T$ and $\sigma_c = 0.013/a^2$. The normalized correlation function is given by

$$C_h(|\mathbf{x}-\mathbf{x}'|) = \frac{\langle h(\mathbf{x}) h(\mathbf{x}') \rangle}{\langle h^2 \rangle} = \frac{\int dq\, W_h(q) J_0(q|\mathbf{x}-\mathbf{x}'|)}{\int dq\, W_h(q)}. \tag{21}$$

Since, in contrast to $W_\sigma(q)$, $W_h(q)$ is a rapidly decreasing function of q with a maximum at $q = q_m$,

$$C_h(|\mathbf{x}-\mathbf{x}'|) \approx J_0(q_h|\mathbf{x}-\mathbf{x}'|), \tag{22}$$

where $q_h \approx q_m = \pi/L$. Indeed Eq. (22) is in excellent agreement with the numerical calculation of Eq. (21) shown in Fig. 4, where the correlation functions of the height undulations are depicted for various values of $\langle \sigma \rangle$ lower than the critical value $\langle \sigma \rangle_c$.

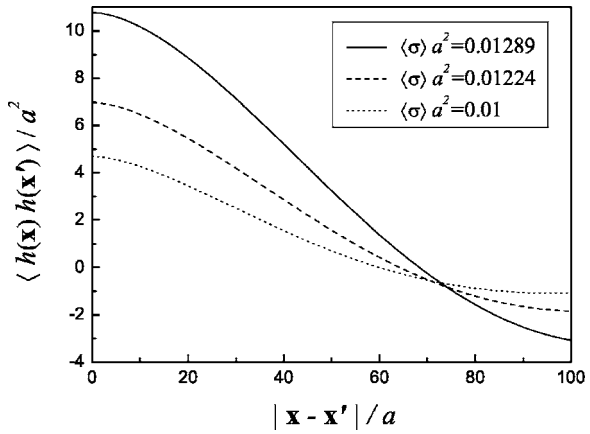

FIG. 4. The static correlation function of height undulations $\langle h(\mathbf{x}) h(\mathbf{x}') \rangle$ for three different charge densities: $\langle \sigma \rangle a^2 = 1.289 \times 10^{-2}$ (solid line), 1.224×10^{-2} (dashed line), and 1.0×10^{-2} (dotted line). The membrane bending rigidity is chosen as $\kappa = 24 k_B T$.

In Fig. 4, the oscillation beyond the system size L is meaningless and is cut off. In accordance with linear response theory, the correlation curve represents the deformation of the membrane from its planar shape induced in response to a small applied force. The large budding over the entire membrane of size L found here is due to the long-range Coulomb repulsion. As the excess surface charge density increases, the size of the bud increases, because by budding separation between the charges increases and the Coulomb repulsion decreases. As the density approaches the critical value $\langle \sigma \rangle_c$, the membrane tends to be very soft, inducing bending instability, where a minute perturbation causes the membrane to spontaneously form a large bud.

III. DYNAMICS AND TIME CORRELATION FUNCTIONS

The charge density, as it is a conserved variable, constitutes a slowly varying degree of freedom. The height undulation, which is the collective excitation of lipid conformation, is another slow variable. The dynamics of slow degrees of freedom are naturally modeled by Langevin-like equations where all the other fast degrees of freedom are treated as random noises [20]. The charge density variation on the membrane evolves via a diffusion equation of Cahn-Hilliard type [21],

$$\frac{\partial}{\partial t} \delta\sigma(\mathbf{x}, t) = \mathcal{D} \nabla_{\mathbf{x}}^2 \left(\frac{\delta \mathcal{H}}{\delta(\delta\sigma(\mathbf{x}))} \right) + \xi_\sigma(\mathbf{x}, t), \tag{23}$$

where $\mathcal{D}$ is the Onsager coefficient simply related to the diffusivity D as shown next, and $\xi_\sigma(\mathbf{x}, t)$ is taken to be the Gaussian random noise that satisfies the fluctuation-dissipation theorem [21]

$$\langle \xi_\sigma(\mathbf{x}, t) \xi_\sigma(\mathbf{x}', 0) \rangle = -2 k_B T D \nabla_{\mathbf{x}}^2 \delta(\mathbf{x} - \mathbf{x}') \delta(t). \tag{24}$$

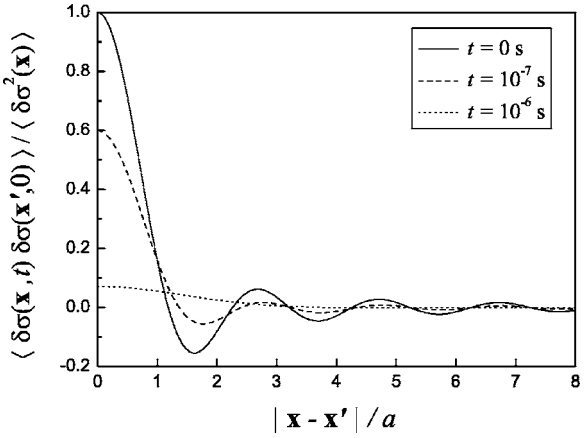

FIG. 5. The normalized dynamic correlation function of charge density fluctuations $\langle \delta\sigma(\mathbf{x},t)\delta\sigma(\mathbf{x}',0)\rangle/\langle\delta\sigma^2(\mathbf{x})\rangle$ for three different times: $t=0$ (solid line), 10^{-7} (which is about the time of diffusion over the Bjerrum length ℓ_B^2/D; dashed line), and 10^{-6} s (dotted line). The parameters are chose as $\chi/a^2=20$ and diffusion coefficient $D=10^6$ nm^2/s.

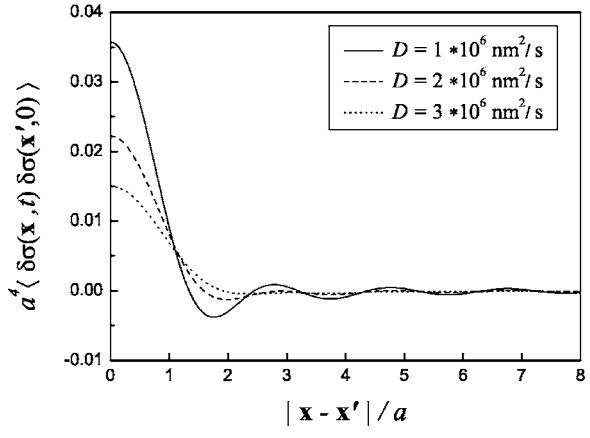

FIG. 6. The dynamic correlation function of charge density fluctuations $\langle \delta\sigma(\mathbf{x},t)\delta\sigma(\mathbf{x}',0)\rangle$ at $\chi/a^2=10$ and $t=10^{-7}$ s for different diffusion coefficients: $D=1\times10^6$ (solid line), 2×10^6 (dashed line), and 3×10^6 nm^2/s (dotted line).

For analytical tractability we consider the Fourier transform as

$$\frac{\partial}{\partial t}\delta\sigma(\mathbf{q},t) = -\mathcal{D}q^2\frac{\delta\mathcal{H}}{\delta(\delta\sigma^*(\mathbf{q}))} + \xi_\sigma(\mathbf{q},t), \tag{25}$$

which can be written, using our model Hamiltonian [Eq. (2)], as

$$\frac{\partial}{\partial t}\delta\sigma(\mathbf{q},t) = -D_e(q)q^2\delta\sigma(\mathbf{q},t) + \xi_\sigma(\mathbf{q},t). \tag{26}$$

Here $D_e(q)=D(1+2\pi\ell_B/\chi q)=D(1+(\lambda q)^{-1})$ is the renormalized diffusivity, which is larger by the factor $(\lambda q)^{-1}$ than $D=\mathcal{D}\chi/\beta$, the diffusivity the charged lipids would have in the absence of the Coulomb interaction. $\xi_\sigma(\mathbf{q},t)$ is the random noise in Fourier space with the variance $\langle\xi_\sigma(\mathbf{q},t)\xi_\sigma^*(\mathbf{q},0)\rangle = 2k_BTDq^2\delta(t)$ and is uncorrelated with $\delta\sigma(\mathbf{q},0)$. From the above equation, one gets the time correlation function as

$$\langle\delta\sigma(\mathbf{q},t)\,\delta\sigma^*(\mathbf{q},0)\rangle = \langle|\delta\sigma(\mathbf{q})|^2\rangle e^{-t/\tau_\sigma(q)}, \tag{27}$$

and thus its real-space expression as

$$\langle\delta\sigma(\rho,t)\,\delta\sigma(0,0)\rangle = \frac{1}{2\pi}\int dq\; W_\sigma(q)J_0(q\rho)e^{-t/\tau_\sigma(q)}, \tag{28}$$

where $\rho=|\mathbf{x}-\mathbf{x}'|$, and $\tau_\sigma(q)=[Dq^2(1+1/\lambda q)]^{-1}$ is the characteristic relaxation time of the density fluctuation with the wave mode q. Figure 5 shows the dynamic correlation function at three different times, with χ and D fixed. The correlation decays to zero as time elapses due to diffusion of the charges. For a fixed $\chi/a^2=10$, the case of moderate charged lipid density, and the three different values of diffusivities given therein, Fig. 6 depicts the correlation at $t=10^{-7}$ s, which is comparable to the time of lipid diffusion over the length a. It is shown that, as the diffusivity increases, the correlation naturally relaxes faster.

Focusing on the time dependence, we consider the equal-position normalized dynamic correlation (autocorrelation) function as

$$C_\sigma(t) = \frac{\langle\delta\sigma(\mathbf{x},t)\,\delta\sigma(\mathbf{x},0)\rangle}{\langle\delta\sigma^2(\mathbf{x})\rangle}. \tag{29}$$

If we turn off the electrostatic interaction, $1/\lambda q=0$,

$$C_\sigma(t) \sim a^2\int_{q_m}^{q_M} qe^{-Dq^2t}dq \sim \frac{a^2}{Dt}\int_{\pi^2Dt/L^2}^{\pi^2Dt/a^2} e^{-y}dy. \tag{30}$$

For $\pi^2Dt/L^2 \ll 1$ and $\pi^2Dt/a^2 \gg 1$, i.e., $a^2/D \ll t \ll L^2/D$, the integral tends to be dimensionless, so that we have

$$C_\sigma(t) \sim a^2/Dt, \tag{31}$$

that is, the autocorrelation of charge density decays via two-dimensional free diffusion.

Now consider the case of strong electrostatic interaction such that $1/\lambda q$, the interaction-induced enhancement of the diffusivity, is much larger than unity for all values of q, i.e., $\lambda q_m \ll 1$ or $\lambda \ll a$. Then the autocorrelation

$$\begin{aligned}\langle\delta\sigma(\mathbf{x},t)\,\delta\sigma(\mathbf{x},0)\rangle &= \frac{\lambda}{2\pi\chi}\int_{q_m}^{q_M} dq\; q^2e^{-Dqt/\lambda} \\ &= \frac{\lambda}{2\pi\chi}\left(\frac{Dt}{\lambda}\right)^{-3}\int_{Dq_mt/\lambda}^{Dq_Mt/\lambda} dz\; z^2e^{-z}\end{aligned} \tag{32}$$

where $z=Dqt/\lambda$. In the time $\lambda a/D \ll t \ll \lambda L/D$, the integral in Eq. (32) tends to be dimensionless so that we have

$$\langle\delta\sigma(\mathbf{x},t)\,\delta\sigma(\mathbf{x},0)\rangle \sim \frac{\lambda}{\chi}\left(\frac{\lambda}{Dt}\right)^3 \tag{33}$$

or

$$C_\sigma(t) \sim \left(\frac{a\lambda}{Dt}\right)^3, \tag{34}$$

which is much smaller than the membrane would have with the electrostatic interaction turned off. Figure 7 shows the

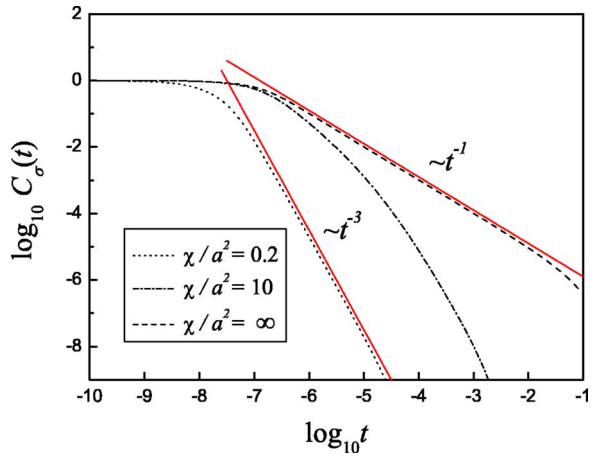

FIG. 7. (Color online) The normalized autocorrelation function of charge density fluctuations $C_\sigma(t)=\langle \delta\sigma(\mathbf{x},t)\delta\sigma(\mathbf{x},0)\rangle/\langle \delta\sigma^2(\mathbf{x})\rangle$ as a function of time for three different values of $\chi:\chi/a^2=\infty$ (neutral membrane; dashed line), 10 (dash-dotted line), and 0.2 (dotted line). The two solid lines represent the power law decays t^{-1} and t^{-3}, in the $C_\sigma(t)$, respectively. The diffusion coefficient is $D=10^6$ nm^2/s. Only for this figure, a membrane with the size of $L/a=10^3$ is considered.

numerical values of charge autocorrelation, Eq. (29), in logarithmic scales, and indicates the different regimes of its power law decay analyzed above. As the electrostatic interaction gets stronger (χ/a^2 gets smaller), the enhanced charge density diffusion dramatically lowers the correlation at long times.

As much as charge density relaxation is characterized by charge diffusion, the undulation relaxation is governed by hydrodynamic dissipation into the viscous fluid. Within linearized hydrodynamics (assuming small deviation from equilibrium) in an incompressible fluid ($\nabla\cdot\mathbf{u}=0$), the fluid velocity $\mathbf{u}(\mathbf{r})$ at one point $\mathbf{r}$ is related to the force density $\mathbf{f}(\mathbf{r}')$ at another point $\mathbf{r}'$ through the Stokes solution in the form

$$\mathbf{u}(\mathbf{r}) = \int d^3\mathbf{r}\, \mathcal{O}(\mathbf{r},\mathbf{r}')\cdot\mathbf{f}(\mathbf{r}'), \tag{35}$$

where $\mathcal{O}(\mathbf{r},\mathbf{r}')$ is the Oseen tensor

$$\mathcal{O}_{ij}(\mathbf{r},\mathbf{r}') = \frac{1}{8\pi\eta|\mathbf{r}-\mathbf{r}'|}\left(\delta_{ij}+\frac{(\mathbf{r}_i-\mathbf{r}_i')(\mathbf{r}_j-\mathbf{r}_j')}{|\mathbf{r}-\mathbf{r}'|^2}\right) \tag{36}$$

representative of the hydrodynamic interaction. The force density, localized on the surface of the membrane, is given as $f(\mathbf{r})=-\delta\mathcal{H}/\delta h(\mathbf{r})$ so that the fluid velocity normal to the surface is given by [22]

$$\mathbf{u}_n(\mathbf{x}) = -\frac{1}{(2\pi)^2}\int d^2\mathbf{q}\, e^{-i\mathbf{q}\cdot\mathbf{x}}\frac{1}{4\eta q}\frac{\delta\mathcal{H}}{\delta h^*(\mathbf{q})}. \tag{37}$$

Assuming no permeation of the fluid through the membrane, the normal fluid velocity is equal to the temporal change of undulation height,

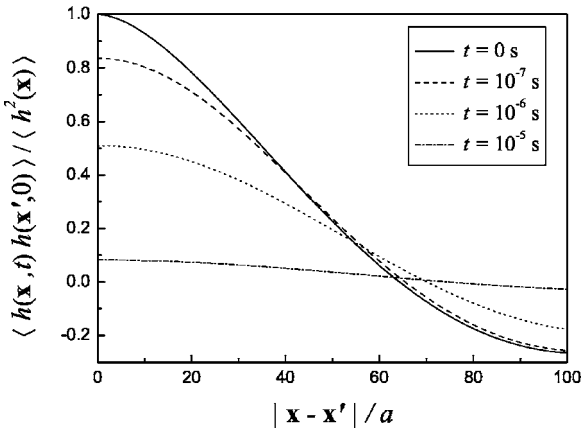

FIG. 8. The normalized dynamic correlation function of height undulations $\langle h(\mathbf{x},t)h(\mathbf{x}',0)\rangle/\langle h^2(\mathbf{x})\rangle$ at different times: $t=0$ (solid line), 10^{-7} (dashed line), 10^{-6} (dotted line), and 10^{-5} s (dash-dotted line). The charge density and bending rigidity are $\langle\sigma\rangle a^2=0.012\,24$ and $\kappa=24k_BT$, respectively.

$$\frac{\partial h(\mathbf{q},t)}{\partial t} = u_n(\mathbf{q},t). \tag{38}$$

The stochastic equation for height fluctuation is then given by

$$\frac{\partial h(\mathbf{q},t)}{\partial t} = -\frac{1}{4\eta q}\frac{\delta\mathcal{H}}{\delta h^*(\mathbf{q})} + \xi_h(\mathbf{q},t), \tag{39}$$

where $\xi_h(\mathbf{q},t)$ is the random thermal noise satisfying

$$\langle \xi_h(\mathbf{q},t)\xi_h^*(\mathbf{q},0)\rangle = \frac{2k_BT}{4\eta q}\delta(t). \tag{40}$$

Using the Hamiltonian Eq. (5), the dynamical equation becomes the linear Langevien equation

$$\frac{\partial h(\mathbf{q},t)}{\partial t} = -\frac{1}{\tau_h(\mathbf{q})}h(\mathbf{q},t) + \xi_h(\mathbf{q},t), \tag{41}$$

from which the correlation function is derived as

$$\langle h(\mathbf{q},t)h^*(\mathbf{q},0)\rangle = \langle|h(\mathbf{q})|^2\rangle e^{-t/\tau_h(\mathbf{q})}. \tag{42}$$

Here, $\tau_h(\mathbf{q})=4\eta\beta q/M(\mathbf{q})=4\eta/\kappa(q^3-q_c^3)$ is the relaxation time of undulation with wave number q. The dynamic correlation function for height fluctuations in real space,

$$\langle h(\mathbf{x},t)h(\mathbf{x}',0)\rangle = \frac{1}{2\pi}\int dq\, W_h(q)J_0(q\rho)e^{-t/\tau_h(\mathbf{q})}, \tag{43}$$

and the normalized dynamic correlation function,

$$C_h(t) = \frac{\langle h(\mathbf{x},t)h(\mathbf{x},0)\rangle}{\langle h^2(\mathbf{x})\rangle} = \frac{\int dq\, W_h(q)e^{-t/\tau_h(\mathbf{q})}}{\int dq\, W_h(q)}, \tag{44}$$

can be obtained in the same way as for the density fluctuation.

Figure 8 depicts the normalized dynamic correlation function for the excess charge density $\langle\sigma\rangle a^2=1.224\times10^{-2}$ at dif-

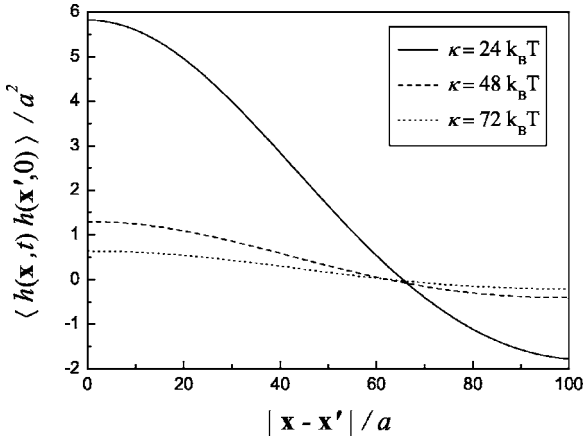

FIG. 9. The dynamic correlation function of height undulations $\langle h(\mathbf{x},t)h(\mathbf{x},0)\rangle$ for different membrane bending rigidities: $\kappa=24k_BT$ (solid line), $48k_BT$ (dashed line), and $72k_BT$ (dotted line). The parameters are chosen as $\langle\sigma\rangle a^2=1.224\times10^{-2}$ and $t=10^{-7}$ s.

ferent times: $t=0$, 10^{-7}, 10^{-6}, and 10^{-5} s. Also it is shown that the correlation relaxes in time with a rate increasing with the bending rigidity (Fig. 9). As the excess density increases approaching the critical density, defined by Eq. (11), the amplitude of the correlation, Eq. (43), diverges rapidly as a signature of undulation instability discussed before. On the other hand, the correlation tends not to be easily relaxed in time as shown in Fig. 10, which can be explained as follows. The $W_h(q)$ in Eq. (19) is dominated by $q_h\approx q_m$, the smallest wave number as discussed before, and thus, within the assumption of a single relaxation time, Eq. (43) is roughly given by

$$\langle h(\rho,t)h(0,0)\rangle \approx \langle h^2\rangle J_0(q_m\rho)e^{-t/\tau_h(q_m)}, \tag{45}$$

with $\tau_h(q_m)=4\eta L^3/\pi^3\kappa\epsilon$ and $\epsilon=1-(q_c/q_m)^3$. As the surface charge density approaches the critical value $\langle\sigma\rangle_c$, $\epsilon\to0$ and $\tau_h\to\infty$. This is qualitatively in good agreement with the numerical data shown in Fig. 10. With recourse to the time-dependent linear response theory, the above result implies

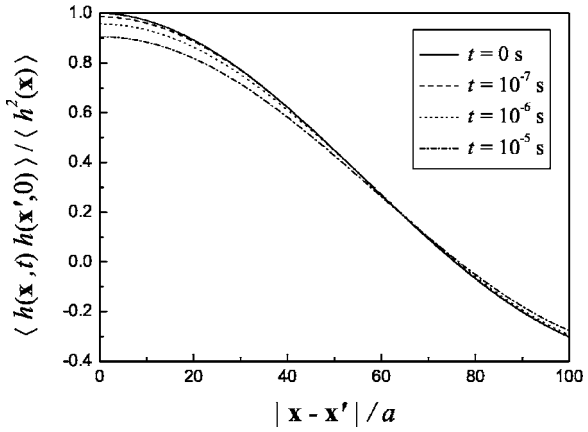

FIG. 10. The normalized dynamic correlation function of height undulations $\langle h(\mathbf{x},t)h(\mathbf{x}',0)\rangle/\langle h^2(\mathbf{x})\rangle$ for $\langle\sigma\rangle=\langle\sigma\rangle_c$ at different times: $t=0$ (solid line), 10^{-7} (dashed line), 10^{-6} (dotted line), and 10^{-5} s (dash-dotted line). The membrane bending rigidity is $\kappa=24k_BT$.

that a large bud, which formed easily upon perturbation near the instability condition, persists even after the perturbation is removed. Physically, this is due to long-range Coulomb repulsion between like charges, which can be reduced by bending.

To focus on the effect of electrostatics on the time dependence, we consider the dynamic autocorrelation function $C_h(t)=\langle h(\mathbf{x},t)h(\mathbf{x},0)\rangle/\langle h^2\rangle$, and equivalently the related mean square undulation

$$\Delta(t)=\langle[h(\mathbf{x},t)-h(\mathbf{x},0)]^2\rangle=2\langle h^2\rangle[1-C_h(t)], \tag{46}$$

which is more relevant to the dynamic structure factor probed by scattering experiments. This can be written as

$$\Delta(t)=\frac{1}{\pi\beta\kappa}\int_{q_m}^{q_M}dq\frac{1}{q^3-q_c^3}(1-e^{-(\kappa t/4\eta)(q^3-q_c^3)}). \tag{47}$$

Its time derivative, which is twice time-dependent diffusivity of the displacement, can be more manageable:

$$\frac{\partial\Delta(t)}{\partial t}=\frac{1}{4\pi\beta\eta}\int_{q_m}^{q_M}dq\,e^{-(\kappa t/4\eta)(q^3-q_c^3)}$$
$$=\frac{k_BT}{4\pi\eta}\left(\frac{\kappa t}{4\eta}\right)^{-1/3}e^{(\kappa q_c^3/4\eta)t}\int_{y_m}^{y_M}dy\,e^{-y^3}, \tag{48}$$

where $y^3=\kappa q^3t/4\eta$. At short times when $y_M=(\kappa q_M^3t/4\eta)^{1/3}\ll1$ $(t\ll\eta a^3/\kappa)$ and thus $e^{\kappa q_c^3t/4\eta}\approx1$, the integrand in Eq. (48) can be expanded for small y so that

$$\frac{\partial\Delta}{\partial t}\approx2\frac{k_BT}{8\eta a}, \tag{49}$$

which is nothing but the Stokes-Einstein relation between diffusivity and hydrodynamic friction $8\eta a$. Also,

$$\Delta(t)\approx\frac{k_BT}{4\eta a}t. \tag{50}$$

This result means that the short-time behavior of the undulation is free diffusion of each lipid with an effective hydrodynamic radius in the order of a, irrespective of the net charge of the membrane. At intermediate times, $\eta a^3/\kappa\ll t\ll\eta L^3/\kappa(y_m\ll1, y_M\gg1)$, the integrand in Eq. (48) is definite, and $e^{\kappa q_c^3t/4\eta}\approx1$ again,

$$\frac{\partial\Delta(t)}{\partial t}\sim\frac{k_BT}{\eta}\left(\frac{\kappa t}{4\eta}\right)^{-1/3}\sim\frac{k_BT}{\eta d(t)}, \tag{51}$$

and

$$\Delta(t)\sim\frac{k_BT}{\kappa}d^2\sim\langle h^2\rangle_0\left(\frac{t}{\tau_2}\right)^{\alpha}, \tag{52}$$

where $\alpha=2/3$ and the effective hydrodynamic radius $d(t)\sim(\kappa t/4\eta)^{1/3}$ grows in time in the range $a\ll d(t)\ll L$. For a neutral membrane, the above result is well known and confirmed experimentally [14,23,24]. The subdiffusive behavior $(\alpha<1)$ is attributed to coupling of the tagged point to a bending mode of the membrane. Remarkably there is no effect of the electrostatic interaction whatever the charge den-

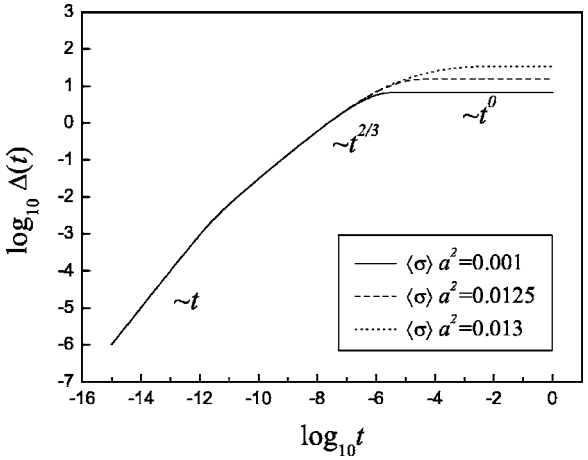

FIG. 11. The mean square undulation Δ as a function of time for different charge densities: $\langle\sigma\rangle a^2=0.001$ (solid line), 0.0125 (dashed line), and 0.013 (dotted line). The used parameters are $\kappa=24k_BT$ and $L/a=100$.

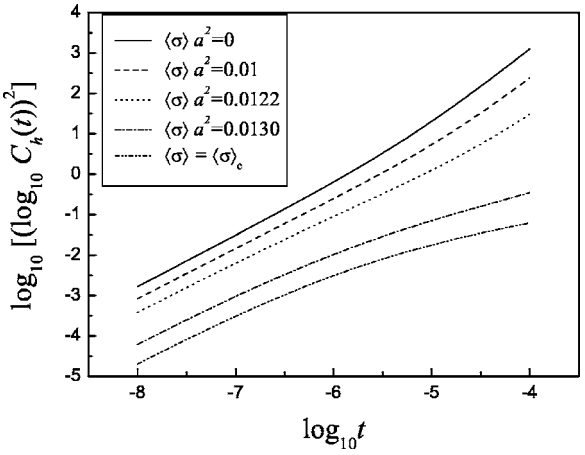

FIG. 12. The normalized autocorrelation function of height undulation $C_h(t)=\langle h(\mathbf{x},t)h(\mathbf{x},0)\rangle/\langle h^2(\mathbf{x})\rangle$ vs time for different charge densities: $\langle\sigma\rangle a^2=0$ (solid line), 0.01 (dashed line), 0.0122 (dotted line), and 0.0130 (dash-dotted line), and $\langle\sigma\rangle=\langle\sigma\rangle_c$ (dash-dot-dotted line). The membrane bending rigidity is set as $\kappa=24k_BT$.

sity in this time regime, as indeed demonstrated in the numerical plot of $\Delta(t)$, Eq. (47) (Fig. 11). At long times where $t\gg\eta L^3/\kappa$, however, the universality with regard to charge mentioned above is broken; Eq. (48) can be integrated (with $y\gg 1$) to

$$\frac{\partial\Delta}{\partial t}=\langle h^2\rangle_0 t^{-1}e^{-t/\tau_h(q_m)}. \tag{53}$$

Compared to Eq. (51), this means that the subdiffusive behavior of the height displacement gets stronger depending upon the excess charge density, eventually giving the equilibrium value $\Delta=2\langle h^2\rangle$. Integrating Eq. (53) further to the long time $t\gg\tau_h(q_m)$, we find

$$\Delta(t)=2\langle h^2\rangle\left(1-\gamma\frac{\tau_h(q_m)}{t}e^{-t/\tau_h(q_m)}\right), \tag{54}$$

where $\gamma\sim\langle h^2\rangle_0/\langle h^2\rangle$. The approach to equilibrium can therefore be very slow for charge density close to the instability, where $\tau_h(q_m)$ tends to infinity.

In each time regime studied above, the autocorrelation function $C_h(t)=1-\Delta(t)/2\langle h^2\rangle$ manifests distinct decays. (i) At short times, $0<t\ll\eta a^3/\kappa$, $C_h(t)\sim e^{-t/\tau_1}$ where $\tau_1\sim\eta L^2 a/\kappa$. (ii) For $\eta a^3/\kappa\ll t\ll\eta L^3/\kappa$, $C_h(t)\sim e^{-(t/\tau_2)^{3/2}}$ with $\tau_2\sim\eta L^3/\kappa$. (iii) For $t\gg\tau_h(q_m)$, $C_h(t)\sim(\tau_h/t)e^{-t/\tau_h(q_m)}$. This is demonstrated in the numerical plot of $C_h(t)$ in Fig. 12.

IV. SUMMARY AND REMARKS

We have investigated the static and dynamic correlation functions of surface charge density and height fluctuations in a fluid membrane with a finite net excess charge. The membrane is immersed in a viscous fluid so that different elements of the membrane couple with one another not only via electrostatic interaction but also via hydrodynamic interaction. We used a mesoscopic Hamiltonian which incorporates these fluctuations at the Gaussian level. For the case where the bilayer is symmetric, the two fluctuations are found to be decoupled in the Hamiltonian, and hence in their static and dynamic correlation functions.

In the charge fluctuation correlation, there exists a short-range damped oscillation with a period of the order of distance between lipid heads, which is given by the short-wavelength cutoff in this coarse-grained theory. This charge oscillation is due to the hard-core effect combined with the Coulomb attraction, whose amplitude, according to the theory, is independent of excess charge density but increases with the total number density of the surface charges. This is in accord with the result for three-dimensional ionic fluids previously studied using a microscopic theory. The decay of the oscillation in time is characterized by the lateral charge diffusivity enhanced by the Coulomb interaction. Due to this, the autocorrelation of the charge density decays much faster (t^{-3}) than in simple diffusion (t^{-1}) of neutral lipids at long times.

On the other hand, the correlation function of the height undulation has the shape of a bud over the entire membrane size characterized by the long-wavelength cutoff of the theory. This bud formation, which grows as the excess charge density increases, is attributed to the long-range Coulomb repulsion. As the density increases to a critical value, the repulsion induces a bending instability, wherein the membrane becomes very soft and a large bud forms spontaneously upon a minute perturbation. As shown in the time correlation of the height undulation, the relaxation of the large bud that has formed is slow and, at the critical density, becomes infinitely slow. This remarkable effect of the electrostatic repulsion is also manifested as subdiffusive motion of the undulation much stronger than in neutral membranes at long times approaching equilibrium. In contrast, the growth of the mean-square undulation at shorter times is irrespective of the net charge, obeying power laws (t and $t^{2/3}$).

Our mesoscopic Hamiltonian at the Gaussian level, a straightforward generalization of the standard model for neutral membranes to include electrostatic interactions, may be the first step toward a more comprehensive theory. Despite its simplicity, it allows us to predict the nontrivial and intriguing effects of electrostatics and fluctuations. We know of no experimental work on charged membranes to compare with our predictions. In order to study the interesting effects of coupling between charge density and surface undulation within the Gaussian level, one has to consider the electrostatic asymmetry of a bilayer, which is closer to biological situations. Incorporation of this aspect as well as a realistic ionic environment remains as a future challenge.

ACKNOWLEDGMENTS

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