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Buckling and nonlocal elasticity of charged membranes

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The elastic behavior of an interacting, and, in specific, of a charged flexible membrane is considered. In the first part of this paper the effective nonlocal elastic energy of a membrane due to a pairwise and arbitrary intra-membrane interaction is derived. Nonlocal elasticity is included to all orders, this description, therefore, corresponds to an infinite resummation of the standard gradient expansion. In the second part, the pair interaction between segments of an (on average) neutral membrane consisting of mobile positive and negative charges is derived both field theoretically in the Gaussian approximation and using a simple ion-pairing approximation. This model might also apply to strongly charged membranes with strongly condensed counter ions. The resulting contribution to the elastic energy is negative and thus favors undulations of the membrane. The bending modulus is extracted from the large-scale or small-momentum behavior of the elastic kernel and found to be comparable to k_BT for the case where ion pairing is dominant. The large-momentum elastic response exhibits a markedly different scaling than the small-momentum regime and sensitively depends on the small-distance cutoff and thus on molecular details.

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I. INTRODUCTION

The description of flexible membranes in terms of their elastic moduli is a widely used concept that sets a platform for developing theoretical concepts and interpreting experimental results [1,2]. The bending rigidity of a membrane can be varied by various means, for example, by adsorbing particles [3] or polymers [4], by anchoring polymers by one end to the membrane [5,6], or by adding stiff components to the bilayer [7].

Some time ago, it was realized by Winterhalter and Helfrich [8], that the electrostatic repulsion between different parts of a charged membrane leads to a contribution to the bending rigidity. This discovery spurned an immense activity on the elastic behavior of charged membranes. Whereas in the initial calculation by Winterhalter and Helfrich and subsequent generalizations to arbitrary geometries [9], the electrostatic interactions were treated on the linear Debye-Hückel level, the full nonlinear mean-field calculation was performed by Mitchell and Ninham [10] and Lekkerkerker [11]. The electrostatic coupling between the two monolayers that make up the lipid bilayers was also investigated [12,13], and the case of mobile charges on the membrane was shown to modify the effective bending rigidity [14]. Stacks of charged membranes were considered in a number of papers [15–17], these studies were later also extended to include the case of no added salt [18,19]. In all these calculations, the electrostatic interactions were considered on a mean-field level. The bending rigidity was found to be positive for all cases considered, meaning that the repulsive electrostatic interactions make the membranes effectively stiffer. Since the Gaussian bending energy is negative, spontaneous vesiculation is expected for low salt and high surface charge densities, as indeed observed in experiments with charged membranes [20–23].

A new theoretical mechanism for a modification of the bending rigidity of charged membranes was identified by Lau and Pincus, who considered a membrane consisting of equal amounts of mobile cationic and anionic lipid molecules [24]. Similar experimental systems have been studied in detail by Kaler and co-workers [25,26] and been found to exhibit spontaneous vesiculation as well. Such a membrane is on average neutral, and a mean-field treatment would give no energetic contribution at all. However, taking into account correlations on a Gaussian level, a negative contribution to both the normal and Gaussian bending rigidities was obtained [24], so that such (*salty*) membranes should exhibit spontaneous vesiculation as well as enhanced undulations even in the planar geometry. These results were corroborated by calculations based on the strongly correlated character of the condensed counter ions [27]. It was also argued that this model has some relevance for strongly charged membranes, since in this case the counter ions are tightly bound to the membrane and render a quasi-neutral, two-dimensional layer of mobile ions [24]. This mechanism, therefore, also favors formation of vesicles for strongly charged membranes, but one has to keep in mind that spontaneous vesiculation already results on the mean-field level and it is, therefore, difficult to judge whether fluctuations are responsible for vesiculation or not. Very recently, however, it was shown experimentally that strongly charged surfactant bilayers exhibit some superstructure consisting of undulating layers, therefore, indicative of a negative bending rigidity [28,29]. Clearly, this effect cannot be explained on the mean-field level, since mean-field theory predicts a positive bending rigidity; on the other hand, this superstructure might very well be caused by the charge-fluctuation mechanism introduced by Lau and Pincus [24].

For neutral membranes, and in the case of attractive long-ranged interactions, one expects a negative contribution to the bending rigidity, which could, if strong enough, also induce undulating membrane superstructures [30–32]. This line of thought was followed up by Brinkmann and Helfrich, who considered the effect of van der Waals interactions on the bending rigidity [33,34]. Membrane superstructures have indeed been observed in experiments with neutral membranes [35]. This experimental observation is backed up by a host of previous indications of some sort of membrane superstructure [36]. In previous theoretical investigations, a negative bending rigidity was shown to lead to spherical, saddlelike, or tubular shapes, depending on the type of stabilizing higher-order term [37]. In a different attempt to explain membrane superstructures, a negative fourth-order curvature term was assumed, stabilized by yet a higher-order curvature term, leading to typical egg-carton-like superstructures [38]. Spiky phases of smooth membranes have been investigated in the context of a more general model for fluctuating surfaces [39].

In previous calculations aimed at extracting elastic constants from some type of interacting-membrane model, the energy of a membrane was either (i) calculated for the planar, spherical, and cylindrical geometries, from which the elastic constants can be derived, or (ii) it was calculated for a sinusoidally deformed sheet, from which the spectrum of the elastic energy can be obtained (which gives the elastic coefficients as the coefficients of a small-momentum expansion).

Our aim in this paper is twofold:

(i) We derive a general formula that relates the pair potential between membrane segments with the full nonlocal elastic energy of membrane deformation. From the spectrum of this elastic energy, the bending rigidity follows as the fourth-order coefficient in a small-momentum expansion. The full nonlocal expression also allows to consider the nonperturbative regime where the local gradient expansion fails for long-ranged interactions [40]. Clearly, this approach only works for cases where the pair-potential is the dominant contribution to the deformation energy of a membrane. We demonstrate explicitly that our formula is analogous to the nonlocal persistence-length contribution derived by Barrat and Joanny for the case of interacting polymers [41]. A similar theory as ours has been developed recently for semiflexible polymers, where a buckling instability was found for sufficiently attractive pair-potentials [42].

(ii) We also calculate the effective pair-interaction between segments of a membrane consisting of equal amounts of mobile cationic and anionic lipids. We do this in the presence of salt in the bulk and, therefore, generalize the original calculation by Lau and Pincus [24], which was for zero salt concentration. In the Gaussian approximation the resulting negative contribution to the bending rigidity is rather small and never outweighs the mechanic bending rigidity [43]. However, on the Gaussian level one neglects multiloop contributions. In the strong coupling case, and this is where the Gaussian approximation fails severely, the physics is dominated by strongly bound ions pairs, which is missed by the Gaussian theory that treats ions as point particles. We, therefore, devise a second approximation, in which all ions are assumed to form pairs. Inserting the interaction between rotating dipoles, which is nothing but the two-dimensional Keesom contribution to the van der Waals interaction, into our expression for the elastic energy spectrum, we see that the negative bending energy contribution is quite sizable and can induce membrane buckling.

II. ELASTICITY CAUSED BY PAIRWISE INTERACTIONS

Neglecting overhangs, the shape of a membrane can be parameterized by a single-valued function $h(\mathbf{R})$ as a function of the two-dimensional coordinate $\mathbf{R}=(x,y)$. Assuming that membrane segments interact via a pair potential $v(r)$ which only depends on the distance r between membrane segments in three-dimensional space, the full interaction energy of a deformed membrane can be written as

$$E[h]=\frac{1}{2}\int_A d^2\mathbf{R}\int_A d^2\mathbf{R}'\,\sqrt{1+[\boldsymbol{\nabla}h(\mathbf{R})]^2}\,\sqrt{1+[\boldsymbol{\nabla}h(\mathbf{R}')]^2}\times v\{\sqrt{(\mathbf{R}-\mathbf{R}')^2+[h(\mathbf{R})-h(\mathbf{R}')]^2}\}. \tag{1}$$

All potentials and energies are measured in units of the thermal energy k_BT throughout this paper. We explicitly assume the shape fluctuations to be area conserving, i.e., the membrane does not become locally thinner upon shape changes, which leads to the square-root prefactor in the bilinear form. In this expression the integration extends over the projected area A of the membrane, which is related to the true area of the membrane A_0 by

$$A_0=\int_A d^2\mathbf{R}\sqrt{1+[\boldsymbol{\nabla}h(\mathbf{R})]^2}. \tag{2}$$

In the following we will perform a systematic, nonlocal expansion of the energy (1) in powers of the membrane shape h according to

$$E[h]=E[0]+\int_{A_0} d^2\mathbf{R}h(\mathbf{R})G(\mathbf{R})+\frac{1}{2}\int_{A_0} d^2\mathbf{R}\int_{A_0} d^2\mathbf{R}'\,h(\mathbf{R})h(\mathbf{R}')K(\mathbf{R},\mathbf{R}')+O(h^3), \tag{3}$$

where the functions defined in this expansion are

$$G(\mathbf{R})=\left.\frac{\delta E[h]}{\delta h(\mathbf{R})}\right|_{h=0}, \tag{4}$$

$$K(\mathbf{R},\mathbf{R}')=\left.\frac{\delta^2 E[h]}{\delta h(\mathbf{R})\,\delta h(\mathbf{R}')}\right|_{h=0}. \tag{5}$$

One notes that we perturb around the true area of the membrane A_0, which is an important point. As a consequence, the boundary of the integration domain in Eq. (1) depends via Eq. (2) on the displacement field h and thus gives an extra contribution in the functional derivatives in Eqs. (4) and (5). For a pair potential the linear term in h vanishes and thus $G=0$. The quadratic kernel $K(\mathbf{R},\mathbf{R}')$ contains four contributions

$$K(\mathbf{R},\mathbf{R}')=-\frac{v'(|\mathbf{R}-\mathbf{R}'|)}{|\mathbf{R}-\mathbf{R}'|}+\delta(\mathbf{R}-\mathbf{R}')\int_{A_0}d^2\tilde{\mathbf{R}}\frac{v'(|\tilde{\mathbf{R}}-\mathbf{R}|)}{|\tilde{\mathbf{R}}-\mathbf{R}|}-\nabla^2\delta(\mathbf{R}-\mathbf{R}')\int_{A_0}d^2\tilde{\mathbf{R}}v(|\tilde{\mathbf{R}}-\mathbf{R}|)+\nabla^2\delta(\mathbf{R}-\mathbf{R}')\int_{A_0}d^2\tilde{\mathbf{R}}v(|\tilde{\mathbf{R}}-\mathbf{R}_b|), \tag{6}$$

where the coordinate point $\mathbf{R}_b$ is located on the boundary of the integration domain A_0. At this point we let the integration area A_0 go to infinity in which case the kernel $K(\mathbf{R},\mathbf{R}')$ only depends on the distance $\mathbf{R}-\mathbf{R}'$. We obtain after some algebra

$$K(\mathbf{R})=-\frac{v'(|\mathbf{R}|)}{|\mathbf{R}|}+\int d^2\tilde{\mathbf{R}}\left[\delta(\mathbf{R})+\frac{\tilde{\mathbf{R}}^2}{4}\nabla^2\delta(\mathbf{R})\right]\frac{v'(|\tilde{\mathbf{R}}|)}{|\tilde{\mathbf{R}}|}. \tag{7}$$

The two-dimensional Fourier transformation of the kernel reads

$$K(q)=2\pi\int_0^\infty ds\left[1-\frac{q^2s^2}{4}-\mathcal{J}_0(qs)\right]v'(s), \tag{8}$$

and we obtain our final result after another partial integration

$$K(q)=\pi\int_0^\infty ds[q^2s-2q\mathcal{J}_1(qs)]v(s), \tag{9}$$

which is the announced relation between the nonlocal elastic kernel $K(q)$ and the membrane interaction $v(r)$. The integrand has a regular expansion in even powers of the momentum q, which leads to the following expansion of the elastic kernel:

$$K(q)=\frac{\pi q^4}{8}\int_0^\infty ds v(s)s^3-\frac{\pi q^6}{192}\int_0^\infty ds v(s)s^5+O(q^8). \tag{10}$$

A number of points are noteworthy: (i) It is seen that the quadratic term in q, which corresponds to an effective surface tension, vanishes, as it should because presence of this term would indicate breaking of the rotational invariance. This stands in clear contrast to similar calculations for an interface, where the surface tension is the leading term [40]. (ii) The leading term of Eq. (10), which corresponds to a curvature energy, is positive for repulsive forces and negative for attractive forces. In the latter case, a buckling instability is expected for sufficiently soft membranes. (iii) For short-ranged potentials, the momentum expansion in Eq. (10) converges term by term. For power-law interactions only a few terms will be finite, making a full expansion impossible. Still, the exact expression for the elastic kernel in Eq. (9), which retains the full momentum dependence and thus nonlocal terms to all orders, converges for all potentials, which for small distances diverge weaker than $v(s)\sim s^{-4}$ and for large distances decay faster than $v(s)\sim s^{-2}$. Since possible ultraviolet divergences can be removed by introducing a suitable small-distance cutoff, it follows that the description in terms of a nonlocal elastic modulus gives sensible results for almost all interaction potentials, as will be discussed in more detail in Sec. IV.

A. Analogy with interacting polymers

In this section we will discuss the connection of the result in Eq. (9) to the analogous expansion for interacting polymers performed by Joanny and Barrat [41]. They derived for an inextensible polymer that interacts via the two-point interaction $w(r)$ the following nonlocal contribution to the persistence length ℓ:

$$\ell(s)=-\frac{1}{6}\int_0^\infty dx\frac{x^3}{x+s}w'(x+s). \tag{11}$$

The one-dimensional Fourier transformation yields

$$\ell(q)=\frac{2}{q^4}\int_0^\infty dx\left[1-\frac{q^2x^2}{2}-\cos(qx)\right]\frac{w'(x)}{x}, \tag{12}$$

which is quite similar to our expression in the two-dimensional case (8) except that the persistence length is divided by the momentum to the fourth power. To make the connection manifest, we use the fact that the one-dimensional deformed polymer can be viewed as a cut through a membrane, with an effective interaction $w(r)$, which is obtained after integration of the interaction $v(r)$ over the transverse coordinate according to

$$w(s)=\int_{-\infty}^\infty dx v(\sqrt{s^2+x^2}). \tag{13}$$

In fact, inserting the interaction (13) into expression (12), we exactly obtain Eq. (8) divided by q^4. This is not surprising, since in Gaussian order, no mode-mixing occurs and, therefore, a single-mode expansion with a wave vector pointing along a definite direction yields the same kernel as our general expansion done in the last section. Clearly, this equivalence will disappear at next-leading order in the vertex functions, which, however, is not pursued in this paper.

III. GAUSSIAN THEORY FOR INTERACTIONS WITHIN A SALTY MEMBRANE

In this section we consider the partition function of a salty membrane, i.e., of a flexible two-dimensional layer that is on average neutral and contains mobile positive and negative ions. The main goal here will be to derive the effective pair potential between two segments of such a membrane within Gaussian theory, which can then be used as an input into our nonlocal elasticity theory developed in the last section.

The Gaussian field theory for a flexible layer that contains salt ions and is described by a height function $h(\mathbf{R})$ reads

$$Z[h]=\int\frac{\mathcal{D}\phi}{Z_v}\exp\left\{-\frac{1}{2}\int d^3\mathbf{r}\int d^3\mathbf{r}'\,\phi(\mathbf{r})v_{\rm DH}^{-1}(\mathbf{r},\mathbf{r}')\phi(\mathbf{r}')\right\}, \tag{14}$$

where Z_v is the partition function of the inverse Coulomb operator, $Z_v \sim \sqrt{\det v}$. This second-order expansion corresponds to the Debye-Hückel (DH) theory generalized to an interfacial geometry. The higher-order terms in the fluctuating field ϕ that we neglect contain nonlinear effects (such as present in the Poisson-Boltzmann theory), but also higher-order correlation effects. These higher-order terms have recently been considered for the bulk situation in a systematic field-theoretic expansion [44]. The ion-pairing approximation, introduced in Sec. IV B, is a heuristic approach that is capable of dealing with these nonlinear effects. It is important to note that the DH theory in the present formulation, although it neglects nonlinear effects, goes beyond the mean-field (Poisson-Boltzmann) approach in that correlations and fluctuations are included on a Gaussian level. The kernel $v_{\rm DH}^{-1}$ is the functional inverse of the DH potential and is defined by [45]

$$v_{\rm DH}^{-1}(\mathbf{r},\mathbf{r}') \equiv v_{\rm C}^{-1}(\mathbf{r}-\mathbf{r}') + \kappa^2 \delta(\mathbf{r}-\mathbf{r}')/4\pi\ell_B + \kappa_= \sqrt{1+[\nabla h(\mathbf{R})]^2}\,\delta[z-h(\mathbf{R})] \times \delta(\mathbf{r}-\mathbf{r}')/4\pi\ell_B, \tag{15}$$

where $v_{\rm C}(r) = \ell_B/r$ is the Coulomb potential and $\ell_B = e^2/4\pi\varepsilon k_B T$ is the Bjerrum length. The screening length in the bulk, κ^{-1}, is defined in the standard way by

$$\kappa^2 = 4\pi\ell_B \sum_j (q_j)^2 c_j, \tag{16}$$

where q_j and c_j are the valency and concentration of ionic species j. A second length scale emerges, $\kappa_=^{-1}$, which is defined by

$$\kappa_= = 4\pi\ell_B \sum_j (q_j^=)^2 c_j^=, \tag{17}$$

where $q_j^=$ and $c_j^=$ are the valency and surface density of ions located in the membrane. The full partition function (14) with an arbitrary position of the ion-containing surface h is intractable. So we intend to use the perturbative treatment from the last section, for which we need as an input the pair interaction between membrane segments calculated for the planar reference membrane configuration. Since the membrane position in the planar state constitutes a symmetry plane, no perpendicular force component is present, and the only potential contribution comes from a membrane displacement along the membrane surface (which is analogous to saying that the electrostatic forces generate no out-of-plane torque; note that this is different in situations where the up-down symmetry is broken as, for example, for charged interfaces between two different media). To calculate the effective interaction between membrane segments we define a new partition function that includes a lateral displacement of membrane segments,

$$Z = \int \frac{\mathcal{D}\phi}{Z_v} \exp\left\{ -\frac{1}{2}\int d^3\mathbf{r} \int d^3\mathbf{r}'\, \phi(\mathbf{r}) v_{\rm DH}^{-1}(\mathbf{r},\mathbf{r}')\phi(\mathbf{r}') - \frac{\kappa_=}{8\pi\ell_B}\int d^3\mathbf{r}\,\delta(z) g(\mathbf{R})\phi^2(\mathbf{r}) \right\}. \tag{18}$$

The weight function $g(\mathbf{R})$ is defined as

$$g(\mathbf{R}) = \delta(\mathbf{R}+\mathbf{a}) - \delta(\mathbf{R}) + \delta(\mathbf{R}-\mathbf{R}_0-\mathbf{a}) - \delta(\mathbf{R}-\mathbf{R}_0), \tag{19}$$

and corresponds to the displacement of two membrane segments, which are at a distance $\mathbf{R}_0$ by a small step $\mathbf{a}$ each (which we assume to point along the direction of the distance vector). In the limit of small incremental displacement $\mathbf{a}$ the weight function can be written as

$$g(\mathbf{R}) = \mathbf{a}\boldsymbol{\nabla}\,\delta(\mathbf{R}-\mathbf{R}_0) - \mathbf{a}\boldsymbol{\nabla}\,\delta(\mathbf{R}) + O(a^2). \tag{20}$$

The second derivative of the effective interaction between membrane segments, which we denote by $v(\mathbf{R})$, then follows as

$$-v''(\mathbf{R}_0) = \left.\frac{\ln Z - \ln Z(a=0)}{a^2}\right|_{a=0}, \tag{21}$$

where Z denotes the modified partition function defined in Eq. (18). Expanding the partition function in powers of a and using Wicks theorem, the second derivative of the interaction potential is

$$v''(\mathbf{R}_0) = -\frac{\kappa_=^2}{32\pi^2\ell_B^2}\frac{\partial^2}{\partial R_0^2}\langle \phi(\mathbf{R})\phi(\mathbf{R}+\mathbf{R}_0)\rangle^2. \tag{22}$$

Integrating both sides twice, omitting any integration constants, the final result for the membrane pair potential is

$$v(\mathbf{R}_0) = -\frac{\kappa_=^2}{32\pi^2\ell_B^2} v_{\rm DH}^2(\mathbf{0},\mathbf{R}_0), \tag{23}$$

where $v_{\rm DH}$ is given by Eq. (15) and using a planar membrane $h=0$. It remains to actually calculate $v_{\rm DH}(\mathbf{r},\mathbf{r}')$, which is complicated because of the broken translational invariance in the z direction. Since the system still has translational invariance parallel to the plane, we use $\mathbf{r}=(\mathbf{R},z)=(x,y,z)$ and may write

$$v_{\rm DH}(\mathbf{r},\mathbf{r}') = \int \frac{d^2\mathbf{p}}{(2\pi)^2} e^{\imath\mathbf{p}\cdot(\mathbf{R}-\mathbf{R}')} v_{\rm DH}(z,z',\mathbf{p}), \tag{24}$$

with a similar transformation for the inverse potential $v_{\rm DH}^{-1}$.

The solution can be calculated in a straightforward manner and is given by [45]

$$v_{\mathrm{DH}}(z,z',\mathbf{p})=\frac{2\pi\ell_B}{\sqrt{\kappa^2+p^2}}\Bigg[\exp[-|z-z'|\sqrt{\kappa^2+p^2}]-\frac{\kappa_=}{2\sqrt{\kappa^2+p^2}+\kappa_=}\exp[-(|z|+|z'|)\times\sqrt{\kappa^2+p^2}]\Bigg]. \tag{25}$$

In the limit of two points confined to the salty plane the kernel becomes

$$v_{\mathrm{DH}}(z=0,z'=0,\mathbf{p})=\frac{4\pi\ell_B}{2\sqrt{\kappa^2+p^2}+\kappa_=}. \tag{26}$$

The Debye-Hückel interaction in real space follows by a two-dimensional Fourier transformation and only depends on the lateral distance R between the two points, it reads

$$v_{\mathrm{DH}}(\mathbf{R})=\ell_B\int_0^\infty\frac{dp\,p\,\mathcal{J}_0(pR)}{\sqrt{\kappa^2+p^2}+\kappa_=/2}, \tag{27}$$

where $\mathcal{J}_0$ is the Bessel function of first kind [46]. In the absence of salt in the bulk, i.e., for $\kappa=0$, the integral can be calculated in closed form and leads to [47]

$$v_{\mathrm{DH}}(R)=\frac{\ell_B}{R}\,\frac{\pi\ell_B\kappa_=}{4}\left(N_0\left[\frac{R\kappa_=}{2}\right]-\mathbf{H}_0\left[\frac{R\kappa_=}{2}\right]\right), \tag{28}$$

where N_0 and $\mathbf{H}_0$ denote the Neumann and the Struve functions, respectively [46]. The asymptotic behavior is

$$v_{\mathrm{DH}}(R)\simeq\frac{\ell_B}{R}+\frac{\ell_B\kappa_=}{2}\ln[R\kappa_=], \tag{29}$$

for $R\ll\kappa_=^{-1}$, and

$$v_{\mathrm{DH}}(R)\simeq\frac{4\ell_B}{\kappa_=^2R^3}, \tag{30}$$

for $R\gg\kappa_=^{-1}$. We see that screening is for large separations much weaker than in the case of a three-dimensional salt solution, resulting in a DH interaction that is in fact long ranged. In the presence of salt ions in the embedding space the behavior is modified at large separations. The behavior now depends on the relative salt concentration in the interface and in the bulk: for $\kappa>\kappa_=$, that means for large bulk salt concentration, one has a behavior described by Eq. (29) for short separations $R<\kappa^{-1}$ and the regular DH interaction

$$v_{\mathrm{DH}}(R)=\frac{\ell_Be^{-\kappa R}}{R}, \tag{31}$$

for $R>\kappa^{-1}$; in this case the salt ions in the plane are relatively unimportant. In the opposite limit, $\kappa<\kappa_=$, for small bulk salt concentration, one obtains Eq. (29) for short separations $R<\kappa_=^{-1}$, Eq. (30) for $R>\kappa_=^{-1}$, and a crossover between Eqs. (30) and (31) at $R\sim\kappa^{-1}\ln[\kappa_=/\kappa]$.

IV. RESULTS

In this section we present results for the effective bending rigidity of a salty membrane. We also look at the full nonlocal behavior of the elastic modulus. In specific, we will see that for large momenta a modified effective elastic behavior results. In the first part, we will do the analysis for the salty membrane in the Gaussian approximation, as derived in the previous section. In the second part, we will derive an approximation that should be valid in the strong-coupling limit, namely, we will consider the positive and negative ions to form strongly bound dipole pairs in the membrane plane. The effective interaction between rotating dipoles gives an effective interaction that is one contribution to the van der Waals energy. In the latter case, the contribution to the bending rigidity is much larger.

A. Gaussian approximation

The effective interaction between membrane segments is determined by Eqs. (23) and (27). For sufficiently large concentration of ions in membrane, $\kappa_=>\kappa$, the effective interaction is given by

$$v(\mathbf{R})\simeq-\frac{\kappa_=^2}{32\pi^2}\begin{cases}\dfrac{1}{R^2} & \text{for}\quad R<\dfrac{2}{\kappa_=}\\[2ex] \dfrac{16}{\kappa_=^4R^6} & \text{for}\quad \dfrac{2}{\kappa_=}<R<\dfrac{2\ln(\kappa/2\kappa_=)}{\kappa},\\[2ex] \dfrac{\mathrm{e}^{-2\kappa R}}{R^2} & \text{for}\quad \dfrac{2\ln(\kappa/2\kappa_=)}{\kappa}<R\end{cases} \tag{32}$$

whereas for very small membrane ion concentration $\kappa_=<\kappa$ we obtain the result

$$v(\mathbf{R})\simeq-\frac{\kappa_=^2e^{-2\kappa R}}{32\pi^2R^2}. \tag{33}$$

The potential Eq. (32) contains an intermediate range where the presence of membrane ions is important and changes the functional form to a R^{-6} dependence. Note that this functional form is similar to the van der Waals interaction.

In Fig. 1 we plot the rescaled kernel $\tilde{K}=K\kappa_=^{-4}$ in the limit of vanishing bulk ion concentration $\kappa=0$ as determined by Eqs. (9), (23), and (27) as a function of the rescaled momentum $\tilde{q}=q\kappa_=^{-1}$. As is clearly seen, the bending rigidity contribution is negative, as expected for an attractive interaction. In Fig. 1(b) we plot $\tilde{K}/\tilde{q}^4$ that goes to a constant for small values of the momentum, demonstrating that indeed the small momentum behavior is dominated by the bending rigidity. Figure 1(c) demonstrates that the large scale behavior is described by the behavior $\tilde{K}(\tilde{q})\sim\tilde{q}^2\ln(\tilde{q})$ and thus very different from the low-momentum behavior.

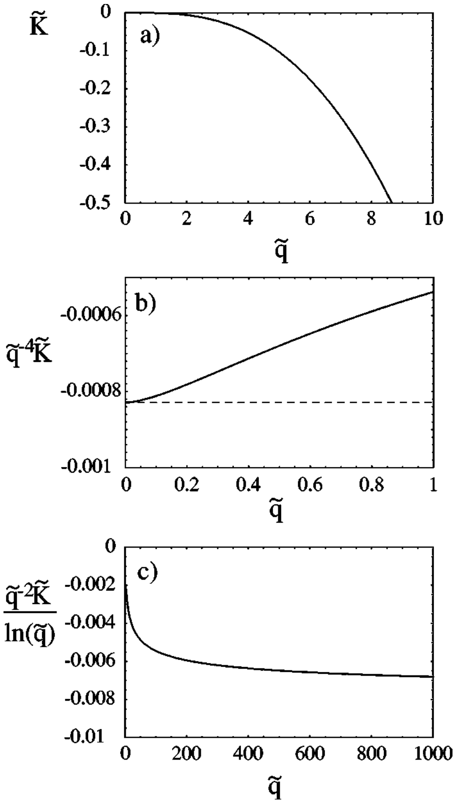

FIG. 1. Momentum-dependent elastic rescaled kernel $\tilde{K} = K\kappa_=^{-4}$ as a function of the rescaled momentum $\tilde{q} = q\kappa_=^{-1}$ for a membrane containing positive and negative ions in the Gaussian approximation with no added salt in the bulk. The plot in (b) shows that the small-momentum limit is correctly given by Eq. (35). The plot in (c) demonstrates that the large-momentum behavior obeys a different power law.

In the presence of bulk salt, and using the expansion (10), the bending rigidity follows as

$$K(q) \simeq -\frac{\kappa_=^2 q^4}{1024\pi\kappa^2} + O(\kappa_=^4/\kappa^4), \tag{34}$$

for the case of low membrane-ion density, $\kappa_= \ll \kappa$, and

$$K(q) \simeq -\frac{q^4}{384\pi} + O(\kappa_=^2/\kappa^2), \tag{35}$$

in the limit of high membrane-ion density, for $\kappa_= \gg \kappa$. The asymptotic law (35) is denoted by a broken line in Fig. 1(b).

Remarkably, for large membrane ion concentration, the effective bending rigidity, which is the prefactor of the q^4 term in Eq. (35), goes to a constant value. This saturation is due to the screening done by membrane ions themselves and is of course completely missed by approaches that neglect the screening of interactions due to correlations of membrane ions. It is also seen that the contribution to the bending rigidity is never larger than roughly 1/1000 in units of k_BT and is, therefore, not large enough by itself to cause membrane buckling since membranes have usually a bending rigidity of the order of or larger than thermal energy. What transpires, however, is that the effective elastic energy has a much slower momentum dependence for large momenta than it does for small momenta. The present calculation is on the Gaussian level. Nonlinear effects, such as ion pairing, are neglected and lead to an underestimation of the contribution to the bending rigidity. This is so because the neglect of ion-pairing overestimates the power of ions to screen the interaction. In the following section we present a heuristic analysis that aims at lifting this deficiency.

B. Dipole-dipole interaction

In the following we treat a membrane which contains ions that form ion pairs, i.e., a membrane with mobile and rotating surface dipoles. The applications of this model are manifold, since lipid bilayers contain zwitterionic headgroups that indeed exhibit large dipole moments. In the present context, we wish to interpret this model as an approximation for the strong-coupling limit where ions are so strongly bound to each other that they can be treated as dipoles in which the two charges are separated by a distance u.

To proceed, the interaction between two dipoles is given by

$$w(r,\theta_1,\theta_2,\phi) = -\frac{u^2\ell_B}{r^3}[2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\phi], \tag{36}$$

where θ_1 and θ_2 are the polar angles with respect to the connecting line between the two dipoles and ϕ is the mutual azimuthal angle. The dipole strength in reduced units is denoted by the length u.

The effective interaction $\overline{w}(r)$ between two freely rotating dipoles is obtained by averaging over all angles according to

$$\overline{w}(r) = -\ln\int_0^{2\pi}\frac{d\phi}{2\pi}\int_0^{2\pi}\frac{d\theta_1}{2\pi}\int_0^{2\pi}\frac{d\theta_2}{2\pi}\exp[-w(r,\theta_1,\theta_2,\phi)], \tag{37}$$

which corresponds to the Keesom contribution to the van der Waals interaction. The integrals in Eq. (37) cannot be done in closed form, however, with certain, unimportant modifications we can come up with simple close-form expressions that capture the fundamental physics of the averaging done in Eq. (37).

First, motivated by the calculation done in Sec. III, we will assume that the dipoles lie in the plane that contains the connecting line between the dipoles. Therefore, $\phi = 0$. The interaction (36) can be written as

$$w(r,\theta_1,\theta_2) = -\frac{u^2\ell_B}{r^3}[\tfrac{3}{2}\cos(\theta_1+\theta_2) + \tfrac{1}{2}\cos(\theta_1-\theta_2)], \tag{38}$$

and the averaging over the two angle θ_1 and θ_2 in Eq. (37) leads to

$$\overline{w}(r) = -\ln(\mathcal{I}_0[u^2\ell_B/2r^3]\mathcal{I}_0[3u^2\ell_B/2r^3]), \tag{39}$$

with the limiting behavior

$$\overline{w}(r) \simeq -\begin{cases} \dfrac{u^2\ell_B}{r^3} & \text{for} \quad r<(u^2\ell_B)^{1/3} \\ \dfrac{5u^4\ell_B^2}{8r^6} & \text{for} \quad (u^2\ell_B)^{1/3}<r. \end{cases} \tag{40}$$

To make the resulting functional form of the interaction even simpler, we now assume both dipoles to rotate in planes perpendicular to the connecting line, i.e., we set $\theta_1=\theta_2=\pi/2$. The interaction (36) is, therefore, given by

$$w(r,\phi)=\frac{u^2\ell_B\cos\phi}{r^3}, \tag{41}$$

and the averaging (37) leads to

$$\overline{w}(r)=-\ln(\mathcal{I}_0[u^2\ell_B/r^3]). \tag{42}$$

The limiting behavior of this expression is

$$\overline{w}(r) \simeq -\begin{cases} \dfrac{u^2\ell_B}{r^3} & \text{for} \quad r<(u^2\ell_B)^{1/3} \\ \dfrac{u^4\ell_B^2}{4r^6} & \text{for} \quad (u^2\ell_B)^{1/3}<r, \end{cases} \tag{43}$$

and we again obtain a r^{-6} decay for large separations, as expected for van der Waals type of interactions. The asymptotic form of the interaction given by (37) with all three interactions integrated over will be similar to our results for the simplified cases. For a collection of many dipoles one expects multibody effects, and in specific one expects the two-body interaction to be effectively weakened due to the coupling to other dipoles. We remind ourselves that it is a similar coupling between mobile ions that changes the DH potential at an interface containing mobile ions from a $1/r$ decay to a $1/r^3$ decay at large separations, see Eq. (30). However, in the present case, this effect is expected to be much smaller, since dipoles are much less effective in screening than free charges. First of all, it is known that the presence of a dielectric (dipolar) medium only changes the prefactor of the charge-charge interaction and not the type or power of decay. This is true if the dielectric medium is distributed over the entire three-dimensional space. In the present case the rotating dipoles are confined to a plane, and the long-range response functions are not modified for large separations, not even the prefactors [48]. We, therefore, can neglect the presence of other rotating dipoles in calculating the effective interaction, at least for large separations [49].

The effective interaction between membrane segments is proportional to the dipole density squared. Assuming that all salt ions form dipoles, the dipole density equals the salt density $c_{=}$ in the membrane layer. We obtain for the effective interaction between two membrane segments covered with rotating dipoles [where for numerical convenience we take the somewhat simpler expression (42)]

$$v(r)=-c_{=}^2\ln(\mathcal{I}_0[u^2\ell_B/r^3]). \tag{44}$$

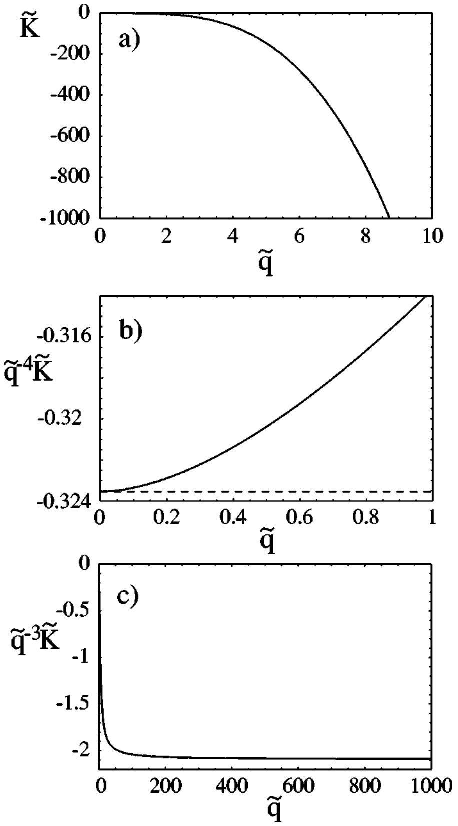

FIG. 2. Momentum-dependent elastic rescaled kernel $\tilde{K}=Kc_{=}^{-2}$ as a function of the rescaled momentum $\tilde{q}=q(u^2\ell_B)^{1/3}$ for a membrane containing positive and negative ions in the ion-paring approximation. The plot in (b) shows that the small-momentum limit is correctly given by Eq. (45). The plot in (c) demonstrates that the large-momentum behavior obeys a different power law.

In Fig. 2 we plot the rescaled kernel $\tilde{K}=Kc_{=}^{-2}$ as determined by Eqs. (9) and (44) as a function of the rescaled momentum $\tilde{q}=q(u^2\ell_B)^{1/3}$. As is clearly seen, the bending rigidity contribution is negative, as expected for attractive interactions. In Fig. 2(b) we plot $\tilde{K}/\tilde{q}^4$ that goes to a constant for small values of the momentum, similarly to our results for the Gaussian calculation displayed in Fig. 1(b). Using the expansion (10) the bending rigidity is determined by

$$K(q)\simeq -0.323\,55c_{=}^2q^4u^{8/3}\ell_B^{4/3}, \tag{45}$$

which is denoted by a broken line and agrees with the asymptotic behavior of the full kernel displayed in Fig. 2(b). Figure 2(c) demonstrates that the large scale behavior is described by the behavior $\tilde{K}(\tilde{q})\simeq -2\tilde{q}^3$ and thus intermediate in scaling between a bending energy and a surface tension.

A rough estimate for the maximal value of the numerical prefactor in Eq. (45) can be obtained by assuming a dipole length of the order $u\approx\ell_B$ and a close-packed array of ions, $c_{=}\approx 1/u^2$, in which case one has $K(q)\approx -q^4/3$. This corresponds to a negative contribution to the bending rigidity of 1/3 (in units of the thermal energy), which for a bilayer has to be multiplied by a factor of 2 and might be large enough to lead to the undulations observed for soft surfactant layers in Refs. [28,29].

To obtain an independent estimate for the appropriate prefactor of the interaction in Eq. (45) we remind ourselves that the van der Waals interaction between two membrane unit volumina goes like $w(r)=A/\pi^2 r^6$, where A is the dimensionless Hamaker constants, which for membranes in water is of the order of unity (in units of thermal energy). The van der Waals interaction between two membrane segments of thickness d goes like $v(r)=Ad^2/\pi^2 r^6$ for large separations. Comparing this with the long-range behavior of Eq. (42) we obtain the relation $c_{=}^2 u^4 \ell_B^2 = 4d^2 A/\pi^2$. We assume that the Hamaker constant only considers contributions due to fluctuating dipoles. We can thus eliminate the density of ions from the elastic energy expression (45) and obtain

$$K(q) \simeq -\frac{0.131\,13 d^2 A q^4}{(u^2 \ell_B)^{2/3}}. \tag{46}$$

Assuming realistic values for the membrane thickness, $d \approx 3$ nm, Bjerrum length, $\ell_B \approx 0.7$ nm, and the dipole length, $u \approx 0.4$ nm, the bending rigidity contribution becomes

$$K(q)/q^4 \approx -5A. \tag{47}$$

We see that the negative contribution to the bending rigidity can be comparable to unity and thus induce a buckling transition of flexible membranes if the corresponding Hamaker constant A is large enough. We hasten to add that the result for the leading q^4 term of the elastic energy depends sensitively on the small-distance behavior of the interaction. For the present case of rotating dipoles, this interaction diverges as r^{-3} for small separations, see Eq. (42), which gives an integrable but quite large contribution to the bending rigidity. For a different cutoff a different result will be obtained.

V. DISCUSSION

In this paper we introduce a method to calculate, based on an arbitrary pairwise interaction between membrane segments, the effective nonlocal elastic modulus for membrane deformations. We use this method to calculate the momentum-dependent energy spectrum $K(q)$ for deformations of a neutral membrane containing mobile positive and negative ions. This calculation is done (i) in the Gaussian approximation, which should be valid when the fraction of strongly bound ion pairs is small, and (ii) in the ion-pair approximation, where all ions are assumed to form tightly bound ion pairs. Both calculations give qualitatively the same behavior (with the ion-pair approximation yielding a larger prefactor to the bending energy contribution), exhibiting a negative elastic kernel, i.e., $K(q)<0$. For small momenta (large length scales) the elastic energy is characteristic of a bending energy, i.e., it behaves as $K(q) \sim -q^4$. For large momenta the elastic energy shows a weaker dependence on the momentum: We obtain $K(q) \sim -q^3$ for the ion-pairing approximation and $K(q) \sim -q^2 \ln q$ for the Gaussian approximation. Assuming that the interaction-induced bending rigidity contribution is indeed large enough such as to overcompensate the bare bending rigidity, what will be the structure of the membrane? Adding the interaction-induced elastic energy due to dipolar interaction, proportional to $K(q) \sim -c_{=}^2 (u^2 \ell_B)^{4/3} q^4$ for small wave vectors and $K(q) \sim -c_{=}^2 (u^2 \ell_B) q^3$ for large wave vectors (compare Fig. 2), and the bare mechanical bending energy, proportional to $K_0 q^4$, there will be a maximally instable wave vector at some length scale of the order $\lambda^* \sim K_0 c_{=}^{-2} (u^2 \ell_B)^{-1}$. Assuming that there are higher-order terms in the membrane displacement that will stabilize the membrane shape, this suggests that the membrane shows undulations of this wavelength λ^*. These findings, therefore, might help to explain the recently observed undulations of strongly charged membranes [28,29] and the superstructures frequently observed with neutral phospholipids [36]. In this respect it is worth repeating that even neutral lipids contain large dipole moments due to their zwitterionic nature.

Comparing our result for the bending rigidity within the Gaussian approximation, Eq. (35), with the result by Lau and Pincus [24], we note that the results differ by a factor of 16 and a logarithmic term. It is conceivable that the difference is due to the fact that we perform a perturbative expansion (to second order of the membrane displacement field h) around a flat reference state, whereas Lau and Pincus evaluated the free energies of cylindrical and spherical shapes in a large radius expansion. This issue deserves further studies.

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