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Renormalization of membrane rigidity by long-range interactions

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We consider the renormalization of the bending and Gaussian rigidity of model membranes induced by long-range interactions between the components making up the membrane. In particular we analyze the effect of a finite membrane thickness on the renormalization of the bending and Gaussian rigidity by long-range interactions. Particular attention is paid to the case where the interactions are of a van der Waals type.

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I. INTRODUCTION

The Helfrich theory [1] for the bending elastic energy of a membrane gives the local elastic energy to be

$$dH_{Hel} = \left[\frac{1}{2}\kappa_b(c_1 + c_2)^2 + \kappa_g c_1 c_2\right] dA, \tag{1}$$

where dA is the local area element and c_1 and c_2 are the principle local curvatures. In the above, κ_b is the bending rigidity and κ_g is the Gaussian rigidity. One expects that both these rigidities are principally generated by short-range lipid-lipid interactions. Clearly however, κ_b and κ_g will also depend on long-range interactions between the membrane components such as van der Waals and electrostatic interactions. Unlike short-range interactions, these long-range interactions can in some cases be modified rather easily; for example, one can screen electrostatic interactions by adding electrolyte to the system.

In the Monge gauge, adapted for small height fluctuations about a flat membrane, the simplest Helfrich Hamiltonian [1] used to describe the bending energy of a membrane, whose height fluctuations in the direction perpendicular to the projection plane are written as $z = h(\mathbf{x})$, corresponds to the case $\kappa_g = 0$ and is given by

$$H_{Hel} = \frac{\kappa_b}{2}\int_{A_0} d\mathbf{x}(\nabla^2 h(\mathbf{x}))^2. \tag{2}$$

A number of authors have considered the problem of renormalization of bending and Gaussian rigidities of membranes due to long-range interactions [2–8]. The somewhat related problem of the renormalization of the rigidity of liquid-vapor interfaces by long-range van der Waal interactions has also been examined in Ref. [9]. Clearly this renormalization is important in determining membrane morphology and is thus of great physical and biological importance. Positive bending rigidities hinder the formation of tubelike and spherical vesicles. A negative Gaussian rigidity could lead to the spontaneous formation of spherical vesicles, and indeed some experiments on charged membranes exhibit this spontaneous vesicle formation [10]. A negative contribution to the bending rigidity will lead to enhanced membrane fluctuations, and this in turn will lead to a modification of the effective Casimir-like interaction between membrane inclusions such as transmembrane proteins; see, for example, Ref. [11].

The first effects of long-range interactions on membrane rigidity were studied in the context where the membrane has a surface charge, more precisely an inner and outer surface charge. These systems were first studied using the Poisson Boltzmann mean field theory in its linearized form [2] and subsequently in its full nonlinear form [3,5]. In the case of fixed symmetric surface charge (with respect to the two surfaces of the membrane) it is found in these studies that renormalization of the bending rigidity is positive; however, the renormalization of the Gaussian rigidity is found to be negative. At the mean field level, even in the presence of a screening electrolyte solution, the effective interaction between like charged surfaces is repulsive, and the increase of the bending rigidity is thus easy to understand from a physical point of view. The reduction of the Gaussian rigidity in these systems is less obvious to understand from a more intuitive standpoint. The general conclusion coming from the studies of charged membranes is that the presence of surface charges can favor their buckling and perhaps induce the formation of spherical vesicles.

The literature on the renormalization of membrane rigidity by long-range interactions contains a few contradictory results, some of which this paper will try to partially resolve. Firstly a number of authors predict that nonretarded van der Waals interactions between the membrane components will lead to a reduction of κ_b [7,8]. These nonretarded interactions are attractive and the general formalism developed by Netz [7] predicts that attractive pairwise intermembrane interactions will lead to a reduction of κ_b. This seems eminently reasonable from a physical perspective; attractive interactions favor points on the membrane becoming closer together and thus a flat sheet which is rolled into a cylinder should have a lower energy. This reasoning is, however, rather deceptive; indeed we shall later see that while attractive forces favor the formation of a cylinder from a plane sheet, they may actually inhibit the formation of a spherical vesicle.

From Eq. (1) we see that taking a flat membrane and rolling it up to form a cylindrical surface of length L and radius R costs a bending free energy given by

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$$H_b = \frac{\kappa_b \pi L}{R}. \tag{3}$$

As mentioned above, it seems clear that at a fixed surface area, if the interaction is attractive then it is energetically favorable to form a cylinder from a flat sheet if the only energies involved are due to attractive long-range interactions between the membrane components. Hence, if this is the case, the renormalization of κ_b above should be negative. In a recent paper [8] we showed that this is indeed the case, in agreement with Netz [7] who used his approach for a generic pairwise potential applied to the case of effective dipole-dipole interactions. In Ref. [8] the static van der Waals interactions are taken into account via the difference in the dielectric constant of the membrane of finite thickness and the surrounding bulk, e.g., water, using the Lifshitz theory [12]. If δ is the membrane thickness, we showed that for large R and when the dielectric constant of the membrane ϵ_M is close to the dielectric constant of water ϵ_W, the van der Waals contribution to the free energy can indeed be seen as a renormalization of the bending rigidity, i.e., the free energy is given by Eq. (3) with

$$\kappa_b = -\frac{k_B T}{\pi}\frac{\Delta^2}{64}[3\ \ln(\Lambda\delta) + 0.02954], \tag{4}$$

where $\Delta = (\epsilon_W - \epsilon_M)/(\epsilon_W + \epsilon_M)$ and $\Lambda \sim 1/a$ where a is a microscopic cutoff scale. In an older paper [4], the same system was analyzed and the resulting κ_b was predicted to be positive, implying a membrane stiffening due to the van der Waals interactions. More precisely in Ref. [4] it is predicted that, for large R, $H_b \sim \text{const.} \times \ln(R\Lambda)/R$. The difference between the results of Ref. [8] and Ref. [4] can be traced to the fact that the expression for the free energy given in Ref. [4] does not go to zero when the thickness δ of the membrane goes to zero, i.e., when no membrane is present. When the result of Ref. [4] is normalized to give zero when $\delta = 0$ then the result of Ref. [8] is obtained. The apparent logarithmic behavior in the result of Ref. [4] is found to disappear, although the mechanism is very subtle and involves some very lengthy analysis. The calculation of Ref. [8] also predicts that the renormalization of κ_b is negative for arbitrarily large differences in dielectric constants, i.e., beyond the dilute approximation where the description in terms of an effective pairwise interaction is no longer valid.

An electroneutral membrane of infinitesimal thickness containing monovalent charges, such as a 1-1 electrolyte, has been studied in Ref. [6]. In this study the surrounding medium is taken to be a nonionic solvent (a somewhat unlikely situation). It was shown that for this system a cylindrical geometry has a bending free energy due to the charges of

$$H_b = -\frac{k_B T L}{24R}\ln(R/\lambda_D). \tag{5}$$

Here, $1/\lambda_D = 8\pi n_0 l_B$ where l_B is the Bjerrum length and n_0 is the (positive/negative) surface charge density of the membrane. This predicts an R dependent bending rigidity

$$\kappa_b = -\frac{k_B T}{24\pi}\ln(R/\lambda_D). \tag{6}$$

Subsequently Netz analyzed this problem in his general formalism where the area elements of the membrane interact via a generic pairwise interaction. In order to do this he was obliged to calculate an effective pairwise interaction for the system. He found that for this particular system

$$\kappa_b = -\frac{k_B T}{384\pi}. \tag{7}$$

It is interesting to ask, what is the origin of these differences? In the method of Ref. [6] one looks at the fluctuations about the mean field and effectively calculates a functional determinant related to the surface charge fluctuations. In this calculation the energy of a flat membrane is explicitly subtracted off to yield the bending energy. In the Netz formalism the energy is expanded to quadratic order in small height fluctuations about a flat membrane, the perturbation being taken about the true area of the membrane as opposed to the projected area. Possible reasons for the observed discrepancy, assuming both calculations to be formally correct, are

(i) There is an ensemble difference: the energy of a flat membrane is only explicitly subtracted off in the calculation of Ref. [6].

(ii) As pointed out by Netz [7], his calculation is done as a perturbation about a flat membrane but the calculation of Ref. [6] is explicitly done for a cylindrical (and spherical geometry). This could lead to a difference.

(iii) The effective interaction needs to be calculated in this system and there could be a difference in the approximations used.

In what follows we shall show that the formalism of Netz can be applied with an explicit subtraction of a flat membrane energy of same area and that, under rather weak assumptions, the same result is recovered. This cannot therefore be at the origin of the disagreement. In addition we show that for a general potential V between membrane components a calculation done in a cylindrical geometry agrees with the result of Netz based on a perturbation about a flat plane; however, the potential V must be of sufficiently short range. This result makes sense as the low momentum height fluctuations correspond to regions of low and slowly varying curvature, and it is thus unlikely that this could lead to a difference, at least for short-range potentials. We then use the geometric method of calculation to compute the Gaussian rigidity κ_g by examining the case of a sphere. In some cases the formulas for κ_b and κ_g obtained for an infinitesimally thin membrane need to be regularized by a short distance cutoff in the potential V. However membranes have a finite thickness and it is thus interesting to investigate the effect of a finite membrane thickness to see if this regularizes the rigidity renormalizations. The renormalization of rigidities for finite membrane thickness are therefore also derived via the geometric route.

As an application we carry out the calculation of the renormalization of the bending and Gaussian rigidities of a membrane of finite thickness δ having a differing dielectric constant to that of its surrounding medium. This calculation is carried out in the dilute limit where the two dielectric constants are close to each other and is equivalent to computing the effect of the zero frequency van der Waals interactions. In this calculation the effective pairwise van der Waals interaction is regularized with a real space cutoff, as opposed to the Fourier space cutoff employed in the eigenmode expansion of Ref. [8]. The result of this calculation with a real space cutoff is strictly identical to that of Eq. (4) up to the definition of the cutoff scale. The contribution to the Gaussian rigidity is also computed and found to be positive and with leading divergence in the small cutoff, again denoted by a, of the form δ^2/a^2.

II. THE NETZ APPROACH EXPLICITLY RENORMALIZED WITH RESPECT TO A FLAT MEMBRANE

Here we revisit the approach of Netz for the computation of the renormalization of the bending rigidity of a close to planar membrane by long-range interactions. The argument we give is slightly different in that we use a formalism which calculates the energy of a fluctuating membrane with respect to that of a flat membrane with no fluctuations but with the same surface area. Reassuringly this approach gives exactly the same result. We imagine a membrane with projected area A_0 in the Monge gauge over the region $\mathbf{x} \in A_0$ and of height $h(\mathbf{x})$ in the z direction at that point. If the membrane is allowed to fluctuate in the z direction then the bending energy due to these fluctuations is given by the following:

$$H_b = \frac{1}{2}\int_{A_0\times A_0} d\mathbf{x}d\mathbf{x}'\sqrt{1+[\nabla h(\mathbf{x})]^2}\sqrt{1+[\nabla h(\mathbf{x}')]^2}V \times(\sqrt{(\mathbf{x}-\mathbf{x}')^2+[h(\mathbf{x})-h(\mathbf{x}')]^2}) - \frac{1}{2}\int_{A\times A} d\mathbf{x}d\mathbf{x}'V(\sqrt{(\mathbf{x}-\mathbf{x}')^2}) \tag{8}$$

Note that the dimensions of V as defined above are thus $[E]/[L^4]$, E denoting energy and and L length. In the case where V is a purely energetic interaction then H_b is a purely energetic term However, if V is an effective interaction induced by thermodynamic effects, (e.g., presence of electrolyte when the membrane is charged or static van der Waals interactions), then it will have a temperature dependence and H_b is thus strictly speaking a free energy. The real area (as opposed to the projected area) of the membrane is given by

$$A = \int_{A_0} d\mathbf{x}\sqrt{1+[\nabla h(\mathbf{x})]^2} \tag{9}$$

and the second term in Eq. (8) corresponds to the subtraction of the energy of a flat membrane of the same area, which can be thought of as a flat bulk membrane from which the membrane we study is drawn from. To quadratic order in the height fluctuations h we obtain

$$H = \frac{1}{2}\int_{A_0\times A_0} d\mathbf{x}d\mathbf{x}'V(|\mathbf{x}-\mathbf{x}'|) - \frac{1}{2}\int_{A\times A} d\mathbf{x}d\mathbf{x}'V(|\mathbf{x}-\mathbf{x}'|) + \frac{1}{2}\int_{A_0\times A_0} d\mathbf{x}d\mathbf{x}'V(|\mathbf{x}-\mathbf{x}'|)[\nabla h(\mathbf{x})]^2 + \frac{1}{4}\int_{A_0\times A_0} d\mathbf{x}d\mathbf{x}'\frac{V'(|\mathbf{x}-\mathbf{x}'|)}{|\mathbf{x}-\mathbf{x}'|}[h(\mathbf{x})-h(\mathbf{x}')]^2, \tag{10}$$

where the second term depends on h through the area A, which to this quadratic order is given by

$$A = A_0 + \frac{1}{2}\int_{A_0} d\mathbf{x}[\nabla h(\mathbf{x})]^2. \tag{11}$$

This expression may be simplified in the limit of large A_0 if the following integrals over all R^2 converge:

$$v_0 = \int d\mathbf{x}V(|\mathbf{x}|) = 2\pi\int_0^\infty dr rV(r) \tag{12}$$

$$v_1 = \int d\mathbf{x}\frac{V'(|\mathbf{x}|)}{|\mathbf{x}|} = 2\pi\int_0^\infty drV'(r) = 2\pi[V(\infty)-V(0)]. \tag{13}$$

The above integrals converge when $V(0)$ is finite, which can be ensured via a suitable regularization scheme, and when $V(r)$ tends to zero quicker than $1/r^2$ for large r. In this case we find

$$H = \frac{1}{2}\int_{A_0\times A_0} d\mathbf{x}d\mathbf{x}'h(\mathbf{x})G(\mathbf{x}-\mathbf{x}')h(\mathbf{x}'), \tag{14}$$

where the operator G is given by

$$G(\mathbf{x}) = -\frac{v_0}{2}\nabla^2\delta(\mathbf{x}) + v_1\delta(\mathbf{x}) - \frac{V'(|\mathbf{x}|)}{|\mathbf{x}|}. \tag{15}$$

The two-dimensional Fourier transform of G is given by

$$\tilde{G}(q) = v_1 + \frac{v_0 q^2}{2} - 2\pi\int_0^\infty drV'(r)J_0(qr), \tag{16}$$

where

$$J_0(qr) = \frac{1}{2\pi}\int_0^{2\pi} d\theta\exp[iqr\cos(\theta)] \tag{17}$$

is a Bessel function of the first kind [13]. This result may be written as

$$\tilde{G}(q) = 2\pi\int_0^\infty dr\left(1-\frac{q^2r^2}{4}-J_0(qr)\right)V'(r), \tag{18}$$

recovering the result of Netz [7] by using the identities

$$2\pi\int_0^\infty drV'(r) = v_1 \tag{19}$$

and

$$\pi\int_0^\infty dr r^2 V'(r) = -v_0, \tag{20}$$

where the second assumption is valid providing that $\lim_{r\to\infty} V(r) r^2 = 0$. An integration by parts can be used to rewrite Eq. (18) as [7]

$$\tilde{G}(q) = 2\pi\int_0^\infty dr (q^2 r - 2qJ_1(qr))V(r). \tag{21}$$

The small q expansion of Eq. (21) gives

$$\tilde{G}(q) = \frac{\pi q^4}{8}\int_0^\infty dr V(r) r^3 + O(q^6). \tag{22}$$

Going back to real space this low momentum term gives a contribution to the simplest form of Helfrich energy, as given by Eq. (2), of

$$\Delta_{Hel} = \frac{\delta\kappa_b}{2}\int_{A_0\times A_0} d\mathbf{x}(\nabla^2 h(\mathbf{x}))^2, \tag{23}$$

where

$$\delta\kappa_b = \frac{\pi}{8}\int_0^\infty dr V(r) r^3, \tag{24}$$

is therefore interpreted as the renormalization of the membrane bending rigidity.

III. GENERAL CALCULATION FOR CYLINDERS AND SPHERES

In a cylindrical geometry the energy for an interaction V between membrane components with the corresponding energy of a flat membrane of the same area subtracted off is the bending energy. For sufficiently short-range interactions it is given by

$$H_b = \frac{2\pi R L}{2}\left[\int_{-\infty}^{\infty} dz \int_{-\pi}^{\pi} R\, d\theta\, V\left(\sqrt{4R^2\sin^2\left(\frac{\theta}{2}\right) + z^2}\right) - 2\pi\int_0^\infty dr r V(r)\right]. \tag{25}$$

The fact that the potential is short ranged is used in setting the limits of the z integration in the first integral at ±∞ and the limits of the r integration in the second integral (for the flat membrane) at 0 and ∞. In the first integral the only contribution that will be present for a short-range potential will be from the region $\theta\approx 0$, more specifically the region where $\theta = \alpha/R$ and where $\alpha\sim O(1)$. Making this change of variables and expanding the sin, we obtain the first integral in the above to be

$$I = \int_{-\infty}^{\infty} dz \int_{-\pi R}^{\pi R} d\alpha V\left(\sqrt{\alpha^2 - \frac{\alpha^4}{R^2} + O(1/R^4) + z^2}\right). \tag{26}$$

To leading order in $1/R$ this is

$$I = \int_{-\infty}^{\infty} dz \int_{-\pi R}^{\pi R} d\alpha\left[V(\sqrt{\alpha^2 + z^2}) - \frac{\alpha^4}{24R^2\sqrt{\alpha^2 + z^2}} V'(\sqrt{\alpha^2 + z^2})\right]. \tag{27}$$

For large R this can be written as

$$I = \int_0^\infty dr \int_0^{2\pi} d\theta\left[r V(r) - \frac{r^4\cos^4(\theta)}{24R^2} V'(r)\right], \tag{28}$$

where we have written $\alpha = r\cos(\theta)$ and $z = r\sin(\theta)$. We thus find that to leading order

$$H_b = \frac{\pi\delta\kappa_b L}{R} \tag{29}$$

with

$$\delta\kappa_b = -\frac{1}{24}\int_0^{2\pi} d\theta\cos^4(\theta)\int_0^\infty dr r^4 V'(r) = \frac{\pi}{8}\int_0^\infty dr r^3 V(r). \tag{30}$$

Therefore we see that the calculation in an explicitly cylindrical geometry agrees with that obtained by the formalism of Netz. This makes it unlikely that the disagreement between Refs. [6,7] is due to a difference of topology, at least for suitably short-range potentials. However the long-range nature of the potential may play a crucial role in the case of a salty membrane with no external electrolyte. In the calculations presented above, one sees clearly that the first order contribution to the bending energy comes from local curvature. This means that the energy associated with a given point comes from the local curvature about that point. For a sphere, for example, one is clearly neglecting the contributions from the sphere which come from the interactions with points on the opposite side. If the potential V has no intrinsic scale and has a power law form $V(r)\sim 1/r^\alpha$ at large r, then the contribution from a point due to points opposite to it is of the order $R^{2-\alpha}$ where the term R^2 is the area term. This means that this contribution is negligible for $\alpha > 2$, but plays an role for $\alpha\leq 2$. Indeed one sees that the first order term in the energy of the system per unit area, which corresponds to the flat membrane is given by $2\pi\int_0^\infty r dr V(r)$ and this is clearly divergent when $\alpha\leq 2$. Furthermore it is clear from Eq. (13) that even the analysis about the flat membrane breaks down in the case $\alpha < 2$.

Let us now consider the same calculation but for a sphere. For suitably short-range potentials the bending energy of the sphere is given by

$$\begin{aligned} H_b &= 2\pi R^2\left[R^2\int_0^{\pi}\sin(\theta)d\theta\int_0^{2\pi}d\phi V(R\sqrt{2-2\cos(\theta)}) - 2\pi\int_0^{\infty}drrV(r)\right] \\ &= 4\pi^2R^2\left[\int_0^{2R}drrV(r) - \int_0^{\infty}drrV(r)\right] \\ &= -4\pi^2R^2\int_{2R}^{\infty}drrV(r), \end{aligned} \tag{31}$$

where to obtain the above we have made the change of variables $2-2\cos(\theta)=r^2/R^2$. We see from Eq. (31) that if the potential V decays exponentially, or faster than exponentially, as a function of R, then the bending energy has an exponential, or faster than exponential, decay. For a sphere Eq. (1) tells us that the bending energy takes the form

$$H_b = 8\pi\kappa_b + 4\pi\kappa_g. \tag{32}$$

For short-range potentials the above calculation implies that the presence of a long, but finite range, interaction does not renormalize the bending energy of a sphere to first order; rather, we conclude that $\delta\kappa_g=-2\delta\kappa_b$—so the renormalization of the Gaussian rigidity is of the opposite sign to that of the bending rigidity. We note that the signs of these results are in agreement with the results on charged membranes [2,5]. It is interesting to note the calculations based on perturbations about a flat plane do not indicate any renormalization of the Gaussian rigidity by long-range interactions. This must be due to the inherently topological nature of the Gaussian bending energy [14], which is insensitive to the geometry of the system and only depends on the membrane topology. It is thus normal that this energy is not picked up by a local perturbative analysis. Notice that if V is negative, and decaying at $R\to\infty$ sufficiently quickly, then the bending energy is actually positive—at variance with the intuition that attractive interactions favor bending.

IV. MEMBRANES OF FINITE THICKNESS

In reality the membrane will always have a finite thickness. In the case of a cylinder we will examine the effect of long-range interactions on the bending rigidity of a cylindrical shell C of uniform thickness δ. We will take the outer radius of the cylinder to be at $R+\delta/2$ and the internal radius at $R-\delta/2$. If the cylinder is of length L then the volume of the shell is $2\pi RL\delta$. The energy of the cylinder is now given by

$$H = \frac{1}{2}\int_{C\times C}d\mathbf{r}_1 d\mathbf{r}_2 V(|\mathbf{r}_1-\mathbf{r}_2|). \tag{33}$$

Note that the potential V as defined above is now due to the interaction of volumes and not areas, it thus has physical dimensions $[E]/[L^6]$. The energy above can be written as

$$H = \pi L\int r_1 r_2 dr_1 dr_2 d\theta dz V \times(\sqrt{(r_1-r_2)^2+2r_1r_2[1-\cos(\theta)]+z^2}). \tag{34}$$

where in the above the integration ranges are $(R-\delta/2,R+\delta/2)$ for r_1 and r_2, $(-\pi,\pi)$ for θ and $(-\infty,\infty)$ for z. One now makes the change of variables $\theta=\alpha/\sqrt{r_1r_2}$, and recalling that r_1 and r_2 are of order R, expand the argument of V to fourth order in α to obtain

$$H = \pi L\int\sqrt{r_1r_2}dr_1dr_2dzd\alpha\left[V(\sqrt{(r_1-r_2)^2+z^2+\alpha^2}) - \frac{\alpha^4}{24r_1r_2}\frac{V'(\sqrt{(r_1-r_2)^2+z^2+\alpha^2})}{\sqrt{(r_1-r_2)^2+z^2+\alpha^2}}\right]. \tag{35}$$

Again taking the limits of the α integrations to $\pm\infty$, carrying out the θ integration, then replacing the coordinates (α,z) by the radial coordinates (r,θ') and writing $r_i=R+x_i$ for $i=1$ and 2 we find that to order $1/R$

$$\begin{aligned} H = \pi LR\int dx_1dx_2rdrd\theta'\Bigg[&\left(1+\frac{1}{2R}(x_1+x_2)+\frac{1}{2R^2}x_1x_2 - \frac{1}{8R^2}(x_1+x_2)^2\right)V(\sqrt{(x_1-x_2)^2+r^2}) \\ &- \frac{1}{24R^2}r^3\cos^4(\theta')\frac{V'(\sqrt{(x_1-x_2)^2+r^2})}{\sqrt{(x_1-x_2)^2+r^2}}\Bigg]. \end{aligned} \tag{36}$$

Now carrying out the θ' integration and an integration by parts on the last term above we obtain

$$H = H_{bulk} + H_b, \tag{37}$$

where H_{bulk} is the bulk energy dependent only on the volume and given by

$$H_{bulk} = 2\pi^2LR\int dx_1dx_2rdrV(\sqrt{(x_1-x_2)^2+r^2}), \tag{38}$$

and H_b is the bending energy given by

$$H_b = \frac{\pi^2L}{8R}\int dx_1dx_2rdr(r^2-2(x_1-x_2)^2)V(\sqrt{(x_1-x_2)^2+r^2}). \tag{39}$$

Note that in the above, the x_1 and x_2 integrations are over $(-\delta/2,\delta/2)$. The above result can be simplified slightly by changing variables and writing $w=x_1-x_2$ and $u=x_2+x_1$, and noting that for w positive the integration range for the variable u is then over $(-\delta+w,\delta-w)$. Therefore for a generic function $f(x,y)$ even in both its arguments we have

$$\int dx_1dx_2f(x_1-x_2,x_1+x_2) = \int_0^{\delta}dw\int_{-\delta+w}^{\delta-w}duf(w,u). \tag{40}$$

Using this change of variables we then obtain

$$H_b = \frac{\pi^2 L\delta}{4R}\int_0^\delta dw(\delta - w)\int_0^\infty rdr(r^2 - 2w^2)V(\sqrt{w^2 + r^2}). \tag{41}$$

If we take the limit of small δ we obtain

$$H_b = \frac{\delta^2\pi^2 L}{8R}\int r^3 dr V(r), \tag{42}$$

provided the above integral is finite and providing that the integration by parts carried out on the last term of Eq. (36) is valid. We note that this result is in agreement with Eq. (30) as the effective interaction between unit areas for thin shells, i.e., for small δ, is $\delta^2 V$.

The result Eq. (41) yields a bending rigidity (here we explicitly include all the integration limits)

$$\kappa_b = \frac{\pi\delta}{8}\int_0^\delta dw(\delta - w)\int_0^\infty rdr(r^2 - 2w^2)V(\sqrt{w^2 + r^2}). \tag{43}$$

The same calculation can be carried out for a sphere and one finds that the total energy is given by

$$H = 4\pi^2\int r_1^2 dr_1 r_2^2 dr_2 \sin(\theta)d\theta V \times(\sqrt{(r_1 - r_2)^2 + 2r_1 r_2[1 - \cos(\theta)]}), \tag{44}$$

where the r_1 and r_2 integrations are over $(R-\delta/2, R+\delta/2)$. One now makes the change of variables

$$r^2 = 2r_1 r_2(1 - \cos(\theta)), \tag{45}$$

which gives

$$H = \pi^2\int rdrdr_1 dr_2[(r_1 + r_2)^2 - (r_1 - r_2)^2]V(\sqrt{(r_1 - r_2)^2 + r^2}), \tag{46}$$

where for large R the limits of the r integration can be taken to be $(0,\infty)$. Now writing $r_1 = R + x_1$ and $r_2 = R + x_2$ then switching to the variables u and w as above we find

$$H = \pi^2\int_0^\delta dw\int_{-\delta+w}^{\delta-w} du[(2R + u)^2 - w^2]\int_0^\infty rdrV(\sqrt{r^2 + w^2}). \tag{47}$$

Now carrying out the u integral yields

$$H = 8\pi^2 R^2\int_0^\delta dw(\delta - w)\int_0^\infty rdrV(\sqrt{r^2 + w^2}) + \pi^2\int_0^\delta dw(\delta - w)\left[\frac{2}{3}\delta^2 - \frac{4}{3}\delta w - \frac{4}{3}w^2\right]\times\int_0^\infty rdrV(\sqrt{r^2 + w^2}). \tag{48}$$

Now to obtain the bending energy we must subtract the bulk energy from this result. The area of the flat membrane necessary to form this sphere is of radius given by

$$A_S(R) = \frac{4\pi}{3\delta}\left(\left(R + \frac{\delta}{2}\right)^3 - \left(R - \frac{\delta}{2}\right)^3\right) = 4\pi R^2 + \frac{\pi\delta^2}{3}. \tag{49}$$

The energy of a flat membrane of this area is then given by

$$H_{bulk} = \frac{1}{2}\times A_S(R)\times 2\pi\int_0^\delta dw 2(\delta - w)\int_0^\infty rdrV(\sqrt{r^2 + w^2}) = \left[8\pi^2 R^2 + \frac{2\pi^2\delta^2}{3}\right]\int_0^\delta dw(\delta - w)\int_0^\infty rdrV(\sqrt{r^2 + w^2}). \tag{50}$$

In calculating $H_b = H - H_{bulk}$ we see that the term proportional to the surface area cancels and we are left with

$$H_b = -\frac{4\pi^2}{3}\int_0^\delta dww(\delta^2 - w^2)\int_0^\infty rdrV(\sqrt{r^2 + w^2}), \tag{51}$$

which thus implies

$$2\kappa_b + \kappa_g = -\frac{\pi}{3}\int_0^\delta dww(\delta^2 - w^2)\int_0^\infty rdrV(\sqrt{r^2 + w^2}). \tag{52}$$

The result of Eq. (51) is rather significant as it shows that a spherical vesicle has a nonzero bending energy at large R when one takes into account the finite thickness of the membrane. When δ is small and the corresponding integrals turn out to be finite, we may ignore the w dependence in the argument of V in Eq. (52) to obtain a formula analogous to Eq. (42),

$$2\kappa_b + \kappa_g = -\frac{\pi\delta^4}{12}\int_0^\infty rdrV(r). \tag{53}$$

V. EFFECT OF DIFFUSE VAN DER WAALS INTERACTIONS

Here we consider the problem where the membrane of finite thickness has a different dielectric constant to that of the external media/solvent. We take the dielectric constant of the membrane to be ϵ' while the external medium has dielectric constant ϵ. This difference in dielectric gives rise to a thermal Casimir effect which is a static van der Waals interaction. In general these interactions are not pairwise, but in the diffuse limit, where $\epsilon - \epsilon'$ is small, the pairwise part of the interaction is the dominant one.

For a system volume C having dielectric constant ϵ' in an external medium of dielectric constant ϵ, the partition function for the thermal fluctuations of the zero frequency Matsubara modes of the electrostatic field is given by [12,15–17]

$$Z = \int d[\phi]\exp(S_0 + \Delta S), \tag{54}$$

where

$$S_0 = -\frac{\epsilon}{2}\int d\mathbf{x}(\nabla\phi)^2 \tag{55}$$

and

$$\Delta S = -\frac{\epsilon' - \epsilon}{2}\int_C d\mathbf{x}(\nabla\phi)^2. \tag{56}$$

Note that in S the integral is over all space but in ΔS the integral is only over the volume C containing the media of differing dielectric constant to the exterior. As the action in Eq. (54) is quadratic, the partition function can be written as a functional determinant; however, for general geometries, this calculation is rather complicated. In the case where ΔS is small one may carry out a cumulant expansion to second order which gives for the free energy F of the system

$$F - F_0 = -k_BT\left(\langle\Delta S\rangle_0 + \frac{1}{2}\langle\Delta S^2\rangle_{0,c}\right). \tag{57}$$

Here F_0 is simply the vacuum free energy in the absence of the membrane C. The subscript 0 indicates that the expectation is taken with respect to the vacuum measure S_0 and thus

$$\langle\phi(\mathbf{x})\phi(\mathbf{y})\rangle_0 = G_0(\mathbf{x}-\mathbf{y}), \tag{58}$$

where G_0 is the Green's function of the free theory with action S_0 and the subscript c denotes the connected part. Now we note that the first term of Eq. (57) is simply a term proportional to the volume of the system and thus does not contribute to the bending free energy. The dilute approximation to the bending free energy is thus

$$H = -\frac{k_BT}{2}\langle\Delta S^2\rangle_{0,c}. \tag{59}$$

In general if one writes

$$\Delta S = \int_C d\mathbf{x}R[\phi(\mathbf{x})], \tag{60}$$

then we obtain

$$H = -\frac{k_BT}{2}\int_C d\mathbf{x}d\mathbf{y}\langle R[\phi(\mathbf{x})]R[\phi(\mathbf{y})]\rangle_{0,c}, \tag{61}$$

which means that the effective pairwise potential V is given by

$$V(\mathbf{x}) = -k_BT\langle R[\phi(\mathbf{x})]R[\phi(\mathbf{0})]\rangle_{0,c}. \tag{62}$$

In the case of a difference in dielectric constants we thus obtain the potential

$$V(\mathbf{x}) = -k_BT\frac{(\epsilon-\epsilon')^2}{4}\beta^2\langle[\nabla\phi(\mathbf{x})]^2[\nabla\phi(\mathbf{0})]^2\rangle_{0,c}. \tag{63}$$

Now using the fact that $G_0(\mathbf{x}) = G_0(r)$ where $r = |\mathbf{x}|$ we obtain

$$\langle[\nabla\phi(\mathbf{x})]^2[\nabla\phi(\mathbf{0})]^2\rangle_{0,c} = \frac{4}{r^2}\left(\frac{dG_0}{dr}\right)^2 + 2\left(\frac{d^2G_0}{d^2r}\right)^2. \tag{64}$$

Here the Green's function G_0 is given by

$$G_0(\mathbf{x}) = -\frac{1}{4\pi\epsilon\beta|\mathbf{x}|}, \tag{65}$$

and thus we obtain

$$V(\mathbf{x}) = -\frac{A}{|\mathbf{x}|^6}, \tag{66}$$

where

$$A = 3k_BT\frac{(\epsilon-\epsilon')^2}{16\pi^2\epsilon^2} \approx 3k_BT\frac{\Delta^2}{4\pi^2}, \tag{67}$$

where $\Delta = (\epsilon-\epsilon')/2\epsilon \approx (\epsilon-\epsilon')/(\epsilon+\epsilon')$ to leading order in $\epsilon-\epsilon'$. This, as is to be expected, recovers the standard form of the unretarded van der Waals interaction.

We now examine the bending rigidity of a membrane of finite thickness δ with this interaction. We regularize the interaction by writing

$$V(\mathbf{x}) = -\frac{A}{(\mathbf{x}^2+a^2)^3}, \tag{68}$$

where a is a short-scale cutoff. Substituting this into Eq. (43) the r integration is easily performed to yield, after some algebra,

$$\kappa_b = -\frac{3k_BT\Delta^2}{64\pi}\int_0^\delta dw(\delta-w)\left[\frac{2a^2}{(a^2+w^2)^2} - \frac{1}{a^2+w^2}\right], \tag{69}$$

which then gives

$$\kappa_b = -\frac{3k_BT\Delta^2}{128\pi}\ln\left(\frac{\delta^2+a^2}{a^2}\right). \tag{70}$$

We see that, as with the eigenmode expansion method of Ref. [8], for small cutoff a the bending rigidity has the form

$$\kappa_b = -\frac{3k_BT\Delta^2}{64\pi}\ln\left(\frac{\delta}{a}\right), \tag{71}$$

and that the above result is identical to Eq. (4) up to a rescaling of the microscopic cutoff a.

The calculation for the sphere is also straightforward to carry out and one obtains

$$\kappa_g + 2\kappa_b = \frac{k_BT\Delta^2}{32\pi}\left[\frac{\delta^2}{a^2} - \ln\left(\frac{\delta^2+a^2}{a^2}\right)\right], \tag{72}$$

which, along with Eq. (70), gives

$$\kappa_g = \frac{k_BT\Delta^2}{64\pi}\left[2\frac{\delta^2}{a^2} + \ln\left(\frac{\delta^2+a^2}{a^2}\right)\right]. \tag{73}$$

Note that from Eq. (72) total bending energy for the sphere is positive for all values of δ/a. We see from Eq. (70) that the renormalization of κ_b due to static van der Waals interactions is rather weak. Although the result depends on the short-scale cutoff it does so only logarithmically. Physically realistic values of δ and a, corresponding to the membrane thickness and a typical dipole size or dipole separation gives at most an $O(k_BT)$ renormalization of κ_b [8]. This is much smaller than the experimental values obtained for κ_b which tend to be between 3 and 30 k_BT [14]. However Eq. (73) predicts a κ_g which depends strongly on δ and it is conceivable that van der Waals interactions make a significant contribution to κ_g. Unfortunately few experimental measurements or estimates exist for κ_g.

VI. CONCLUSIONS

In this paper we have revisited the problem of the renormalization of the bending and Gaussian rigidities of membranes by long-range interactions. These renormalizations may be calculated via a geometric approach applied to cylindrical and spherical geometries. The result obtained for κ_b is found to agree with that found for a perturbative analysis about a flat membrane in a general approach proposed by Netz [7]. We also rederived the Netz result for a flat membrane by considering an ensemble where the membrane is thought of as being drawn from a reservoir of flat nonfluctuating membrane showing the equivalence of the two approaches from an ensemble point of view. Using the geometric approach we obtained the general result for an infinitesimally thin membrane that $\kappa_g=-2\kappa_b$, i.e., the somewhat surprising result that the Gaussian rigidity is renormalized by a long-range potential with a sign opposite to the bending rigidity. This effect has also been seen in more specific mean-field studies of charged membranes. We then derived analogous formulas for the bending and Gaussian rigidity when the membrane has a finite (but small relative to the radii of curvature) thickness. Finally we calculated the bending and Gaussian rigidities induced by the thermal Casimir force, or static van der Waals interactions, for a dilute system. In agreement with our previous studies we find a negative contribution to the bending rigidity but with exactly the same functional dependence on the thickness δ of the membrane and the microscopic cutoff a when a is small compared to δ. This agreement is reassuring as although microscopic details are dominating the physics they are doing so in a rather universal way which is insensitive to the regularization scheme being employed. The Gaussian rigidity is found to undergo a positive renormalization due to van der Waals interaction. This renormalization exhibits a strong divergence as $a\to 0$ behaving as δ^2/a^2. As pointed out in Ref. [8], van der Waals interactions only weakly favor the formation of tubelike structures, such as *t*-tubules, and it is unlikely that they can stabilize cylindrical geometries thermodynamically. However if these structures are formed via another physical or biological mechanism, then attractive van der Waals forces may contribute to their stability in that they will impede the formation of spherical budding instabilities and thus enhance the metastability of these structures. Whether this enhancement of metastability is significant depends the value of δ/a and contributions of a similar functional form which will come from the nonzero frequency frequency Matsubara modes which are responsible for the fluctuating part of the van der Waals interaction.

A final comment on the conflicting results of Eq. (6) and Eq. (7) for the renormalization of the bending rigidity of a salty membrane is in order. In the case of a system with salt outside, the bare interaction induced between the membrane components, in the diffuse limit where the salt concentration within the membrane is small, behaves as $\exp(-2mr)/r^2$ where m is the external Debye mass. In this limit the two results should give the same result as the interaction is sufficiently short range. In the Netz approach an effective pairwise interaction is computed; however, in the eigenmode expansion of Lau and Pincus it is clear from their calculation that they are summing all terms in the eigenmode expansion and not just those which correspond to the dilute-pairwise limit. Concretely the logarithms in the expressions given in Ref. [6] are not expanded to second order. This means that their result is inherently taking into account multiple scattering events and thus nonpairwise interactions. All the same, one should bear in mind that the physical situation where one has salt in the membrane but none outside is rather unlikely.

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