Some observations on the renormalization of membrane rigidity by long-range interactions

D.S. Dean(1) and R.R. Horgan (2)
(1) IRSAMC, Laboratoire de Physique Quantique, UMR CNRS 5152, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cedex 04, France
(2) DAMTP, CMS, University of Cambridge, Cambridge, CB3 0WA, UK
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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

In the Monge gauge the simplest Helfrich Hamiltonian \[ H_{\text{Hel}} = \frac{\kappa_b}{2} \int_{\mathbb{A}} d\mathbf{x} (\nabla^2 h(\mathbf{x}))^2 . \] (1)

Here \( \kappa_b \) is the bending rigidity and it is principally generated by short range lipid-lipid interactions. Clearly however \( \kappa_b \) 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.

A number of authors have considered the problem of renormalization of bending and Gaussian rigidities due to long-range interactions [2, 3, 4, 5, 6, 7, 8]. Clearly this renormalization is important in determining membrane morphology and is thus of great physical and biological importance. The first effects studied were those due to the presence of a surface charge on the membrane surface, 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 non-linear 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, 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 stand point. 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 non retarded van der Waals interactions between the membrane components will lead to a reduction of \( \kappa_b \) [7, 8]. These non-retarded interactions are attractive and the general formalism developed by Netz [7] predicts that attractive pair-wise inter-membrane interactions will lead to a reduction of \( \kappa_b \). 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.

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

\[ H_b = \frac{\kappa_b \pi L}{R} . \] (2)

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 $\kappa_b$ 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 [6] 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 [2]. If $\delta$ is the membrane thickness, we showed that for large $R$ and when the dielectric constant of the membrane $\epsilon_M$ is close to the dielectric constant of water $\epsilon_W$, 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. (2) with

$$\kappa_b = -\frac{k_B T \Delta^2}{\pi} \left[ 3 \log(\Lambda \delta) + 0.02954 \right],$$

where $\Delta = (\epsilon_W - \epsilon_M)/(\epsilon_W + \epsilon_M)$ and $\Lambda \sim 1/a$ where $a$ is a microscopic cut-off scale. In an older paper [4] the same system was analyzed and the resulting $\kappa_b$ was predicted to be positive, implying a membrane stiffening due to the van der Waals interactions. More precisely in [4] it is predicted that, for large $R$, $H_b \sim \text{Const.} \times \ln(RA)/R$. The difference between the results of [8] and [4] can be traced to the fact that the expression for the free energy given in [4] does not go to zero when the thickness $\delta$ of the membrane goes to zero, i.e., when no membrane is present. When the result of [4] is normalized to give zero when $\delta = 0$ then the result of [8] is obtained. The apparent logarithmic behavior in the result of [4] is found to disappear, although the mechanism is very subtle and involves some very lengthy analysis. The calculation of [8] also predicts that the renormalization of $\kappa_b$ 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 electro-neutral membrane of infinitesimal thickness containing monovalent charges, such as a 1-1 electrolyte, has been studied in [6]. In this study the surrounding medium is taken to be a non-ionic 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

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

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

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

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 and effective pairwise interaction for the system. He found that for this particular system

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

It is interesting to ask what is the origin of these differences. In the method of [8] 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

- There is an ensemble difference: the energy of a flat membrane is only explicitly subtracted off in the calculation of [8].
- As pointed out by Netz [7], his calculation is done as a perturbation about a flat membrane but the calculation of [8] is explicitly done for a cylindrical (and spherical geometry). This could lead to a difference.
- 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 \( \kappa_g \) by examining the case of a sphere. In some cases the formulas for \( \kappa_b \) and \( \kappa_g \) obtained for an infinitesimally thin membrane need to be regularized by a short distance cut-off 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 renormalization the bending and Gaussian rigidities of a membrane of finite thickness \( \delta \) 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 cut-off, as opposed to the Fourier space cut-off employed in the eigen-mode expansion of \( \kappa_g \). The result of this calculation with a real space cut-off is strictly identical to that of Eq. (1) up to the definition of the cut-off scale. The contribution to the Gaussian rigidity is also computed and found to be positive and with leading divergence in the small cut-off, again denoted by \( a \), of the form \( \delta^2/a^2 \).

## 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 \( x \in A_0 \) and of height \( h(x) \) 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:

\[
H_b = \frac{1}{2} \int_{A_0 \times A_0} dxdx' \sqrt{1 + (\nabla h(x))^2} \sqrt{1 + (\nabla h(x'))^2} V \left( \sqrt{(x - x')^2 + (h(x) - h(x'))^2} \right) - \frac{1}{2} \int_{A \times A} dxdx' V \left( \sqrt{(x - x')^2} \right) \tag{7}
\]

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:

\[
A = \int_{A_0} dx \sqrt{1 + (\nabla h(x))^2} \tag{8}
\]

and the second term in Eq. (7) 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

\[
H = \frac{1}{2} \int_{A_0 \times A_0} dxdx' V(|x - x'|) - \frac{1}{2} \int_{A \times A} dxdx' V(|x - x'|) + \frac{1}{2} \int_{A_0 \times A_0} dxdx' V(|x - x'|) (\nabla h(x))^2 + \frac{1}{4} \int_{A_0 \times A_0} dxdx' \frac{V'(|x - x'|)}{|x - x'|} (h(x) - h(x'))^2, \tag{9}
\]

the second term depends on \( h \) through the area \( A \) which to this quadratic order is given by

\[
A = A_0 + \frac{1}{2} \int_{A_0} dx (\nabla h(x))^2. \tag{10}
\]

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

\[
v_0 = \int dV V(|x|) = 2\pi \int_0^\infty dr rV(r) \tag{11}
\]
\( v_1 = \int d\mathbf{x} \frac{V'(|\mathbf{x}|)}{|\mathbf{x}|} = 2\pi \int_0^\infty dr V'(r) = 2\pi (V(\infty) - V(0)). \) (12)

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

\[
H = \frac{1}{2} \int_{A_0 \times A_0} dx dx' h(x) G(x - x') h(x'),
\] (13)

where the operator \( G \) is given by

\[
G(x) = -\frac{v_0}{2} \nabla^2 \delta(x) + v_1 \delta(x) - \frac{V'(|x|)}{|x|}.
\] (14)

The two dimensional Fourier transform of \( G \) is given by

\[
\tilde{G}(q) = v_1 + \frac{v_0 q^2}{2} - 2\pi \int_0^\infty dr V'(r) J_0(qr)
\] (15)

where

\[
J_0(qr) = \frac{1}{2\pi} \int_0^{2\pi} d\theta \exp(i q r \cos(\theta))
\] (16)

is a Bessel function of the first kind [10]. This results may be written as

\[
\tilde{G}(q) = 2\pi \int_0^\infty dr \left(1 - \frac{q^2 r^2}{4} - J_0(qr)\right) V'(r),
\] (17)

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

\[
2\pi \int_0^\infty dr V'(r) = v_1
\] (18)

and

\[
\pi \int_0^\infty dr r^2 V'(r) = -v_0,
\] (19)

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. (17) as [11]

\[
\tilde{G}(q) = 2\pi \int_0^\infty dr \left(q^2 r - 2 q J_1(qr)\right) V(r).
\] (20)

The small \( q \) expansion of Eq. (20) gives

\[
\tilde{G}(q) = \frac{\pi q^4}{8} \int_0^\infty dr V(r)r^3 + O(q^6).
\] (21)

Going back to real space this low momentum term gives a contribution to the Helfrich energy of

\[
\Delta_{Hef} = \frac{\delta\kappa_b}{2} \int_{A_0 \times A_0} d\mathbf{x} (\nabla^2 h(\mathbf{x}))^2
\] (22)

where

\[
\delta\kappa_b = \frac{\pi}{8} \int_0^\infty dr V(r)r^3,
\] (23)

is 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

$$H_b = \frac{2\pi RL}{2} \left[ \int_{-\infty}^{\infty} dz \int_{-\pi}^{\pi} Rd\theta V \left( \sqrt{4R^2\sin^2(\frac{\theta}{2}) + z^2} \right) - 2\pi \int_{0}^{\infty} dr r V(r) \right]$$

(24)

The fact that the potential is short ranged is used in setting the limits of the $z$ integration in the first integral at $\pm \infty$ and the limits of the $r$ integration in the second integral (for the flat membrane) at 0 and $\infty$. In the first integral the only contribution that will be present for a short range potential will be from the region $\theta = 0$, 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

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

(25)

To leading order in $1/R$ this is

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

(26)

For large $R$ this can be written as

$$I = \int_{0}^{\infty} dr \int_{0}^{2\pi} d\theta \left[ r V(r) - \frac{r^4 \cos^4(\theta)}{24R^2} V'(r) \right],$$

(27)

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

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

(28)

with

$$\delta \kappa_b = \frac{1}{24} \int_{0}^{2\pi} d\theta \cos^4(\theta) \int_{0}^{\infty} dr \ r^4 \frac{\partial V}{\partial r}.$$

(29)

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 [7] and [6] 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 $2\pi \int_{0}^{\infty} r dr V(r) \ r^3 V(r)$ and this is clearly divergent when $\alpha \leq 2$. Furthermore it is clear from Eq. [22] 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

$$H_b = 2\pi R^2 \left[ R^2 \int_{0}^{\pi} \sin(\theta) d\theta \int_{0}^{2\pi} d\phi \ V \left( R\sqrt{2 - 2\cos(\theta)} \right) - 2\pi \int_{0}^{\infty} dr r V(r) \right]$$

(24)
\[ H = 4\pi^2 R^2 \left[ \int_0^{2R} dr \ r V(r) - \int_0^\infty dr \ r V(r) \right] \]
\[ = -4\pi^2 R^2 \int_{2R}^\infty dr \ r V(r), \quad (30) \]

where to obtain the above we have made the change of variables \( 2 - 2\cos(\theta) = r^2/R^2 \). We see from Eq. (30) 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 the bending energy takes the form
\[ H_b = 8\pi \kappa_b + 4\pi \kappa_g, \quad (31) \]

where \( \kappa_b \) is the bending rigidity and \( \kappa_g \) is the Gaussian rigidity [11]. 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]. 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 [11], 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 \( \delta \). 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
\[ H = \frac{1}{2} \int_{\mathcal{C} \times C} d\mathbf{r}_1 d\mathbf{r}_2 V(|\mathbf{r}_1 - \mathbf{r}_2|), \quad (32) \]

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
\[ H = \pi L \int r_1 r_2 d\mathbf{r}_1 d\mathbf{r}_2 d\theta d\mathbf{z} V \left( \sqrt{(r_1 - r_2)^2 + \alpha^2} \right), \quad (33) \]

where in the above the integration ranges are \((R - \delta/2, R + \delta/2)\) for \( r_1 \) and \( r_2 \), \((-\pi, \pi)\) for \( \theta \) and \((-\infty, \infty)\) for \( z \). One now makes the change of variables \( \theta = \alpha/\sqrt{r_1 r_2} \), and recalling that \( r_1 \) and \( r_2 \) are of order \( R \), expand the argument of \( V \) to fourth order in \( \alpha \) to obtain
\[ H = \pi L \int \sqrt{r_1 r_2} dr_1 dr_2 dz d\alpha \left[ V \left( \sqrt{(r_1 - r_2)^2 + \alpha^2} \right) - \frac{\alpha^4}{24 r_1 r_2} V'' \left( \sqrt{(r_1 - r_2)^2 + \alpha^2} \right) \right]. \quad (34) \]

Again taking the limits of the \( \alpha \) integrations to \( \pm \infty \), carrying out the \( \theta \) integration, then replacing the coordinates \((\alpha, z)\) by the radial coordinates \((r, \theta')\) and writing \( r_i = R + x_i \) for \( i = 1 \) and \( 2 \) we find that to order \( 1/R \)
\[ H = \pi LR \int dx_1 dx_2 dr d\theta' \left[ (1 + \frac{1}{2R} (x_1 + x_2) + \frac{1}{2R^2} x_1 x_2 - \frac{1}{8R^2} (x_1 + x_2)^2) V \left( \sqrt{(x_1 - x_2)^2 + r^2} \right) \right. \]
\[ \left. \quad - \frac{1}{24R^2} r^2 \cos^4(\theta') \frac{V'' \left( \sqrt{(x_1 - x_2)^2 + r^2} \right)}{\sqrt{(x_1 - x_2)^2 + r^2}} \right]. \quad (35) \]

Now carrying out the \( \theta' \) integration and an integration by parts on the last term above we obtain.
\[ H = H_{bulk} + H_b \quad (36) \]
where $H_{\text{bulk}}$ is the bulk energy dependent only on the volume and given by

$$H_{\text{bulk}} = 2\pi^2 LR \int dx_1 dx_2 r dr r V \left( \sqrt{(x_1 - x_2)^2 + r^2} \right), \quad (37)$$

and $H_b$ is the bending energy given by

$$H_b = \frac{\pi^2 L}{8R} \int dx_1 dx_2 r dr (r^2 - 2(x_1 - x_2)^2) V \left( \sqrt{(x_1 - x_2)^2 + r^2} \right). \quad (38)$$

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

$$\int dx_1 dx_2 f(x_1 - x_2, x_1 + x_2) = \int_0^\delta du \int_{-\delta + w}^{\delta - w} f(w, u). \quad (39)$$

Using this change of variables we then obtain

$$H_b = \frac{\pi^2 L}{4R} \int_0^\delta dw (\delta - w) \int_0^\infty rdr (r^2 - 2w^2) V \left( \sqrt{w^2 + r^2} \right). \quad (40)$$

If we take the limit of small $\delta$ we obtain

$$H_b = \frac{\delta^2 \pi^2 L}{8R} \int r^3 dr \ V(r), \quad (41)$$

provided the above integral is finite and providing that the integration by parts carried out on the last term of Eq. 35 is valid. We note that this result is in agreement with Eq. 20 as the effective interaction between unit areas for thin shells, i.e. for small $\delta$, is $\delta^2 V$.

The result Eq. 40 yields a bending rigidity (here we explicitly include all the integration limits)

$$\kappa_b = \frac{\pi \delta}{8} \int_0^\delta dw (\delta - w) \int_0^\infty rdr (r^2 - 2w^2) V \left( \sqrt{w^2 + r^2} \right). \quad (42)$$

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

$$H = 4\pi^2 \int r_1^2 dr_1 r_2^2 dr_2 \sin(\theta) d\theta \ V \left( \sqrt{(r_1 - r_2)^2 + 2r_1 r_2 (1 - \cos(\theta))} \right) \quad (43)$$

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

$$r^2 = 2r_1 r_2 (1 - \cos(\theta)) \quad (44)$$

which gives

$$H = \pi^2 \int rdr dr_1 dr_2 \left[ (r_1 + r_2)^2 - (r_1 - r_2)^2 \right] V \left( \sqrt{(r_1 - r_2)^2 + r^2} \right), \quad (45)$$

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

$$H = \pi^2 \int_0^\delta dw \int_{-\delta + w}^{\delta - w} du \left[ (2R + u)^2 - w^2 \right] \int_0^\infty rdr V \left( \sqrt{r^2 + w^2} \right). \quad (46)$$

Now carrying out the $u$ integral yields

$$H = 8\pi^2 R^2 \int_0^\delta dw (\delta - w) \int_0^\infty rdr V \left( \sqrt{r^2 + w^2} \right) \quad (47)$$

$$+ \pi^2 \int_0^\delta dw (\delta - w) \left[ \frac{2}{3} \delta^2 - \frac{4}{3} \delta w - \frac{4}{3} w^2 \right] \int_0^\infty rdr V \left( \sqrt{r^2 + w^2} \right). \quad (47)$$
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

\[ A_S(R) = \frac{4\pi}{3\delta} \left( (R + \frac{\delta}{2})^3 - (R - \frac{\delta}{2})^3 \right) \]

\[ = 4\pi R^2 + \frac{\pi\delta^2}{3} \] (48)

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

\[ H_{bulk} = \frac{1}{2} A_S(R) \times 2\pi \int_{0}^{\delta} dw \frac{2(\delta - w)}{4\pi R} \int_{0}^{\infty} rdr V\left( \sqrt{r^2 + w^2} \right) \]

\[ = \left[ 8\pi^2 R^2 + \frac{2\pi^2\delta^2}{3} \right] \int_{0}^{\delta} dw \frac{\delta - w}{\sqrt{r^2 + w^2}} \int_{0}^{\infty} rdr V\left( \sqrt{r^2 + w^2} \right) \] (49)

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

\[ H_b = -\frac{4\pi^2}{3} \int_{0}^{\delta} dw \frac{w}{\sqrt{\delta^2 - w^2}} \int_{0}^{\infty} rdr V\left( \sqrt{r^2 + w^2} \right), \] (50)

which thus implies

\[ 2\kappa_b + \kappa_g = -\frac{\pi}{3} \int_{0}^{\delta} dw \frac{w}{\sqrt{\delta^2 - w^2}} \int_{0}^{\infty} rdr V\left( \sqrt{r^2 + w^2} \right) \] (51)

The result Eq. (50) is rather significant as it shows that a spherical vesicle has a non-zero bending energy at large \( R \) when one takes into account the finite thickness of the membrane. When \( \delta \) is small and the corresponding integrals turn out to be finite we may ignore the \( w \) dependence in the argument of \( V \) in Eq. (51) to obtain a formula analogous to Eq. (41):

\[ 2\kappa_b + \kappa_g = -\frac{\pi\delta^4}{12} \int_{0}^{\infty} rdr V(r). \] (52)

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 \( \epsilon' \) while the external medium has dielectric constant \( \epsilon \). 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 \( \epsilon' \) in an external medium of dielectric constant \( \epsilon \), the partition function for the thermal fluctuations of the zero frequency Matsubara modes of the electrostatic field is given by

\[ Z = \int d[\phi] \exp (S_0 + \Delta S) \] (53)

where

\[ S_0 = -\frac{\epsilon}{2} \int d\mathbf{x}(\nabla \phi)^2 \] (54)

and

\[ \Delta S = -\frac{\epsilon' - \epsilon}{2} \int_C d\mathbf{x}(\nabla \phi)^2. \] (55)

Note that in \( S \) the integral is over all space but in \( \Delta S \) the integral is only over the volume \( C \) containing the media of differing dielectric constant to the exterior. As the action in Eq. (53) 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 $\Delta S$ is small one may carry out a cumulant expansion to second order which gives for the free energy $F$ of the system

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

(56)

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

$$\langle \phi(x) \phi(y) \rangle_0 = G_0(x - y),$$

(57)

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. (56) 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

$$H = -\frac{k_B T}{2} \langle \Delta S^2 \rangle_{0,c},$$

(58)

In general if one writes

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

(59)

then we obtain

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

(60)

which means that the effective pairwise potential $V$ is given by

$$V(\mathbf{x}) = -k_B T \langle R[\phi(\mathbf{x})] R[\phi(0)] \rangle_{0,c}$$

(61)

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

$$V(\mathbf{x}) = -k_B T \frac{(\epsilon - \epsilon')^2}{4} \beta^2 \langle (\nabla \phi(\mathbf{x}))^2 (\nabla \phi(0))^2 \rangle_{0,c}$$

(62)

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

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

(63)

Here the Green’s function $G_0$ is given by

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

(64)

and thus we obtain

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

(65)

where

$$A = 3k_B T \frac{(\epsilon - \epsilon')^2}{16\pi^2 \epsilon^2}$$

$$\approx 3k_B T \frac{\Delta^2}{4\pi^2}$$

(66)

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 $\delta$ with this interaction. We regularize the interaction by writing

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

where $a$ is a short-scale cutoff. Substituting this into Eq. (42) the $r$ integration is easily performed to yield, after some algebra,

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

which then gives

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

We see that, as with the eigen-mode expansion method of [8], for small cut-off $a$ the bending rigidity has the form

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

and that the above result is identical to Eq. (3) up to a rescaling of the microscopic cut-off $a$.

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

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

which along with Eq. (68) gives

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

Note that from Eq. (71) total bending energy for the sphere is positive for all values of $\delta/a$. We see from Eq. (70) that the renormalization of $\kappa_b$ due to static van der Waals interactions is rather weak. Although the result depends on the short scale cut-off it does so only logarithmically. Physically realistic values of $\delta$ and $a$, corresponding to the membrane thickness and a typical dipole size or dipole separation gives at most an $O(k_BT)$ renormalization of $\kappa_b$ [11]. This is much smaller than the experimental values obtained for $\kappa_b$ which tend to be between $3 - 30 k_BT$ [11]. However Eq. (72) predicts a $\kappa_g$ which depends strongly on $\delta$ and it is conceivable that van der Waals interactions make a significant contribution to $\kappa_g$. Unfortunately few experimental measurements or estimates exist for $\kappa_g$.

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 $\kappa_b$ is found to agree with that found for a perturbative analysis about a flat membrane in a general approach proposed by Netz [2]. 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 non-fluctuating 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 $\delta$ of the membrane and the microscopic cut-off $a$ when $a$ is small compared to $\delta$. 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 strongly divergent as $a \to 0$ behaving as $\delta^2/a^2$. As pointed out in [8], van der Waals interactions only weakly favor the formation of tube-like 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 $\delta/a$ and contributions of a similar functional form which will come from the non-zero frequency frequency Matsubara modes which are responsible for the fluctuating part of the van der Waals interaction.

A final comment on the conflicting results Eq. (5) and Eq. (6) 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 eigen-mode expansion of Pincus and Lau it is clear from their calculation that they are summing all terms in the eigen-mode expansion and not just those which correspond to the dilute-pairwise limit. Concretely the logarithms in the expressions given in [6] are not expanded to second order. This means that their result is inherently taking into account multiple scattering events and thus non-pairwise interactions. All the same one should bare in mind that the physical situation where one has salt in the membrane but non outside is rather unlikely.

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