MEMBRANE STIFFNESS FROM VAN DER WAALS FORCES ☆

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We calculate the contribution to the membrane curvature stiffness of the charge fluctuations in the membrane and its environment. It is found to be logarithmically divergent in the membrane thickness, positive for the mean curvature and negative for the Gaussian curvature, with a proportionality factor involving the dispersive properties of the materials.

1. In membrane physics, van der Waals forces which have their origin in the charge fluctuations of the dielectric materials of the system [1] govern a variety of important phenomena. At intermediate distances r of 10–100 Å they appear as a $1/r^2$ attractive potential [2] which is responsible for the existence of the many layered phases in systems of soap and water or soap, oil, and water (in the latter case ruining the effectiveness of tertiary oil recovery). At shorter distances, they are defeated by repulsive hydration forces. At very long distances, the finite travel time of the electromagnetic waves (retardation) cuts down on high frequency fluctuations. Between two far separated stacks of membranes this manifests itself in a crossover from $-1/r^2$ to $-1/r^3$ between 100 Å and 1000 Å [2]. For pairs of individual membranes, the falloff is more rapid. Salt in the aqueous environment makes the falloff exponential over the Debye length.

The most important counteragent of the van der Waals forces are the undulation forces [3]. They attempt to increase the distance between membranes so as to create space for configurational entropy and amount to a repulsive $1/r^2$ potential if r is smaller than the order of the de Gennes persistence length $\xi \approx 300$ Å [#1] (which is the length scale over which a membrane appears as a smooth surface, due to its curvature stiffness). The transitions between layered phases are mostly due to an interplay between these two forces [5], and its thorough understanding is crucial for an eventual predictability of many important processes.

The most obvious origin of curvature stiffness is the molecular structure. It is easy to visualize how rod-like molecules orthogonal to the surface create resistence to bending, and we have constructed simple field theoretic models which demonstrate this quantitatively [6]. These models also simulate nicely the reduction of surface tension in oil–water interfaces by soap molecules. Another part of the stiffness stems from the electric forces due to surface dipoles or charges. This also has been demonstrated in the above models [6].

In this note we want to draw attention to the fact that besides fighting effectively undulation forces, the van der Waals forces also renormalize the molecular stiffness properties of a membrane, depending on the dielectric properties of the materials involved. We shall demonstrate that they stiffen the membrane while reducing simultaneously the energy associated with the Gaussian curvature. The integral over the Gaussian curvature depends only on the topology of the surface and is proportional to $1-h$ where h is the number of handles of surface. The decrease of the associated stiffness by van der Waals forces implies a favorization of bubbles over multiply connected surfaces.

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#1 The crossover from this regime to the exponential falloff at larger distance, when the surface looks wrinkled, is calculated in ref. [14].

The curvature stiffness generated by van der Waals forces has an important property which must be emphasized at this place. Due to the long-range nature of the dispersive forces it *cannot* be represented in the local Helfrich form [7]

$$E=\frac{1}{\alpha}\int d^2\xi\sqrt{g}\,(c_1+c_2)^2+\frac{1}{\bar{\alpha}}\int d^2\xi\sqrt{g}\,c_1c_2\,,$$

where $c_1(\xi)$, $c_2(\xi)$ are the principal curvatures. Instead, the energy will be a bilocal integral

$$\int d^2\xi\sqrt{g}\int d^2\xi'\,\sqrt{g'}\,c_i(\xi)\,e_{ij}(\xi,\xi')\,c_j(\xi')\,,$$

with a long-range kernel $e_{ij}(\xi,\xi')$.

In the present note we shall not give a complete study of the non-local properties of this energy but consider only the global effects of the van der Waals forces upon the curvature stiffness. We shall calculate the energy difference between a spherical or a cylindrical membrane and their planar limits. Neglecting retardation effects, the fluctuation energy density of the electric potential in a dielectric medium is given by

$$f=\frac{k_BT}{2A}\sum_{n=-\infty}^{\infty}\operatorname{tr}\ln[-\epsilon(\omega_n)\nabla^2]\,, \tag{1}$$

where $\epsilon(\omega)$ is the frequency dependent dielectric constant, $\omega_n=2\pi/k_BT$, $n=0,\pm1,\pm2$ are the Matsubara frequencies (T=temperature), and "tr" denotes the functional trace. For an ensemble of damped oscillators of charge e',

$$\epsilon(\omega)=1+4\pi\frac{e^2}{m}\sum_i(\omega_i^2-\omega^2-i\gamma_j)^{-1}\,.$$

For $\omega\to\infty$, this behaves like $\epsilon(\omega)\sim1-\omega_p^2/\omega^2$ where ω_p is the plasma frequency with $\omega_p^2=4\pi e^2N/m$.

2. For a layered structure with the geometry

ϵ_1, for $z\in(-\infty,-d/2)$,

ϵ, for $z\in(-d/2,d/2)$,

ϵ_2, for $z\in(d/2,\infty)$,

the tr ln is the logarithm of the secular determinant of the solutions of the Poisson equation $-\epsilon\nabla^2\psi=0$ in this geometry. Let us denote the two independent solutions by $I=e^{kz}e^{i\boldsymbol{k}\cdot\boldsymbol{\xi}}$, $K=e^{-kz}e^{i\boldsymbol{k}\cdot\boldsymbol{\xi}}$, where $\boldsymbol{\xi}$ and $\boldsymbol{k}$ are transverse coordinates and momenta, respectively. The general solution is $aI+bK$. The boundary conditions require that $\partial_\xi\varphi$ and $\epsilon\partial_z\varphi$ be continuous everywhere, giving the secular equations

$$z=-d/2:\quad a\Delta_1+b=0\,,$$

$$z=d/2:\quad a+b\Delta_2=0\,, \tag{2a}$$

with (a prime denoting $\partial/\partial z$)

$$\Delta_1=\frac{(\epsilon_1-\epsilon)II'}{\epsilon_1I'K-\epsilon IK'}\,,\quad \Delta_2=\frac{(\epsilon_2-\epsilon)KK'}{\epsilon_2IK'-\epsilon I'K}\,, \tag{2b}$$

the first being evaluated at $z=-d/2$, the second at $z=d/2$. Hence $\Delta_i(\omega,kd)=(\epsilon_i-\epsilon)/(\epsilon_i+\epsilon)e^{kd}$ and we find for $\operatorname{tr}\ln[-\epsilon(\omega)\nabla^2]$ the integrals

$$A\sum_{n=-\infty}^{\infty}\int\frac{d^2k}{(2\pi)^2}\ln[1-\Delta_1\Delta_2(\omega_n,kd)]$$

$$=\frac{A}{2\pi d^2}\sum_{n=-\infty}^{\infty}\int_0^\infty dx\,x\ln[1-\Delta_1\Delta_2(\omega_n,x)]\,, \tag{3}$$

where A is the total area of the interface. When inserted into (1) this gives the well-known $1/d^2$ formula $f=H/12\pi d^2$, determining the Hamaker constant H in terms of the spectral properties of $\epsilon(\omega)$.

3. Consider now a spherical modification of this configuration with a dielectric shell between $R_\pm=R\pm d/2$. Then I, K in (2) are to be replaced by r^l, r^{-l-1} and

$$\Delta_1^s=\frac{(\epsilon_1-\epsilon)lR_-^{2l+1}}{\epsilon_1l+\epsilon(l+1)}\,,$$

$$\Delta_2^s=\frac{(\epsilon_2-\epsilon)(l+1)R_\mp^{-(2l+1)}}{\epsilon_2(l+1)+\epsilon l}\,. \tag{4}$$

Let us denote the tr ln by S: for the sphere it reads explicitly

$$S^s=\sum_{n=-\infty}^{\infty}\sum_{l=0}^{\infty}(2l+1)\ln(1-\Delta_1^s\Delta_2^s)\,. \tag{5}$$

For cylinders, formulas (2) hold with K being the modified Bessel functions $I_m(x_\mp)$, $K_m(x_\mp)$ ($x=kR_\mp$). Using the Wronskian $I_mK_m'-K_mI_m'=-1/x$ we write $\Delta_{m,1,2}^c$ as

$$\Delta_{m,1}^c=\frac{(\epsilon_1-\epsilon)x(I_m^2)'}{\epsilon_1+\epsilon+(\epsilon_1-\epsilon)x(I_mK_m)'}\,,$$

$$\Delta^{c}_{m,2}=\frac{-(\epsilon_2-\epsilon)x(K_m^2)'}{\epsilon_2+\epsilon-(\epsilon_2-\epsilon)x(I_mK_m)'}\,, \tag{6}$$

to be evaluated at $x_\pm$, respectively. The relevant sum for the cylinder is then

$$S^c=\sum_{n,m=-\infty}^{\infty}\int_0^{\infty}\frac{dx}{\pi}\ln(1-\Delta^c_{m,1}\Delta^c_{m,2})\,. \tag{7}$$

In the limit $d\to 0$, $R_+=R_-$, $x_+=x_-$, and S^s, S^c are pure numbers.

The energy densities are $f=(k_BT/2)\{S^s/4\pi R^2, S^c/2\pi R^2\}$ and amount to pure curvature energies. For $d\neq 0$ there will be higher corrections in powers of d/R which will be ignored.

4. We shall employ the same definition of α, $\bar\alpha$ for surfaces of constant curvatures c_1, c_2 in the non-local case as in Helfrich's local expressions. Then, subtracting from (5), (7) the sum (3) of the planar $R=\infty$ (configuration) we find the formulas for the van der Waals generated stiffness constants,

$$\frac{1}{\alpha}=\frac{k_B}{2}\frac{1}{\pi}\Delta S^c,\quad \frac{2}{\alpha}+\frac{1}{\bar\alpha}=\frac{k_B}{2}\frac{1}{4\pi}\Delta S^s\,, \tag{8}$$

where ΔS^s, ΔS^c are the subtracted sums. After expanding the logarithm $\ln(1-x)$ in a power series we find for the spherical case

$$\Delta S^s\approx-\sum_{n=-\infty}^{\infty}\sum_{p=1}^{\infty}\sum_{l=0}^{\infty}(2l+1)\frac{1}{p}\left(\frac{\rho}{1-\rho}\right)^p \times\left(\frac{a_\alpha}{l+\alpha}-\frac{a_\beta}{l+\beta}\right)^p, \tag{9}$$

where in the limit of zero thickness d we have

$$\rho=\frac{(\epsilon_1-\epsilon)(\epsilon_2-\epsilon)}{(\epsilon_1+\epsilon)(\epsilon_2+\epsilon)},\quad a_\alpha=\frac{(\epsilon+\epsilon_2)\epsilon\epsilon_1}{(\epsilon+\epsilon_1)(\epsilon^2-\epsilon_1\epsilon_2)},$$

$$a_\beta=a_\alpha\,(1\leftrightarrow 2),\quad \alpha=\frac{\epsilon}{\epsilon_1+\epsilon},\quad \beta=\frac{\epsilon_2}{\epsilon_2+\epsilon}.$$

For small differences between the dielectric constants ϵ_1, ϵ_2, also ρ is small and we can truncate the p-sum after $p=1$, thus finding

$$\Delta S^s\approx\sum_{n=-\infty}^{\infty}\{(a_\alpha-a_\beta)\zeta(0) +[(1-2\alpha)a_\alpha\zeta(1,\alpha)-(\alpha\leftrightarrow\beta)]\}\,, \tag{10a}$$

where $\zeta(z,q)=\sum_{l=0}^{\infty}(l+q)^{-z}$ and $\zeta(z)=\zeta(z,1)$ is Riemann's zeta function ($\zeta(0)=-1/2$). We can also write $\zeta(1,\alpha)$ in terms of digamma functions

$$\psi(\alpha-1)=-\gamma-\sum_{l=0}^{\infty}[(l+\alpha)^{-1}-(l+1)^{-1}]$$

as $\zeta(1,\alpha)=L-\psi(\alpha-1)$ where $L=\psi(l_{max}+2)$ is a logarithmically divergent sum $\sum_0^\infty(l+1)^{-1}-\gamma$. At a finite but small membrane thickness $d\ll R$, it would be the following finite expression

$$\sum_0^\infty(l+1)^{-1}(R_-/R_+)^{2l+1}-\gamma\sim-\ln(1-R_-/R_+)^{-\gamma}$$
$$\sim\ln(R/2de^{\gamma})\,.$$

Thus, the membrane thickness acts as a short-distance cutoff in the sum over dispersive waves.

For $\epsilon_1=\epsilon_2$ we have $a_\alpha=a_\beta$,

$$(1-2\alpha)a_\alpha=-(1-2\beta)a_\beta=-\frac{\epsilon_1\epsilon}{(\epsilon_1+\epsilon)^2}$$

so that ΔS^s is simply

$$\Delta S^s\approx\sum_{n=-\infty}^{\infty}\left(-\frac{\epsilon_1\epsilon}{(\epsilon_1+\epsilon)^2}[\zeta(1,\alpha)+\zeta(1,\beta)]\right), \tag{10b}$$

with the logarithmic divergence $-[\epsilon_1\epsilon/(\epsilon_1+\epsilon)^2]2L+\dots$ .In general, the factor in front of L is

$$-\frac{\epsilon[\epsilon_2(\epsilon+\epsilon_1)^3(\epsilon-\epsilon_2)+(1\leftrightarrow 2)]}{(\epsilon^2-\epsilon_1\epsilon_2)(\epsilon+\epsilon_1)^2(\epsilon+\epsilon_2)^2}\,.$$

Consider now the cylindrical case, where (a prime denoting d/dx)

$$\Delta S^c=-\sum_{n=-\infty}^{\infty}\sum_{p=1}^{\infty}\sum_{m=-\infty}^{\infty}\int_0^\infty\frac{dx}{\pi}\frac{1}{p}\left(\frac{\rho}{1-\rho}\right)^p \times[c_m(x)-1]^p\,, \tag{11}$$

with

$$c_m=-x^2(I_m^2)'(K_m^2)' \times\left(1+\frac{\epsilon_1-\epsilon}{\epsilon_1+\epsilon}x(I_mK_m)'\right)^{-1} \times\left(1-\frac{\epsilon_2-\epsilon}{\epsilon_2+\epsilon}x(I_mK_m)'\right)^{-1},$$

which are all >0 for the usual situation $|\epsilon_1-\epsilon|<\epsilon_1+\epsilon$, $|\epsilon_2-\epsilon|<\epsilon_2+\epsilon$.

Let us evaluate this expression to lowest order in the differences between ϵ, ϵ_1, ϵ_2, which amounts to taking $p=1$ only and neglecting the denominators in c_m. For $m\geqslant 2$ we use the expansions, especially good for large m,

$$I_m(mz)=(2m\pi/t)^{-1/2}\mathrm{e}^{m\eta}\left(1+\sum_{k=1}^{\infty}\frac{u_k(t)}{m^k}\right),$$

$$K_m(mz)=(2m/\pi t)^{-1/2}\left(1+\sum_{k=1}^{\infty}\frac{(-1)^k u_k(t)}{m^k}\right)e^{m\eta}$$

$$I'_m(mz)=(2m\pi t)^{-1/2}\mathrm{e}^{m\eta}z^{-1}\left(1+\sum_{k=1}^{\infty}\frac{v_k(t)}{m^k}\right),$$

$$K'_m(mz)=(2mt/\pi)^{-1/2}\mathrm{e}^{-m\eta}z^{-1}\times\left(1+\sum_{k=1}^{\infty}\frac{(-1)^k v_k(t)}{m^k}\right), \quad (12)$$

where $t=(1+z^2)^{-1/2}$, $\eta=\sqrt{2+z^2}+\ln[z/(1+\sqrt{1+z^2}]$, and we obtain an expansion

$$c_m=[2(u_2+v_2)-u_1^2-v_1^2]/m^2+[(2u_4-2u_1u_3+u_2^2+2u_2u_2-u_2u_1^2+\tfrac{1}{2}u_1^2v_1^2)+(u\to v)]/m^4+\mathrm{O}(1/m^6).$$

The coefficients $u_k(t)$, $v_k(t)$ are the well-known Debeye polynomials, so that c_m starts out as $c_m=-(t^2-1)^2/4m^2+\dots$. If we set $z=\mathrm{tg}\,\varphi$, $t=\cos\varphi$, the integral $\int_0^\infty \mathrm{d}x/\pi$ can be rewritten as

$$\frac{1}{m}\int_0^{\pi/2}\frac{\mathrm{d}\varphi}{\pi}\frac{1}{\cos^2\varphi},$$

and with

$$\int_0^{\pi/2}\frac{\mathrm{d}\varphi}{\pi}\cos^{2n}\varphi=\frac{(2n-1)!!}{2(2n)!!}$$

we find, after some algebra [#2],

$$\int_0^\infty\frac{\mathrm{d}x}{\pi}(c_m-1)\equiv i_m$$

$$=\frac{1}{2}\left(-\frac{3}{2^5m}+\frac{3^3}{2^{12}m^3}-\frac{3^3\times 47}{2^{19}n^5}+\frac{3^4\times 3631}{2^{27}m^7}-\frac{3^3\times 4661317}{2^{35}m^9}+\frac{0.0097}{m^{11}}-\frac{0.0371}{m^{13}}+\frac{0.1934}{m^{15}}-\frac{1.3131}{m^{17}}+\frac{11.2552}{m^{19}}+\dots\right). \quad (13)$$

This expression holds only for sufficiently large m, say, $m\geqslant M$. We therefore introduce the slightly modified ζ-function

$$\tilde{\zeta}(k)\equiv\sum_{n=M}^{\infty}\frac{1}{n^k}\equiv\zeta(k)-1-\frac{1}{2^k}-\dots-\frac{1}{(M-1)^k}$$

and we can write the sum over i_m for all $m\neq 0, \pm 1, \pm 2$, as

$$\sum_{|m|\geqslant M}^{\infty} i_m=-\frac{3}{2^5}\tilde{\zeta}(1)+\frac{3^3}{2^{12}}\tilde{\zeta}(3)+\dots. \quad (14)$$

The terms with low $m<M$, $m=0, \pm 1, \pm 2, \dots, \pm(M-1)$ cannot be calculated using (12), (13) in (11) but have to be evaluated numerically. It will be sufficient to choose $M=3$, so that we only need the extra numerical integrals

$$i_0=-0.2677,\quad i_{|1|}=-0.0401,\quad i_{|2|}=-0.0213. \quad (15a)$$

Together with (13) this gives

$$\Delta S^c\approx[i_0+2i_1+2i_2-\tfrac{3}{32}\tilde{\zeta}(1)+\tfrac{27}{4096}\tilde{\zeta}(3)+\dots]\times\sum_{n=-\infty}^{\infty}\rho(\omega_n). \quad (15b)$$

In order to judge the convergence of the sum (14) we notice that when evaluating the sum of $\tilde{\zeta}$'s starting with $\frac{27}{4096}\tilde{\zeta}(3)\approx 0.000508$ up to $\tilde{\zeta}(19)$, we find 0.000495, not much different from the leading $\zeta(3)$ term. Thus, although we are dealing with an asymptotic series, the convergence up to m^{-19} is very good. As a further check of the convergence we increase M to 4 and perform one more i_m numerically, and find $2i_3=-0.0286$, while $\tilde{\zeta}(1)$ contributes $-\frac{3}{32}\frac{1}{3}\approx -0.0313$ less than before, with the remaining series giving 0.00026 instead of 0.000495. Combining these

[#2] The floating point coefficients in (13) are, in terms of prime factors, $3^3\times 1580096099/2^{42}m^{11}-3^5\times 31\times 89\times 191\times 163243/2^{49}m^{13}+3^3\times 587\times 202021\times 17410307/2^{58}m^{15}-3^3\times 19\times 9011\times 41920060200673/2^{67}m^{17}+3^4\times 262474917337070723537543/2^{74}m^{19}$.

numbers we see that the final result differs only in the fourth digit implying an excellent convergence.

The term $\bar{\zeta}(1)$ contains the same logarithmic divergence, L, as $\zeta(1, \alpha)$ in the spherical case. Inserting S^c, S^s into (8) shows that for $\epsilon \sim \epsilon_1$, ϵ_2, the mean and the Gaussian curvature constants receive the following logarithmically divergent contributions from the van der Waals forces

$$\frac{1}{\alpha} \approx \frac{k_B T}{2\pi} \frac{3}{32} L \sum_{n=-\infty}^{\infty} \rho(\omega_n) ,$$

$$\frac{1}{\bar{\alpha}} \approx \frac{k_B T}{2\pi} \times -\frac{5}{16} L \sum_{n=-\infty}^{\infty} \rho(\omega_n) . \qquad (16)$$

The first equation implies that van der Waals forces stiffen membranes. Thus they counteract the thermal softening due to the nonlinearities in the curvature energy [8] $1/\alpha = 1/\alpha_0 - (k_B T/2\pi) \times \frac{3}{2} L$. Also the decrease of $1/\bar{\alpha}$ acts in the opposite direction of the non-linearities in the curvature energy [9]. It tries to impede surfaces with a large number of handles, just as the elastic forces within the membranes]10].

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