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Flexural Rigidity of a Liquid Surface

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The energy of a mass of liquid is evaluated asymptotically in powers of the range of the intermolecular potential divided by a typical dimension of the liquid. The leading term is the internal energy, proportional to the liquid volume. The second term is the energy of surface tension, proportional to the area of the liquid surface. The third term is proportional to an integral over this surface of the square of the mean curvature of the surface minus one-third of its Gaussian curvature. This new term has exactly the form of the bending energy of a thin elastic plate. Comparing it with the bending energy yields expressions for the flexural rigidity and the Poisson ratio of the liquid surface. This flexural rigidity of the surface leads to new terms in the equation of equilibrium of the liquid surface, in addition to the usual surface tension terms.

KEY WORDS: Surface tension; flexural rigidity.

1. INTRODUCTION

The macroscopic theory of surface tension is based upon the assumption that a liquid surface behaves mechanically like an isotropic elastic membrane with a constant tension σ. This tension manifests itself as a force per unit length normal to any curve in the surface, or equivalently as an energy per unit area of the surface. From either of these characterizations, the effect of surface tension on the equations of motion or on the equations of equilibrium of a surface can be deduced. Since the work of Young(1) and Laplace(2) in 1805 it has been known that this macroscopic theory can be derived from a molecular theory. That theory yields an expression for the coefficient of surface tension σ in terms of intermolecular potentials.

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From the same molecular theory we shall show that a liquid surface also behaves mechanically like an elastic plate with a constant flexural rigidity D. This flexural rigidity is manifested in moments which oppose bending of the interface, or equivalently in an energy per unit area of surface proportional to the square of the mean curvature minus one-third of the Gaussian curvature of the surface. The flexural rigidity leads to extra terms in the equation governing the motion or the equilibrium of a surface. The theory yields an expression for D in terms of the intermolecular potentials and also determines the Poisson ratio of the surface.

The energy of bending is smaller than the energy associated with surface tension by the square of the ratio of the scale length of the intermolecular potential to a radius of curvature of the surface. Therefore it is relatively unimportant except where the radius of curvature is small, as it may be near a contact line, in small droplets, etc.

2. MOLECULAR THEORY OF SURFACE ENERGY

Young$^{(1)}$ and Laplace$^{(2)}$ showed that the surface tension results from the different intermolecular forces acting from the two sides on molecules at or near an interface. To describe this phenomenon quantitatively it is convenient to consider the energy of the substances on the two sides of the interface in thermal equilibrium. Let us call them substances 1 and 2, and let them occupy regions D_1 and D_2, respectively, separated by a surface S_{12}.

From a molecular point of view, the distribution of the molecules of the two substances is described by $\rho_{ij}^{(2)}(x, y)$, the two-particle density of molecules of types i and j at x and y, respectively, and the corresponding one-particle densities $\rho_1(x)$ and $\rho_2(y)$. We assume that far from the interface in region D_i, $\rho_i(x)$ tends to the constant value ρ_i^0, and $\rho_{ii}^{(2)}(x, y)$ tends to $(\rho_i^0)^2 g_{ii}(|x-y|/\varepsilon)$, while for $j \neq i$, ρ_j, ρ_{ij}, and ρ_{jj} all tend to zero. Hence $g_{ii}(|x-y|/\varepsilon)$ is the radial distribution function of substance i.

Let $\varepsilon^{-3}\varphi_{ij}(|x-y|/\varepsilon)$ be the intermolecular potential between a molecule of substance i at x and a molecule of substance j at y with ε denoting the range of the potential. Then for $i \neq j$ the total interaction energy of i with j is given by

$$V_{ij} = \varepsilon^{-3} \int_D \int_D \rho_{ij}^{(2)}(x, y)\, \varphi_{ij}(|x-y|/\varepsilon)\, dx\, dy \tag{1}$$

Here $D = D_1 \cup D_2$. By setting $i = j$ in (1) we obtain V_{ii}, which is twice the energy of interaction of molecules of i with each other. In addition, let there be an external potential $U_i(x)$ of a molecule of substance i at position x. Then the total external potential energy V_i of substance i is

$$V_i = \int_{D_i} \rho_i U_i(x)\, dx \tag{2}$$

Thus E, the total interaction energy of the two substances with themselves and with each other, plus the external potential energy, is

$$E = \sum_{i=1}^{2} V_i + \frac{1}{2} \sum_{i,j=1}^{2} V_{ij} \tag{3}$$

We shall evaluate E asymptotically for ε small compared to the dimensions of the regions D_i. To do so, we use a typical dimension l of D_1 as the unit of length, and then $\varphi_{ij}(r/\varepsilon)$ becomes $\varphi_{ij}[(r/l)(\varepsilon/l) = \varphi_{ij}(r'/\varepsilon')$, where $r' = r/l$ and $\varepsilon' = \varepsilon/l$. Now we omit the primes and (1)–(3) are unchanged, but ε denotes the ratio of the range of the intermolecular potential to l. Thus our goal is to evaluate $E(\varepsilon)$ for ε small.

In order to obtain the result in the simplest way, without unnecessary complications, we shall make an approximation to $\rho_{ij}^{(2)}$ analogous to that which was suggested by Green[3] for $i = j$, and which has been used by Berry.[4] It is to write

$$\rho_{ij}^{(2)}(x, y) = \rho_i(x)\, \rho_j(y)\, g_{ij}(|x-y|/\varepsilon) \tag{4a}$$

where

$$\rho_i(x) = \begin{cases} \rho_i^0 & \text{for} \quad x \in D_i \\ 0 & \text{for} \quad x \notin D_i \end{cases} \tag{4b}$$

With this approximation V_{ij} and V_i become

$$V_{ij} = \varepsilon^{-3} \int_{D_j} \int_{D_i} \rho_i^0 \rho_j^0 g_{ij}(|x-y|/\varepsilon)\, \varphi_{ij}(|x-y|/\varepsilon)\, dx\, dy \tag{5}$$

$$V_i = \int_{D_i} \rho_i^0\, U_i(x)\, dx \tag{6}$$

Next we assume that $\varphi_{ij}(r/\varepsilon)$ tends to zero so rapidly as r increases that the first few moments of φ_{ij} exist. We denote the kth moment of $\rho_i^0 \rho_j^0 \varphi_{ij}(r)\, g_{ij}(r)$ by ϕ_{ij}^k, which is given by

$$\phi_{ij}^k = \rho_i^0 \rho_j^0 \int_0^\infty r^{2+k} \varphi_{ij}(r)\, g_{ij}(r)\, dr \tag{7}$$

Now we rewrite V_{ii} by integrating x over all of R^3 and subtracting the integral over $R^3 - D_i$:

$$V_{ii} = \varepsilon^{-3} \int_{D_i} \int_{R^3} (\rho_i^0)^2 \, \varphi_{ii}(|x-y|/\varepsilon) \, g_{ii}(|x-y|/\varepsilon) \, dx \, dy$$

$$- \varepsilon^{-3} \int_{D_i} \int_{R^3 - D_i} (\rho_i^0)^2 \, \varphi_{ii}(|x-y|/\varepsilon) \, g_{ii}(|x-y|/\varepsilon) \, dx \, dy \qquad (8)$$

The integral over x in the first term is just the constant $4\pi\phi_{ii}^0$. Therefore the y integration yields the volume v_i of D_i. Thus, (8) becomes

$$V_{ii} = 4\pi v_i \phi_{ii}^0 - \varepsilon^{-3} \int_{D_i} \int_{R^3 - D_i} (\rho_i^0)^2 \, \varphi_{ii}(|x-y|/\varepsilon) \, g_{ii}(|x-y|/\varepsilon) \, dx \, dy \qquad (9)$$

We observe that the integrand in (9) differs appreciably from zero only when both x and y are near the interface between D_i and $R^3 - D_i$. Therefore we can anticipate that the leading term in the expansion of the integral will be proportional to the area of the interface. Similarly the leading term in the integral in (5) will be proportional to the area of the interface S_{ij} between D_i and D_j.

We have evaluated these integrals asymptotically in powers of ε, for ε small (see the Appendix for some of the details). The simplest results are obtained when the interfaces are smooth, without edges or corners, and with all their dimensions of order unity. Then from (5) we obtain

$$V_{ij} = \varepsilon \pi \phi_{ij}^1 \int_{S_{ij}} dA + \varepsilon^3 \frac{\pi}{8} \phi_{ij}^3 \int_{S_{ij}} \left(-H^2 + \frac{K}{3} \right) dA + O(\varepsilon^4) \qquad (10)$$

Here S_{ij} is the surface separating D_i and D_j, H is the mean curvature of S_{ij}, and K is its Gaussian curvature. Similarly from (9) we get

$$V_{ii} = 4\pi v_i \phi_{ii}^0 - \varepsilon \pi \phi_{ii}^1 \int_{S_{ii}} dA - \varepsilon^3 \frac{\pi}{8} \phi_{ii}^3 \int_{S_{ii}} \left(-H^2 + \frac{K}{3} \right) dA + O(\varepsilon^4) \qquad (11)$$

We now combine the terms associated with the interface S_{ij}, which occur in V_{ii}, V_{ij}, and V_{jj}. This yields the energy associated with S_{ij}. Then $\tilde{E}$, the part of E associated with the volumes v_i and v_j and with S_{ij}, but not with other interfaces, is given by

$$\tilde{E} = \int_{D_i} \rho_i^0 U_i(x) \, dx + \int_{D_j} \rho_j^0 U_j(y) \, dy + 2\pi (v_i \phi_{ii}^0 + v_j \phi_{jj}^0)$$

$$- \varepsilon \frac{\pi}{2} \gamma_{ij}^1 \int_{S_{ij}} dA - \frac{\pi}{16} \varepsilon^3 \gamma_{ij}^3 \int_{S_{ij}} \left(-H^2 + \frac{K}{3} \right) dA + O(\varepsilon^4) \qquad (12)$$

Here γ_{ij}^{k} is defined by

$$\gamma_{ij}^{k}=\phi_{ii}^{k}+\phi_{jj}^{k}-2\phi_{ij}^{k} \tag{13}$$

The third integral on the right side of (12) is proportional to the area of S_{ij}, and the coefficient of proportionality is the surface tension σ_{ij}. It is given by

$$\sigma_{ij}=\frac{\varepsilon\pi}{2}\gamma_{ij}^{1}=\frac{\varepsilon\pi}{2}(\phi_{ii}^{1}+\phi_{jj}^{1}-2\phi_{ij}^{1}) \tag{14}$$

This result for σ_{ij} is essentially that of Fowler.(5,6) A more accurate calculation of σ_{ij}, without the approximation (4), was made by Kirkwood and Buff(7) and Buff.(8)

The last integral on the right-hand side of (12) is proportional to the integral of the square of the mean curvature minus one-third of the Gaussian curvature. The potential energy of bending of a thin elastic plate is given by the similar integral(9)

$$\int_{S}\frac{D}{2}[4H^{2}-2(1-\nu)K]\,dA \tag{15}$$

Here ν is the Poisson ratio of the plate material and D is its flexural rigidity:

$$D=\frac{2}{3}\frac{Eh^{3}}{(1-\nu^{2})} \tag{16}$$

The plate thickness is h and Young's modulus of the material is E. Comparison of the last integral in (12) with (15) shows that they become identical if ν and D are defined by

$$\nu=\frac{1}{3} \tag{17a}$$

$$D_{ij}=\frac{\pi}{32}\varepsilon^{3}\gamma_{ij}^{3}=\frac{\pi\varepsilon^{3}}{32}(\phi_{ii}^{3}+\phi_{jj}^{3}-2\phi_{ij}^{3}) \tag{17b}$$

Thus, in addition to behaving like a membrane with respect to stretching, a liquid surface or interface also behaves like a thin elastic plate with respect to bending.

To supplement the asymptotic expansion of E given by (12), we shall now evaluate E exactly when S_{12} is a sphere of radius R with substance 1 inside it and substance 2 outside. We assume the outer boundary of D_2 is far from S_{12} and we shall not include the energy associated with it. First we shall evaluate the potential $\Pi(y)$ at any point y in region D_2 due to the particles inside the sphere. It is given by

$$\begin{aligned}\Pi_{ij}(|y|) = {} & 2\pi \int_{(|y|-R)/\varepsilon}^{(|y|+R)/\varepsilon} \rho_i^0 \rho_j^0 r^2 \varphi_{ij}(r)\, g_{ij}(r)\, dr \\ & - \frac{\pi\varepsilon}{|y|} \int_{(|y|-R)/\varepsilon}^{(|y|+R)/\varepsilon} \rho_i^0 \rho_j^0 r^3 \varphi_{ij}(r)\, g_{ij}(r)\, dr \\ & - \frac{\pi(|y|^2 - R^2)}{\varepsilon |y|} \int_{(|y|-R)/\varepsilon}^{(|y|+R)/\varepsilon} \rho_i^0 \rho_j^0 r \varphi_{ij}(r)\, g_{ij}(r)\, dr \end{aligned} \tag{18}$$

where $|y| \geqslant R$ is measured from the center of the sphere. This expression reduces to that of Rayleigh$^{(10)}$ when $|y| = R$.

The energy associated with the sphere of radius R is now given by

$$E = \tfrac{1}{2}[E_{11} + E_{22} + 2E_{12}] + V_1 + V_2 \tag{19a}$$

where

$$E_{11} = 4\pi v_1 \int_0^\infty (\rho_1^0)^2 r^2 \varphi_{11}(r)\, g_{11}(r)\, dr - 4\pi \int_R^\infty \Pi_{11}(r) r^2\, dr \tag{19b}$$

$$E_{22} = 4\pi v_2 \int_0^\infty (\rho_2^0)^2 r^2 \varphi_{22}(r)\, dr - 4\pi \int_R^\infty \Pi_{22}(r) r^2\, dr \tag{19c}$$

$$E_{12} = 4\pi \int_R^\infty \Pi_{12}(r) r^2\, dr \tag{19d}$$

Upon using (18) in (19) and evaluating the integrals, we obtain an exact expression for the energy of a sphere of radius R containing substance 1 surrounded by medium 2. It is

$$\begin{aligned} E = {} & V_1 + V_2 + 2\pi\{v_1 \phi_{11}^0(2R/\varepsilon) + v_2 \phi_{22}^0(2R/\varepsilon)\} \\ & - 2\pi^2 R^2 \{\phi_{11}^1(2R/\varepsilon) + \phi_{22}^1(2R/\varepsilon) - 2\phi_{12}^1(2R/\varepsilon)\} \\ & + (\varepsilon^3 \pi^2/6)\{\phi_{11}^3(2R/\varepsilon) + \phi_{22}^3(2R/\varepsilon) - 2\phi_{12}^3(2R/\varepsilon)\} \\ & + 2\pi(v_2 - v_1)\{\phi_{22}^0(\infty) - \phi_{22}^0(2R/\varepsilon)\} \end{aligned} \tag{20}$$

where

$$\phi_{ij}^k(T) = \rho_i^0 \rho_j^0 \int_0^T r^{2+k} \varphi_{ij}(r)\, g(r)\, dr \tag{21}$$

If ε is much smaller than the radius of curvature of the interface, then $2R/\varepsilon \gg 1$ and (20) can be simplified. Then it agrees with our asymptotic result (12) when the two radii of curvature are taken equal, so that $H = 1/R$, $K = 1/R^2$, and the surface area of the sphere is $4\pi R^2$.

Fowler and Guggenheim$^{(6)}$ used a similar method to calculate the energy of a planar liquid–vapor interface.

3. EQUATION FOR THE INTERFACE

At low temperature an equilibrium configuration of the two substances considered in Section 2 is a configuration that minimizes the total energy E. The configuration is constrained to have a specified mass $\rho_i^0 v_i$ of substance i, for $i = 1, 2$. Since the ρ_i^0 are given constants, it follows that $\operatorname{vol} D_i$, the volume of the domain D_i, must have the specified value v_i. Therefore the interface S_{ij} between the domains D_i and D_j must be such that the energy E is minimized among all pairs of domains with

$$\operatorname{vol} D_i = v_i, \qquad i = 1, 2 \tag{22}$$

To find the interface S_{ij} we introduce the Langrange multipliers λ_i and consider the functional

$$E + \sum_{i=1}^{2} \lambda_i (\operatorname{vol} D_i - v_i) \tag{23}$$

Then we use in (23) the asymptotic expansion (12) for E. Next we vary S_{ij} in the resulting expression and we obtain the Euler equation

$$\begin{aligned} &\rho_i U_i(x) - \rho_j U_j(x) + 2\pi(\phi_{ii}^0 - \phi_{jj}^0) \\ &\quad + \varepsilon\pi\gamma_{ij}^1 H + \frac{\varepsilon^3\pi}{16}\gamma_{ij}^3 \{\Delta_s H + 2H^3 - 2HK\} = \lambda_i - \lambda_j \end{aligned} \tag{24}$$

Here Δ_s is the surface Laplacian. The variation of (23) with respect to λ_i yields (22). These equations (22) and (24) for S_{ij} and the λ_i must be supplemented by suitable boundary conditions where S_{ij} meets a solid boundary.

To derive the boundary conditions, we reconsider (23) without expanding the V_{ii} and V_{ij}. Instead we derive the Euler equation for S_{ij} directly from (23) using the exact expression (1) for V_{ij} and (9) for V_{ii}. In this way we obtain

$$\begin{aligned}
&\rho_i^0 U_i(x) - \rho_j^0 U_j(x) + \varepsilon^{-3} \int_{D_i} (\rho_i^0)^2\, \varphi_{ii}(|x-y|/\varepsilon)\, g_{ii}(|x-y|/\varepsilon)\, dy \\
&\quad - \varepsilon^{-3} \int_{D_j} (\rho_j^0)^2\, \varphi_{jj}(|x-y|/\varepsilon)\, g_{jj}(|x-y|/\varepsilon)\, dy \\
&\quad + \varepsilon^{-3} \int_{D_j} \rho_i^0 \rho_j^0 \varphi_{ij}(|x-y|/\varepsilon)\, g_{ij}(|x-y|/\varepsilon)\, dy \\
&\quad - \varepsilon^{-3} \int_{D_i} \rho_i^0 \rho_j^0 \varphi_{ij}(|x-y|/\varepsilon)\, g_{ij}(|x-y|/\varepsilon)\, dy = \lambda_i - \lambda_j \qquad (25)
\end{aligned}$$

This expression holds right up to any solid boundary or other interface which intersects S_{ij}. Therefore it can be used to derive boundary conditions for (24), such as the contact angle condition, by including in $U_i(x)$ the potential due to the solid boundary.

Away from solid boundaries or intersection points, (25) can be simplified by asymptotically evaluating the integrals in it. The expansion of the typical integral in (25) is given by

$$\begin{aligned}
&\varepsilon^{-3} \int_{D} \rho_i^0 \rho_j^0 \varphi_{ij}(|x-y|/\varepsilon)\, g_{ij}(|x-y|/\varepsilon)\, dy \\
&\quad = 2\pi\phi_{ij}^0 + \pi\varepsilon\phi_{ij}^1 H + \frac{\pi}{16}\varepsilon^3 \phi_{ij}^3 \{\Delta_s H + 2H^3 - 2HK\} + O(\varepsilon^4) \qquad (26)
\end{aligned}$$

When (26) is used in (25), it yields the result (24) again. This consistency is a verification of the correctness of the various asymptotic and variational calculations.

We conclude by noting that the exact equation for the interface S_{ij} is the integral equation (25). When expanded for ε small, at points away from solid boundaries and intersections, it yields the differential equation (24). By matching the solution of this differential equation to the solution of the initegral equation valid near a solid boundary or a line of intersection, boundary conditions for the differential equation can be obtained.

The differential equation (24) contains the usual surface tension term, the external potential term, and new terms of order ε^3. These new terms raise the order of the equation to fourth order, so that additional boundary conditions are needed beyond the usual contact angle condition. They can be found by higher-order matching of the solutions of the integral equation and the differential equation.

When the surface S_{ij} is a sphere of radius R, then $H = R^{-1}$ and $K = R^{-2}$, so $\Delta_s H = 0$ and $2H^3 - 2HK = 0$. In this case the terms of order ε^3 in (24) vanish. This example has a bearing on an argument of

Rayleigh.(10) He calculated the pressure in a spherical cavity of arbitrary radius R exactly, without assuming that R is small compared to ε. His procedure was just that which we used in the previous section to evaluate the energy of a spherical surface. Then he expanded the pressure for R large compared to ε, and showed that there was no term of order R^{-3} in the result. He pointed out that a calculation of Fuchs(11) which yields a term of order R^{-3} "does not appear to harmonize" with this result. We see that there are such additional terms in (24) for a general surface, but that they just cancel out for a spherical surface. Apparently Fuch's terms of order R^{-3} did not vanish in this case.

4. CONCLUSION

We have shown that the energy of the surface of a substance or of the interface between two substances contains a bending energy contribution. Thus the surface or interface has a flexural rigidity. It is determined in terms of the intermolecular potentials and the radial distribution functions of the substances on one side of the surface or on the two sides of the interface. The Poisson ratio of the surface or interface is shown to be 1/3. The flexural rigidity also leads to an additional term of fourth order in the equation of equilibrium of the surface or interface. Therefore another boundary condition is needed in addition to the contact angle condition. A method for determining that condition from an "exact" integral equation for the surface or interface has been proposed.

APPENDIX

The asymptotic evaluation of the integrals apprearing in Eqs. (5) and (26) is simplified by choosing coordinates that lie on the interface. Consider a surface $\mathbf{X}(u, v)$, where u and v are surface parameters, with the unit normal $\mathbf{n}(u, v)$. Then any point x near the surface can be parametrized by u, v, and t, where

$$x = \mathbf{X}(u, v) + t\mathbf{n}(u, v) \tag{A.1}$$

Now $\mathbf{X}_u$, $\mathbf{X}_v$, and $\mathbf{n}$ are linearly independent vectors with their first fundamental form coefficients given by(12)

$$E = \mathbf{X}_u \cdot \mathbf{X}_u, \qquad G = \mathbf{X}_v \cdot \mathbf{X}_v, \qquad F = \mathbf{X}_u \cdot \mathbf{X}_v \tag{A.2}$$

We choose u and v such that $\mathbf{X}_u$ and $\mathbf{X}_v$ lie in principal directions of curvature. Then they are orthogonal ($F \equiv 0$) and the Weingarten equations reduce to

$$\begin{aligned} \mathbf{n}_u + k_1 \mathbf{X}_u &= 0 \\ \mathbf{n}_v + k_2 \mathbf{X}_v &= 0 \end{aligned} \tag{A.3}$$

Here k_1 and k_2 are the principal normal curvatures at (u, v).

Now we consider the integral appearing in (5), namely

$$V_{ij} = \varepsilon^{-3} \int_{D_j} \int_{D_i} \rho_i^0 \rho_j^0 \varphi_{ij}(|x-y|/\varepsilon)\, g_{ij}(|x-y|/\varepsilon)\, dx\, dy \tag{A.4}$$

We write

$$\mathscr{H}(|x-y|^2/\varepsilon^2) = \rho_i^0 \rho_j^0 \varphi_{ij}(|x-y|/\varepsilon)\, g_{ij}(|x-y|/\varepsilon) \tag{A.5}$$

Next we let

$$y = \mathbf{X}(u', v') + t'\mathbf{n}(u', v') \tag{A.6}$$

lie in the region D_j below the surface $\mathbf{X}(u, v)$ and

$$x = \mathbf{X}(u, v) + t\mathbf{n}(u, v) \tag{A.7}$$

lie in the region D_i above the surface. Then (A.4) becomes

$$\begin{aligned} V_{ij} = \varepsilon^{-3} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv \int_{0}^{\infty} dt \int_{-\infty}^{\infty} du' \int_{-\infty}^{\infty} dv' \int_{-\infty}^{0} dt' \\ \times \mathscr{H}(|x-y|^2/\varepsilon^2)\, J(u, v, t)\, J(u', v', t') \end{aligned} \tag{A.8}$$

Here $J(u, v, t)$ is the Jacobian of the transformation, given by

$$J(u, v, t) = [1 - 2H(u, v)t + t^2 K(u, v)](EG)^{1/2} \tag{A.9}$$

while $H = (k_1 + k_2)/2$ and $K = k_1 k_2$ are the mean and Gaussian curvatures, respectively.

To simplify the integral (A.8), we note that the integrand differs from zero only when both x and y are near the interface $\mathbf{X}(u, v)$. Therefore we introduce the new scaled independent variables τ, τ', σ_1, and σ_2 defined by

$$t = \varepsilon\tau, \qquad t' = \varepsilon\tau', \qquad u' = u + \varepsilon\sigma_1, \qquad v' = v + \varepsilon\sigma_2 \tag{A.10}$$

Then we expand all the terms appearing in the integrand in (A.8) in powers of ε. This calculation in straightforward, but quite involved, and is easily automated using a symbolic manipulation package. We write the result as

$$V_{ij} = \varepsilon I_1 + \varepsilon^2 I_2 + \varepsilon^3 I_3 + O(\varepsilon^4) \tag{A.11}$$

For I_1 we get

$$I_1 = \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv \int_{-\infty}^{0} d\tau' \int_{-\infty}^{\infty} d\sigma_1 \int_{-\infty}^{\infty} d\sigma_2 \int_{0}^{\infty} d\tau \times EG\mathscr{H}(\sigma_1^2 E + \sigma_2^2 G + (\tau - \tau')^2) \tag{A.12a}$$

Upon integrating over σ_1 and σ_2, we find that I_1 simplifies to

$$I_1 = 2\pi \int_{S_{ij}} dA \int_0^{\infty} r\,dr \int_{-\infty}^{0} d\tau' \int_0^{\infty} d\tau\, \mathscr{H}(r^2 + (\tau - \tau')^2) \tag{A.12b}$$

By introducing the new variables $a = \tau - \tau'$ and $b = \tau + \tau'$ we can write I_1 as

$$I_1 = \pi \int_{S_{ij}} dA \int_0^{\infty} r\,dr \int_0^{\infty} da \int_{-a}^{a} \mathscr{H}(r^2 + a^2)\,db \tag{A.13}$$

Integrating over both a and b gives the final result

$$I_1 = \pi \int_0^{\infty} r^3 \mathscr{H}(r^2)\,dr \int_{S_{ij}} dA \tag{A.14}$$

In a similar way, after integrating over σ_1 and σ_2, we get for I_2,

$$I_2 = -4\pi \int_{S_{ij}} dA \int_0^{\infty} r\,dr \int_{-\infty}^{0} d\tau' \int_0^{\infty} d\tau \times 2H(\tau + \tau')\{2\mathscr{H}(r^2 + (\tau - \tau')^2) + \mathscr{H}'(r^2 + (\tau - \tau')^2) r^2\} \tag{A.15}$$

The integrand in (A.15) is odd in $(\tau + \tau')$, so $I_2 = 0$.

For I_3, after integrating over σ_1, σ_2, τ, and τ', and integrating by parts, we get

$$I_3 = \pi \int_S dA \int_0^{\infty} r^5\,dr\, \mathscr{H}(r^2) \left\{ -\frac{1}{8} H^2 + \frac{7}{24} K - \frac{1}{16} \times \left[\frac{E_v^2}{E^2 G} + \frac{G_u^2}{E G^2} + \frac{E_v G_v}{G^2 E} + \frac{E_u G_u}{E^2 G} - \frac{E_{vv}}{EG} - \frac{G_{uu}}{EG} \right] \right\} \tag{A.16}$$

The last term in the integrand can be reduced to $4K$ by using Gauss's theorema egregium$^{(12)}$ relating the Gaussian curvature to E and G, namely,

$$K = k_1 k_2 = -\frac{1}{2(EG)^{1/2}} \left[\frac{\partial}{\partial v} \left(\frac{E_v}{(EG)^{1/2}} \right) + \frac{\partial}{\partial u} \left(\frac{G_u}{(EG)^{1/2}} \right) \right] \tag{A.17}$$

Then (A.16) becomes

$$I_3 = \frac{\pi}{8}\int_0^\infty r^5 \mathscr{H}(r^2)\,dr \int_S \left(-H^2 + \frac{K}{3}\right) dA \tag{A.18}$$

To calculate the integral apprearing in (26), namely

$$\begin{aligned} &\varepsilon^{-3} \int_D \rho_i^0 \rho_j^0 \varphi_{ij}(|x-y|/\varepsilon)\, g_{ij}(|x-y|/\varepsilon)\, dy \\ &\quad = \varepsilon^{-3} \int_D \mathscr{H}(|x-y|^2/\varepsilon^2)\, dy \end{aligned} \tag{A.19}$$

the precedure is similar. In surface coordinates the integral becomes

$$\begin{aligned} &\varepsilon^{-3} \int_D \rho_i^0 \rho_j^0 \varphi_{ij}(|x-y|/\varepsilon)\, g_{ij}(|x-y|/\varepsilon)\, dy \\ &\quad = \varepsilon^{-3} \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv \int_{-\infty}^{0} dt\, \mathscr{H}(|x-y|^2/\varepsilon^2)\, J(u, v, t) \end{aligned} \tag{A.20}$$

Again it is straightforward to expand the integral as before, but we must keep one more term. The algebra becomes quite complicated, so we will not present it. To simplify the final result, we use the following expression for the surface Laplacian:

$$\Delta_s \Phi = \frac{1}{(EG)^{1/2}} \left[\frac{\partial}{\partial u}\left(\frac{G\Phi_u}{(EG)^{1/2}}\right) + \frac{\partial}{\partial v}\left(\frac{E\Phi_v}{(EG)^{1/2}}\right) \right] \tag{A.21}$$

We also use the compatability conditions satisfied by the parameters u and v,

$$(\mathbf{n} \cdot \mathbf{X}_{uu})_v = HE_v \tag{A.22a}$$

$$(\mathbf{n} \cdot \mathbf{X}_{vv})_u = HG_u \tag{A.22b}$$

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