Wilhelmy plate artifacts in elastic monolayers

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The conventional method of measuring surface pressure in a Langmuir trough experiment is the Wilhelmy plate.[1] The plate measures the net tension on the surface. The reported surface pressure Π is then the tension γ_0 of the bare liquid minus the measured Wilhelmy tension. The method gives reliable measurements of the tension for a liquidlike surface that supports only isotropic stress.[1] It is also used to characterize monolayers that show clear signs of anisotropic stress by wrinkling or folding.[2,3] Pocivavsek *et al.*[4] explained this folding as a simple mechanical buckling phenomenon. However, such buckling requires compressive stress in the monolayer, whereas the measured Wilhelmy stress where folding was observed was tensile.[5] Earlier work[3] showed that the Wilhelmy stress disagrees with other measures of stress when this stress or the elasticity tensor is anisotropic. In Appendix A of Ref. 5 some of the present authors argued that the Wilhelmy stress in an elastic membrane differs from the stress far from the plate even in an isotropic situation. Using a simplified two-dimensional model of the Wilhelmy measurement, they argued that the Wilhelmy stress could be tensile while the overall stress was compressive. Though this conclusion is correct, the derivation is incorrect. This note offers a corrected analysis.

In Appendix A of Ref. 5 the Langmuir trough was modeled as a circular enclosure containing the monolayer-bearing liquid surface. The Wilhelmy plate is modeled as a small circular ring of radius a at the center. The ring contracts and measures the resulting radial tension. The mistaken analysis was based on the statement that in equilibrium the radial derivative ∂_r of the radial stress σ_{rr} is zero. This incorrect statement invalidates the derivation. To correct the derivation we begin with the correct equilibrium condition[6]

$$\partial_r \sigma_{rr} = (\sigma_{\phi\phi} - \sigma_{rr})/r, \tag{1}$$

where $\sigma_{\phi\phi}$ is the azimuthal stress. In the symmetric situation presumed here, the principal stresses are in the radial and azimuthal directions, so that $\sigma_{r\phi}=0$. This equation expresses the balance of radial forces on a small annular wedge subtending an angle $\Delta\phi$ and having an annular width Δr. For a liquid interface $\sigma_{rr}=\sigma_{\phi\phi}$, so that σ_{rr} is uniform, as expected. In an extremely anisotropic material for which $\sigma_{\phi\phi}=0$, Eq. (1) implies that $\sigma_{rr}\sim 1/r$, as required.

As before we may use this equilibrium condition to infer the displacement field $u(r)$. We shall assume that this $u(r)$ is entirely radial in direction and independent of ϕ, so that it retains the symmetry of the boundaries. We also suppose that the elasticity of the material is isotropic. Evidently $u(r)$ determines the principal strains $\gamma_{rr}=\partial_r u$ and $\gamma_{\phi\phi}=u/r$. As before the linear elastic relationship between σ and γ can be expressed as

$$\sigma_{rr} = A\gamma_{rr} + B\gamma_{\phi\phi}, \quad \sigma_{\phi\phi} = B\gamma_{rr} + A\gamma_{\phi\phi}. \tag{2}$$

Using these expressions in the equilibrium condition (1), we obtain

$$u'' + u'/r - u/r^2 = 0, \tag{3}$$

where primes denote r derivatives. This equation is homogeneous in r and has power-law solutions r and $1/r$. Thus the general solution can be written as $u(r)=C[r+b^2/r]$. We note that the elastic coefficients B and A do not appear in Eq. (3). This reflects the strong equilibrium constraints on elastic sheets; it is a property of the Föppl von Kármán equations[7] that describe such sheets in generality.

To mimic the action of a Wilhelmy plate, we contract the inner circle so as to produce a negative (inward) displacement $u(a)$ and a tensile stress $\sigma_{rr}(a)$. We now ask how this measured stress at a compares to the stress at the distant outer ring. Using the expression for $u(r)$ above, we infer

$$\sigma_{rr}(r) = AC[(1+B/A) - (b/r)^2(1-B/A)]. \tag{4}$$

In like manner we find that the hydrostatic stress $\sigma_{rr}+\sigma_{\phi\phi}$ is simply $2C(A+B)$. A compressive stress at large r implies $C<0$. If the b term is sufficiently large, it can outweigh the constant term in Eq. (4) and produce a tensile radial stress at the inner ring. This evidently is not possible in a liquid interface, for which $B/A=1$. However in an elastic interface with $B<A$, the stress reverses sign whenever

$$b/a > \sqrt{(1+B/A)/(1-B/A)}. \tag{5}$$

We propose that this may be the situation when folding is observed in a Langmuir trough whose Wilhelmy plate is measuring a positive nominal tension.

Though this model lends plausibility to the notion that the Wilhelmy stress differs from ambient stress in an elastic monolayer, it is far from adequate to quantify this difference, as noted in Ref. 5. The actual Wilhelmy geometry differs strongly from this model. Neither the outer boundary nor the plate are radially symmetric. The shape of the outer boundary is likely not important since the distortion found above falls off far from the plate. As for the plate itself, we expect the distortion to be concentrated at the two ends of the strip, where azimuthal compression is necessary. Still, it seems likely that a strip of width a has a distortion for $r > a$ comparable to that of a cylinder of diameter a.

Another experimental effect complicates quantitative predictions. The measured Wilhelmy pressures[5] differ from the required net compression by over 10 mN/m. Such a large difference would create substantially greater fluidity near the plate than that of the monolayer as a whole.

Despite the shortcomings of this model, it suggests that Wilhelmy plate measurements should not be taken as faithful measures of hydrostatic stress when the monolayer has an elastic character. Reinterpreting these previous Wilhelmy plate measurements may alter our physical picture of some reported monolayer phenomena.

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