Derivation of the Laplace equation

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Sammendrag

This note presents a derivation of the Laplace equation which gives the relationship between capillary pressure, surface tension, and principal radii of curvature of the interface between the two fluids.

First, several mathematical results of space curves and surfaces will be derived as a necessary basis. It is shown that at each point of a surface there are two principal, normal sections (two planes) that are perpendicular with the line of intersection being the surface normal. The cuts of the two planes with the surface define two space curves that each have their centers of curvature on the surface normal.

The Laplace equation is derived (1) by the concept of virtual work to extend the interface, and (2) by force balance on a surface element.

Introduction

The Laplace equation[1]

$$p_c = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right), \qquad (1)$$

gives an expression for the capillary pressure p_c, i.e. the pressure difference over an interface between two fluids in terms of the surface tension σ and the principal radii of curvature, R_1 and R_2. This expression is often encountered in the literature covering the concepts of capillary pressure and wettability since it is quite general.

The expression in parenthesis in Eq. 1 is a geometry factor. At equilibrium, each point on the interface has the same geometry factor. The simple expression reflects the fact that for an arbitrary, *smooth* surface, the curvature at any point is defined by assigning radii of curvature, R_1 and R_2, in two planes, called *principal curvature sections*. The two planes are normal to each other and their line of intersection is the surface normal at the chosen point. Also, the curvature of an arbitrary normal section may be expressed in terms of the principle curvatures.

With sufficient knowledge of the mathematical properties of surfaces, the Laplace equation may easily be derived either by the principle of minimum energy or by requiring force equilibrium.

The nomenclature is only for the last section, the derivation of Laplace's equation from physical principles. In the first section, which covers mathematical properties of curves and surfaces, all entities are dimensionless and defined in the text.

Curvature of Surfaces

Surface and Curves

Most of this section follows the exposition of space curves in the textbook by Tambs Lyche[2].

Let $\mathbf{r}$ denote the radius vector from the origin of the Cartesian coordinate system (x, y, z) with unit vectors $(\mathbf{i}, \mathbf{j}, \mathbf{k})$. A surface S may be defined by the vector equation

$$\mathbf{r} = \mathbf{f}(u, v) = \varphi(u, v)\mathbf{i} + \psi(u, v)\mathbf{j} + \chi(u, v)\mathbf{k}, \qquad \dots\dots\dots\dots\dots \quad (2)$$

or in parameter form

$$x = \varphi(u, v), \quad y = \psi(u, v), \quad z = \chi(u, v), \qquad \dots\dots\dots\dots\dots\dots \quad (3)$$

where φ, ψ and χ are functions of the two parameters u and v. If the two first equations in Eq. 3 are solved for u and v and substituted in the third equation, we get z expressed as a function of x and y, the usual way to represent a surface. However, the parameter form is a very useful representation of a surface for description of curvature characteristics.

If we set $u = u(t)$ and $v = v(t)$ we get the vector equation $\mathbf{r} = \mathbf{f}(t)$ for a curve (a space curve) on the surface, or in parameter form:

$$x = \varphi(t), \quad y = \psi(t), \quad z = \chi(t),$$

where t is a parameter. By assumption, all functions are twice differentiable with continuous second order derivatives. A curve or surface represented by functions fulfilling this requirement is called *smooth*.

Definitions

Arc Length. If $\mathbf{f}(t)$ is differentiable with continuous derivative in the interval $[a,b]$, then the arc length L is defined by

$$L = \int_a^b |\dot{\mathbf{f}}(t)| dt,$$

where the dot denotes differentiation with respect to t. If $t \in [a, b]$ and we set $s = \int_a^t |\dot{\mathbf{f}}(t)| dt$, we get the arc differential $ds = |\dot{\mathbf{f}}(t)| dt = \pm |d\mathbf{r}|$. Then s is a continuous function of t that increases from 0 to L when t increases from a to b. Instead of t, s could be used as a parameter to represent the curve. By this *taxameter* form, many formulas are especially simple, e.g. $|\mathbf{r}'| = |d\mathbf{r}/ds| = 1$.

Tangent to a Curve. The vector $\mathbf{t} = d\mathbf{r}/ds = \mathbf{r}'$ is defined as the *tangent vector* of the space curve $\mathbf{r} = \mathbf{f}(t)$. Since $|\mathbf{t}| = 1$, $\mathbf{t}$ is a unity vector along the tangent of the curve.

Curvature. The *curvature* K of a curve is defined by $K = |d\mathbf{t}/ds| = |d^2\mathbf{r}/ds^2| = |\mathbf{r}''|$, or simply $K = |\mathbf{f}''(s)|$, the curve being on taxameter form.

Radius of Curvature. The radius of curvature R of a space curve C is defined by $R = 1/K$.

Principal Normal to a Curve. The *principal normal* $\mathbf{h}$ of a curve is defined by $\mathbf{h} = \mathbf{r}''/|\mathbf{r}''| = \mathbf{r}''/K$. Since $\mathbf{r}'^2 = 1$ it follows that $\mathbf{r}' \cdot \mathbf{r}'' = 0$, and hence $\mathbf{h}$ is normal to $\mathbf{t}$ (and the curve).

Normal of a Surface. The *surface normal* $\mathbf{n}$ to a surface at a point is defined by $\mathbf{n} = \mathbf{r}_u \times \mathbf{r}_v / |\mathbf{r}_u \times \mathbf{r}_v|$. Here $\mathbf{r}_u$ and $\mathbf{r}_v$ denotes partial derivatives of $\mathbf{r}$ with respect to u and v, cf. Eq. 2. The total differential $d\mathbf{r}$ is given by

$$d\mathbf{r} = \mathbf{r}_u du + \mathbf{r}_v dv,$$

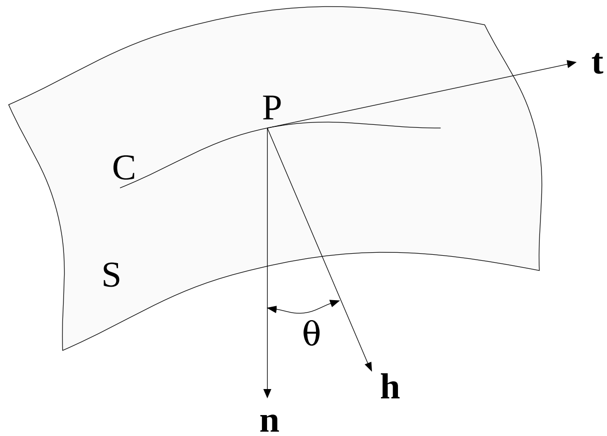
and for the space curve on the surface, $u = u(t)$ and $v = v(t)$. From the definition of $\mathbf{t}$, $d\mathbf{r}$ is along $\mathbf{t}$, and it is easily seen that $d\mathbf{r} \cdot \mathbf{n} = 0$. That is, $\mathbf{n}$ is normal to all curves on the surface drawn through the selected point.

Normal Plane and Normal Section. A plane through the normal to a surface, i.e. the normal is lying in the plane, is called a *normal plane* The cut between a normal plane and the surface is a curve on the surface and is called a *normal section*.

Curvature of a Normal Section

Again, let $\mathbf{r} = \mathbf{f}(u, v)$ a surface S and $\mathbf{r} = \mathbf{f}(u(t), v(t))$ a space curve C on S. From the definitions, we have $K\mathbf{h} = d\mathbf{t}/ds$. Multiplying by $\mathbf{n}$ gives

$$\frac{d\mathbf{t}}{ds}\mathbf{n} = K \cos\theta,$$



Figur 1: Surface S, curve C through point P, tangent to the curve, surface normal and principal normal to the curve

where θ is the angle between the principal normal to C and the surface normal at the chosen point P, Fig. 1.

Since $\mathbf{n} \cdot \mathbf{t} = 0$, we get by differentiation

$$\mathbf{n}\frac{d\mathbf{t}}{ds} + \frac{d\mathbf{n}}{ds}\mathbf{t} = 0,$$

and thereby

$$K = -\frac{1}{\cos\theta}\frac{d\mathbf{n}}{ds}\mathbf{t} = -\frac{1}{\cos\theta}\frac{d\mathbf{n}\cdot d\mathbf{r}}{ds^2}.$$

From the definition of $\mathbf{n}$, we have $\mathbf{r}_u\mathbf{n} = 0$, $\mathbf{r}_v\mathbf{n} = 0$. Differentiating with respect to u and v, we get

$$\begin{array}{ll} \mathbf{r}_u\mathbf{n}_u + \mathbf{r}_{uu}\mathbf{n} = 0, & \mathbf{r}_v\mathbf{n}_u + \mathbf{r}_{uv}\mathbf{n} = 0, \\ \mathbf{r}_u\mathbf{n}_v + \mathbf{r}_{uv}\mathbf{n} = 0, & \mathbf{r}_v\mathbf{n}_v + \mathbf{r}_{vv}\mathbf{n} = 0. \end{array}$$

Since

$$d\mathbf{n} = \mathbf{n}_u du + \mathbf{n}_v dv, \quad d\mathbf{r} = \mathbf{r}_u du + \mathbf{r}_v dv,$$

we have

$$\begin{aligned} d\mathbf{n}\cdot d\mathbf{r} &= \mathbf{r}_u\mathbf{n}_u du^2 + (\mathbf{r}_u\mathbf{n}_v + \mathbf{r}_v\mathbf{n}_u)du\,dv + \mathbf{r}_v\mathbf{n}_v dv^2 \\ &= -(\mathbf{r}_{uu}\mathbf{n}\,du^2 + 2\mathbf{r}_{uv}\mathbf{n}\,du\,dv + \mathbf{r}_{vv}\mathbf{n}\,dv^2), \end{aligned}$$

and we get

$$K = \frac{1}{\cos\theta}\frac{L\,du^2 + 2M\,du\,dv + N\,dv^2}{E\,du^2 + 2F\,du\,dv + G\,dv^2}, \qquad \ldots\ldots\ldots\ldots \quad (4)$$

when

$$\begin{aligned} ds^2 &= d\mathbf{r}^2 = (\mathbf{r}_u du + \mathbf{r}_v dv)^2 \\ &= \mathbf{r}_u^2 du^2 + 2\mathbf{r}_u\mathbf{r}_v du dv + \mathbf{r}_v^2 dv^2 \end{aligned}$$

and

$$E = \mathbf{r}_u^2, \qquad F = \mathbf{r}_u \mathbf{r}_v, \qquad G = \mathbf{r}_v^2,$$
$$L = \mathbf{r}_{uu}\mathbf{n}, \qquad M = \mathbf{r}_{uv}\mathbf{n}, \qquad N = \mathbf{r}_{vv}\mathbf{n}.$$

We note that the quantities E, F, G, L, M, N only depend on properties of the surface S with no reference to the space curve C on the surface. For all curves C that start out from point P in the same direction, determined by the ratio $dv : du$, the angel θ is the same according to Eq. 4. Conversely, all space curves through P with the same **t** and **h** has the same curvature at P.

If we choose $\theta = 0$, K is the curvature of a normal section, i.e. the principal normal of the curve coincides with the normal to the surface,

$$K = \frac{L\,du^2 + 2M\,du\,dv + N\,dv^2}{E\,du^2 + 2F\,du\,dv + G\,dv^2}. \qquad \text{(5)}$$

Principal Curvature Sections

If K is known, Eq. 5 is a quadratic equation for the ratio $dv : du$, and may be written

$$(L - EK)\,du^2 + 2(M - FK)\,du\,dv + (N - GK)\,dv^2 = 0. \qquad \text{(6)}$$

If this equation has two distinct roots, there will be two normal sections with curvature K. If it has only one root, there exist only one normal section with the given curvature, and if there are no roots, no normal section exists with curvature K. To discern these alternatives, we consider the expression

$$(M - FK)^2 - (L - EK)(N - GK)$$

that is under the square root sign when solving Eq. 6. This expression is generally equal to zero for two values of K, the *principal curvatures* K_1 and K_2. The corresponding normal sections are called the *principal curvature sections*.

After simplifying the last expression, we have to investigate the roots of

$$(EG - F^2)K^2 - (EN - 2FM + GL)K + (LN - M^2) = 0. \qquad \text{(7)}$$

Solving this equation we have to find the square root of

$$(EN - 2FM + GL)^2 - 4(EG - F^2)(LN - M^2).$$

As will be shown, this expression is never negative. Let us assume chosen values for E, F, G, L, N such that the last expression is a function of M, denoted by $\varphi(M)$. It is a polynomial of second degree with the derivative

$$\varphi'(M) = -4F(EN - 2FM + GL) + 8(EG - F^2)M,$$

and $\varphi'(M) = 0$ for $M = M_1 = F(EN + GL)/2EG$. Then $\varphi''(M) = 8EG > 0$, from the definition of E and G, i.e. $\varphi(M)$ has a minimum at $M = M_1$, and after some calculation

$$\varphi(M_1) = \frac{(EG - F^2)(EN - GL)^2}{EG} \geq 0,$$

since $EG - F^2 = \mathbf{r}_u^2\mathbf{r}_v^2 - (\mathbf{r}_u\mathbf{r}_v)^2 = (\mathbf{r}_u \times \mathbf{r}_v)^2 \geq 0$. Actually, we will assume that $EG - F^2 > 0$ since otherwise $\mathbf{r}_u$ or $\mathbf{r}_v$ is the null vector or they are parallel. Then $\varphi(M)$ can only be zero if $EN = GL$ and $M = M_1$, i.e. $GM = FN$. We then have

$$\frac{L}{E} = \frac{N}{G} = \frac{M}{F},$$

and from Eq. 5 the curvature K is independent of du and dv and equal to L/E. A point where the curvature is the same for all normal sections is called a *navel point* of the surface.

For a point P on the surface that is not a navel point, Eq. 7 will have two distinct roots, K_1 and K_2, as postulated above.

Principal Curvature Sections are Orthogonal

Substitution of $K = K_1$ or $K = K_2$ into Eq. 6 results in a quadratic expression of the general form $(Adu + Bdv)^2$, since the equation has single roots for these values of K. Its derivative with respect to dv then has to be zero for the same values of K, that is

$$(M - FK)du + (N - GK)dv = 0,$$

or

$$K = \frac{Mdu + Ndv}{Fdu + Gdv}.$$

Substituting this expression into Eq. 6, we get

$$(EM - FL)du^2 + (EN - GL)dudv + (FN - GM)dv^2 = 0.$$

From this equation we get the two directions $dv_1 : du_1$ and $dv_2 : du_2$ (or the inverted ratios if $FN - GM = 0$), for the two principal curvature sections. Using rules for the sum and product of the roots of a quadratic equation, we get

$$\frac{dv_1}{du_1} + \frac{dv_2}{du_2} = -\frac{EN - GL}{FN - GM}, \quad \frac{dv_1}{du_1}\frac{dv_2}{du_2} = \frac{EM - FL}{FN - GM}.$$

We also have

$$d\mathbf{r}_1 = \mathbf{r}_u du_1 + \mathbf{r}_v dv_1, \quad d\mathbf{r}_2 = \mathbf{r}_u du_2 + \mathbf{r}_v dv_2,$$

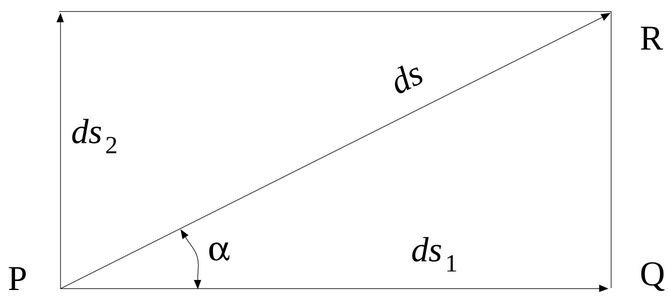
and hence

$$\begin{aligned}
d\mathbf{r}_1 \cdot d\mathbf{r}_2 &= \mathbf{r}_u^2 du_1 du_2 + \mathbf{r}_u\mathbf{r}_v(du_1 dv_2 + du_2 dv_1) + \mathbf{r}_v^2 dv_1 dv_2 \\
&= \left[E + F\left(\frac{dv_1}{du_1} + \frac{dv_2}{du_2}\right) + G\frac{dv_1}{du_1}\frac{dv_2}{du_2}\right] du_1 du_2 \\
&= \left[E - F\frac{EN - GL}{FN - GM} + G\frac{EM - FL}{FN - GM}\right] du_1 du_2 \\
&= \frac{E(FN - GM) - F(EN - GL) + G(EM - FL)}{FN - GM} du_1 du_2 \\
&= 0,
\end{aligned}$$

i.e. the principal curvature sections are orthogonal. (One can easily show that this is the case also for $FN - GM = 0$).

A Theorem of Euler

A theorem of Euler[3] states that the curvature of an arbitrary normal section may be expressed by the curvatures of the principal sections. Let ds_1 and ds_2 be the arc differentials of the two pricipal sections and ds the arc differential in a normal section at an angle α with ds_1, Fig. 2.



Figur 2: Arc differentials along a normal section and the two principal curvature sections

Generally, if $\Phi(u, v)$ is a function of u and v, we have

$$\Phi(\mathrm{R}) - \Phi(\mathrm{P}) = \Phi(\mathrm{R}) - \Phi(\mathrm{Q}) + \Phi(\mathrm{Q}) - \Phi(\mathrm{P}),$$

or

$$\frac{\Phi(\mathrm{R}) - \Phi(\mathrm{P})}{ds} = \frac{\Phi(\mathrm{R}) - \Phi(\mathrm{Q})}{ds_1}\frac{ds_1}{ds} + \frac{\Phi(\mathrm{Q}) - \Phi(\mathrm{P})}{ds_2}\frac{ds_2}{ds},$$

and letting ds_1 and ds_2 approach zero,

$$\frac{d\Phi}{ds} = \frac{d\Phi}{ds_1}\frac{ds_1}{ds} + \frac{d\Phi}{ds_2}\frac{ds_2}{ds} = \frac{d\Phi}{ds_1}\cos\alpha + \frac{d\Phi}{ds_2}\sin\alpha.$$

We now apply this general expression to $\mathbf{r}$ and $\mathbf{n}$ and get

$$\begin{aligned} \mathbf{t} &= \frac{d\mathbf{r}}{ds} = \mathbf{t}_1\cos\alpha + \mathbf{t}_2\sin\alpha \\ & \frac{d\mathbf{n}}{ds} = \frac{d\mathbf{n}}{ds_1}\cos\alpha + \frac{d\mathbf{n}}{ds_2}\sin\alpha, \end{aligned}$$

and by scalar multiplying these two expressions,

$$\begin{aligned} -K &= \mathbf{t}\frac{d\mathbf{n}}{ds} \\ &= \mathbf{t}_1\frac{d\mathbf{n}}{ds_1}\cdot\cos^2\alpha + \left(\mathbf{t}_1\frac{d\mathbf{n}}{ds_2} + \mathbf{t}_2\frac{d\mathbf{n}}{ds_1}\right)\sin\alpha\cos\alpha + \mathbf{t}_2\frac{d\mathbf{n}}{ds_2}\cdot\sin^2\alpha \\ &= -K_1\cos^2\alpha - K_2\sin^2\alpha + \left(\mathbf{t}_1\frac{d\mathbf{n}}{ds_2} + \mathbf{t}_2\frac{d\mathbf{n}}{ds_1}\right)\sin\alpha\cos\alpha. \end{aligned}$$

Since $\mathbf{n}\cdot\mathbf{t}_1 = \mathbf{n}\cdot\mathbf{t}_2 = 0$, we get

$$\mathbf{t}_1\frac{d\mathbf{n}}{ds_2} + \mathbf{n}\frac{\mathbf{t}_1}{ds_2} = 0, \quad \mathbf{t}_2\frac{d\mathbf{n}}{ds_1} + \mathbf{n}\frac{\mathbf{t}_2}{ds_1} = 0.$$

The curves C_1 and C_2 are embedded in two orthogonal planes, $\mathbf{t}_1\cdot\mathbf{t}_2 = 0$, and $\mathbf{t}_1$ is independent of s_2. Therefore $d\mathbf{t}_1/ds_2 = 0$ and likewise $d\mathbf{t}_2/ds_1 = 0$, and we get Euler's result

$$K = K_1\cos^2\alpha + K_2\sin^2\alpha. \qquad (8)$$

Let us now choose another normal section at an angle $\alpha + \pi/2$ with ds_1 and denote the corresponding arc differential by $ds_\perp$ since it is at an angle $\pi/2$ with ds. For the corresponding curvature $K_\perp$ we get from Eq. 8

$$\begin{aligned} K_\perp &= K_1\cos^2(\alpha+\pi/2) + K_2\sin^2(\alpha+\pi/2) \\ &= K_1\sin^2\alpha + K_2\cos^2\alpha. \end{aligned}$$

By summation, we the get

$$K + K_\perp = K_1 + K_2, \qquad (9)$$

that is, the sum of the curvatures of two orthogonal normal sections is constant, equal to the sum of the curvatures of the principal sections.

The Laplace Equation

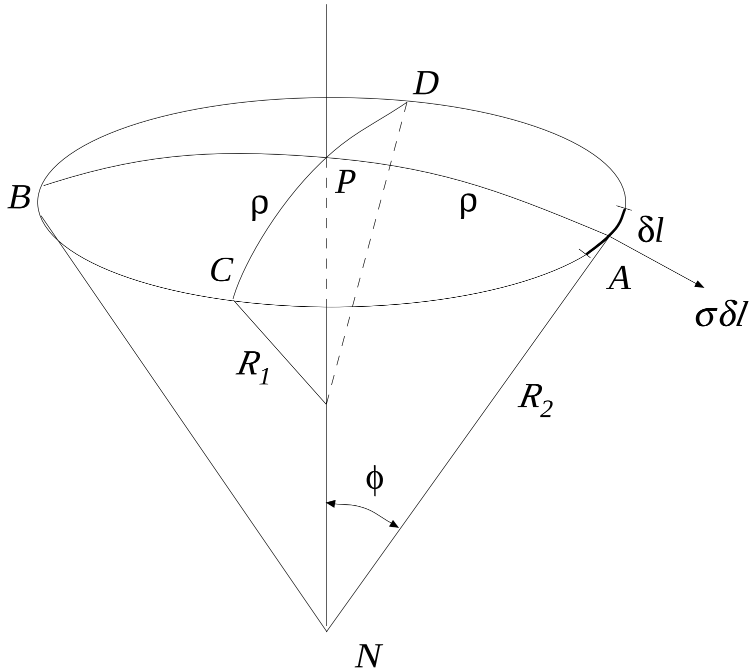
The Laplace equation may be derived either by minimization of energy or by summing all forces to zero. We will do both here although the concept of force in connection with surface tension may be somewhat obscure. The force approach follows the derivation of Defay and Prigogine[4] and the energy approach is taken from the book by Landau and Lifshitz[5]. In both cases it is assumed that the interface is without thickness and that the interfacial tension is constant.

Force Equilibrium

Consider a point P on the surface, Fig. 3, and draw a curve at a constant distance ρ from P. This curve forms the boundary of a cap for which we shall find the equilibrium condition as ρ tends to zero.

Through P we draw the two principal curvature sections AB and CD on the surface. Their radii of curvature at P are R_1 and R_2. At the point A, an element δl of the boundary line is subjected to a force $\sigma\delta l$ whose projection along the normal PN is

$$\sigma\delta l\sin\phi = \sigma\phi\delta l = \sigma\frac{\rho}{R_1}\delta l,$$



Figur 3: Equilibrium of a nonspherical cap.

since ϕ by assumption is small.

If we consider four elements δl of the periphery at A, B, C, and D, they will contribute with a force

$$2\rho\sigma\delta l\left(\frac{1}{R_1}+\frac{1}{R_2}\right).$$

Since this expression by Euler's theorem, Eq. 9, is independent of the choice of AB and CD, it can be integrated around the circumference. Since four orthogonal elements are considered, the integration is made over one quarter of a revolution to give

$$\pi\rho^2\sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right).$$

The force on the surface element caused by the pressure difference over the surface is given by $(p_1 - p_2)\pi\rho^2$, and equating the last two expressions Laplace's equation follows.

Minimum Energy

Let the surface of separation undergo an infinitesimal displacement. At each point of the undisplaced surface we draw the normal. The length of the segment of the normal lying between the points where it intersects the displaced and undisplaced surfaces is denoted by $\delta\zeta$. Then a volume element between the two sufaces is $\delta\zeta df$, where df

is a surface element. Let p_1 and p_2 be the pressures in the two media, and let $\delta\zeta$ be positive if the displacement of the surface is towards medium 2 (say). Then the work necessary to bring about the change in volume is

$$\int(-p_1 + p_2)\delta\zeta\, df.$$

The total work δW in displacing the surface is obtained by adding to this the work connected with the change in area of the surface. This part of the work is proportional to the change δf in area of the surface, and is $\sigma\delta f$, where σ is the surface tension. Thus the total work is

$$\delta W = -\int(p_1 - p_2)\delta\zeta\, df + \sigma\delta f. \qquad (10)$$

The condition for thermodynamical equilibrium is, of course, that δW be zero.

Next, let R_1 and R_2 be the principal radii of curvature at a given point of the surface. We set R_1 and R_2 as positive if they are drawn into medium 1. Then the elements of length (the arc differentials) ds_1 and ds_2 on the surface in its principal curvature sections are increased to $(R_1 + \delta\zeta)ds_1/R_1$ and $(R_2 + \delta\zeta)ds_2/R_2$ when the angles ds_1/R_1 and ds_2/R_2 remain constant, i.e., an expansion normal to the surface (ds_1 is the arc length of a circle with radius R_1, and correspondingly for ds_2). Hence the surface element $df = ds_1 ds_2$ becomes, after displacement,

$$ds_1(1 + \delta\zeta/R_1)ds_2(1 + \delta\zeta/R_2) \cong ds_1 ds_2(1 + \delta\zeta/R_1 + \delta\zeta/R_2),$$

i.e. it changes by $\delta\zeta\, df(1/R_1 + 1/R_2)$. Hence we see that the total change in area of the surface of separation is

$$\delta f = \int \delta\zeta \left(\frac{1}{R_1} + \frac{1}{R_2}\right) df. \qquad (11)$$

Substituting these expressions in Eq. 10 and equating to zero, we obtain the equilibrium condition in the form

$$\int \delta\zeta \left\{(p_1 - p_2) - \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right\} df = 0.$$

This condition must hold for every infinitesimal displacement of the surface, i.e. for all $\delta\zeta$. Hence the expression in braces must be identically equal to zero and Laplace's equation follows.

Nomenclature, for last section

f = area, m^2
l = length of arc, m

p = pressure, Pa
R = principal radius of curvature, m
W = work, J
σ = surface tension, N/m
ς = length along normal, m
ρ = radius of cap, m
ϕ = angle, radians

Subscripts

c = capillary
α = constant
Γ = adsorption (kg surfactant/kg rock)
γ = interfacial tension, N/m

Operators

δ = infinitesimal change

Referanser

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