B_1 = constant defined by Equation (9), cm.$^{-1}$
B_2 = constant defined by Equation (10), cm.$^{-1}$
C_A = concentration of solute in capillary
C_{A0} = concentration of solute in capillary at $z = 0$
C_s = concentration of solute in surroundings
L = capillary length, cm.
L_D, L_{DP}, L_P, L_{PD} = phenomenological coefficients, cm./(sec.)(atm)
P = hydrostatic pressure inside capillary, atm
P^* = dimensionless pressure defined by Equation (13)
P_0 = hydrostatic pressure inside capillary at $z = 0$
P_s = hydrostatic pressure in the surroundings
Q^* = dimensionless axial flow rate, Q_W/Q_{W0}
Q_W = volumetric flow rate of solvent in capillary, cm.^{3}/sec.
Q_{W0} = volumetric flow rate of solvent in capillary at $z = 0$
R = gas law constant
R_1 = inside radius of capillary, cm.
R_2 = outside radius of capillary
R_{lm} = log mean radius of capillary, $(R_2 - R_1)/\ln(R_2/R_1)$
T = absolute temperature, °K
z = axial distance, cm.
z^* = dimensionless axial distance $B_1 z$
α = constant, $(2\pi R_{lm} L_P A_1)^{1/2}$, cm.$^{-1}$
μ = viscosity of solvent, poise
ϕ_1 = dimensionless parameter defined by Equation (12a)
ϕ_2 = dimensionless parameter defined by Equation (12b)
ρ_W = density of solvent (in dilute solutions density of solution), g/cm.^{3}

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Volume-Area Relationship in Capillarity

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If liquid which is in contact with a solid is increased in volume by the amount δV, the change in the surface area of the liquid-vapor interface δA and also in the liquid-solid interface δa is given by the equation

$$H\delta V = \delta A - \cos\theta\,\delta a \tag{1}$$

Melrose pointed out the mathematical nature of this equation for any surface of minimum area at a given volume and proposed the problem of deriving it from mathematical rather than from physical principles (Melrose, 1966).

For the radially symmetric configuration shown in Figure 1, the areas and volume are given by

$$A = \int_{x_0}^{x_1} F\,dx \quad \text{where} \quad F = 2y(1 + y'^2)^{1/2} \tag{2}$$

$$a = 2\int_{x_0}^{c_0} p(1 + p'^2)^{1/2}\,dx + 2\int_{c_1}^{x_1} q(1 + q'^2)^{1/2}\,dx \tag{3}$$

$$V = \int_{x_0}^{x_1} G\,dx \quad \text{where} \quad G = y^2 - p^2 \quad \text{for} \quad x_0 \leqq x \leqq c_0$$

$$G = y^2 \quad \text{for} \quad c_0 \leqq x \leqq c_1$$

$$G = y^2 - q^2 \quad \text{for} \quad c_1 \leqq x \leqq x_1 \tag{4}$$

where the factor π has been deleted for simplicity. If y is a fixed function, then A and V are constants, but if the function y is considered to vary, then A are V are functionals. The differential of a functional is called a variation. Thus δA, δV, and δa are variations in A, V and a, corresponding to a small change from $y(x)$ to $y(x) + h(x)$ where, in addition, y represents a surface of least area corresponding to a fixed volume. Equation (1) can be derived from the calculus of variations.

The variation in area of the liquid-vapor interface having end points which are constrained to lie on $p(x)$ and $q(x)$ is (Gelfand, Fomin, 1963)

$$\delta A = \int_{x_0}^{x_1}\left(F_y - \frac{d}{dx}F_{y'}\right)h\,dx + [F + (q' - y')F_{y'}]_{x=x_1}\delta x_1 - [F + (p' - y')F_{y'}]_{x=x_0}\delta x_0 \tag{5}$$

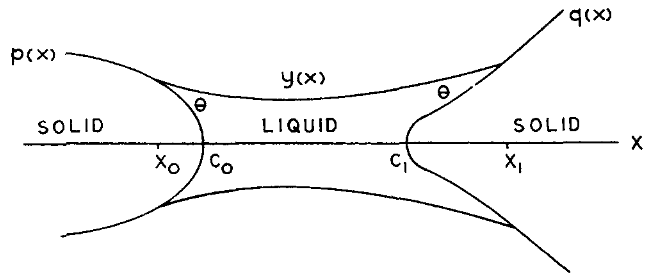

Fig. 1. Liquid in contact with solid.

where the subscripts y and y' represent partial differentiation with respect to y and y'. From the equations

$$[F + (q' - y')F_{y'}]_{x=x_1}\delta x_1 = 2q(1 + y'q')(1 + y'^2)^{-1/2}|_{x=x_1}\delta x_1 \quad (6)$$

$$[F + (p' - y')F_{y'}]_{x=x_0}\delta x_0 = 2p(1 + y'p')(1 + y'^2)^{-1/2}|_{x=x_0}\delta x_0 \quad (7)$$

$$\delta a = 2q(1 + q'^2)^{1/2}\delta x_1 - 2p(1 + p'^2)^{1/2}\delta x_0 \quad (8)$$

$$\cos\theta = (1 + y'q')\,[(1 + q'^2)(1 + y'^2)]^{-1/2}_{x=x_1} \quad (9)$$

$$\cos\theta = (1 + y'p')\,[(1 + p'^2)(1 + y'^2)]^{-1/2}_{x=x_0} \quad (10)$$

it can be seen that

$$[F + (q' - y')F_{y'}]_{x=x_1}\delta x_1 - [F + (p' - y')F_{y'}]_{x=x_0}\delta x_0 = \cos\theta\,\delta a \quad (11)$$

and therefore Equation (5) reduces to

$$\delta A = \int_{x_0}^{x_1}\left(F_y - \frac{d}{dx}F_{y'}\right)h\,dx + \cos\theta\,\delta a \quad (12)$$

Equations (6) and (7) are derived by substituting for F, differentiating, and noting that $y = p$ at x_0 and $y = q$ at x_1. Equation (8) results from the formula for the variation δa, which is analogous to Equation (5). Equations (9) and (10) are derived by noting that the normal to the liquid surface at x_1 is

$$\mathbf{n} = (y'(x_1), -1) \quad (13)$$

while the normal to the solid surface at x_1 is

$$\mathbf{N} = (q'(x_1), -1) \quad (14)$$

and that the scalar product of $\mathbf{n}$ and $\mathbf{N}$ is

$$\mathbf{n}\cdot\mathbf{N} = |\mathbf{n}|\;|\mathbf{N}|\;\cos\theta \quad (15)$$

The variation in volume δV is given by the formula analogous to Equation (5) except that since G is a function only of y, δV does not contain terms in $G_{y'}$.

$$\delta V = \int_{x_0}^{x_1} G_y\,h\,dx + G(x_1)\;\delta x_1 - G(x_0)\;\delta x_0 \quad (16)$$

Furthermore, since $y(x_0) = p(x_0)$ and $y(x_1) = q(x_1)$, then $G(x_0) = G(x_1) = 0$, thus

$$\delta V = \int_{x_0}^{x_1} G_y\,h\,dx \quad (17)$$

Since y is a surface of minimum area A subject to the constraint of constant volume V, F and G satisfy Euler's equation (Gelfand, Fomin, 1963)

$$(F + \lambda G)_y - \frac{d}{dx}(F + \lambda G)_{y'} = 0 \quad (18)$$

where λ is a Lagrangian multiplier. Therefore

$$G_y = \frac{1}{\lambda}\left(\frac{d}{dx}F_{y'} - F_y\right) \quad (19)$$

When G_y is substituted into Equation (17), the variation in volume satisfies

$$-\lambda\delta V = \int_{x_0}^{x_1}\left(F_y - \frac{d}{dx}F_{y'}\right)h\,dx \quad (20)$$

Combining Equations (12) and (20) yields

$$-\lambda\delta V = \delta A - \cos\theta\,\delta a \quad (21)$$

The derivation of Equation (1) is completed by showing that

$$\lambda = -H \quad (22)$$

Equation (22) results from Equation (18) and the equations

$$G_y = 2y \quad (23)$$

$$\frac{d}{dx}F_{y'} - F_y = -2Hy \quad (24)$$

Equation (24) follows from

$$\frac{d}{dx}F_{y'} - F_y = 2(yy'' - 1 - y'^2)(1 + y'^2)^{-3/2} \quad (25)$$

by noting that the right-hand side is $-2Hy$. Equation (25) results from substituting for F from Equation (2) and differentiating.

Nonsymmetric configurations can be treated similarly by using the corresponding parametric variational equations in higher dimensions (Gelfand, Fomin, 1963).

NOTATION

A = area of liquid-vapor interface
a = area of liquid-solid interface
c_0, c_1 = rightmost and leftmost positions of solid surfaces
F = $2y(1 + y'^2)^{1/2}$
G = $y^2 - p^2$ for $x_0 \leq x < c_0$
y^2 for $c_0 \leq x \leq c_1$
$y^2 - q^2$ for $c_1 < x \leq x_1$
H = mean curvature of liquid-vapor interface
h = arbitrary function representing a small increment in y
$\mathbf{N}$ = normal to solid surface
$\mathbf{n}$ = normal to liquid-vapor interface
p, q = functions which when revolved about x axis describe the solid surfaces
V = volume of liquid phase
x = abscissa
x_0, x_1 = points of contact of meniscus with solid surfaces
y = ordinate
δ = change in a quantity, variation, differential of a functional
θ = contact angle
λ = Lagrangian multiplier

Subscripts and Superscripts

y, y' = partial differentiation with respect to y and y'
$'$ (prime) = d/dx

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