Meniscus Shape and Contact Angle

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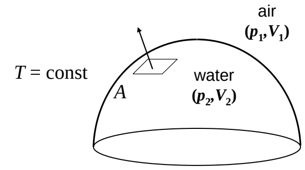
Laplace equation: A thermodynamic interpretation

Work done on the system: $dW = \underbrace{-pdV}_{\text{positive for compression}} + \underbrace{\gamma dA}_{\text{positive for stretching}}$

Change in the energy: $dU = \underbrace{dW}_{\text{work}} + \underbrace{dQ}_{\text{heat}} = -pdV + \gamma dA + TdS$

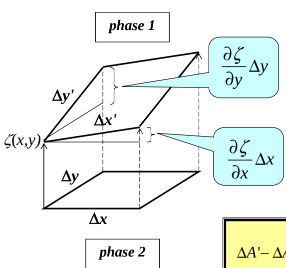
Free energy: $F \equiv U - TS$

$$dF = -pdV + \gamma dA - SdT$$



p - pressure (Pa)
V - volume (m³)
A - surface area (m²)
γ - surface tension (N/m)
T - temperature (K)
S - entropy (J/K)

Laplace equation (cont'd)



Displace a surface element by ζ

$$\Delta A \to \Delta A'$$
$$\Delta A = \Delta x \Delta y; \quad \Delta A' = \Delta x' \Delta y'$$

$$\Delta x' = \sqrt{\Delta x^2 + \left(\frac{\partial\zeta}{\partial x}\Delta x\right)^2} \simeq \left[1 + \frac{1}{2}\left(\frac{\partial\zeta}{\partial x}\right)^2\right]\Delta x$$

$$\Delta y' = \sqrt{\Delta y^2 + \left(\frac{\partial\zeta}{\partial y}\Delta y\right)^2} \simeq \left[1 + \frac{1}{2}\left(\frac{\partial\zeta}{\partial y}\right)^2\right]\Delta y$$

$$\Delta A' - \Delta A = \frac{1}{2}\left[\left(\frac{\partial\zeta}{\partial x}\right)^2 + \left(\frac{\partial\zeta}{\partial y}\right)^2\right]\Delta x \Delta y$$

$$\Delta V_1 = -\Delta V_2 = -\zeta(x,y)\Delta x \Delta y$$

Laplace equation (cont'd)

$$0 = \delta F = -p_1\delta V_1 - p_2\delta V_2 + \gamma\delta A = -(p_1 - p_2)\delta V_1 + \gamma\delta A$$

The thermodynamic potentials are defined for the whole system, but not to one element, i.e.

$$\delta A = \delta\left\{\iint \frac{1}{2}\left[\left(\frac{\partial\zeta}{\partial x}\right)^2 + \left(\frac{\partial\zeta}{\partial y}\right)^2\right]dxdy\right\} = \iint\left\{\frac{\partial\zeta}{\partial x}\delta\left(\frac{\partial\zeta}{\partial x}\right) + \frac{\partial\zeta}{\partial y}\delta\left(\frac{\partial\zeta}{\partial y}\right)\right\}dxdy$$

$$= \iint\left\{\frac{\partial\zeta}{\partial x}\frac{\partial}{\partial x}(\delta\zeta) + \frac{\partial\zeta}{\partial y}\frac{\partial}{\partial y}(\delta\zeta)\right\}dxdy$$

$$= \int\left(\frac{\partial\zeta}{\partial y}\delta\zeta\Big|_{\text{on the boundary}}\right)dx + \int\left(\frac{\partial\zeta}{\partial x}\delta\zeta\Big|_{\text{on the boundary}}\right)dy - \iint\left\{\left(\frac{\partial^2\zeta}{\partial x^2} + \frac{\partial^2\zeta}{\partial y^2}\right)\delta\zeta\right\}dxdy$$

$$= -\iint\left\{\left(\frac{\partial^2\zeta}{\partial x^2} + \frac{\partial^2\zeta}{\partial y^2}\right)\delta\zeta\right\}dxdy$$

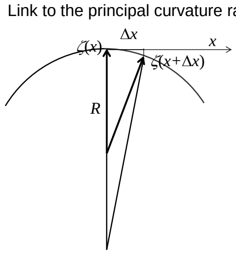
$$\delta V_1 = -\iint \delta\zeta\, dxdy$$

Laplace equation (cont'd)

$$\delta F = \iint\left\{\left[p_1 - p_2 - \gamma\left(\frac{\partial^2\zeta}{\partial x^2} + \frac{\partial^2\zeta}{\partial y^2}\right)\right]\delta\zeta\right\}dxdy = 0$$

$$p_1 - p_2 = \gamma\left(\frac{\partial^2\zeta}{\partial x^2} + \frac{\partial^2\zeta}{\partial y^2}\right)$$

Link to the principal curvature radii



$$\zeta(x + \Delta x) = \zeta(x) + \frac{1}{2}\frac{\partial^2\zeta}{\partial x^2}\Big|_x \Delta x^2$$

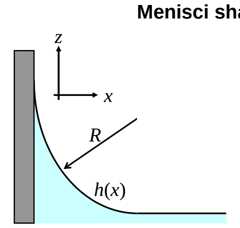
By virtue of the commensurability of triangles

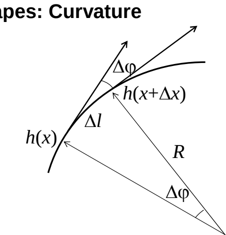
$$\frac{\Delta x}{2R} = \frac{\zeta(x) - \zeta(x + \Delta x)}{\Delta x}$$

$$\frac{1}{R} = -\frac{\partial^2\zeta}{\partial x^2}$$

$$p_2 - p_1 = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

Menisci shapes: Curvature





$$\Delta \tan\varphi \equiv \frac{\Delta\varphi}{\cos^2\varphi} \equiv (1 + \tan^2\varphi)\Delta\varphi = \{1 + [h'(x)]^2\}\Delta\varphi$$

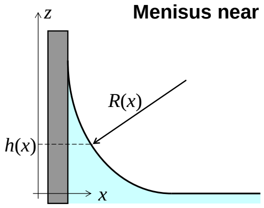
$$\|$$

$$h'(x + \Delta x) - h'(x) \simeq h''(x)\Delta x$$

$$-R\sin\Delta\varphi \simeq -R\Delta\varphi = \Delta l = \sqrt{1 + [h'(x)]^2}\,\Delta x$$

$$R = -\frac{\{1 + [h'(x)]^2\}^{3/2}}{h''(x)}$$

Menisus near a vertical wall



$$\underbrace{\rho g h(x)}_{\text{hydrostatic pressure}} = \underbrace{\frac{\gamma h''(x)}{\left\{1+[h'(x)]^2\right\}^{3/2}}}_{\text{Laplace pressure}}$$

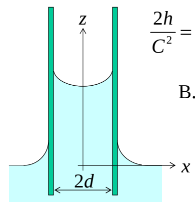
ρ - density of liquid
g - acceleration of gravity
γ - surface tension

$$\times 2h' \;\Rightarrow\; 2\rho g h h' = \frac{2\gamma h' h''}{\left\{1+[h']^2\right\}^{3/2}} \;\Rightarrow\; \rho g \mathrm{d}h^2 = \frac{\gamma \mathrm{d}[h']^2}{\left\{1+[h']^2\right\}^{3/2}}$$

$$\rho g h^2 = \text{const} - \frac{2\gamma}{\sqrt{1+[h']^2}}$$

$$x = -\frac{C}{\sqrt{2}}\,\text{arc cosh}\left(\frac{C\sqrt{2}}{h(x)}\right) + C\sqrt{2-\frac{h^2(x)}{C^2}} + x_0; \qquad C = \sqrt{\frac{2\gamma}{\rho g}}$$

Meniscus in a side-parallel slot



$$\frac{2h}{C^2} = \frac{h''}{\left\{1+[h']^2\right\}^{3/2}} \;\Rightarrow\; \frac{h^2}{C^2} = \text{const} - \frac{1}{\sqrt{1+[h']^2}}$$

B.C.: $h'(0) = 0;\quad h'(d/2) = \text{ctan}\,\theta$

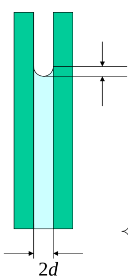
Hence,

$$h(0) = C\sqrt{(\text{const}-1)}$$
$$h(d/2) = C\sqrt{(\text{const}-\sin\theta)}$$

$$x = \int_{h(0)}^{h(x)} \frac{\left(\text{const}-\frac{h^2}{C^2}\right)\mathrm{d}h}{\sqrt{1-\left(\text{const}-\frac{h^2}{C^2}\right)^2}} = \frac{C}{2}\int_0^{C\sqrt{\text{const}-\cos\xi}} \frac{\cos\xi\,\mathrm{d}\xi}{\sqrt{\text{const}-\cos\xi}}$$

const is found from the boundary conditions

A limiting case that everyone is familiar with



$$C = \sqrt{\frac{2\gamma}{\rho g}} >> d$$

$$\Delta h = R - R\sin\theta = \frac{d}{2}(\sec\theta - \tan\theta) << h(0)$$

hence the curvature is nearly constant,

$$h(x) \simeq h(0) + R - \sqrt{R^2 - x^2}$$

i.e. the meniscus is *"hemispherical"*

const >>1

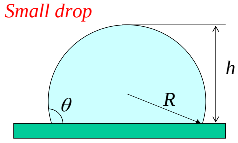
$$d \simeq \frac{C}{\sqrt{\text{const}}}\int_0^{\frac{\pi}{2}-\theta}\cos\xi\,\mathrm{d}\xi = \frac{C}{\sqrt{\text{const}}}\cos\theta$$

$$h(0) \simeq C\sqrt{\text{const}}$$

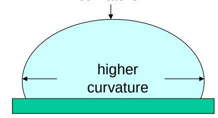
$$\Rightarrow\; h(0) \simeq h(d/2) \simeq \frac{2\gamma\cos\theta}{\rho g d}$$

Drop shape

Small drop

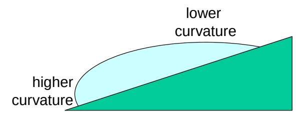


Large drop



$$\rho g h << \frac{2\gamma}{R}$$
$$\Updownarrow$$
$$R << \frac{C}{\sqrt{1+\sin\theta}} \sim C$$

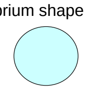
C = 3.7 mm for H_2O
= 2.7 mm for Hg



Minimal surfaces: the Plateau problem

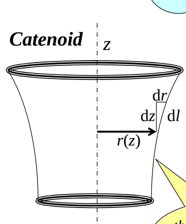
What is the equilibrium shape of liquid drop under zero gravity condition?

Sphere



minimum area (A) for a given volume (V)

Catenoid



$$A = 2\pi\int r\,\mathrm{d}l = 2\pi\int_{z_1}^{z_2} r\sqrt{\mathrm{d}z^2 + \mathrm{d}r^2}$$

$$= 2\pi\int_{z_1}^{z_2} r\sqrt{1+(r')^2}\,\mathrm{d}z \to \min$$

$$r(z) = c_1\cosh\frac{z-c_2}{c_1}$$

the surface of zero average curvature

Catenoid problem: The variational approach

The problem: Find a function $r(z)$ such that

$$A = 2\pi\int_{z_1}^{z_2}\underbrace{r\sqrt{1+(r')^2}}_{F(r,r')}\,\mathrm{d}z \to \min$$

$$r(z) \to r(z) + \varepsilon\varphi(z); \qquad |\varepsilon| \ll 1$$

If $A(\varepsilon)$ has an extremum, $\left.\frac{\mathrm{d}A}{\mathrm{d}\varepsilon}\right|_{\varepsilon=0} = 0$

must be zero

$$A(\varepsilon) = \int_{z_1}^{z_2} F(r+\varepsilon\varphi, r'+\varepsilon\varphi')\mathrm{d}z \cong A(0) + \varepsilon\int_{z_1}^{z_2}\left(\frac{\partial F}{\partial r}\varphi + \frac{\partial F}{\partial r'}\varphi'\right)\mathrm{d}z$$

$$\int_{z_1}^{z_2}\left(\frac{\partial F}{\partial r}\varphi + \frac{\partial F}{\partial r'}\varphi'\right)\mathrm{d}z = \int_{z_1}^{z_2}\frac{\partial F}{\partial r}\varphi\,\mathrm{d}z + \underbrace{\int_{z_1}^{z_2}\frac{\partial F}{\partial r'}\varphi'\,\mathrm{d}z}_{\text{intergrate by parts}} = \varphi\left.\frac{\partial F}{\partial r'}\right|_{z_1}^{z_2} + \int_{z_1}^{z_2}\left(\frac{\partial F}{\partial r} - \frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial F}{\partial r'}\right)\varphi\,\mathrm{d}z$$

Euler-Lagrange equation: $\frac{\partial F}{\partial r} - \frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial F}{\partial r'} = 0$

Catenoid problem: The variational approach (cont'd)

We have defined $F(r,r') = r\sqrt{1+(r')^2}$ i.e. it does not depend on z explicitly.

Then

$$\frac{\mathrm{d}F}{\mathrm{d}z} = \underbrace{\frac{\partial F}{\partial z}}_{\text{is zero}} + \frac{\partial F}{\partial r}\frac{\mathrm{d}r}{\mathrm{d}z} + \frac{\partial F}{\partial r'}\frac{\mathrm{d}r'}{\mathrm{d}z} = \frac{\partial F}{\partial r}r' + \frac{\partial F}{\partial r'}r''$$

Further, from the Euler-Lagrange equation,

$$r'\frac{\partial F}{\partial r} - r'\frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial F}{\partial r'} = 0$$

and so

$$\overbrace{r'\frac{\partial F}{\partial r} \qquad \frac{\partial F}{\partial r'}r''}^{\frac{\mathrm{d}F}{\mathrm{d}z}}$$

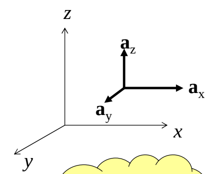
$$r'\frac{\partial F}{\partial r} - r'\frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial F}{\partial r'} + \frac{\partial F}{\partial r'}r'' - \frac{\partial F}{\partial r'}r'' = 0$$

$$\underbrace{- r'\frac{\mathrm{d}}{\mathrm{d}z}\frac{\partial F}{\partial r'} - \frac{\partial F}{\partial r'}r''}_{\frac{\mathrm{d}}{\mathrm{d}z}\left(r'\frac{\partial F}{\partial r'}\right)}$$

$$\frac{\mathrm{d}}{\mathrm{d}z}\left(F - r'\frac{\partial F}{\partial r'}\right) = 0 \quad\Rightarrow\quad F - r'\frac{\partial F}{\partial r'} = \mathrm{const} \quad\Rightarrow\quad r(z) = c_1\cosh\frac{z-c_2}{c_1}$$

Tensors

Let there be three vectors $\mathbf{a}_x$, $\mathbf{a}_y$ and $\mathbf{a}_z$ defined in each point of a space. On rotation of the coordinate system, $x \to x'$, $y \to y'$ and $z \to z'$, the triple of the vectors is transformed as



$$\mathbf{a}_{x'} = \mathbf{a}_x\cos(x,x') + \mathbf{a}_y\cos(y,x') + \mathbf{a}_z\cos(z,x')$$
$$\mathbf{a}_{y'} = \mathbf{a}_x\cos(x,y') + \mathbf{a}_y\cos(y,y') + \mathbf{a}_z\cos(z,y')$$
$$\mathbf{a}_{z'} = \mathbf{a}_x\cos(x,z') + \mathbf{a}_y\cos(y,z') + \mathbf{a}_z\cos(z,z')$$

This defines a 2nd rank tensor $\hat{\mathbf{a}} = (a_{ij})$

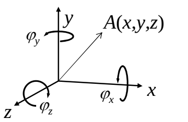
projections of such a tensor on coordinate axes are vectors

Scalar product of a tensor and a vector gives a vector, e.g.

$$\mathbf{B} = \hat{\mathbf{a}}\cdot\mathbf{A}$$
$$B_i = \sum_j a_{ij}A_j$$

projections of a vector on coordinate axes are scalars

An alternative definition of tensors



Representation of a *scalar* (e.g. temperature) does not change on transforming the coordinate system.

Representation of a *vector* (e.g. electric field) changes as

$$\begin{pmatrix}A_{x''}\\A_{y''}\\A_{z''}\end{pmatrix} = \underbrace{\begin{pmatrix}\cos\varphi_{z''} & \sin\varphi_{z''} & 0\\ -\sin\varphi_{z''} & \cos\varphi_{z''} & 0\\ 0 & 0 & 1\end{pmatrix}}_{\text{rotation around } z''}\underbrace{\begin{pmatrix}\cos\varphi_{y'} & 0 & \sin\varphi_{y'}\\ 0 & 1 & 0\\ -\sin\varphi_{y'} & 0 & \cos\varphi_{y'}\end{pmatrix}}_{\text{rotation around } y'}\underbrace{\begin{pmatrix}1 & 0 & 0\\ 0 & \cos\varphi_x & \sin\varphi_x\\ 0 & -\sin\varphi_x & \cos\varphi_x\end{pmatrix}}_{\text{rotation around } x}\begin{pmatrix}A_x\\A_y\\A_z\end{pmatrix}$$

Let $\mathbf{A}$ and $\mathbf{B}$ be two vectors. Introduce a new object $\mathbf{T}$ comprised of pairs A_iB_j

$$\left.\begin{aligned}A_i' &= \sum_j M_{ij}A_j\\ B_k' &= \sum_l M_{kl}B_l\end{aligned}\right\} \quad\Rightarrow\quad T_{ik}' = \sum_{jl} M_{ij}M_{kl}T_{jl}$$

Think of electric polarization $\mathbf{p} = \boldsymbol{\alpha}\cdot\mathbf{E}$

$\mathbf{T}$ is a 2nd rank *tensor* (and has 3^2 = 9 elements)

Pressure tensor

To describe the surface forces, it is convenient to use the ***stress tensor*** $\boldsymbol{\sigma}$

$$\mathbf{F}_{\text{surface}} = \oint_S \boldsymbol{\sigma}\cdot\mathbf{n}\,\mathrm{d}S$$

$$\sigma_{ik} = -p\delta_{ik} + \eta\left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i}\right)$$

Under static conditions,

$$\sigma_{ik} = -p\delta_{ik}$$

which justify introduction of ***the pressure tensor***, $\hat{\mathbf{p}} = -\boldsymbol{\sigma}$

static equilibrium, potential force

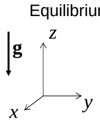
$$\int_V \rho\left(\mathbf{f}(\mathbf{r}) - \frac{\mathrm{d}^2\mathbf{r}}{\mathrm{d}t^2}\right)\mathrm{d}V + \oint_S \boldsymbol{\sigma}\cdot\mathbf{n}\,\mathrm{d}S = 0$$

$$-\rho\nabla U + \nabla\cdot\boldsymbol{\sigma} = 0$$

Pressure tensor (cont'd)

$$\hat{\mathbf{p}} = \begin{pmatrix}p_{11} & p_{12} & p_{13}\\ p_{21} & p_{22} & p_{23}\\ p_{31} & p_{32} & p_{33}\end{pmatrix} \xrightarrow[\text{axes}]{\text{principal}} \begin{pmatrix}p_{11} & 0 & 0\\ 0 & p_{22} & 0\\ 0 & 0 & p_{33}\end{pmatrix}$$

Equilibrium condition for an isotropic liquid in the gravitational field:



$$\hat{\mathbf{p}} = p\hat{\mathbf{I}}; \qquad \frac{\partial p}{\partial x} = \frac{\partial p}{\partial y} = 0; \qquad \frac{\partial p}{\partial z} = -\rho g$$

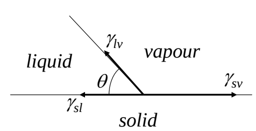
Bakker equation

for symmetric part of the excess surface stress tensor

$$\hat{\boldsymbol{\gamma}} = \int_{-\infty}^{z_0}(p^{\alpha}\hat{\mathbf{I}} - \hat{\mathbf{p}})\mathrm{d}z + \int_{z_0}^{+\infty}(p^{\beta}\hat{\mathbf{I}} - \hat{\mathbf{p}})\mathrm{d}z$$

$$\gamma = \int_{-\infty}^{+\infty}(p_{\perp} - p_{\parallel})\mathrm{d}z$$

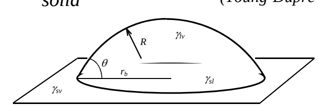
Contact angle



$$\gamma_{sl} + \gamma_{lv}\cos\theta = \gamma_{sv}$$

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

(Young-Dupré equation)



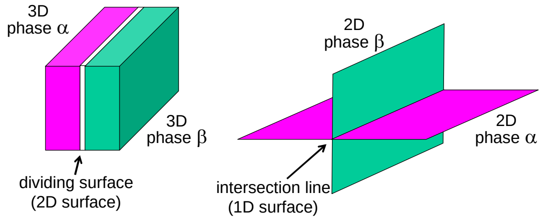
$$E = E_{lv} + E_{sl} + E_{sv}$$
$$E_{lv} = \gamma_{lv}S_{lv} = 2\pi R^2\gamma_{lv}(1-\cos\theta)$$
$$E_{sl} = \gamma_{sl}S_{sl} = \pi R^2\gamma_{sl}\sin^2\theta$$
$$E_{sv} = \gamma_{sv}S_{sv} = const - \pi R^2\gamma_{sv}\sin^2\theta$$

$$R(\theta) = \sqrt[3]{\frac{3V}{\pi(2-3\cos\theta+\cos^3\theta)}}$$

$$\min_{\{\theta\}} E|_{V=const} \qquad \frac{\mathrm{d}E}{\mathrm{d}\theta} = 0$$

$$\cos\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}$$

Linear tension and generalized Young equation



The energy functional:

$$F = \underbrace{-\sum_i \iiint_{V^{(i)}} p^{(i)} \mathrm{d}V^{(i)}}_{\text{bulk effect}} + \underbrace{\sum_{i<j} \iint_{V^{(i)} \cap V^{(j)}} \gamma^{(ij)} \mathrm{d}A^{(ij)}}_{\text{surface effect}} + \underbrace{\sum_{i<j<k} \int_{V^{(i)} \cap V^{(j)} \cap V^{(k)}} \gamma^{(ijk)} \mathrm{d}L^{(ijk)}}_{\text{line effect}}$$

$$\min F \Rightarrow \gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta + \frac{\gamma_{slv}}{r}$$