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Lecture Note

Capillarity

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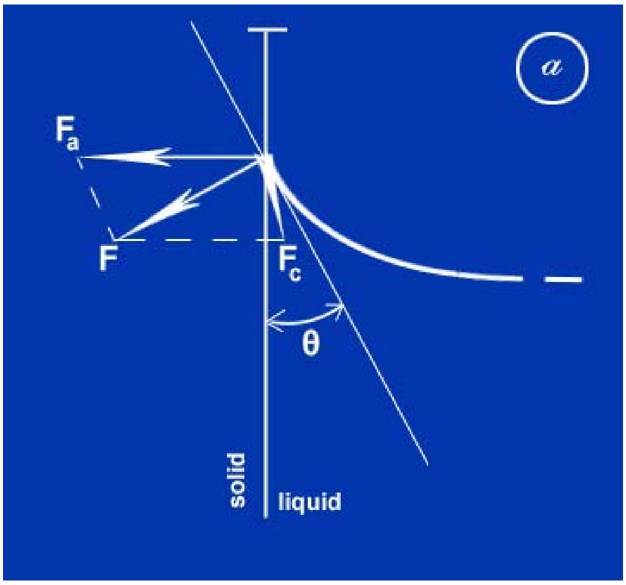
Abstract

Capillarity is an important phenomenon in nature and life. In this note the theory upon which the capillary action relies as well as the interface shapes for certain types of capillary systems under gravity is briefly outlined. Schematic presentations are also given.

Keywords: capillary rise, mean curvature, sessile drop, pendent drop, raised holm.

A tube, the bore of which is so small that it will only admit a hair (Latin capilla) is called a capillary tube. When such a tube of glass, open at both ends, is placed vertically with its lower end immersed in water, the water is observed to rise in the tube, and to stand within the tube at a higher level than the water outside. The action between the capillary tube and the water has been called capillary action, and the name has been extended to many other phenomena which have been found to depend on properties of liquids and solids similar to those which cause water to rise in capillary tubes. The forces which are concerned in these phenomena are those which act between neighboring parts of the same substance, and which are called forces of cohesion, and those which act between portions of matter of different kinds, which are called forces of adhesion. These forces are quite insensible between two portions of matter separated by any distance which we can directly measure. It is only when the distance becomes exceedingly small that these forces become perceptible (J.C.Maxwell [1]).



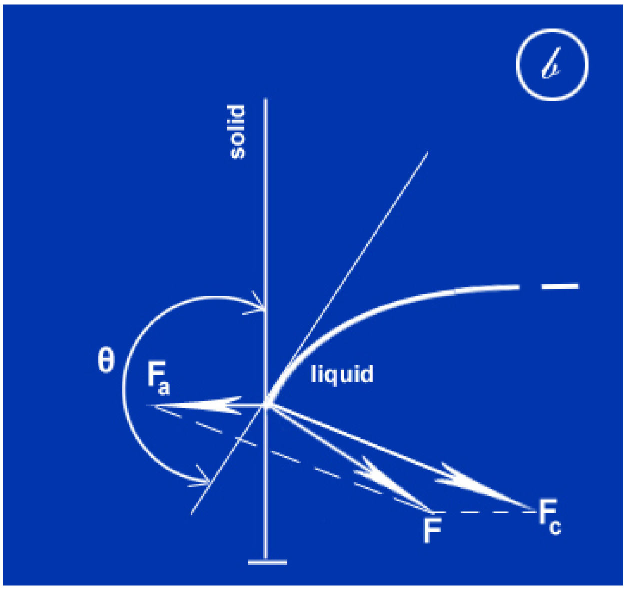


Figure 1. Cohesion and adhesion forces.

Let a marginal molecule common to both the liquid surface that is in contact with a solid and the liquid free surface (Fig.1). On this molecule the cohesion and adhesion forces F_c and F_a will exert a resultant force F. At this point the liquid surface tends to get a position such that to become normal to F. When $F_a > F_c$ the liquid is wetting the solid surface; i.e. the liquid free surface becomes concave near the solid plate and the contact angle $\theta < 90^o$ (Fig.1a). When $F_a < F_c$ the liquid does not wet the solid surface; i.e. the liquid free surface becomes convex near the solid and $\theta > 90^o$ (Fig.1b).

If a liquid is placed inside a solid tube the requirement that the liquid/gas interface must meet the liquid/solid interface at the correct contact angle prevents the surface of the liquid from being plane (Fig.2). The resulting curvature of the surface creates a pressure difference ΔP which is given by the Young-Laplace equation [2-6]:

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$$\Delta P = \gamma j\,, \qquad (1)$$

where γ is the surface tension and j is the mean curvature of the surface. Since the capillary is circular in cross section the meniscus will be approximately hemispherical with radius r_m and $j=2/r_m$. If the liquid meets the wall of the capillary at some angle θ then $r_m=r_c\cos\theta$ where r_c is the capillary radius. In the case of perfect wetting $\theta=0^o$ or:

$$\Delta P = \frac{2\gamma}{r_c}\,. \qquad (2)$$

In any wetting case the liquid will rise [7,8] in a tube until the force acting to pull the liquid upwards is balanced by the weight of the column of liquid supported in the tube [9].

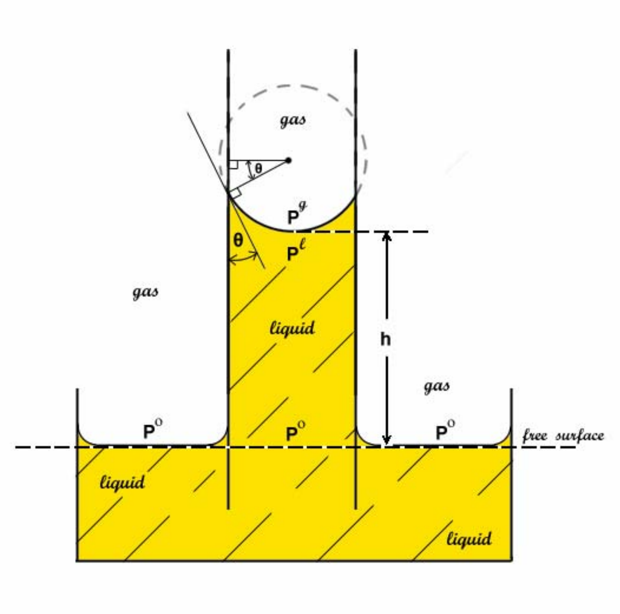

Figure 2. Capillary rise.

The pressure P^g in the gas phase (e.g. air) just above the interface will be equal to:

$$P^g = P^o - \rho_g gh\,, \qquad (3)$$

where P^o is the pressure at the free surface of the liquid, ρ_g is the gas density, g is the acceleration of gravity, and h is the height of liquid column. The pressure P^l in the liquid phase (e.g. water) just beneath the interface will be equal to:

$$P^l = P^o - \rho_l gh\,, \qquad (4)$$

where ρ_l is the density of the liquid. Since $\rho_l>\rho_g$ the pressure existing in the liquid phase beneath the gas/liquid interface is less than the pressure which exists in the gaseous phase above the interface. From hydrostatics this difference in pressure existing across the interface [10] will then be equal to:

$$P^g - P^l = (\rho_l - \rho_g)gh = \Delta\rho gh\,. \qquad (5)$$

On equilibrium Eq.2 and 5 must be equal:

$$\Delta P = \begin{cases} 2\gamma/r \\ \Delta\rho gh \end{cases} \Rightarrow a^2 = \frac{2\gamma}{\Delta\rho g} = rh\,, \qquad (6)$$

where α is the capillary constant.

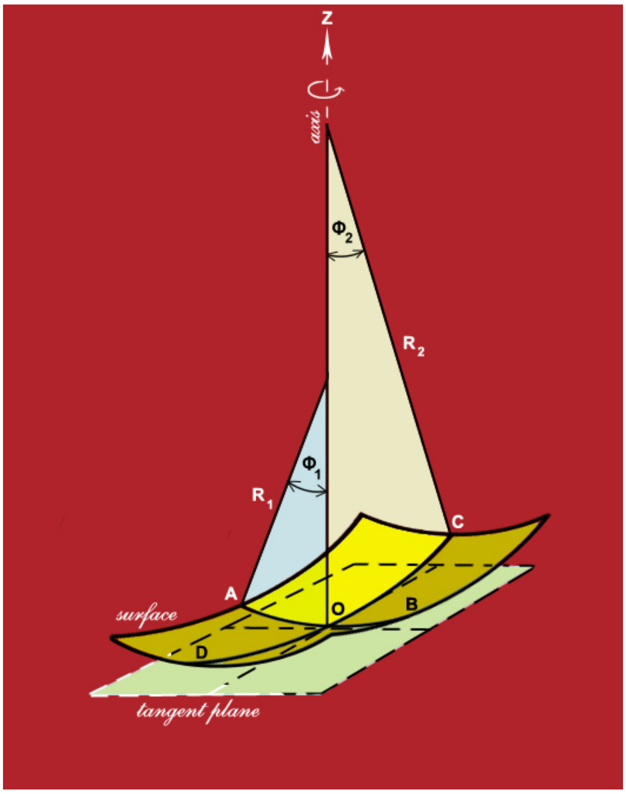

Figure 3. Mean curvature. Let O is a point and Z is the normal to the surface at that point. A plane which contains the normal will eventually intersect the surface to a line of intersection (is not shown). The radius of curvature for this line (which in general will be curved) is that for a circle tangent to the line at point O. Note that this radius is not yet the principal radius. By rotating the plane around the normal the radius of curvature will go through a minimum. Let this minimum corresponds to a line of intersection AB. Then this will be the first principal radius of curvature R_1 at point O. The second principal radius of curvature R_2 is obtained by simply passing a second plane through the surface, also containing the normal, but perpendicular to the first plane where the first principal radius of curvature is defined. This second plane cuts now the surface to CD. The radius of curvature which corresponds to CD is the second principal radius of curvature at point O and is always happened to be of maximum value. The pressure difference ΔP cannot depend upon the manner in which R_1 and R_2 are chosen, however, and it follows that the mean surface curvature J is independent of the directions of the orthogonal planes within which lie osculating circles. In other words if U_1 and U_2 are two radii of curvature (but not the principle ones) corresponding to two unspecified sections at right angles containing the same normal, then at point O: $J=(1/U_1)+(1/U_2)=(1/R_1)+(1/R_2)$.

For air/water interfaces at room temperature α≅4mm. Under the influence of gravity the meniscus will differ from sphericity, however. For very narrow capillaries (i.e. when r<<h) Lord Rayleigh [11] has shown that:

$$a^2 = rh\left(1+\frac{1}{3}\frac{r}{h} - 0.1288\frac{r^2}{h^2} + 0.1312\frac{r^3}{h^3}\cdots\right). \qquad (7)$$

In the general case of capillary rise j and hence ΔP will vary with the location of a point of question on the interface.

For systems at equilibrium in a gravitational field the curvature only varies in the vertical direction (e.g. z). Since h is the height of the liquid column up to the apex of the meniscus then for a point (x, z) on the interface the elevation will be h+z. Therefore $\Delta\rho g(h+z)=\gamma j$ while the capillary constant α may be further used to reduce the involved quantities. The constant α may also be used in several other capillarity problems which require only Δρ and γ. By setting Δρ to be always positive the general formulation [12] of the problem is given as:

$$J = 2(\lambda H - Z). \tag{8}$$

Where $J=\alpha j$, $H=h/\alpha$, $Z=z/\alpha$, and $\lambda=\pm 1$. The parameter λ takes into account the sign of J. Equation 8 is a differential equation which only under certain conditions can be numerically solved. The source of this complication emanates from J and whether or not it is possible to be described analytically [13-23].

At a point on a surface the curvature varies with direction. In general, there are two directions in which the radius of curvature has an absolute maximum and minimum. These are the principal directions and Euler's theorem shows that they are perpendicular [24]. The principal curvatures at the point are the curvatures in these directions (see Fig.3).

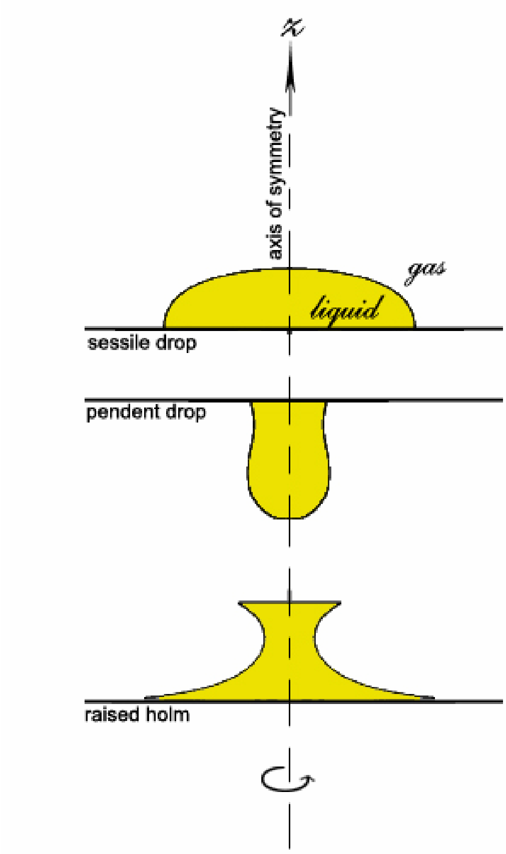

Figure 4. Meridians for axisymmetric fluid bodies in a gravitational field.

In capillarity most of the situations which can be produced under laboratory conditions refer to systems with an axis of rotational symmetry (Fig.4) and for these it is possible to write down explicit expressions for the radii of curvature from analytical geometry. A plane which passes through the axis of revolution will cut the surface under investigation to a meridian section. The meridional principal radius R_1 then swings in the plane of paper i.e. it is the curvature of the meridional profile at the point of question (X, Z). The azimuthal radius of curvature R_2 must then be in the plane perpendicular to that of the paper at the given point i.e. it is obtained by prolonging the normal to the profile until hits the axis of revolution. In the Cartesian form R_1 and R_2 may be defined as the first and second derivatives of Z with respect to X.

$$J = \frac{1}{R_1} + \frac{1}{R_2}, \tag{9}$$

$$\begin{cases} \dfrac{1}{R_1} = \dfrac{\ddot{Z}}{\left(1+\dot{Z}^2\right)^{3/2}} \\ \dfrac{1}{R_2} = \dfrac{\dot{Z}}{X\left(1+\dot{Z}^2\right)^{1/2}} \end{cases}, \dot{Z} = \frac{dZ}{dX}, \text{ and } \ddot{Z} = \frac{d^2 Z}{dX^2}. \tag{10}$$

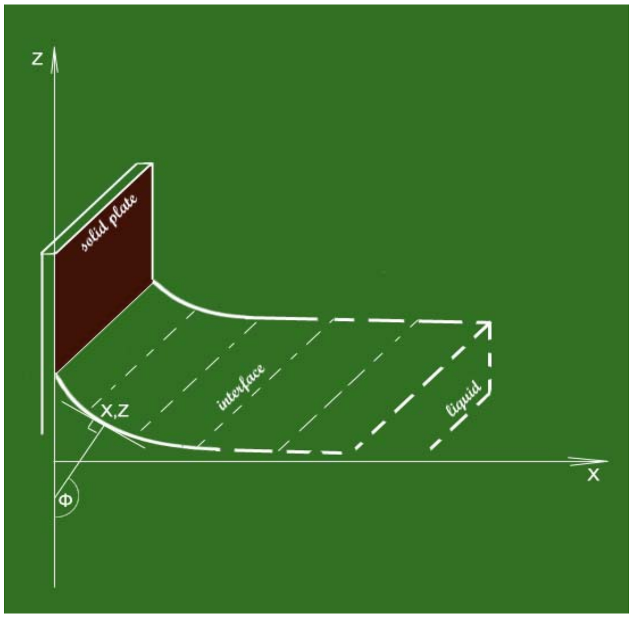

Figure 5. An interface meeting a plane wall (X=0 plane) with some contact angle. The meridian angle Φ is shown.

Alternatively, the meridian angle Φ may be introduced (see Fig.5). Thus:

$$\begin{cases} \dfrac{1}{R_1} = \dfrac{d\Phi}{dS} = \dfrac{d(\sin\Phi)}{dX} = -\dfrac{d(\cos\Phi)}{dZ} \\ \dfrac{1}{R_2} = \dfrac{\sin\Phi}{X}, \dfrac{dX}{dS} = \cos\Phi, \textit{and } \dfrac{dZ}{dS} = \sin\Phi \end{cases} \tag{11}$$

To demonstrate the solution of Eq.8 for a simple case let us assume an interface meeting a vertical plane in the presence of a gravitational field (Fig.5) . Since a capillary action is only possible very near to the plate the rest of the liquid will be asymptotically quite flat and since there is no axis of symmetry the Y direction will be linear even very close to the plate, thus H=0 and $R_2=\infty$. Then Eq.8 takes the form:

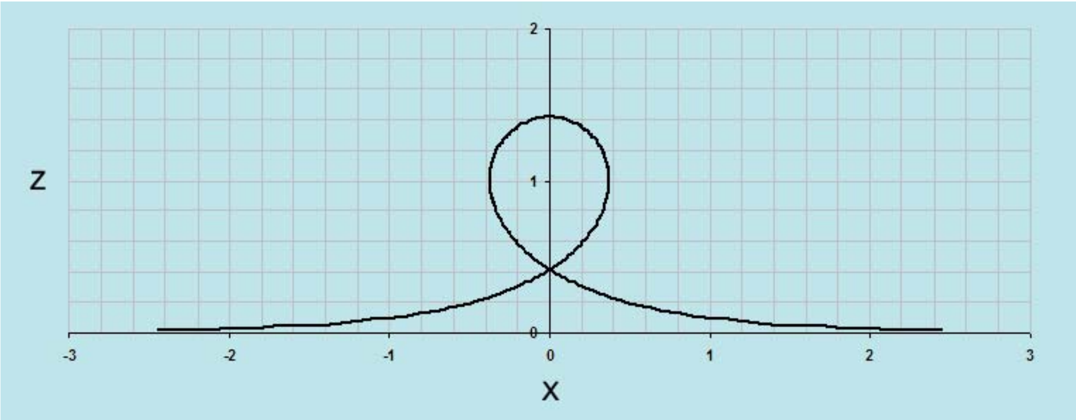

Figure 6. The capillary curve.

$$-\frac{d\Phi}{dS}=\frac{d(\cos\Phi)}{dZ}=2Z\ . \tag{12}$$

Integration of Eq.12 with initial conditions $\Phi=180^o$ and Z=0 gives:

$$Z=\pm\sqrt{1+\cos\Phi}\ . \tag{13}$$

Combining Eq.12 and 13 it comes that:

$$\frac{dS}{d\Phi}=\mp\frac{1}{2\sqrt{1+\cos\Phi}}\ . \tag{14}$$

Multiplying Eq.14 with dX/dS=cosΦ yields:

$$\frac{dX}{d\Phi}=\mp\frac{\cos\Phi}{2\sqrt{1+\cos\Phi}}\ . \tag{15}$$

Integration of Eq.15 gives:

$$X=\frac{1}{\sqrt{2}}\ln\left|\tan\left(\frac{\Phi+180^o}{4}\right)\right|-\sqrt{2}\sin\left(\frac{\Phi}{2}\right)+const. \tag{16}$$

By plotting X vs Z one obtains the capillary curve; Fig.6 shows this curve including negative and positive values with the coordinates conveniently shifted. Equations 13 and 16 may be used to approximate holm meridians while Eq.13 alone gives the height of a large sessile drop. More complicate situations require the use of elliptic integrals of the first and second kind.

In this note, which is the third in a series of lecture motes in colloids and interface science [25, 26], the physics of capillary systems is preliminary reviewed. In general J and hence ΔP will vary with the location of the point (X, Z) on the interface. For systems at equilibrium in a gravitational field the curvature, J, only varies in the vertical direction. For systems such as those in Fig.4, having an axis of symmetry aligned vertically, expressions for J and ΔP give a differential equation which can be solved numerically subject to specified conditions to give the meridian curve (X, Z).

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References and Notes

1. J.C.Maxwell, Capillary Attraction, Encyclopaedia Britannica, 9th Ed., Vol. 5, Samuel L. Hall, New York (1878). See also: J.Plateau, Experimental and theoretical statics of liquids subject to molecular forces only, Gauthier-Villars, Paris (1873); C.V.Boys, Soap-bubbles their colours and the forces which mould them, Society for promoting Christian knowledge, London (1916); Lord Kelvin, Capillary Attraction, Proc.Roy.Inst. London 11 (1886) 483-507; R.Finn, Capillary Surface Interfaces, Notices of the AMS 46 (1999) 770-781.
2. T.Young, An Essay on the Cohesion of Fluids, Phil.Trans.Royal Soc. 95 (1805) 65-87.
3. P.S.Laplace, Theory of Capillary Attraction, Supplements to the 10th book of Celestial Mechanics (1807).
4. P.R.Pujado, C.Huh, L.E.Scriven, On the Attribution of an Equation of Capillarity to Young and Laplace, J.Colloid Interface Sci. 38 (1972) 662-663.
5. M.Pasandideh-Fard, P.Chen, J.Mostaghimi, and A.W.Neumanntic, The generalized Laplace equation of capillarity I. Thermodynamic and hydrostatic considerations of the fundamental equation for interfaces, Adv.Colloid Interface Sci. 63 (1996) 151-178.
6. P.Chen, S.S.Susnar, M.Pasandideh-Fard, J.Mostaghimi, and A.W.Neumann, The generalized Laplace equation of capillarity II. Hydrostatic and thermodynamic derivations of the Laplace equation for high curvatures, Adv.Colloid Interface Sci. 63 (1996) 179-193.
7. B.V.Zhmud, F.Tiberg and K.Hallstensson, Dynamics of Capillary Rise, J.Colloid Interface Sci. 228 (2000) 263–269.
8. J.Bico and D.Quere, Rise of Liquids and Bubbles in Angular Capillary Tubes, J.Colloid Interface Sci. 247 (2002) 162–166.
9. In the non-wetting case the liquid will fall.
10. Also is referred to as capillary pressure, P_c.
11. Lord Rayleigh, On the Theory of Surface Forces, Phil.Mag. 30 (1890) 285-298, 456-475 (1890). Reprinted in Scientific Papers by Lord Rayleigh, Vol. 3, pp. 397-425. Dover Inc., New York (1964).
12. It has been commonly accepted practice to use lower case letters for dimensional quantities and upper case for dimensionless or reduced quantities. Although in this report the notation is consistent

with this practice, in the literature remains a source of confusion. For instance the mean curvature j appears in most of the literature as J careless if it corresponds to a reduced or a non-reduced quantity. The best way to judge whether a quantity is reduced or not is to keep in mind that reduced quantities occur when γ and Δρ are absent.

13. F.Bashforth and J.C.Adams, An Attempt to Test the Theories of Capillary Action, University Press, Cambridge, England (1883).
14. E.A.Boucher, Capillary phenomena: properties of systems with fluid/fluid interfaces, Rep.Prog.Phys. 43 (1980) 497-546.
15. E.A.Boucher, M.J.B.Evans, T.G.J.Jones, The computation of interface shapes for capillary systems in a gravitational field, Adv.Colloid Interface Sci. 27 (1987) 43-79.
16. B.K.Larkin, Numerical Solution of the Equation of Capillarity, J.Colloid Interface Sci. 23 (1967) 305-312.
17. J.Gaydos, Differential geometric theory of capillarity, Colloids and Surf.A: Physchem.Eng.Aspects 114 (1996) 1-22.
18. J. Gaydos and A.W. Neumann, Generalized Theory of Capillarity for Axisymmetric Menisci, Adv.Colloid Interface Sci. 38 (1992) 143-227.
19. L.Boruvka and A.W.Neumann, An Analytical Solution of the Laplace Equation for the Shape of Liquid Surfaces Near a Stripwise Heterogeneous Wall, J.Colloid Interface Sci. 65 (1978) 315-330.
20. Y.Rotenberg, L.Boruvka, and A.W.Neumann, Determination of Surface Tension and Contact Angle from the Shapes of Axisymmetric Fluid Interfaces, J.Colloid Interface Sci. 93 (1983) 169-183.
21. D.N.Staicopolus, The computation of surface tension and of contact angle by the sessile-drop method (II), J.Colloid Sci. 18 (1963) 793-794.
22. D. N. Staicopolus, The computation of surface tension and of contact angle by the sessile-drop method, J.Colloid Sci. 17 (1962) 439-447.
23. G.D.M.MacKay and S.G.Mason, Some effects of interfacial diffusion on the gravity coalescence of liquid drops, J.Colloid Sci. 18 (1963) 674-683.
24. A.W.Adamson, Physical Chemistry of Surfaces, Inter science Publishers, New York (1960).
25. A.Ch.Mitropoulos, What is a surface excess? JESTR 1, 1-3 (2008).
26. E.P.Favvas and A.Ch.Mitropoulos, What is spinodal decomposition? J. Eng. Sci. Tech. Rev. 1, 25-27 (2008).