On the Linear Boundary Energy in Two-Dimensional System

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Introduction.—The energy or the tension along the boundary line at which three phases are brought into contact with each other has been frequently conceived and called as the linear tension. When an oil lens is floating on the free surface of water, for example, the thickness of the lens is determined by the equilibrium between the spreading tendencies of oil and water, F_o^* and F_w^*. Thus, I. Langmuir(1) has assumed that the following equilibrium holds, $F_o^* - F_w^* = \Lambda^*/R$, where R is the radius of the lens and Λ^* is introduced as the linear tension along the periphery of the lens. When a lens has a definite thickness, F_o^* and F_w^* depend

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(1) I. Langmuir, *J. Chem. Phys.*, **1**, 756 (1933).

on the phase boundary tensions superimposed with the gravity force.

When, however, the thickness of the lens diminishes infinitely, the gravity force can be neglected and the spreading tendencies depend only upon the surface pressures themselves. This is a case of a two-dimensional system. In this case, we can define the "linear boundary tension" in two-dimensional system corresponding to the surface tension in the three-dimensional system.

As to the surface films of insoluble substances on water, it is known that there are some cases where the heterogeneous phase equilibrium takes place between the gaseous and the liquid films. In such cases, the presence of the islands of coherent liquid film surrounded by the vapor film has been found.(2) Accordingly, let the surface pressure of the liquid phase be F_1 and that of the vapour phase F_2, then for the equilibrium the following relation must be present,

$$F_1 - F_2 = \Lambda / R \qquad (1)$$

where R is the radius of the island of the liquid film, and Λ is defined as the linear boundary tension of this surface liquid film.(3)

It will not be impossible, radically speaking, to measure the linear boundary tension by some experimental device. However, as it will be seen in the following section, its value is supposed to be very small, so that the experimental technique will hardly be found at present.

The Conception of the Linear Boundary Energy in Two-Dimensional System by the Classical Theory.—The surface tension is deduced from the coherent force of the matter. The general idea has been expressed in the classical theory(4) of Laplace or Gauss. The same theory can be applied to the two-dimensional system, if the "surface mass" could be assumed. Such an assumption may be admitted in the mathematical sense, but physically it seems absurd. However, when we treat a surface film, we can consider it as a two-dimensional system, and the surface mass can be defined as the product of surface density (ρ) and area (S).

Following Gauss's method, we can estimate the potential energy of a condensed film of which area is S_0 and the length of periphery is L_0. Assuming the potential energy between two unit "surface mass" being apart at the distance r as $-\varphi(r)$, the energy between any two small parts of a condensed film, ds and ds', is expressed as $dW = -\rho^2\varphi(r)ds\,ds'$, where ρ is the surface density of the film. The total potential energy of the system is then,

$$W = -\frac{1}{2}\rho^2\iint\varphi(r)ds ds' = -\frac{1}{2}\rho^2\Omega \qquad (2)$$

Integration is carried out seperately regarding to ds and ds'. Thus ds is fixed at first and ds' is expressed by polar coordinate as $ds' = rd\theta_1 dr$ in Fig. 1. Therefore,

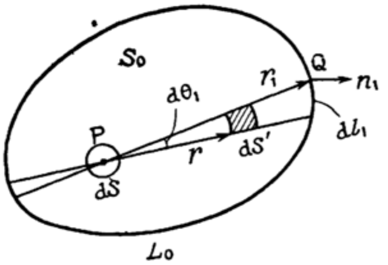

Fig. 1.

$$\Omega = \int ds\int d\theta_1\int_0^{r_1} r\varphi(r)dr \qquad (3)$$

Let us put $\int r\varphi(r)dr = c_1 - \Phi(r)$, where c_1 is a constant, then we will get

$$\begin{aligned}\Omega &= \int ds\int d\theta_1[\Phi(0) - \Phi(r_1)] \\ &= 2\pi\Phi(0)S_0 - \int ds\int\Phi(r_1)d\theta_1 \qquad (4)\end{aligned}$$

Here, let n_1 be a perpendicular to the periphery at Q in Fig. 1, accordingly $r_1 d\theta_1 = dl_1\cos(n_1\wedge r_1)$, and

$$\Omega = 2\pi\Phi(0)S_0 - \iint\frac{\Phi(r_1)\cos(n_1\wedge r_1)}{r_1}dl_1 ds \qquad (4')$$

As ds is also expressed as $r_1 d\theta dr_1$ in Fig. 2,

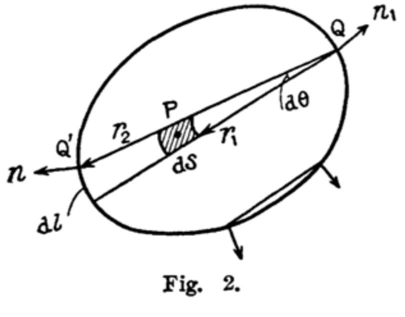

Fig. 2.

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(2) N. K. Adam, "The Physics and Chemistry of Surface", Oxford, 1938.

(3) A heterogeneous phase equilibrium between two kinds of condensed films is also possible to consider, however, it has not been investigated hitherto.

(4) G. Bakker, "Handbuch der Experimental Physik." B. 6, 1928, p. 51.

$$\int \frac{\Phi(r_1)\cos(n_1 \wedge r_1)\mathrm{d}s}{r_1}$$
$$= \int \cos(n_1 \wedge r_1)\mathrm{d}\theta \int_0^{r_2} \Phi(r_1)\mathrm{d}r_1 \qquad (5)$$

Let us again put $\int \varphi(r) r^2 \mathrm{d}r = c_2 - \psi(r)$, where c_2 is a constant, then

$$\int \varphi(r) r^2 \mathrm{d}r = \int \Phi(r)\mathrm{d}r - r\Phi(r) = c_2 - \psi(r)$$

and Eq. (5) is equal to $\psi(0)\int \cos(n_1 \wedge r_1)\mathrm{d}\theta - \int [\psi(r_2) - r_2\Phi(r_2)] \cos(n_1 \wedge r_1)\mathrm{d}\theta$.

Furthermore, let us put $\cos(n_1 \wedge r_1) = \cos\nu$, and since $\mathrm{d}\theta = \mathrm{d}\nu$, so

$$\int \cos(n_1 \wedge r_1)\mathrm{d}\theta = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \cos\nu\,\mathrm{d}\nu = 2.$$

$$\int \frac{\Phi(r_1)\cos(n_1 \wedge r_1)\mathrm{d}s}{r_1} = 2\psi(0)$$
$$- \int [\psi(r_2) - r_2\Phi(r_2)] \cos(n_1 \wedge r_1)\mathrm{d}\theta. \qquad (5')$$

Now when we put $r_2\mathrm{d}\theta = \mathrm{d}l \cos(n \wedge r_2)$ in Fig. 2, the second term in Eq. (5′) will be

$$\int [\psi(r_2) - r_2\Phi(r_2)] \frac{1}{r_2} \cos(n_1 \wedge r_1) \cos(n \wedge r_2)\mathrm{d}l.$$

$$\Omega = 2\pi\Phi(0)S_0 - 2\psi(0)\int \mathrm{d}l_1$$
$$+ \int\int \frac{1}{r_2}[\psi(r_2) - r_2\Phi(r_2)]$$
$$\times \cos(n_1 \wedge r_1)\cos(n \wedge r_2)\,\mathrm{d}l_1\mathrm{d}l. \qquad (6)$$

The value of $\psi(r)$ as well as $\Phi(r)$ decreases rapidly with increasing r, hence $\frac{1}{r}[\psi(r) - r\Phi(r)] \doteqdot 0$ when r is large. When r is small, on the other hand, $\cos(n_1 \wedge r_1)$ and also $\cos(n \wedge r_2)$ approach to zero (cf. Fig. 2). Thus the third term of Eq. (6) vanishes.

$$W = -\pi\rho^2\Phi(0)S_0 + \rho^2\psi(0)L_0 \qquad (7)$$

or
$$W = -HS_0 + \Lambda L_0 \qquad (8)$$

where,
$$H = \pi\rho^2 \int_0^\infty \varphi(r) r\,\mathrm{d}r \qquad (9)$$

$$\Lambda = \rho^2 \int_0^\infty \varphi(r) r^2 \mathrm{d}r \qquad (10)$$

Here, we can define Λ as the total linear boundary energy, corresponding to the total surface energy in the three-dimensional system, and H is the inner surface pressure.

An Estimation of the Value of the Linear Boundary Energy of the Surface Film.—It will be possible to make a rough estimation about the value of the linear boundary energy, when we assume the proper function for $\varphi(r)$ in Eqs. (9) and (10).

Let us consider a monomolecular film, of which equation of state is written as

$$\left(F + \frac{a}{A^2}\right)(A - b) = kT \qquad (11)$$

where F is the surface pressure and A is the area occupied by a molecule. From the statistical consideration of two-dimensional system,(5) a and b are written as

$$\left.\begin{aligned} a &= -\pi \int_D^\infty \mathcal{E}(r) r\,\mathrm{d}r \\ b &= 2\pi(D/2)^2 \end{aligned}\right\} \qquad (12)$$

where $\mathcal{E}(r)$ is the potential energy between two molecules in the film, D is the diameter of a molecule, and the potential diagram is assumed as illustrated in Fig. 3. Remembering that $\varphi(r)$ is the potential energy between two unit surface masses, and $\mathcal{E}(r)$ is that between two molecules, the relation between them is

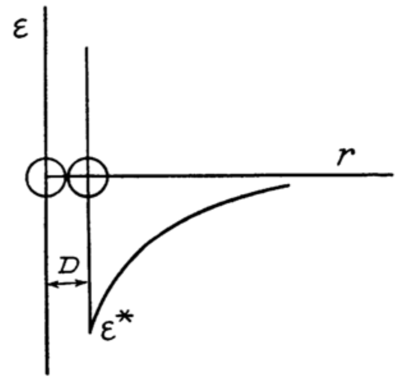

Fig. 3.—The hypothetical potential diagram. $\varepsilon = \infty$ when $r < D$, $\varepsilon = \varepsilon(r)$ when $r > D$, $\varepsilon = \varepsilon^*$ when $r = D$.

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(5) The partition function in two-dimensional system is,

$$Z = \left[\frac{2\pi mkT}{h^2}\right]^N \frac{1}{N!} \int\int \cdots \int \exp[-\Sigma\mathcal{E}(r_{ij})/kT]$$
$$\times \mathrm{d}x_1 \cdots \mathrm{d}y_N = [\quad]\,\phi(T)$$
$$\ln\phi(T) = \ln\left(\frac{1}{N!}\right) + N\ln S_0 - \frac{1}{2}N^2\frac{B}{S_0} + \cdots\cdots$$

where $B = \int_0^\infty 2\pi r(1 - e^{-\varepsilon(r)/kT})\mathrm{d}r$ is the second virial coefficient for two-dimensional system.

$$\varphi(r) \simeq -\frac{1}{m^2}\mathcal{E}(r) = -\mathcal{E}(r)/(A\rho)^2$$

where m is the mass of a molecule. Thus,

$$\int_0^\infty \varphi(r) r\,\mathrm{d}r \simeq \frac{-1}{(A\rho)^2}\int_D^\infty \mathcal{E}(r) r\,\mathrm{d}r$$

$$\int_0^\infty \varphi(r) r^2\,\mathrm{d}r \simeq \frac{-1}{(A\rho)^2}\int_D^\infty \mathcal{E}(r) r^2\,\mathrm{d}r$$

$$H = \frac{-\pi}{A^2}\int_D^\infty \mathcal{E}(r) r\,\mathrm{d}r = \frac{a}{A^2} \qquad (9')$$

$$\Lambda = \frac{-1}{A^2}\int_D^\infty \mathcal{E}(r) r^2\,\mathrm{d}r \qquad (10')$$

We must further assume a proper function for $\mathcal{E}(r)$, and it is assumed as,

$$\mathcal{E}(r) = \mathcal{E}^*(D/r)^6. \qquad (13)$$

Now we can integrate Eqs. (9′) and (10′).

$$H = -\frac{\pi}{A^2}\,\frac{\mathcal{E}^* D^2}{4} \qquad (9'')$$

$$\Lambda = -\frac{1}{A^2}\,\frac{\mathcal{E}^* D^3}{3} \qquad (10'')$$

Considering that, $H = a/A^2$ and $b = 2\pi(D/2)^2$,

$$\Lambda = \frac{4}{3\pi}DH = 0.34\,\frac{a\sqrt{b}}{A^2} \qquad (14)$$

We take, for an example, the data for myristic acid measured by Adam and Jessop.⁽⁶⁾ From the F–A diagram of myristic acid, the equation of state can be written as,

$$\left(F + \frac{18950}{A^2}\right)(A - 15.5) = 397$$

for liquid condensed film, and

$$\left(F + \frac{35500}{A^2}\right)(A - 24.3) = 397$$

for liquid expanded film. Since the true meaning of the expanded film seems unknown, we take the average value for a and b for those two states.

$$\bar{a} = 27\times10^{-29}\ \text{dyne}\cdot\text{cm.}^3,\quad \bar{b} = 20\times10^{-16}\ \text{cm}^2.$$

Inserting those values in Eq. (14),

$$\Lambda = \frac{41\times10^{-37}}{A^2}\ \text{dyne}. \qquad (15)$$

It has been found from the surface potential measurements⁽²⁾ that the region where coherent and gaseous film coexist together is at all areas between 48 and 800 sq. Å. per molecule for myristic acid. In this region, the islands of coherent film are observed as surrounded by gaseous film. Below 48 and above 800 sq. Å., the surface consists entirely of either coherent or gaseous film. Hence, it is reasonable to consider that in the islands of coherent film, the area occupied by a molecule is the order of 48 sq. Å. or less. If we assume 48 sq. Å. for the value of A in Eq. (15), then Λ will be 1.8×10^{-7} dyne (or more) for the islands of myristic acid film.

We have nothing to check the value directly at present. However, the latent heat of surface vaporisation of myristic acid film has been measured as 2457 cal. by J. Sameshima.⁽⁷⁾ From this value, the internal latent heat of surface vaporisation per melecule (q) is known as 13×10^{-14} erg. On the other hand, the value of the total linear boundary energy per molecule (λ) is calculated as,

$$\lambda = (1.8\times10^{-7}) \div [(1\times10^8) \div 2\sqrt{48/\pi}] = 1.4\times10^{-14}\ \text{erg}.$$

It is supposed as reasonable that the value of λ is a certain fraction, not far from 0.5, of q. Thus the estimated value of Λ of myristic acid film seems too small to compare it with the observed value of the heat of surface vaporisation, though the order of the value is reasonable.

Summary

A definition of the linear boundary tension of the two-dimensional film was conceived, which corresponds to the surface tension in the three-dimensional system. The physical meaning of this conception was investigated according to the classical Gauss theory. A rough estimation of this value was made for the surface film of myristic acid.

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(6) N. K. Adam and G. Jessop, *Proc. Roy. Soc. London*, A **112**, 362 (1926).

(7) J. Sameshima, *Proc. Imp. Acad. Japan*, **10**, 155 (1934).