

AN EXAMINATION OF THE BASIC POSTULATES OF SURFACE CHEMISTRY: A VARIATIONAL CALCULUS ANALYSIS OF THE CLASSIC ROTATING DROP EXPERIMENT

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Abstract

A demonstration, using the variational calculus, is given showing that it is impossible to describe the excess free energy in any liquid surface by the use of a single energy parameter, the surface tension, without violating the laws of motion. The addition of the required second parameter, the flexural rigidity, is shown to be adequate to explain published data on the system *n*-hexadecane/glycerol, and to demonstrate that for small radii of curvature, the curvature parameter may contribute orders of magnitude more to the surface energy than the surface tension does.

1. Introduction

This paper has several purposes. It will show that the variational calculus furnishes a very powerful tool for the examination of experimental models, and it will use the free surface energy model as an example by analysing the rotating drop experiment. It will show that it is impossible to represent the free energy in a surface by the surface tension alone without violating the laws of motion. It will show how, in the rotating drop experiment, the mathematical analysis suggests alternative and more satisfactory models for the surface energy. It is hoped that the mathematical strategy outlined will suggest other scientific models to which the variational calculus might contribute in a similar fashion.

When a system, such as the rotating drop, is in a steady-state condition, certain integrals describing the state must be minimized. The determination of the minimal boundary conditions and functional forms can be done using the methods of the variational calculus. Such a determination is not too difficult an extrapolation of the methods for finding the maximum and minimum points of simple curves in elementary calculus. The methods, although extremely powerful, are not familiar to most chemists; it is therefore important that their strengths be demonstrated. Surface chemistry is

a very important example, for if an entity can be isolated, it must have a surface and any reaction between two entities involves their surfaces. So the surface model must be examined to see if the area parameter is enough to describe a surface, as all the important surfaces are highly curved.

If it can be shown in the minimization process that too few measurable parameters lead to a reduction to absurdity, the model must be changed to include at least one additional parameter; however, in order to conform to the requirements of Occam's razor, the model should not have more parameters than are necessary to avoid the reduction to absurdity.

2. The rotating drop

A method for obtaining interfacial free energies by measuring the shape of a drop of fluid in a more dense liquid contained in a rotating horizontal tube was first suggested by Plateau's [1] experiments. Beer [2] had also considered the shape of the drop in some detail, as did Lord Raleigh [3] in 1914. It was not until 1942, however, that Vonnegut [4] first tried to use the method to determine surface tension.

Vonnegut's analysis rested on the assumption that the drop could be treated as though it were a cylinder with hemispherical ends, thus avoiding having to determine the drop shape. The measurement of drop length $2x_0$ is relatively easy, but the measurement of the drop radius $y = f(x)$ is very difficult experimentally and therefore requires theoretical analysis. Further contributions have been made by Silberberg [5], Rosenthal [6], Ross [7], Wade et al. [8] and Princen, Zia and Mason [9]. All of the workers cited made the tacit assumption that the deformation of the drop shape began at zero rate of rotation, an assumption that will be examined in this paper. The beautifully precise experimental work of Princen, Zia and Mason (PZM) will test the mathematical development. Figure 1, from PZM, illustrates the experimental method.

The rotating drop method is admirably suited to our purpose, for only one surface, that between the two phases, is involved so there are no contact angles. In addition, there is no relative motion, in the absence of gravity, of the phases when a steady-state is achieved. More importantly, the initial statement of the problem can be made using only the most basic concepts, so that the introduction of tacit assumptions, such as unnatural boundary conditions, is fairly easily avoided. For example, the assumption that the volume of the drop and of the surrounding phases are constants restricts all the possible potential energy parameters to the interface between the two phases and requires the pressures, both inside and outside the drop, on the axis of rotation, to be independent of the rate of rotation.

If a long tube (see fig. 1), filled with a liquid phase M' of density ρ' containing a drop of an immiscible liquid M'' of lesser density ρ'' , is rotated about its horizontal axis, the drop becomes elongated along the axis of rotation. We assume the absence of

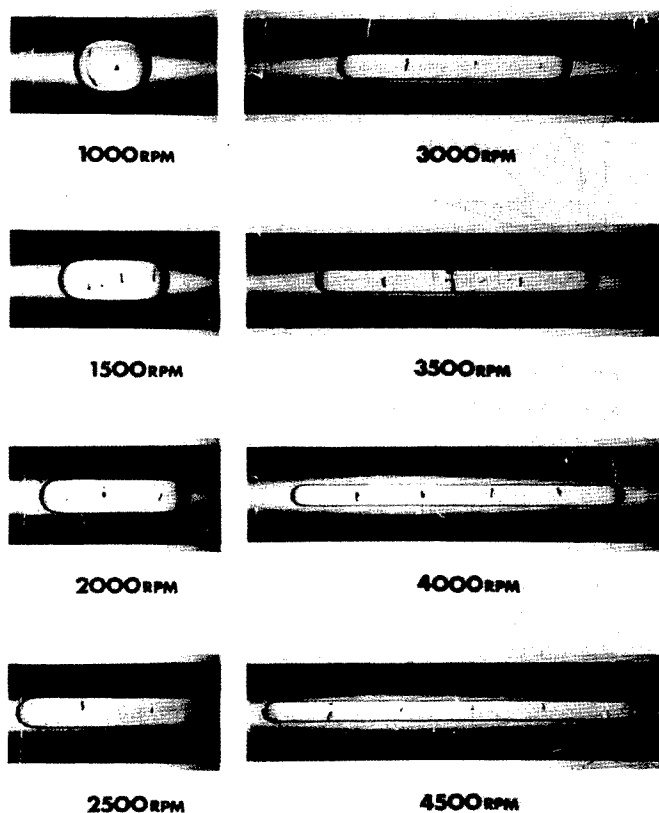


Fig. 1. Photographs of a heptane drop (0.156 cm^3) in glycerol rotating at various speeds.

gravity so that the axis of the drop will coincide with the axis of rotation of the tube. The origin of the coordinate system will be taken at the left end of the drop. Because of symmetry, only half of the drop between the origin and the center of the drop at the x_0 plane need be considered which, fortunately, gives more informative end points to the integral to be minimized. The kinetic energy KE minus the potential energy PE of the drop will be minimum when the system is in the steady-state condition, in accordance with Hamilton's principle. This minimum will result when the integral of $K dx$ from 0 to x_0 is stationary subject to the constraint of the drop volume being constant, that is, independent of the rate of rotation; thus

$$G = \pi \int_0^{x_0} K dx = \int_0^{x_0} \left(\frac{\pi \rho \omega^2 y^4}{4} + 2\pi \sigma y (1 + y_x^2)^{1/2} + \pi \lambda y^2 \right) dx. \quad (1)$$

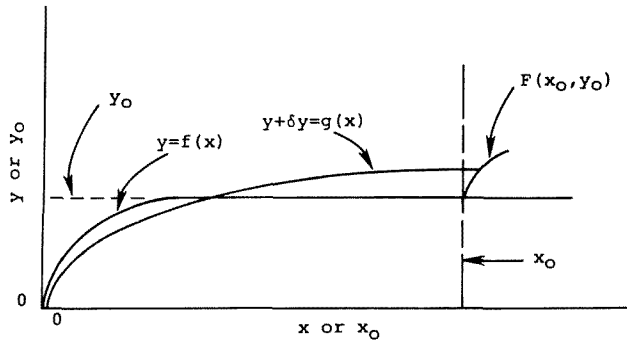


Fig. 2. Possible drop shapes. $f(x)$ = equilibrium curve; $g(x)$ = possible non-equilibrium curve.

The first term in the second integral is $-KE$ available, because of the difference in density $\rho = \rho' - \rho''$ of the two liquids and ω the angular rate of rotation, to do work on the drop. The differential term dKE is determined by solving the kinetic energy of a rotating circular plate. The second term is the dPE of the surface of the drop described by the curve $y = f(x)$ (fig. 2) when it is rotated around the x axis; y_x is the derivative of y with respect to x . The Lagrangian multiplier λ is to be adjusted so that the volume of the drop of density ρ'' and given mass

$$V = 2\pi \int_0^{x_0} y^2 dx = \frac{4}{3} \pi a^3 \tag{2}$$

is maintained constant. $y = f(x)$ represents the equilibrium shape which is to be determined by minimizing eq. (1). We now assume, following standard thermodynamics of surfaces, that σ is the only surface energy parameter and that it is a constant and we determine the consequences of that assumption.

The condition that G be a minimum is the Euler equation (see any variational calculus text [10, 11]):

$$\frac{d}{dx} \left[K - y_x \frac{\partial K}{\partial y_x} \right] = 0 \tag{3}$$

for the case where K does not contain x explicitly. From eq. (3), we may write

$$K - y_x \frac{\partial K}{\partial y_x} = \frac{\rho \omega^2 y^4}{4} + 2y\sigma(1 + y_x^2)^{-1/2} + \lambda y^2 = \text{constant} = 0. \tag{4}$$

The constant is zero, since (4) may be evaluated at the origin where $y = 0$. Equation (3), upon differentiating, becomes

$$\rho\omega^2 y^3 + 2\sigma(1 + y_x^2)^{-1/2} - \frac{2\sigma y y_{xx}}{(1 + y_x^2)^{3/2}} + 2\lambda y = 0. \tag{5}$$

y_{xx} represents the second derivative of y with respect to x .

Subtract eq. (4) from eq. (5) to eliminate $2\sigma(1 + y_x^2)^{-1/2}$ and replace the derivatives with the corresponding angular functions ($y_x = \tan \theta$) to obtain

$$\frac{3}{4} \rho\omega^2 y^2 - \frac{2\sigma d \sin \theta}{dx} + \lambda = 0. \tag{6}$$

Separate the variables and integrate from 0 to x_0 to obtain

$$\frac{3}{4} \rho\omega^2 \int_0^{x_0} y^2 dx + \lambda x_0 = -2\sigma. \tag{7}$$

Equation (7) with eq. (2) gives

$$\frac{\rho\omega^2 a^3}{4} + \frac{\lambda x_0}{2} = -\sigma. \tag{8}$$

Equation (4) may be evaluated at x_0 where dy/dx is zero, because of symmetry, so that

$$-\lambda = \frac{\rho\omega^2 y_0^2}{4} + \frac{2\sigma}{y_0}, \tag{9}$$

which with eq. (8) results in

$$\sigma = \frac{\rho\omega^2}{4} \left[a^3 - \frac{x_0 y_0^2}{2} \right] \frac{y_0}{x_0 - y_0} \tag{10}$$

Equation (10) is an example of an integration to an undetermined, or variable, end point y_0 and we have to determine the values of y_0 in eq. (10) that will determine a constant value of σ , minimize G , and define the shape of the drop. If, for example, the drop were a cylinder capped by hemispheres, the drop would require that

$$x_0 = \frac{2}{3} \left[\frac{a^3}{y_0^2} + \frac{y_0}{2} \right], \tag{11}$$

and this in eq. (10) gives Vonnegut's equation and a variable σ . It does show that the basic assumptions of Vonnegut's treatment are consistent with those of this paper, but that eq. (11) does not give the value of y_0 that minimizes G . We therefore ask the variational calculus to define the value of y_0 to be used in eq. (10) so that δG , the variation of G , equals zero for each of the measured values of x_0 and ω .

To define y_0 and therefore σ , consider the variation of G as the upper end point of the integral, for a given value of ω is allowed to vary; $y + \delta y = g(x)$ in fig. 2 is assumed to represent some varied non-equilibrium curve. We now ask, how does the end point of $y + \delta y$ change along some curve F and meet $y = f(x)$ so as to give a condition that will define the minimum value of G ? We write (ref. [11], ch. 8, sect. 2)

$$\delta G = K_0 dx_0 + \int_0^{x_0} \left(\frac{\partial K}{\partial y} \delta y + \frac{\partial K}{\partial y_x} \delta y_x \right) dx. \quad (12)$$

The subscript 0 indicates the value of the function at x_0 . Equation (12) can be integrated by parts, giving

$$\delta G = K_0 dx_0 + \left(\frac{\partial K}{\partial y_x} \right)_0 \delta y_0 + \int_0^{x_0} \delta y \left(\frac{\partial K}{\partial y} - \frac{d}{dx} \frac{\partial K}{\partial y_x} \right) dx. \quad (13)$$

The part of eq. (13) under the integral sign is an expression of the Euler equation and is therefore zero, so that the condition for G to be stationary with respect to a variation of the end point along the curve $F(x_0, y_0)$ is

$$\delta G = K_0 dx_0 + \left(\frac{\partial K}{\partial y_x} \right)_0 \delta y_0 = 0. \quad (14)$$

Equation (14) can be put in the more useful form (see ref. [11], ch. 8):

$$\delta G = \left(K + (F_{x_0} - y_x) \frac{\partial K}{\partial y_x} \right)_0 = 0, \quad (15)$$

which is called the transversality condition. F_{x_0} is the slope of $F(x_0, y_0)$ at $f(x_0)$, which would require, if $\partial K/\partial y_x$ were not zero, that F_{x_0} , when $\delta G = 0$, be zero. However, since in this case the partial of K with respect to y_x is zero at x_0 , F_{x_0} is not restricted and the conditions for a stationary G are simply that the derivative of σ be zero and $F(x_0, y_0)$ may meet $f(x)$, the assumed equilibrium shape, at any angle and the derivative of eq. (10) gives

$$(a^3 - \frac{3}{2}x_0y_0^2 + y_0^3)x_0dy_0 - \left(a^3 - \frac{y_0^3}{2}\right)y_0dx_0 = 0. \quad (16)$$

If dy_0/dx_0 is finite, then

$$x_0 = \frac{2}{3} \left(\frac{a^3}{y_0^2} + y_0 \right). \quad (17)$$

Equation (17) with eq. (10) then gives

$$\sigma = \frac{\rho\omega^2y_0^3}{4}. \quad (18)$$

If dy_0/dx_0 equals zero,

$$2a^3 = y_0^3 = x_0^3 \quad (19)$$

and only one point is determined and y_{xx} at x_0 must be zero for all values of ω greater than some critical value ω_c , determined by eq. (19), below which y_{xx} at x_0 is not equal to zero and the drop is not distorted, but is stressed.

When eqs. (5), (9) and (17) are combined, y_{xx} is confirmed to be zero for all values above the critical value ω_c , where eq. (19) holds. When $x_0 = y_0$, σ is indeterminate and x_0 and y_0 have lost any meaning as measurable parameters.

To get a feeling for the interpretation of an experiment, we may plot y_0 versus σ in eq. (10) for some measured value of x_0 and ω (see fig. 3, which is a plot of the data of experiment 5, table 1, and compare points A, B and C). A is the point given by Vonnegut's equation. C is the point given by PZM. B is the point resulting from the variational analysis. This comparison is valid since Vonnegut's equation, as has been mentioned, may be derived from eq. (10) and eq. (10) may be derived from PZM's [16] approach. Thus, the variational calculus allows an integral to be minimized to give a minimal function, eq. (10), which is then given a specific value by finding the constant value of the parameter σ through a standard differentiation guided by the variational calculus. The three viewpoints can be united, as will now be shown, by the introduction of a second parameter into the free energy of the surface.

If y_{xx} at x_0 for values of ω greater than ω_c is not zero, σ is slightly smaller than the value given by eqs. (17) and (18) and is not constant as required by the initial assumptions. Further, if λ is evaluated at $y = 0$ in eq. (4) and compared with eq. (9), it is found that the drop radius r at $y = 0$, the end of the drop, is

$$r = 2y_0/3, \quad (20)$$

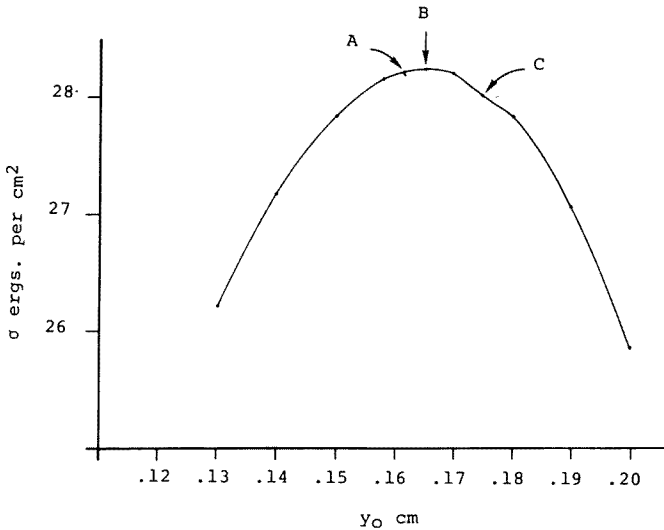


Fig. 3. Plot of eq. (10) at a particular constant x_0 (experiment no. 5). A: from Vonnegut theory; B: from variational calculus; C: from PZM theory.

Table 1

System *n*-hexadecane/glycerol

$V = 0.1900$ cc, $a = 0.35663$ cm, $\rho = 0.485$ gr/cc, $T = 21 \pm 1$ °C

exp.	ω	x_0	y_0 cm		σ ergs/cm ²		
	rad/sec	cm	eq. (17)	eq. (11)	PZM	eq. (18)	KE
1	89.95	0.5240	0.30808	0.26328	28.14	28.68	11.885
2	126.40	0.6715	0.24374	0.22516	27.77	28.05	17.720
3	170.59	0.8930	0.19947	0.19094	27.97	28.00	23.690
4	204.94	1.0860	0.17673	0.17144	28.08	28.11	27.807
5	226.98	1.2165	0.16533	0.16127	27.98	28.23	30.299
6	256.98	1.4095	0.15204	0.14912	28.13	28.14	33.333
7	276.88	1.5455	0.14445	0.14207	27.99	28.02	35.195
8	308.61	1.7650	0.13435	0.13256	28.00	28.00	38.158
9	344.00	2.0310	0.12459	0.12327	27.71	27.75	40.982
10	381.07	2.2895	0.11693	0.11591	28.14	28.15	44.639
11	420.97	2.6000	0.10939	0.10860	28.12	28.13	47.860
12	470.09	2.9980	0.10156	0.10100	28.06	28.07	51.696
Average					28.00	28.10	
					± 0.13	± 0.07	

$\omega_c = 67.43$ rads/sec, $KE_c = 10.66$ ergs, $\phi = 0.106$ ergs/rad.

a result which is approached for long drops in the usual treatment as, for example, that of PZM. However, such a result would mean that by eq. (25), the Laplace equation, the pressure across the drop surface on the axis of rotation would have to increase with the rate of rotation, which is impossible. We have therefore reached a reduction to absurdity, eqs. (19) and (20), and one of the assumptions of eq. (1) must be altered. The most reasonable change to make is the assumption that the free surface energy F^s is a function of the area only.

3. Extension of surface thermodynamics

To examine the ways the required second mechanical parameter in the free surface energy may be introduced, it is sufficient to consider spherical surfaces and define the area A and the volume V thus

$$A = \phi r^2; \quad V = \phi r^3/3; \quad dA = r^2 d\phi + 2r\phi dr; \quad dV = r^3 d\phi/3 + \phi r^2 dr \quad (21)$$

and two equivalent partial differential equations of the free surface energy F^s

$$\left(\frac{\partial F^s}{\partial A}\right)_r dA + \left(\frac{\partial F^s}{\partial r}\right)_A dr = \Delta P dV = \Gamma dA + 2R dr \quad (22)$$

$$\left(\frac{\partial F^s}{\partial A}\right)_\phi dA + \left(\frac{\partial F^s}{\partial \phi}\right)_A d\phi = \Delta P dV = \gamma dA + 2\Phi d\phi, \quad (23)$$

The factor 2 in the last terms allows for the two principal radii of curvature. ΔP is the pressure difference across the surface of tension s of radius r and solid angle ϕ subtending the area A of s .

Equation (22) results in

$$\Gamma = \frac{\Delta P r}{3}, \quad (24)$$

while eq. (23) gives

$$\gamma = \frac{\Delta P r}{2}, \quad (25)$$

the Laplace equation. Therefore, to conserve past data, the proper choice of a new parameter in situations such as this is one that in the past has been held constant, either tacitly or by design, for partial differential equations must be separable in a consistent fashion, both in the laboratory and on paper. Also, the mathematics using

Φ is the same as that normally used in the strength of materials. The surface s is the neutral surface; it is the surface in the surface region as defined by Gibbs [12], which in simple bending has zero stress. The curvature energy may be written [13]

$$dE_{\phi}^s = \frac{\Phi}{2} \left(\frac{1}{r_1} + \frac{1}{r_2} \right)^2 dA, \quad (26)$$

where r_1 and r_2 are the principal radii of curvature of s . s is not the same as the Gibbsian dividing surface which defines the surface region so that the chemical potentials are constant of phase.

By eq. (26) the curvature energy of a sphere is $8\pi\Phi$ and for a cylinder of length x and radius r it is, if Φ is a constant,

$$E_{\phi}^s = \pi\Phi x/r.$$

Before developing the consequences of the analysis further, we might try to get an intuitive feeling for the problem by asking what the flexural rigidity contributes to the physical properties of a drop. Because it is a partial differential equation, eq. (23) defines Φ and γ as the ultimate strengths of the surface. The spring of the surface in bending would be expected to show up in the same way it does in a ping-pong ball, so that small drops of water should bounce off a plane water surface the same way ping-pong balls bounce from a table. The phenomenon is easily observed if a fine spray from a hose falls in a gentle arc on the hood of a car; the effect is very beautiful, as anyone who has washed a car in bright sunshine can attest. In the maximum bubble pressure (MBP) method for measuring γ , the experiment is done at constant ϕ ; we should expect to find that MBP would give different results if the test were made at variable ϕ by using a non-wetted capillary, and this has indeed been reported in ref. [14]. Finally, it has been shown that small drops of liquid water can exist to temperatures as low as forty degrees below zero [15], a phenomenon called cold fog that must be reconciled with the triple point.

To introduce Φ into the analysis rigorously would require adding the term

$$\frac{\Phi}{2} \left(\frac{1}{r_1} + \frac{1}{r_2} \right)^2 y(1 + y_x^2)^{1/2} \quad (28)$$

to eq. (1). Since the radii of curvature involve y_{xx} , the Euler equation will be

$$\frac{\partial K}{\partial y} - \frac{d\partial K}{dx\partial y_x} + \frac{d^2\partial K}{dx^2\partial y_{xx}} = 0, \quad (29)$$

the solution of which, it is hoped, will be the subject of a future paper.

At the critical rate of rotation, we may assume that $\sigma A = \lambda V$, and since λ is given by eq. (9), it may be combined with eq. (19) because no kinetic energy has been used to increase the area, and we have

$$\omega_c^2 = \frac{2\sigma 2^{1/3}}{\rho a^3} (3 - 2^{2/3}). \quad (30)$$

The kinetic energy in a rotating sphere is

$$KE = \frac{4}{15} \pi \rho \omega^2 a^5, \quad (31)$$

which with ω_c from eq. (30) will give the critical energy of rotation.

If the shape of the drop is assumed to be that of a cylinder capped by hemispheres (see fig. 1), y_0 will be given by eq. (11) and for changes of the drop after the critical rate of rotation has been exceeded, we may write

$$KE_c - KE - 4\pi\gamma a^2 + 4\pi\gamma x_0 y_0 - \frac{2\pi\phi}{y_0} (x_0 - y_0) = 0. \quad (32)$$

The difference in sign of the last two terms is required by consideration of the sign of ΔPdV for an experiment at constant ϕ versus the sign of ΔPdV for an experiment at constant A [see eqs. (21) and (22)]. This also shows why r at $y = 0$ can change with ω .

The kinetic energy for the assumed shape is:

$$KE = \frac{4}{15} \pi \rho \omega^2 y_0^5 + \frac{\pi \rho \omega^2 y_0^4}{2} (x_0 - y_0). \quad (33)$$

Because the surface energy of a sphere may be written

$$E^s = \left(\gamma + \frac{2\Phi}{a^2} \right) 4\pi a^2, \quad (34)$$

it will be assumed that the critical energy is used to remove the effect of one principal radii of curvature, and that therefore we may write

$$\sigma = \gamma + \Phi/a^2. \quad (35)$$

Equations (32) and (35) may now be solved simultaneously.

Table 2
Total energy of spherical surfaces *n*-hexadecane/glycerol

$\gamma + 2\Phi/a^2$ ergs/cm ²	Radius cm
27.27	∞
28.94	0.35663
29.63	0.3
30.66	0.25
32.6	0.2
48.5	0.1
112.1	0.05

Table 3
Comparison of interfacial tension measurements by different methods
 $T = 21 \pm 1$ °C

System	σ ergs/cm ²		
	Rotating drop	Pendant drop	Ring tensiometer
Air/glycerol	66.1	64.6	63.4
Heptane/glycerol	28.4	27.8	27.7
<i>n</i> -hexadecane/glycerol	28.0	27.2	27.3

Table 4
 γ as a function of KE_c

exp.	γ ergs/cm ²						
	KE_c						
	11.5	11.0	10.66	9.5	8.0	5.0	0.0
1	24.11	24.95	25.33	26.57	28.19	31.42	36.82
2	26.91	27.12	27.35	27.97	28.76	30.35	33.01
3	27.21	27.35	27.45	27.78	28.21	29.07	30.48
4	27.20	27.30	27.36	27.60	27.90	28.49	29.49
5	27.19	27.27	27.33	27.52	27.76	28.25	29.36
6	27.14	27.21	27.25	27.40	27.59	27.98	28.79
7	27.11	27.17	27.21	27.34	27.50	27.83	28.38
8	27.11	27.16	27.19	27.29	27.43	27.69	28.14
9	27.09	27.13	27.15	27.24	27.34	27.56	27.92
10	27.12	27.19	27.21	27.28	27.37	27.55	27.85
11	27.15	27.22	27.23	27.29	27.36	27.51	27.76
12	27.23	27.25	27.27	27.31	27.37	27.37	27.69
Average	27.14	27.22	27.27	27.41	27.69	28.15	28.99

4. Experimental

The theoretical considerations of this paper are confirmed experimentally by the published results of PZM on the system *n*-hexadecane/glycerol. The results of the measurements are shown in table 1. It will be noticed that the standard deviation of σ by the PZM analysis is approximately twice that from eq. (18). The standard deviations were calculated omitting experiments one and nine, which PZM reported as being most suspect. The smaller deviation for the variational development suggests that it may be theoretically more correct. Further, it will be noted that σ given by the variational method is the maximum value of the partial derivative of σ with respect to y_0 (see fig. 3), a result that makes it, intuitively, more pleasing than any other value.

To test the assumptions of eqs. (33) and (34), the results of table 4 were calculated using different values of KE_c . It can be seen that the value of 10.66 ergs gives a constant value of γ in experiments two through twelve, with an average value that agrees very well with the value of γ by both the pendant drop and the ring tensiometer methods, as shown in table 3 which is PZM's table 4. Measurements by the pendant drop and ring tensiometer methods give γ , since these methods, being calibrated against the capillary rise method, are measurements at constant ϕ , and should be smaller than σ , as shown in table 3 for other systems.

Because γ and σ are constants, experimentally, for y_0 equal to 0.1 cm, table 2 has been given to show how the total surface energy per square centimeter varies with a , the radius of the spherical drop. If the drop were smaller, it might be anticipated that the tension value would be insignificant by comparison with the free energy associated with Φ because the energy per cc of a spherical drop due to the surface energy would be

$$\frac{3\gamma}{a} + \frac{6\Phi}{a^3} \quad ,$$

an amount of energy sufficient to make the existence of cold fog understandable.

5. Conclusions

Because surface science is so all pervading and any entity that can be isolated must have a surface, the results given in this paper need to be amplified. It has been shown [15] that in unsaturated solutions, Φ and γ are functions of the radius of curvature and that the classical adsorption equation is a special case of the more general adsorption equation and holds only for plane surfaces, which are very rare. It must also be remembered that the position of the surface of tension is a function of the radius and will move outward through the surface region as the radius decreases;

therefore, the volume cannot always be assumed to be constant. However, this effect should not become important until the radius of the drop approaches the thickness of the interfacial region.

The difference between the variational development and the treatment by means of an elliptical integration, for example, is that the variational analysis allows an exact solution by way of natural boundary conditions. An elliptical expansion may be thought of as equivalent to the introduction of an unlimited number of additional parameters and of discarding the requirements of Occam's razor. There will, however, be times when a judicious combination of the mathematical methods will be desirable. Such a time might be in the study of the effect of small disturbances, such as those that cause the drop surface to exhibit a wave shape. In this case, a variational treatment combined with a wave solution might give valuable understanding of the ways that a drop absorbs and gives up energy, so that it can act as a model for quantum systems.

It has been shown by a variational calculus analysis that it is impossible to represent the excess free energy in a surface by a single constant parameter, the surface tension, because the concept of a single variable cannot be reconciled with the laws of motion. It has also been shown, using published data, that the extra parameter demanded contributes a very significant amount to the surface energy when the curvature is in the range of the important industrial and biological surfaces such as, for example, emulsions, pigments, fibers, living cells and lung alveoli.

It is believed that the variational calculus offers a valuable tool for the examination of other scientific models in which some functional must be minimized, as in the surface chemistry example.

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