# Thermodynamics of Surface Phase Systems. VII. The Influence of Solid Surface Strain Changes on the Contact Angle Equilibrium and Some Further Comments on Adhesional Wetting Thermodynamics

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A thermodynamic fundamental equation valid for equilibrium contact angle systems is derived that includes a term accounting for the effect of solid surface strain variations. Various contributions to the (mechanical) surface tension difference, $\Delta\gamma$, between the solid-vapor and solid-liquid interfaces are considered. It is concluded that stretching experiments are required in order to confirm the applicability of the approximate fundamental equation implicit in the Gibbs treatment which involves the assumption that surface strain effects are negligible. Some recent determinations of the temperature dependence of equilibrium contact angles are discussed in terms of entropy on basis of the fundamental equation given. It is furthermore concluded that separate measurements of the Gibbs surface excess of the liquid component at the solid-liquid interface are needed to precisely determine the interfacial energy and entropy of this interface.

It is generally accepted that the Gibbs fundamental equation for interfaces, viz.

$$dg^s_{ex} = -S^s_{(1)}dT - \sum_{i=2}^{r} \Gamma_{i(1)}d\mu_i \tag{1}$$

is valid without restrictions for plane liquid-gas and liquid-liquid interfaces. However, it appears to be less well recognized that the validity of this equation for solid-gas and solid-liquid interfaces is limited to cases of constant state of strain of the solid surface.[1-3] In eqn. (1) all symbols have their usual meaning, i.e.

$g^s_{ex} =$ the excess surface free energy per unit area

$S^s_{(1)} =$ the surface phase entropy per unit area

$\Gamma_{i(1)} =$ the superficial density of component i

Subscript $_{(1)}$ denotes that a Gibbs type of surface phase with zero thickness is considered which is positioned in such a way as to make $\Gamma_1 = 0$. A more general equation applicable for some (but not all) solid-fluid interfaces is the following (binary system);

$$dg^s_{ex} = -S^s_{(1)}dT + (\gamma - g^s_{ex})d\varepsilon_s - \Gamma_{2(1)}d\mu_2 \tag{2}$$

where the term involving the differential $d\varepsilon_s = dA/A$ relates to isotropic and homogeneous changes of the solid surface strain.[2] The validity of eqn. (2) is restricted to such plane solid surfaces for which the (mechanical) surface tension, $\gamma$, is a nontensorial property, i.e. to amorphous solid surfaces and to crystal faces with a sufficiently high degree of symmetry.[4]

For fluid-fluid interfaces the surface tension, $\gamma$, and the excess surface free energy per unit area, $g^s_{ex}$ (that physically corresponds to the reversible work of formation of new surface area), are always equal, i.e.

$$\gamma = g^s_{ex} \tag{3}$$

and in this case eqn. (2) reduces to the fundamental eqn. (1). In general, for solid-fluid interfaces, however, $\gamma$ and $g^s_{ex}$ are not equal and the complete thermodynamic treatment should include separate set of equations for both these quantities. For interfaces of this kind, $g^s_{ex}$ is

conveniently interpreted physically as the reversible *cleavage work* per unit area whereas $\gamma$, the surface tension (sometimes called surface stress) has a mechanical significance.

It is evident that the conclusions stated above which were discussed at length in number V and utilized in connection with insoluble surface films in number VI of this series of papers on surface phase thermodynamics [2] should have certain previously not observed consequences with respect to the detailed thermodynamic treatment of contact angle equilibrium. For instance, a clear distinction has rarely been made between $\gamma$- and $g^s_{ex}$-quantities for the solid-vapor and solid-liquid interfaces when deriving Young's equation and its nature of mechanical *and* physico-chemical equilibrium condition is often obscured (*cf.* Ref. 5). Moreover though considered by Gibbs, the problem concerning the effect of solid surface strain changes on the contact angle equilibrium has not received much attention later on.

When treating the contact angle equilibrium on inert solids, Gibbs [1] introduced a surface free energy quantity, $\varrho$, called the superficial tension of the fluid in contact with the solid effectively as $\varrho = g^s_{ex} - g^s_{ex}$ (for clean solid surface plus localized adsorbate) that relates specifically to matter at the interface which is "fluid or movable". He claimed that $\varrho$ is approximately unaffected by variations in the state of strain of the solid surface and he also attributed a mechanical significance to $\varrho$ as "the superficial tension of the fluid in contact with solid". In view of our previous conclusions (*cf.* Ref. 2) concerning the difference between the mechanical effects of localized and mobile adsorption and the influence of solid surface strain changes on adsorbate properties, the Gibbs procedure appears to be reasonable. Still, methods are desirable to test the adequacy of the approximation involved.

In order to elucidate the above-mentioned questions, a rigorous thermodynamic treatment of adhesional wetting is carried through in the present paper using eqn. (2) as the point of departure. The likewise rigorous thermodynamic analysis presented by Melrose [3] of the interrelations between adhesional and immersional wetting is in some respects closely related to this treatment. Melrose, however, based his formalism on eqn. (1).
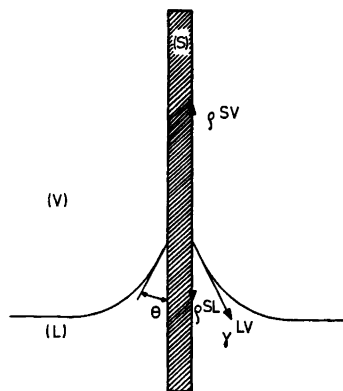


*Fig. 1.* Sketch of the equilibrium contact angle system studied. $\theta$ is the contact angle, $\varrho^{SV}$ and $\varrho^{SL}$ are the superficial tensions of the vapor and the liquid in contact with the solid surface and $\gamma^{LV}$ is the surface tension of the liquid-vapor interface.

*Description of the thermodynamic system studied.* The system subject to investigation is a closed equilibrium contact angle system consisting of a pure *rigid* monocrystalline solid (component 1) with a high symmetry crystal face partly exposed to a pure liquid (component 2) and partly to the vapor of the same liquid (Fig. 1). Alternatively, the solid can be amorphous with a plane and smooth surface. According to the phase rule, this system has only *one* degree of freedom: the temperature $T$. However, at the outset we may formally consider the solid surface strain, $\varepsilon_s$, as a further independent variable though in conformity with Ref. 2 we shall limit the treatment to isotropic and homogeneous reversible strain variations from an approximately unstressed bulk phase state of the solid.

Throughout much of the present paper use will be made of the Gibbs surface phase convention with one dividing surface positioned at the solid surface in such a way that $\Gamma_1 = 0$ in order to completely define the thermodynamic interfacial properties (energy, entropy, mol numbers *etc.*). Thus the surface phase considered only contains component 2. In some connections below, however, it is really more convenient to make use of a Verschaffelt-Guggenheim kind of surface phase with two dividing surfaces, $\Sigma'$ and $\Sigma''$, located somewhere within the homogeneous phases as is shown in Fig. 2
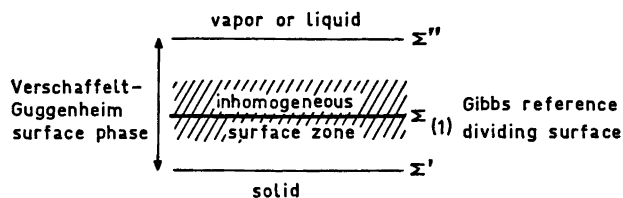
*Fig. 2.* Surface phase according to the Verschaffelt-Guggenheim convention defined by two dividing surfaces $\sum'$ and $\sum''$ located within the homogeneous phases and according to Gibbs defined by the dividing surface $\sum_{(1)}$ positioned so as to make the superficial density of the solid componenen $\Gamma_1$ equal to zero.

(for further details *cf.* paper number I of this series, Ref. 6).

The vapor pressure of the liquid component is assumed to be low enough to warrant that $pV$-terms are negligible for condensed matter. Hence $U(=\text{energy}) \simeq H(=\text{enthalpy})$, $F(=$ Helmholtz free energy$) \simeq G(=\text{Gibbs free energy})$, $f(=\text{molar Helmholtz free energy}) \simeq \mu(=\text{chemical potential})$ *etc.* for all parts of the system except the vapor phase. It is also presupposed (though not strictly required) that the adsorption isotherm for the vapor on the solid surface has such a course that the adsorption can be limited at the saturation vapor pressure. This condition guarantees that the system studied actually constitutes what is normally called a contact angle system, *i.e.* $\theta \neq 0$.[7]

*Definitions.* In conformity with Gibbs' treatment of solid-fluid interfaces (Ref. 1, p. 315) and Ref. 2 the excess surface free energies per unit surface area of the S/V- and S/L-interfaces are *defined* by the expressions

$$g^{SV}_{ex} = F^{SV}_{(1)} - \Gamma^{SV}_{2(1)}\mu_2 \qquad (4)$$

$$g^{SL}_{ex} = F^{SL}_{(1)} - \Gamma^{SL}_{2(1)}\mu_2 \qquad (5)$$

Physically, $g^{SV}_{ex}$ and $g^{SL}_{ex}$ correspond to the reversible work per unit surface area of cleaving the crystal at constant temperature in the vapor and in the liquid, respectively. These in principle measurable quantities are *not* dependent, of course, on the exact choice of surface phase (Ref. 2).

Following Gibbs (Ref. 1, p. 328) we also introduce the *superficial tensions of the vapor and the liquid in contact with the solid surface*, $\varrho^{SV}$ and $\varrho^{SL}$, at equilibrium. Their difference, $\varrho^{SV} - \varrho^{SL} = \Delta\varrho$ is called the *adhesion tension* in accordance with the nomenclature used by

Defay, Prigogine, Bellemans and Everett.[8] Since the external force per unit length acting downwards on the (freely movable) three-phase junction is $\gamma^{LV} \cos \theta$ we obviously have (Fig. 1)

$$\Delta\varrho = \gamma^{LV} \cos \theta \qquad (6)$$

where $\theta$ is the contact angle. This mechanical equilibrium condition is to be considered as the *operational* definition of $\Delta\varrho$. Evidently, the relation $\varrho^{SV} - \varrho^{SL} = \Delta\varrho$ is of little practical utility since $\varrho^{SV}$ and $\varrho^{SL}$ cannot be measured separately. In order to actually determine the *equilibrium* contact angle and hence the adhesion tension $\Delta\varrho$, it is a prerequisite, of course, that all the mass transfer needed for restructuring of the S/L-interface into S/V-interface and *vice versa* proceeds rapidly enough to warrant reversibility.

*Young's equation.* Next we shall show that the cleavage work interpretation of $g^s_{ex}$ favourably may be utilized when deriving Young's equation. At constant temperature, the work required for reversible cleavage of the solid in the vapor phase must be the same as for first reversibly cleaving the solid in the liquid and then reversibly transferring the solid surface so formed to contact with the vapor. Thus it follows that

$$g^{SV}_{ex} - g^{SL}_{ex} = \Delta\varrho \qquad (7)$$

since $\Delta\varrho$ is obviously equal to the reversible work per unit area needed at constant temperature for the transfer process. Making use of eqn. (6) we obtain

$$g^{SV}_{ex} - g^{SL}_{ex} = \gamma^{LV} \cos \theta \qquad (8)$$

*i.e.* Young's equation. It constitutes a physicochemical equilibrium condition that is fulfilled for the equilibrium contact angle only.

In principle at least, all the quantities involved in eqn. (8) are separately measurable. Often, it is incorrectly assumed [9],[10] that $g^{SV}_{ex}$ and $g^{SL}_{ex}$ ($\sigma_{BS}$ and $\sigma_{AS}$ in Gibbs' text) can not be measured separately and that only their difference, equal to the adhesion tension $\Delta\varrho$, is an experimentally accessible thermodynamic variable. However, Bailey, Price and Kay [11] have actually succeeded in directly verifying eqn. (8) by measuring the reversible work of cleaving mica samples in the liquid and vapor phases of water, hexane, decane and by determining the corresponding contact angles.

It results from eqns. (4), (5) and (7) that $\Delta\varrho$ is related to the basic thermodynamic interfacial properties in the following way,

$$\Delta\varrho = \Delta F_{(1)} - \Delta\Gamma_{2(1)}\mu_2 . \qquad (9)$$

where

$$\Delta F_{(1)} = F_{(1)}^{SV} - F_{(1)}^{SL} \qquad (10)$$

$$\Delta\Gamma_{2(1)} = \Gamma^{SV}_{2(1)} - \Gamma^{SL}_{2(1)} \qquad (11)$$

Hence, $\Delta\varrho$ equals the surface phase free energy difference per unit area between the S/V- and S/L-interfaces corrected for the free energy associated with the corresponding difference in superficial density of component 2.

*The thermodynamic fundamental equation for an equilibrium contact angle system.* Taking into consideration that $T$ and $\mu_2$ cannot be varied independently for two-component contact angle systems, eqn. (2) should be modified as follows for the S/V- and S/L-interfaces, respectively.

$$dg^{SV}_{ex} = -(S^{SV}_{(1)} - \Gamma^{SV}_{2(1)}s^{L}_2)dT + (\gamma^{SV} - g^{SV}_{ex})d\varepsilon_s \qquad (12)$$

$$dg^{SL}_{ex} = -(S^{SL}_{(1)} - \Gamma^{SL}_{2(1)}s^{L}_2)dT + (\gamma^{SL} - g^{SL}_{ex})d\varepsilon_s \qquad (13)$$

Here we have inserted the obvious relationship

$$d\mu_2 = -s^{L}_2 dT \qquad (14)$$

Forming the difference between eqns. (12) and (13) and taking eqn. (7) into account, yields the resulting equation

$$d(\Delta\varrho) = -(\Delta S_{(1)} - \Delta\Gamma_{2(1)}s^{L}_2)dT + (\Delta\gamma - \Delta\varrho)d\varepsilon_s \qquad (15)$$

where $\Delta\gamma$ is the surface tension difference $\gamma^{SV} - \gamma^{SL}$ and $\Delta S_{(1)}$ is defined analogously to $\Delta F_{(1)}$.

This equation is the thermodynamic fundamental equation for the kind of equilibrium contact angle system considered in this paper. It includes two derivatives of special interest, namely

$$\left(\frac{\partial(\Delta\varrho)}{\partial\varepsilon_s}\right)_T = \Delta\gamma - \Delta\varrho \qquad (16)$$

$$\frac{d(\Delta\varrho)}{dT} = -(\Delta S_{(1)} - \Delta\Gamma_{2(1)}s^{L}_2) + (\Delta\gamma - \Delta\varrho)\frac{d\varepsilon_s}{dT} \qquad (17)$$

Eqn. (16) is the counterpart in this connection to the well-known Shuttleworth equation [4] valid for a pure solid surface whereas eqn. (17) gives the temperature coefficient of the adhesion tension. We should note, in particular, that in certain cases (*e.g.* using elastomers) it might well be feasible to obtain an experimental estimate of the partial derivative $(\partial(\Delta\varrho)/\partial\varepsilon_s)_T$ and thus by using eqn. (16), also an estimate of $\Delta\gamma$.

Eqn. (17) is applicable for a free (unstressed) solid and it includes a correction term that accounts for the influence of the solid surface strain change associated with a change of temperature. The relative magnitude of this correction term is generally not known but can be obtained, in principle at least, on basis of stretching experiments and using eqn. (16). In this way the assumption implied in Gibbs' treatment concerning the approximate independence of $\Delta\varrho$ with respect to variations of the state of strain of the solid surface could actually be tested. The correction is likely to be small, however, on grounds that will next be discussed with reference to some oversimplified structural models of the S/V- and S/L-interfaces.

*Discussion of the various contributions to $\Delta\gamma$.* For a Vershaffelt-Guggenheim kind of surface phase that is bounded by two dividing surfaces, $\Sigma'$ and $\Sigma''$, positioned within the homogeneous phases, we have the following definition of $\gamma$,

$$\gamma = \left(\frac{\partial F^s}{\partial A}\right)_{T,n^s_1,n^s_2} \qquad (18)$$

where $F^s$, $n^s_1$ and $n^s_2$ are *total* surface phase quantities. Very schematically, we may picture the structures of the S/V- and S/L-interfaces as is shown in Fig. 3 with a mobile adsorption layer on top of a localized adsorption layer. Assuming that the adsorbent is inert it is possible to make a clearcut division of $F^s$ in two
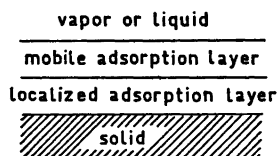
vapor or liquid

mobile adsorption layer

localized adsorption layer

solid

*Fig. 3.* Schematic interfacial structure of the S/V- and S/L-interfaces.

parts, $F^{so}{}_1$ for the pure solid surface and $F^s{}_2$ for the adsorbate. Evidently, the $F^{so}{}_1$-parts of $F^s$ are the same for the S/V- and S/L-interfaces independently of $\varepsilon_s$ and in such a case there is no resulting contribution to $\Delta\gamma$ due to the solid surface itself.

In general, $F^s{}_2$ cannot be split in parts associated with the localized and mobile adsorption layers, respectively, in a similar straightforward way because the presence of the mobile adsorbate is likely to affect the thermodynamic properties of the localized adsorbate. Still, for the purpose of discussion we may suppose that it is possible to estimate $F^s{}_2(\mathrm{loc})$ and $F^s{}_2(\mathrm{mob})$ separately in some way such that

$$F^s{}_2(\mathrm{loc}) + F^s{}_2(\mathrm{mob}) = F^s{}_2 \qquad (19)$$

where the interaction free energy between the localized and mobile layers is ascribed to the mobile layer. Now, since the structures and thermodynamic properties of the S/V- and S/L-*mobile* adsorption layers must be rather different it is reasonable to assume that the corresponding localized adsorption layers are also somewhat different in the same respects. Though very little is actually known about these matters it is likely that the effect of solid surface strain changes on $F^s{}_2(\mathrm{loc})$ is inherently small when the adsorbent-adsorbate interaction is comparatively weak (*cf.* Ref. 2). So, we might tentatively conclude, referring to eqn. (18), *i.e.*

$$\Delta\gamma = \frac{\partial}{\partial A}(F^{\mathrm{SV}} - F^{\mathrm{SL}}) = \frac{\partial}{\partial A}(F^{\mathrm{SV}}{}_2 - F^{\mathrm{SL}}{}_2) \qquad (20)$$

that for many such systems there can be a small contribution, $\Delta\gamma(\mathrm{loc})$, to $\Delta\gamma$ arising from the two rather similar localized adsorption layers. For systems with filled localized adsorption layers, however, it is clear that $\Delta\gamma(\mathrm{loc}) \approx 0$, because in such a case is $F^{\mathrm{SV}}{}_2(\mathrm{loc}) - F^{\mathrm{SL}}{}_2(\mathrm{loc}) \approx 0$.

Concerning the contribution to $\Delta\gamma$ from the mobile adsorption layers, it is evident that

$\Delta\varrho$ *i.e.* the difference between the superficial tensions of the vapor and the liquid in contact with the solid, in most cases constitutes the major contribution. However, there may also be a certain contribution, $\Delta\gamma(\mathrm{mob})$, due to the change of the state of the mobile adsorption layers associated with a solid surface strain variation (*cf.* Ref. 2). This conclusion holds true, of course, irrespective of whether the mobile adsorption layers are in direct contact with the solid surface or if they are formed on top of localized adsorption layers. Consequently, there are reasons in favour of the assumption effectively stated by Gibbs that

$$\Delta\gamma - \Delta\varrho \approx \Delta\gamma(\mathrm{loc}) + \Delta\gamma(\mathrm{mob}) \qquad (21)$$

is a relatively small quantity and, in particular, since $d\varepsilon_s/dT$ normally is $10^{-5} - 10^{-4}/\mathrm{K}$ for solids that the last term of eqn. (17) is often negligible. However, in order to ascertain this rather qualitatively based conclusion, experiments are needed aiming at the determination of the partial derivative $[\partial(\Delta\varrho)/\partial\varepsilon_s]_T$ so that a comparison can be made of the relative magnitudes of $d(\Delta\varrho)/dT$ and $[\partial(\Delta\varrho)/\partial\varepsilon_s]_T d\varepsilon_s/dT$.

*The temperature dependence of $\Delta\varrho$ and $\theta$.* In most cases the leading term in eqn. (17) presumably is

$$\Delta S_{(1)} - \Delta\Gamma_{2(1)}s^{\mathrm{L}}{}_2 = S^{\mathrm{SV}}{}_{(1)} - S^{\mathrm{SL}}{}_{(1)} - (\Gamma^{\mathrm{SV}}{}_{2(1)} -$$

$$\Gamma^{\mathrm{SL}}{}_{2(1)})s^{\mathrm{L}}{}_2 \approx - \frac{d(\Delta\varrho)}{dT} \qquad (22)$$

Though formally (but not explicitly) included in the Melrose treatment,[3] it appears that the implications of this term with respect to the temperature dependence of $\Delta\varrho$ and $\theta$ have not been elaborated previously. In this section we will indicate that on basis on eqn. (22) it is possible to qualitatively account entropy-wise for some observed $d(\Delta\varrho)/dT$-values.

For systems with comparatively weak adsorbent-adsorbate interaction and *extensive* adsorption on the solid surface from the vapor the following relations should hold because of the considerable density difference between the vapor and liquid phases

$$\Gamma^{\mathrm{SV}}{}_{2(1)} \simeq \Gamma^{\mathrm{SV}}{}_2 \gg \Gamma^{\mathrm{SL}}{}_{2(1)} \qquad (23)$$

$$S^{\mathrm{SV}}{}_{(1)} - S^{\mathrm{SL}}{}_{(1)} \approx S^{\mathrm{SV}}{}_2/A = \Gamma^{\mathrm{SV}}{}_2 s^{\mathrm{SV}}{}_2 \qquad (24)$$

Also, the approximate eqn. (24) is applicable only so far as there is no large entropy effect on

the liquid adjacent to the solid due to the interaction with the solid surface. Consequently, from eqn. (22) we obtain

$$\frac{d(\Delta\varrho)}{dT} \equiv \gamma^{LV}\frac{d\cos\theta}{dT} + \frac{d\gamma^{LV}}{dT}\cos\theta \approx$$
$$- \Gamma^{SV_2}(s^{SV_2} - s^{L_2}) \qquad (25)$$

When the adsorption in contact with the vapor is mobile we normally expect that $s^{SV_2} - s^{L_2} > 0$ and thus that $d(\Delta\varrho)/dT$ is a negative quantity. Concerning the resulting sign of $d\theta/dT$ we find that no general statement can be made in this case; it will be determined by the sign of the sum of $\Gamma^{SV_2}(s^{SV_2} - s^{L_2})$ and $(d\gamma^{LV}/dT)\cos\theta$.

A common situation of particular interest is the case of low degree of adsorption at the solid-vapor interface. Then the approximations

$$\Gamma^{SV_2}, \Gamma^{SL_{2(1)}} \approx 0 \qquad (26)$$

$$S^{SV_{(1)}} - S^{SL_{(1)}} \approx - (S^{SL_{(1)}} - S^{So_{(1)}}) = - S^{SL_{2(1)}} \qquad (27)$$

may well be fulfilled. It follows from eqn. (22) that $d(\Delta\varrho)/dT \approx S^{SL_{2(1)}}$ under these circumstances. We can expect that $S^{SL_{2(1)}}$ normally is a positive quantity when the adsorbent-adsorbate interaction is weak compared with the cohesional interaction in the liquid. Then $d\theta/dT$ will be $< 0$ at least for $\theta < 90°$. The naphthalene-water system studied by Jones and Adamson [12] between 10 and 80 °C appears to be of this kind with $\Delta\varrho$ close to zero and $d(\Delta\varrho)/dT = 0.13$ erg/cm², K. We note that $S^{SL_{(2)}}$ ($= - d\gamma^{LV}/dT$) for the liquid-vapor interface of water is of similar magnitude, $\sim 0.15$ erg/cm². K. The corresponding interfacial energy value for the naphthalene-water interface, $U^{SL_{2(1)}}$, as obtained on basis of eqn. (9) is 37 erg/cm².

When there is relatively strong adsorbent-adsorbate interaction, however, $S^{SL_{2(1)}}$ may become negative as a consequence of local ordering of the liquid at the interface. In such a case a negative value of $d(\Delta\varrho)/dT$ is predicted and a resulting positive sign of $d\theta/dT$ is possible for $\theta < 90°$. The system $CS_2$ on monocrystalline ice studied by Adamson, Shirley and Kunichika [13] is presumably of this latter kind with $d\theta/dT = 0.35°/K$ within the temperature range $- 50$ to $- 5$ °C. This value would correspond to $S^{SL_{2(1)}} = - 0.25$ erg/cm², K and is indicative of an ordering effect of the (polar) ice surface on

liquid $CS_2$. The corresponding $U^{SL_{2(1)}}$ -value is $- 94$ erg/cm².

*Evaluation of the thermodynamic properties of the S/L-interface.* From a more fundamental point of view contact angle measurements are important in the first place because equilibrium contact angle data are needed for the evaluation of the basic thermodynamic properties of the S/L-interface. Thus, when $U^{SV_{2(1)}} = U^{SV_{(1)}} - U^{So_{(1)}}$, $S^{SV_{2(1)}} = S^{SV_{(1)}} - S^{So_{(1)}}$ and $\Gamma^{SV_{2(1)}}$ of the S/V-interface are known at the saturation vapor pressure through adsorption measurements and $\Delta\varrho$ and $d(\Delta\varrho)/dT$ have been determined, $S^{SL_{2(1)}} - \Gamma^{SL_{2(1)}}s^{L_2}$, $F^{SL_{2(1)}} - \Gamma^{SL_{2(1)}}\mu_2$ and $U^{SL_{2(1)}} - \Gamma^{SL_{2(1)}}u^{L_2}$ can all be obtained (approximately) by means of eqns. (22) and (9).

It appears, however, that adsorption and contact angle measurements must be supplemented with a separate determination of $\Gamma^{SL_{2(1)}}$ in order to enable the precise evaluation of $U^{SL_{2(1)}}$ and $S^{SL_{2(1)}}$. Possibly, such a determination can be carried out by measuring the volume change, $\Delta V$, generally occurring at cleavage of the solid in the liquid. For a Verschaffelt-Guggenheim surface phase this volume change is given by the expression

$$\Delta V = V^{SL} - n^{SL_1}v^{S_1} - n^{SL_2}v^{L_2} \qquad (36)$$

or, for a Gibbsian surface phase $(V^{SL}, n^{SL_1} = 0)$

$$\Delta V/\Delta A = - \Gamma_{2(1)}v^{L_2} \qquad (37)$$

where $\Delta A$ is the surface area formed at cleaving. To the present author's knowledge no such experiments have ever been reported. In most cases, $\Gamma^{SL_{2(1)}}$ is presumably a rather small quantity but this is not to say that terms like $\Gamma^{SL_{2(1)}}s^{L_2}$ etc. always are negligible compared with $S^{SL_{2(1)}}$ etc.

## CONCLUSIONS

The main conclusions of the formal investigation presented in this paper are:

(i) results of elastic stretching experiments are needed on the change of the equilibrium contact angle due to a surface strain variation in order to estimate the error involved when applying the fundamental equation for contact angle systems resulting from the Gibbs thermodynamic treatment;

(ii) when interpreting $\theta = \theta(T)$ data it is advantageous to base the discussion on the thermodynamic fundamental equation for contact angle systems and to carry it through in terms of interfacial entropy;

(iii) for the precise evaluation of the interfacial energy and entropy of the solid-liquid interface, the surface excess of the liquid component at this interface must be separately measured.

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