Problems of surface thermodynamics

A.I.Rusanov

Mendeleev Centre, Leningrad 199034, USSR

Abstract The modern forms of key equation of surface thermo-
dynamics are analysed. The generalized Laplace equation in-
cludes anisotropy of surface tension and the second order cur-
vature terms. The generalized Young equation includes the line
work and the line curvature. The generalized Gibbs adsorption
equation for solid surfaces includes anisotropy of surface ten-
sion and of chemical potentials and is written also in terms
of surface work. Universal interrelations between surface ener-
gy, cohesive energy, and the vaporization heat are derived,
and their dependence on the surface structure of matter is es-
tablished. The role of the surface and line tensions in formu-
lation of the equilibrium and stability conditions is discuss-
ed.

INTRODUCTION

The work of formation of unit area of an interface is the main quan-
tity of the surface thermodynamics. The process of formation of a new
surface can be carried out in two possible ways: as stretching an
initial surface and doing work against the forces of surface tension
or as cutting off (clearing) a body and doing work against cohesional
forces. Designating the first work as γ and the second work as ϵ ,
one may say that, for anisotropic surfaces, γ may depend on the
direction on the surface, whereas ϵ is, evidently, a scalar quan-
tity (ϵ may be dependent of the direction of the crystallographic
plane, but not of the direction of the surface).

Gibbs (ref.1) first recognized the difference between γ and ϵ
for the case of solids. As was shown by the authors (ref.2), this dif-
ference is caused by the nonuniformity of chemical potentials near the
surface, i.e. by the absence of the diffusional equilibrium which is
attained especially slowly for solids. Diffusion is absent at all in
the model of a perfectly elastic body with all particles to be consi-
dered as fixed in the crystalline lattice. As for real solids at low
temperatures, diffusion proceeds slowly and often is not completed
after the time of experiment. A difference between γ and ϵ is
obvious to exist not only for solids, but also for nonequilibrium
fluid surfaces for which the diffusional equilibrium has not yet been
established. Moreover, this difference appears also for the equilibri-
um surface of a polar liquid if the liquid is subjected to the action
of an external electric field (ref.3). However, $\gamma = \epsilon$ for an
equilibrium liquid in the absence of a field.

The pressure anisotropy exists both in equilibrium and nonequilibrium
surface layers. But the anisotropy of pressure causes the anisotropy
of chemical potentials. This important statement of the surface ther-
modynamics was formulated first by Podstrigach (ref.4) and Stuke
(ref.5). The author's approach to the chemical potential anisotropy
and the difference between γ and ϵ was published earlier (ref.6).

Now we turn to the problem of reformulation of thermodynamic relationships recognizing the difference between γ and ϵ. Shuttleworth (ref.7) first began to discuss this problem. In particular, he pointed out that the two key equations of the classical theory of capillarity, the Laplace equation and the Young equation, refer to different quantities. The Laplace equation should be expressed in terms of surface tension, γ, and the Young equation in terms of ϵ. Let us consider the modern forms of this relationships.

THE GENERALIZED LAPLACE EQUATION

The mechanical state of an anisotropic surface is characterized by the surface tension tensor (the excess surface stress tensor), $\hat{\gamma}$, and surface tension γ is given by the trace of tensor $\hat{\gamma}$:

$$\gamma = (\gamma_{11} + \gamma_{22})/2 \tag{1}$$

γ_{11} and γ_{22} are the principal values of tensor $\hat{\gamma}$. If we now imagine that a surface element between phases α and β is shifted along the normal, N, the work of a small deformation will be

$$(p_N^\beta - p_N^\alpha) A \, dN + \gamma_{11}L_2 \, dL_1 + \gamma_{22}L_1 \, dL_2 +$$
$$A \, C_1 \, dc_1 + A \, C_2 \, dc_2 + Am \, g \, dh \tag{2}$$

where p_N is the normal pressure in the adjacent phase (α or β), $A = L_1L_2$ area of the surface element with principal linear dimensions L_1 and L_2, c_1 and c_2 the principal curvatures of the element, C_1 and C_2 the corresponding coefficients, m the excess of mass per unit area, g the acceleration of gravity, h the hight of the element. The first term is the work produced by the bulk phases while shifting the surface element. The second and the third terms represent the work of stretching or contracting the surface element while it moves along the normal. Simultaneously, the curvature of the element changes, which yields the work given by the fourth and the fifth terms. The last term corresponds to the work of a displacement of the surface element in the gravitational field.

The Laplace equation is a mechanical equilibrium condition which means that the total force acting on the surface element is zero. Respectively, the work of elementary deformation of the element is also zero. Equalizing (2) to zero with taking into account the geometrical relationships $dN = d(1/c_1) = d(1/c_2)$, $dL_i = L_ic_id(1/c_i)(i = 1,2)$, and $dh/dN = \cos\gamma$, we get the generalized Laplace equation

$$P_N^\alpha - P_N^\beta = \gamma_{11}c_1 + \gamma_{22}c_2 - C_1c_1^2 - C_2c_2^2 + mg\cos\gamma \tag{3}$$

where γ is the angle between the vertical and the normal to the surface. It is seen from eq.(3) that the normal pressure difference in adjacent phases is caused by the curvature and the inclination of the surface.

In the absence of the gravitational field, eq.(3) changes into the result by Rusanov and Krotov (ref.8)

$$P_N^\alpha - P_N^\beta = \gamma_{11}c_1 + \gamma_{22}c_2 - C_1c_1^2 - C_2c_2^2 \tag{4}$$

Two last terms may be neglected if the surface curvature is not great.

Then eq.(4) is reduced to the formula derived earlier by Krotov, Rusanov, and Blinowski (ref.9)

$$p_N^\alpha - p_N^\beta = \gamma_{11} c_1 + \gamma_{22} c_2 \tag{5}$$

In the case of an isotropic surface, $\gamma_{11} = \gamma_{22} = \gamma$. If the adjacent bulk phases are also isotropic, normal pressure p_N may be replaced with isotropic pressure p in a bulk phase. Then eq.(3) becomes

$$p^\alpha - p^\beta = \gamma (c_1 + c_2) - C_1 c_1^2 - C_2 c_2^2 + mg \cos \gamma \tag{6}$$

In the absence of gravity, eq.(6) changes into Buff's formula (ref.10)

$$p^\alpha - p^\beta = \gamma (c_1 + c_2) - C_1 c_1^2 - C_2 c_2^2 \tag{7}$$

Neglecting the second and the third terms on the right-hand side of eq.(6) for a slightly curved surface, eq.(6) is reduced to Gibbs' equation (ref.1, p.281, eq.(613))

$$p^\alpha - p^\beta = \gamma (c_1 + c_2) + mg \cos \gamma \tag{8}$$

It should be noted that the transition from (6) to (8) is also possible for a strongly curved surface if it is spherical and the surface of tension is chosen as a dividing surface (then $C_1 = C_2 = 0$).

The modern data on the self-adsorption of liquids (see, e.g., ref.11) lead to the conclusion that the gravitational term in the generalized Laplace equation is very small. For instance, the self-adsorption of water at $20^\circ C$ is $\Gamma \approx -2.5 \times 10^{-6}$ moles/m^2 and m = Γ м $\approx -4.5 \times 10^{-8}$ kg/m^2 (м is the molar mass). Then the second term on the right-hand side of eq.(8) even with cos $\gamma = 1$ becomes comparable with the first one (at $\gamma = 72.75$ mN/m) at curvature radii about 330 km. The curvature of real menisci is many orders higher, so that the gravitational term in (8) is negligible. Retaining only the leading term in the right-hand side, eq.(8) is reduced to the classical Laplace equation

$$p^\alpha - p^\beta = \gamma (c_1 + c_2) \tag{9}$$

The Laplace equation determines the shape of the surface of capillary bodies and makes the basement for many methods of measuring surface tension. It should be noted that the influence of gravity on the shape of the surface may be essential for macroscopic bodies with a considerable difference in density between phases α and β because pressures in the bulk phases change under the action of gravity.

EQUILIBRIUM AT THE THREE PHASE CONTACT LINE. THE GENERALIZED YOUNG EQUATION

If several interfaces meet each other at the same line, the mechanical equilibrium condition is expressed as the force balance

$$\sum_k \vec{f}_k = 0 \tag{10}$$

where $\vec{f}_k$ is the force per unit length of the line produced by the kth surface. Let the mechanical state of the kth surface be given by the surface tension tensor, $\hat{\gamma}_k$. Then force $\vec{f}_k$ is determined as a scalar product of tensor $\hat{\gamma}$ and the unit vector, $\vec{\nu}$, of the normal

to a given element of the line:

$$\vec{f}_k = \hat{\gamma}_k \cdot \vec{\nu}_k \tag{11}$$

Substituting (11) into (10), we express the mechanical equilibrium condition at the phase contact line through the surface tension tensor of converging surfaces:

$$\sum_k \hat{\gamma}_k \cdot \vec{\nu}_k = 0 \tag{12}$$

According to (11), for the case of isotropic surfaces, force f_k is equal to surface tension γ_k :

$$\vec{f}_k = \gamma_k (\hat{1} \cdot \vec{\nu}_k) = \gamma_k \vec{\nu}_k \equiv \vec{\gamma}_k \tag{13}$$

and eq.(12) changes into the known vectorial Neumann equation

$$\sum_k \vec{\gamma}_k = 0 \tag{14}$$

which holds at each element of the phase contact line. Equation (14) is called Neumann's triangle in case of the three-phase line.

Molecular structure and the pressure tensor field have been changed at the phase contact line, which results in appearance of line tension, τ , an one-dimensional analog of surface tension. Line tension is directed along the phase contact line and contributes to the mechanical equilibrium condition if the line is curved. More accurately, eq. (12) is written as

$$\sum_k \hat{\gamma}_k \cdot \vec{\nu}_k + \tau c \vec{n} = 0 \tag{15}$$

and eq. (14) for isotropic surfaces becomes, respectively,

$$\sum_k \vec{\gamma}_k + \tau c \vec{n} = 0 \tag{16}$$

where c is the local line curvature, $\vec{n}$ the vector of the principal normal of the line. It is seen from (15) and (16) that the correction related to line tension depends on the line curvature and becomes important only for large curvatures. If the line is straight, the correction is zero and eqs.(12) and (14) are valid.

The mechanical equilibrium conditions expressed in (12), (14)-(16) are applicable only to fluid systems where tensions exist usually at interfaces and their linear boundaries and cannot be in the bulk as in the case of solids. But if at least one phase is solid, internal stresses arise in the bulk of a solid under the influence of surface forces near the phase contact line, and these stresses should be included into the force balance, eq.(10). The simplest example is a drop (L) on a flat surface between a solid (S) and a gas (V) with contact angle θ. In the absence of the drop, tension γ_{SV} acts on the solid surface (double subscripts refer to the corresponding interfaces). When the drop is present, there appears the additional force $\vec{\gamma}_{LV} + \vec{\gamma}_{SL} + \vec{\gamma}_{SV} + \tau c \vec{n}$ which, being applied to the solid surface, will cause internal stresses in the solid. There are no doubts about the reality of this force since it leads to two experimentally observable phenomena: (i) rapid deformation of a solid along the three-phase line with

formation of a ridge which is noticeable for bodies with a low elasticity modulus; (ii) slow diffusion of the substance of a solid to the three-phase line (more noticeable at higher temperatures) which also leads to the ridge formation (diffusion is caused by lowering chemical potentials in the region of the three-phase line due to internal stresses). It is not difficult to understand that the force given by the left-hand side of eq.(16), may be compensated by internal stresses in a solid at any given value of contact angle θ. Hence, the mechanical equilibrium condition at the three-phase line on a solid is not related to a definite contact angle. This is the principal difference between the cases of solid and liquid phases. In both cases, the drop in a final equilibrium state adopts the shape of a lens, but contact angle is determined by eq.(16) (i.e. by a set of surface tensions γ_k in case of a large drop) only for a liquid substrate.

Thus, mechanical equilibrium for the wetting of a solid is possible, in principle, at an arbitrary value of contact angle. By contrast, thermodynamic equilibrium is attained at a unique definite value of contact angle. This equilibrium angle θ can be found from the condition of a minimum of free energy for the three-phase system. The most complete solution of this variational problem, including line tension and gravity, for an arbitrary relief of a solid surface results in the generalized Young equation (ref.12):

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta + (\varkappa/r + \partial \varkappa / \partial r) \, |\cos \varphi| \qquad (17)$$

where $\varkappa$ is the thermodynamic analog of line tension τ and the one-dimensional analog of σ (the work of formation of a unit length of the three-phase line), r the local curvature radius of the three-phase line, φ the inclination angle of the solid surface at the three-phase line. The thermodynamic equilibrium condition, eq.(17), is expressed in terms of σ. In contrast to γ, σ is sensitive to surface straines, but not to stresses. Since deformation is very small for solids, local values of σ_{SV} and σ_{SL} in eq.(17) may be considered to be the same as far from the three-phase line, i.e. to be determined only by the nature of surfaces.

For a flat horizontal surface of a solid, the generalized Young equation becomes

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta + \varkappa/r + \partial \varkappa / \partial r \qquad (18)$$

If radius r is not very small and the dependence of $\varkappa$ on r is negligible, eq.(18) changes into the result by Shcherbakov and Ryasantsev (ref.13):

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta + \varkappa/r \qquad (19)$$

The role of the third term on the right-hand side of (17)-(19) depends on the value of line work $\varkappa$ and on the line curvature. If a solid surface is easily deformable, an effective value of $\varkappa$ may be several orders higher than the usual values (about 10^{-10} H), which leads to the experimentally observable influence of the line term on contact angle (ref.14). By contrast, $\varkappa$ for solids with a high elasticity modulus (glasses, crystals, metals, etc.) is so small that the third term in the right-hand side of eq.(19) is negligible for macroscopic drops. Then eq.(19) changes into the classical Young equation

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta \qquad (20)$$

or, if we remember that $\sigma_{LV} = \gamma_{LV}$ for a fluid interface,

$$\sigma_{SV} = \sigma_{SL} + \gamma_{LV} \cos \theta \qquad (21)$$

Quantities σ_{SV} and σ_{SL} include contributions from adsorbed films on a solid surface. The presence of such films as well of gravity does

not influence the form of the Young equation, though the drop shape is dependent of gravity. The matter is that eqs.(17)-(21) express only a boundary condition (mathematically, this is the transversality condition in the variational problem on the equilibrium shape of a drop on a solid surface).

THE GENERALIZED GIBBS ADSORPTION EQUATION

Additionally to the two key relationships of the classical theory of capillarity, the Laplace and Young equations, Gibbs introduced one more relationship of fundamental importance, the adsorption equation. However, the adsorption equation was derived by him only for fluid interfaces. For a flat horizontal surface, the Gibbs adsorption equation is

$$d\gamma = d\mathfrak{G} = -\bar{s}\,dT - \sum_i \Gamma_i\,d\mu_i \qquad (22)$$

where $\bar{s}$ is excess entropy per unit area, T temperature, Γ_i and μ_i the adsorption and the chemical potential of the ith component, respectively.

In the case of a solid, quantities γ and $\mathfrak{G}$ are different, and, consequently, there should be a separate adsorption equation for each of this quantities (ref.2). Surface tension in the kth direction on a surface is defined as an excess stress

$$\gamma_k = -\int (p_k - p_k^{\alpha,\beta})\,dz \qquad (23)$$

where $p_k^{\alpha,\beta}$ is the pressure component p_k^α for the part of surface layer on the side of phase α and the pressure component p_k^β for the part of surface layer on the side of phase β as considered with respect to the dividing surface, z is the normal to the surface coordinate, integration is carried out over the whole thickness of surface layer. If the equimolecular surface of a solid (i.e., the surface satisfying the condition of zero-adsorption of the solid $\Gamma_j = 0$) is chosen as a dividing surface, quantities γ_k and $\mathfrak{G}$ are related to each other by the expression (ref.6)

$$\mathfrak{G} = \gamma_k + \int (\mu_{j(k)} - \mu_{j(k)}^{\alpha,\beta})\,c_j\,dz \qquad (24)$$

where $\mu_{j(k)}$ is the chemical potential of the solid in the kth direction, c_j the local concentration of the substance of the solid, superscript α,β is read as α while integrating over the part of surface layer adjacent to phase α and as β while integrating over the part of surface layer adjacent to phase β.

Additionally to the substance of the solid, there may be other components in surface layer which may be adsorbed and desorbed and move freely passing from surface layer to the surroundings. Such component are called mobil (let us denote them with subscript i). Quantity $\mathfrak{G}$ is defined with respect to mobil components as the surface density of grand thermodynamic potential:

$$\mathfrak{G} = \bar{u} - T\bar{s} - \sum_i \mu_i \Gamma_i \qquad (25)$$

where $\bar{u}$ is excess energy per unit area, μ_i and Γ_i chemical potentials and adsorptions for mobil components, respectively.

The fundamental equation for the energy, U, of a uniform thin layer is

$$dU = TdS - (\hat{p} : d\hat{e})V + \hat{\mu}_j : d\hat{N}_j + \sum_i \mu_i \, dN_i \qquad (26)$$

where S is the entropy of the layer, V its volume, $\hat{p}$ the pressure tensor, $\hat{e}$ the strain tensor (symbol ":" means the scalar product of tensors), μ_j the chemical potential tensor of the substance of the solid, N_j and $d\hat{N}_j$ the amount of the substance of the solid and its tensorial change (ref.6), respectively (the work of bringing in the substance into volume of given dimensions depends on direction in the case of a solid).

To derive the adsorption equation for a solid surface, let us subdivide surface layer into the set of parallel elementary layers and apply eq. (26) to each elementary layer implying tangential changes. The difference between eq.(26) for each elementary layer in the part of surface layer on the side of phase $\propto$ with respect to the dividing surface (the equimolecular surface) and the same equation for phase $\propto$ may be written as

$$d(U - U^\propto) = Td(S - S^\propto) - \left[(\hat{p} - \hat{p}^\propto) : d\hat{e} \right] V +$$
$$+ (\hat{\mu}_j - \hat{\mu}_j^\propto) : d\hat{N}_j + \hat{\mu}_j^\propto : d(N_j - N_j^\propto) +$$
$$+ \sum_i \mu_i \, d(N_i - N_i^\propto) \qquad (27)$$

The tangential strain is assumed here to be the same for all elementary layers.

Considering only tangential changes, eq.(24) may be written

$$\int (\hat{\mu}_j - \hat{\mu}_j^{\propto,\beta}) \, c_j dz = \mathfrak{S}\hat{1} - \hat{\gamma} \qquad (28)$$

where $\hat{1}$ is the unit tensor. Proceeding now to excess quantities, i.e. integrating eq.(27) over the $\propto$ -region of surface layer and an analogous equation over the β -region (with respect to the dividing surface), and also using (23) and (28), we obtain

$$d\bar{U} = Td\bar{S} + (\hat{\gamma} : d\hat{e})A - (\hat{\gamma} - \mathfrak{S}\hat{1})A : d\hat{N}_j/N_j + \sum_i \mu_i \, d\bar{N}_i \qquad (29)$$

where excess quantities are marked with a bar. Substituting $\bar{U} = \bar{u}A$ and expressing $\bar{u}$ through $\mathfrak{S}$ with the aid of eq.(25) yields

$$d\mathfrak{S} = -\bar{s}_{(j)} \, dT + (\hat{\gamma} - \mathfrak{S}\hat{1}) : (d\hat{e} - d\hat{N}_j/N_j) - \sum_i \Gamma_{i(j)} \, d\mu_i \qquad (30)$$

where subscript (j) refers to the equimolecular surface of a solid. This is an analog (for quantity $\mathfrak{S}$) of the Gibbs adsorption equation, quantity γ changing in accordance with eq.(24).

For a simple enlargement in size without a change in the shape of a body, $d\hat{e} = d\hat{N}_j/N_j$. Thus, difference $d\hat{e} - d\hat{N}_j/N_j$ is non-zero only for real deformations. One may fix the amount of a solid, N_j, as it occurs often in practice, say, in adsorption processes. Then, any change of tensor $\hat{e}$ means deformation, and eq.(30) becomes (ref.2).

$$d\mathfrak{S} = - \bar{s}_{(j)} \, dT + (\hat{\gamma} - \mathfrak{S}\hat{1}) : d\hat{e} - \sum_i \Gamma_{i(j)} \, d\mu_i \qquad (31)$$

or, for an isotropic solid (ref.15),

$$d\mathfrak{S} = - \bar{s}_{(j)} dT + (\gamma - \mathfrak{S}) \, d\ln A - \sum_i \Gamma_{i(j)} \, d\mu_i \qquad (32)$$

Equations (30)-(32) differ from the Gibbs adsorption equation for
fluids only in their mechanical term, i.e. the second term on the
right-hand side. It is interesting that this term disappears not only
for liquids when $\gamma = \varsigma$, but also for solids in the absence of
deformation. For a rigid solid, eq.(30) takes the traditional form of
the adsorption equation

$$d\varsigma = -\bar{s}_{(j)} dT - \sum_i \Gamma_{i(j)} d\mu_i \qquad (33)$$

with the only difference that $\varsigma \neq \gamma$. The equations for ς for
liquids and rigid solids look similarly. However, they differ in their
practical usage. In the case of liquids, ς is determined directly
from experiment due to the condition $\varsigma = \gamma$, and eq. (33) is used for
the calculation of surface entropy and adsorption. In the case of so-
lids, it is experimentally easier to measure adsorption, and eq.(33)
may be applied to compute a change in ς due to adsorption.

INTERRELATIONS BETWEEN SURFACE ENERGY, COHESIVE ENERGY, AND THE VAPORIZATION HEAT

As is known, all surface quantities are dependent of the structure of
surface layer and, hence, it is not easy to relate them to bulk quan-
tities. If so, is it possible to find a universal interrelation bet-
ween surface and cohesive energies (the latter may be characterized by
the vaporization heat)? Many investigations was done to answer this
question. The first result was the known Stefan rule (ref.16) claiming
that surface tension (Harkins (ref.17) replaced surface tension by sur-
face energy) corresponds to the half of cohesive bonds in the bulk. The
most general equation relating the cohesive energy density, w , to
surface energy was derived by the author (ref.18).

We give first the definition: the cohesive energy of a system, U_c ,
is a difference between the internal energy of the system and that of
the gas of the same molecules in the limit of zero density at the same
temperature. If e_i is the energy per mole of the ith component of the
gas, the total energy of a two-phase system may be represented as

$$U = U_c + \sum_i e_i N_i \qquad (34)$$

where N_i is the total number of moles of the ith component in the sys-
tem. Respectively, the excess surface energy is

$$\bar{U} = \bar{U}_c + \sum_i e_i \bar{N}_i \qquad (35)$$

The excess surface cohesive energy, $\bar{U}_c$, is defined as

$$\bar{U}_c = U_c - w^\beta V + (w^\beta - w^\alpha) V \qquad (36)$$

where V is volume, α and β are the phase symbols.

Volume V and all other excess quantities in eq.(35) depend on the po-
sition of the dividing surface. If we choose the position where the con-
dition holds

$$\sum_i e_i N_i = 0 \qquad (37)$$

(this is the equimolecular surface in case of an one-component sys-
tem), eq.(35) is reduced to

$$\bar{U} = \bar{U}_c \qquad (38)$$

This means, in particular, that the specific surface energy, $\bar{u}$, is

the excess cohesive energy per unit area for the equimolecular dividing surface in an one-component system.

For the dividing surface given by (37) (position 1), eqs. (36) and (38) yield

$$\overline{U} = U_c - w^{\beta} V + (w^{\beta} - w^{\alpha}) V_1^{\alpha} \tag{39}$$

and for the dividing surface satisfying condition $\overline{U}_c = 0$ (position 2)

$$0 = U_c - w^{\beta} V + (w^{\beta} - w^{\alpha}) V_2^{\alpha} \tag{40}$$

Subtracting (40) from (39), we get

$$\overline{U} = (w^{\beta} - w^{\alpha}) \Delta V \tag{41}$$

where $\Delta V = V_1^{\alpha} - V_2^{\alpha}$ is the volume between the two positions of the dividing surface. From here

$$\overline{u} = (w^{\beta} - w^{\alpha}) \Delta V/A \tag{42}$$

where A is the area of the dividing surface given by (37) (the equimolecular surface in case of an one-component system). Equation (42) is a rigorous universal relationship relating surface energy to the difference of the cohesive energy densities in the adjacent bulk phases. The linear parameter $\Delta V/A$ depending on the structure of surface layer plays the role of a coefficient.

At a given shape of an interface, parameter $\Delta V/A$ may be expressed through the distance between the above two positions of the dividing surface. For a spherical interface

$$\Delta V/A = \Delta r \left[1 - \Delta r/r_1 + (\Delta r/r_1)^2 /3 \right] \tag{43}$$

where $\Delta r = r_1 - r_2$, r_1 and r_2 are the radii of the dividing surfaces satisfying the conditions (37) and $U_c = 0$, respectively. For a flat (or a slightly curved) interface

$$\Delta V/A = \Delta z = z_1 - z_2 \tag{44}$$

where z_1 and z_2 are the normal coordinates of the two dividing surfaces. The substitution of (44) into (42) yields

$$\overline{u} = (w^{\beta} - w^{\alpha}) \Delta z \tag{45}$$

The apparent simplicity of eqs.(42) and (45) is deceptive. Even in the case of one component, the calculation of parameter $\Delta V/A$ demands knowledge of the local density profiles of matter, $c(x,y,z)$, and of cohesive energy, $w(x,y,z)$, inside surface layer. It is seen from the expression

$$\Delta V = \iiint \{[c(x,y,z) - c^{\beta}] /(c^{\alpha} - c^{\beta}) -$$
$$- [w(x,y,z) - w^{\beta}]/(w^{\alpha} - w^{\beta})\} \, dxdydz \tag{46}$$

In the case of a flat interface, local densities   c   and   w   depend
only on   z, and eq.(46) becomes

$$\Delta z = \int \{ [c(z) - c^\beta] / (c^\alpha - c^\beta) - $$
$$- [w(z) - w^\beta] / (w^\alpha - w^\beta) \} \, dz \qquad (47)$$

The integrand in eqs.(46) and (47) becomes zero inside the bulk phases,
so integration is carried out actually only over the nonuniform sur-
face layer. Since both the dividing surfaces are located inside sur-
face layer, distance Δz should not exceed the effective thickness of
surface layer which is of order of molecular or atomic dimensions for
an one-component system far from the critical point.

If phase β is vacuum (or a gas), $c^\beta = 0$ and $w^\beta = 0$ so that eqs.
(42) and (46) may be written as

$$\bar{u} = - w^\alpha \Delta V / A \qquad (48)$$

$$\Delta V = N/c^\alpha - U_c/w^\alpha = \iiint [1 - u_c(x,y,z)/u_c^\alpha] \, x$$
$$[c(x,y,z)/c^\alpha] \, dxdydz \qquad (49)$$

or, for a flat surface,

$$\bar{u} = - w^\alpha \Delta z \qquad (50)$$

$$\Delta z = \int [1 - u_c(z)/u_c^\alpha] [c(z)/c^\alpha] \, dz \qquad (51)$$

where $u_c = w/c$ is cohesive energy per mole. Since $|u_c(z)| < |u_c^\alpha|$,
we obtain from (51) a very important result: $\Delta z > 0$ which means
that the dividing surface of zero cohesive energy is situated always
deeper in a condensed body than the equimolecular surface. As a con-
sequence, using also the obvious condition $w^\alpha < 0$ in (50), we come
to the conclusion that surface energy is positive: $\bar{u} > 0$.

Now we relate surface energy to the vaporization heat. The molar heat
of phase transition $\alpha \rightarrow \beta$ is given by the enthalpy change

$$\Delta h = h^\beta - h^\alpha = h_v^\beta / c^\beta - h_v^\alpha / c^\alpha \qquad (52)$$

where   h   is molar enthalpy, h_v the enthalpy density, and   c   the to-
tal number of moles of all components per unit volume. We have

$$h_v = u_v + p = w + \sum_i e_i c_i + p \qquad (53)$$

where u_v is energy density, p   pressure, and c_i the concentration of
the ith component. From (42), (52), and (53), we obtain

$$\bar{u} = [c^\alpha \Delta h + w^\beta (1 - c^\alpha / c^\beta) + p^\alpha - c^\alpha p^\beta / c^\beta - $$
$$- \sum_i e_i (c_i^\alpha - c_i^\beta c^\alpha / c^\beta)] \Delta V / A \qquad (54)$$

This is a general equation relating surface energy to the enthalpy ef-
fect of phase transition or to the phase transition heat (which is -
Δh). For an one-component system, $c_i = c$, so the kinetic energy

term in (54) disappears reducing eq. (54) to

$$\bar{u} = \left[c^{\alpha} \Delta h + w^{\beta} (1 - c^{\alpha}/c^{\beta}) + \right.$$
$$\left. + p^{\alpha} - c^{\alpha} p^{\beta}/c^{\beta} \right] \Delta V/A \tag{55}$$

If phase β is vacuum or a gas far from the critical point ($w^{\beta} \approx 0$, $p^{\beta}/c^{\beta} \approx RT$, $RTc^{\alpha} \gg p^{\alpha}$), eq.(55) becomes

$$\bar{u} = c^{\alpha} (\Delta h - RT) \Delta V/A = (\Delta h - RT) \Delta V/A \, v^{\alpha} \tag{56}$$

where v^{α} is the molar volume of a condensed phase. For a flat surface, eq.(56) is

$$\bar{u} = (\Delta h - RT) \Delta z/v^{\alpha} \tag{57}$$

For liquids $\bar{u}$, Δh, and v^{α} can be determined directly from experiment, and eq. (57) allows calculations of parameter Δz characterizing the structure of surface layer. It has been found (ref.18) that Δz is usually several times smaller than the average intermolecular distance in the bulk phase of a liquid.

SURFACE AND LINE CHARACTERISTIC IN STABILITY CONDITIONS

The condition of stable equilibrium of an arbitrary system was formulated by Gibbs as

$$d U = 0, \quad \Delta U > 0, \quad d^2 U \geqslant 0 \ (S,V,N_i \ - \text{const}) \tag{58}$$

where the volume constancy is meant generally as fixation of the external boundaries of the system. Detailing condition (58), Gibbs came to the stability condition for bulk phases (ref.1, p.111, eq.171)

$$\Delta T \Delta S - \Delta p \Delta V + \sum_i \Delta \mu_i \Delta N_i > 0 \tag{59}$$

from where the conditions follow of thermal

$$\Delta T \Delta S > 0 \tag{60}$$

mechanical

$$\Delta p \Delta V < 0 \tag{61}$$

and material stability

$$\sum_i \Delta \mu_i \Delta N_i > 0 \tag{62}$$

Inequality (59) was derived without considering surface phenomena. Stability conditions for surface layers and heterogeneous systems (ref.11, Ch.1) and the role of line characteristics in stability (ref. 19) were analysed later by the author. As it was shown, the conditions of thermal and material stability, (60) and (62), maintain, but the mechanical stability condition takes another form when surface and line characteristics are taken into account.

The fundamental equation for the energy of a heterogeneous system may be derived by summation of the corresponding equations for phases and interfaces which are well known for the state of equilibrium. We consider the case when phases and interfaces are internally equilibrium, but they are not in equilibrium with each other. Then we obtain the fundamental equation

$$dU = \sum TdS - \sum pdV + \sum \gamma dA + \sum \tau dL +$$
$$+ \sum L(\partial \tau / \partial r) dr + \sum \sum_i \mu_i dN_i \qquad (63)$$

where γ is surface tension, A the dividing surface area (Gibbs' surface of tension is used as a dividing surface for curved interfaces), τ line tension, L and r are the length and the curvature radius of a portion of the dividing line, respectively. Summation is carried out over all elements of the system. Partial derivative $\partial \tau / \partial r$ may be regarded as related to variation of the position of the dividing line at a fixed physical state of the system. The analogous term for γ is absent in eq. (63) because we refer γ and A to the surface of tension for which $\partial \gamma / \partial r = 0$. For the dividing line, there also exists the notion of the line of tension for which $\partial \tau / \partial r = 0$ (ref. 11). However, it is not certainty that the line of tension coincides with the intersection line of the surfaces of tension for different interfaces if they intersect. This intersection line is a natural dividing line in our consideration, so we have to set $\partial \tau / \partial r \neq 0$.

By differentiating, we obtain from eq. (63)

$$d^2U = \sum dT dS - \sum dp dV + \sum d\gamma dA +$$
$$\sum d\tau dL + \sum d(L \partial \tau / \partial r)dr + \sum \sum_i d\mu_i dN_i \qquad (64)$$

After the substitution of (64) into (58), we come to the necessary condition of internal stability of a heterogeneous system:

$$\sum dTdS - \sum dp dV + \sum d\gamma dA + \sum d\tau dL +$$
$$+ \sum d(L \partial \tau / \partial r)dr + \sum \sum_i d\mu_i dN_i \geqslant 0$$
$$(S, V, N_i - const) \qquad (65)$$

and, in particular, to the condition of mechanical stability

$$- \sum dpdV + \sum d\gamma dA + \sum d\tau dL + \sum d(L \partial \tau / \partial r) dr \geqslant 0 \quad (66)$$

However, expression (66) is written correctly only under the condition that variables V,A,L, and r are independent. In practice, they are often related each to others due to, e.g., a given shape of a body or other restrictions. This is of no importance for the mechanical equilibrium condition following from (58) and (63)

$$- \sum pdV + \sum \gamma dA + \sum \tau dL + \sum L(\partial \tau / \partial r) dr = 0 \qquad (67)$$

because of the invariancy of the first differential form. But if we differentiate (67) again, it is important to know whether quantities V,A,L, and r depend on each other or on other quantities. If they are functions, terms $\sum pd^2V$, $\sum d^2A$, $\sum \tau d^2L$, and $\sum L(\partial \tau / \partial r)d^2r$ prove to be lost in (66). That is why the mechanical stability condition should be written in a more general form as

$$d\left[- \sum pdV + \sum \gamma dA + \sum \tau dL + \sum L(\partial \tau / \partial r) dr \right] \geqslant 0 \quad (68)$$

At fixed volumes of phases, conditions (67) and (68) become an analog of the generalized Gibbs - Curie principle:

$$\sum \gamma \, dA + \sum \tau \, dL + \sum L(\partial \tau / \partial r) \, dr = 0 \qquad (69)$$

$$d\left[\sum \gamma \, dA + \sum \tau \, dL + \sum L(\partial \tau / \partial r) \, dr \right] \geqslant 0 \qquad (70)$$

In the absence of linear boundaries, conditions (69) and (70) are reduced to

$$\sum \gamma \, dA = 0, \quad \sum d\gamma \; dA + \sum \gamma \, d^2 A \; \geqslant \; 0 \qquad (71)$$

For a single closed surface, condition (71) becomes

$$dA = 0, \quad \gamma \, d^2 A \; \geqslant \; 0 \qquad (72)$$

which means that the stable shape of a body corresponds to a minimum of the surface area at positive surface tension, and to a maximum of the surface area at negative surface tension. In the case of liquids, condition $\gamma = \sigma < 0$ means a complete instability when a body is dispersed spontaneously up to molecular dimensions. In the case of solids, the signs of γ and σ may differ. If $\gamma < 0$, a body is stretched, but if $\sigma > 0$ at the same time, the body can remain undestroyed and stable.

By analogy, in the case of a pure two-dimensional phase transition (we may use here the line of tension and set $\partial \tau / \partial r = 0$), the condition of the stable mechanical equilibrium at constant surface areas is

$$\sum \tau \, dL = 0, \quad \sum d\tau \; dL + \sum \tau \, d^2 L \; \geqslant \; 0 \qquad (73)$$

For a closed line boundary of a single two-dimensional phase, we obtain from (73)

$$dL = 0 \, , \quad \tau \, d^2 L \; \geqslant \; 0 \qquad (74)$$

It follows from (74) that the two-dimensional phase region should have a minimal perimeter, i.e. be a circle, under condition $\tau > 0$. If τ were negative, there would be self-dispersion and disappearence of a two-dimensional phase. Thus, experimental observations of macroscopic two-dimensional phases give an evidence of the positive sign of τ in two-dimensional phase processes.

A sessile drop, α, between phases β (a gas) and γ (a substrate) is the simplest example of a system containing both curved surfaces and lines. Let surface $\alpha\beta$ be curved and surfaces $\alpha\gamma$ and $\beta\gamma$ flat so that $dA^{\alpha\gamma} = - dA^{\beta\gamma}$. The generalized Gibbs - Curie principle is written in this case as (ref.19)

$$(\sigma^{\alpha\gamma} - \sigma^{\beta\gamma})dA^{\alpha\gamma} + \sigma^{\alpha\beta} dA^{\alpha\beta} + \sum \varpi \, dL + \sum L (\partial \varpi / \partial r) \, dr = 0 \quad (75)$$

$$(d\sigma^{\alpha\gamma} - d\sigma^{\beta\gamma})dA^{\alpha\gamma} + d\sigma^{\alpha\beta} dA^{\alpha\beta} + \sum d\varpi \, dL + \sum \varpi \, d^2 L +$$

$$+ \sum d(L\partial\varpi / \partial r) \, dr + (\sigma^{\alpha\gamma} - \sigma^{\beta\gamma}) \, d^2 A^{\alpha\gamma} + \sigma^{\alpha\beta} d^2 A^{\alpha\beta} \geqslant 0 \qquad (76)$$

where we use σ instead of γ and ϖ instead of τ because the

substrate may be solid. Applying (76) to a change of the shape of the linear boundary at fixed area $A^{\alpha\gamma}$ and all fixed ς , we come to the condition

$$\sum \varkappa\, d^2 L + \sum (\partial \varkappa / \partial r)\, dr\, dL + \varsigma^{\alpha\beta}\, d^2 A^{\alpha\beta} \geqslant 0 \quad (77)$$

For a fixed position of the linear boundary, we obtain the stability condition

$$\varsigma^{\alpha\beta} > 0,\ d^2 A^{\alpha\beta} \geqslant 0 \qquad\qquad (78)$$

which means that surface area $A^{\alpha\beta}$ should be minimal for any fixed position of the three-phase line. We cannot fix area $A^{\alpha\beta}$ at constant volume of the drop since any change of the drop shape in accompanied by a change of its surface area, namely $A^{\alpha\beta}$ if $A^{\alpha\gamma}$ is fixed. That is why there is no separate stability condition for $\varkappa$ or τ . Even their negative values are not excluded at the three-phase line.

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