NUMERICAL CALCULATION OF SURFACE-FREE ENERGIES OF SOLIDS

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I. Basic concepts

1. *The boundary layer and the surface phase*

The properties of solids are known to be greatly influenced by their surface properties in many practically important cases. In the last decades the development of solid state physics was extended to the physics of solid surfaces. In the present paper it will be tried to outline some important aspects of this new branch of science, especially the calculation of the surface free energy, its most important characteristic will be dealt with.

A short review of literature data will be followed by the description of our own methods.

Let us regard a thermodynamic system, consisting of two bulk phases, in its stable equilibrium state. The local physical properties as density of energy or densities of components will be then functions of space co-ordinates. These continuous functions will have constant values inside the bulk phases, but they will show a rather great interphase gradient. The surfaces bordering this region from the side of the bulk phases will be called phase boundaries, and the region itself will be denoted as the boundary layer. The typical thickness of the boundary layer is to some few a hundred Angstroms [1] so that it is some 6—8 orders smaller than the linear sizes of the bulk phases on its two sides.

In the most common approximation the boundary layer is treated as one of constant thickness t. Assuming a co-ordinate axis z in the direction normal to one of the phase boundaries, to every point of this axis in the boundary layer a surface may be assigned. These will be called as boundary surfaces, and each of them may be characterized by its dimensionless co-ordinate $\lambda \equiv z/t$ and with its area $\Omega(\lambda)$. In this approximation it is postulated that local physical properties are constant within a surface. Their values, however, differ on the different surfaces so that according to the well-known definition of Gibbs each such surface may be regarded as a different phase.

Let us regard an extensive thermodynamic quantity A_i. In the usual cases, in a K component mixture A_i is one of the following quantities: entropy

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S, volume V, component mole numbers $N_j (j = 1, 2, \ldots, K)$. In solids the independent components of the deformation tensor (multiplied by V) have to be taken into account instead of V, because of their anisotropy. (In our treatment anisotropy will not be dealt with directly in a first approximation. This is a usual procedure in the thermodynamics of solids.)

The surface excess of A_t will be defined by the relationship:

$$a_i^s(\lambda) = \frac{t}{\Omega(\lambda)} \left[\int_0^\lambda [\varrho_i(\lambda) - \varrho_i^I] \Omega(\lambda) d\lambda + \int_\lambda^1 [\varrho_i(\lambda) - \varrho_i^{II}] \Omega(\lambda) d(\lambda) \right] \tag{1}$$

here $\varrho_i(\lambda)$ is the actual density while the bulk phases are denoted by I and II, respectively. Dimension of a_i^s is extensive quantity per unit surface.

It is well known that all the equilibrium macroscopic properties of a bulk phase are described by the free energy function $F(T, V, N_1, \ldots, N_K)$. An analogous function results from calculating surface excesses of $F, V, N_1, \ldots, N_K$ by relation (1). So the boundary layer may be characterized the same way as a homogeneous phase, and it may be called surface phase. There is, however, fundamental difference between bulk and surface phases: unlike the former, the latter are imhomogeneous, further, free energy function of the latter is not independent of the free energy functions of the phases in its neighbourhood.

Dependence of a_i^s on λ may be excluded in two ways. First, there exists λ_0 giving minimum (always positive one) of the surface excess of F, second, there exist λ_j giving zero value of the surface excess of N_j. The first condition will give Gibbs's surface of tension which is the actual physical surface. As an example: in liquid argon the λ_1 surface was lying at 3.6 A° distance from the λ_0 surface in the direction of the gaseous phase [2].

2. Surface free energy and surface tension

Let us regard a process involving constant T, N_j^s ($j = 1, 2, \ldots, K$) and t, where the surface of tension is displaced by $d\lambda$. (Such a change may be caused by the change of the densities and shapes of the bulk phases e.g.) The change of the surface excess of F will be then:

$$df^s = \left(\frac{\partial f^s}{\partial \Omega} \right)_{T, N_1^s, N_2^s, \ldots, N_K^s} d\Omega = \gamma d\Omega \tag{2}$$

where quantity γ will be called the surface free energy. (Here the term corresponding to $\partial f^s/\partial \lambda$ will be missing, according to the definitions of the surface of tension.) Quantity γ consist of two parts:

$$\gamma = \gamma_0 + \gamma' \tag{3}$$

the first term (surface tension) corresponds to the work needed to enlarge the surface at constant shape, while the second to the work needed to change the shape of the surface at constant area. Quantity γ' is zero in plastic fluid surfaces but it is not in elastic solid surfaces, so that in solids γ and γ_0 may differ by as much as 100%, and this difference is very much dependent on the material's character [3].

From equation (1) it is obvious that, the surface free energy changes always by F^s/Ω (where F^s is the actual excess free energy of the surface phase), provided that only surface properties are changed.

Another aspect of surface free energy may be described by regarding the differential of the quantity F^t, the total free energy of the two-phase system at the transfer of dN_j^s moles of components j at constant temperature (s is the sign of the surface phase while b is the sign of the bulk phase):

$$dF^t = \sum_{j=1}^{K} (\mu_j^s - \mu_j^b)dN_j^s + \gamma \sum_{j=1}^{K} \Phi_j dN_j^s \qquad (4)$$

Chemical potentials are defined here by

$$\mu_j^b \equiv \left(\frac{\partial F^b}{\partial N_j^b}\right)_{T,V^b,N_{i\neq j}^b} \qquad (5)$$

$$\tilde{\mu}_j^s \equiv \left(\frac{\partial F^s}{\partial N_j^s}\right)_{T,N_{i\neq j}^s,\Omega} \qquad (6)$$

Partial molar surfaces are:

$$\Phi_j \equiv \left(\frac{\partial \Omega}{\partial N_j^s}\right)_{T,N_{i\neq j}^s} \qquad (7)$$

From the condition of equilibrium

$$dF^t = 0 \qquad (8)$$

we have

$$\tilde{\mu}_j^s = \mu_j^b + \gamma \Phi_j \quad (j = 1, 2, \ldots, K) \qquad (9)$$

That is, surface free energy multiplied by the component partial molar surface is the isothermal reversible work needed to bring one mole of component j from the bulk phase under consideration into the surface phase.

3. Surface free energy as an efficient characteristic of surfaces and its connection with other surface properties

The two most efficient methods describing solid surfaces, namely the thermodynamical and the quantum mechanical, lead to the surface excess

energy in direct or indirect way. The surface excess (internal) energy u_s is determined from the surface free energy γ through the surface Gibbs—Helmholtz equation in thermodynamics:

$$u_s = \gamma - T\frac{d\gamma}{dT} \tag{10}$$

Solutions of the Schrödinger equation give the total energy of the system (solid + surface), but there are several methods (e.g. [5, 6]) for determining of the surface excess energy from this by substraction of the bulk energy.

Surface physical investigations of our research group have led to the conclusion that many surface physical properties are in connection with the surface free energy. Some examples will be given now.

The difference between surface and bulk compositions in many component systems is described by equations

$$\frac{x_i^s}{x_i^b} = e^{\frac{\gamma\Phi_i - \gamma_i^0\Phi_i^0 + (l+m)\mu_{ei}^b(x_i^b) - l\mu_{ei}^b(x_i^b)}{RT}} \tag{11}$$

$$(i = 1, 2, \ldots, K)$$

and

$$\frac{x_i^s}{x_i^b} = e^{\frac{\gamma - \gamma_i^0}{RT}\Phi_i} \tag{12}$$

$$(i = 1, 2, \ldots, K)$$

where γ is the mixture surface free energy, γ_i^0 and Φ_i are the surface free energy of the pure component and its partial molar surface, μ_{ei} is the excess chemical potential, l is the fraction of nearest neighbours in the surface while m is the fraction of missing nearest neighbours on the surface. Research made in this direction gave satisfactory results so far [4, 11].

Solutions of Schrödinger's equation for a localized perturbation of the periodic potential describe localized electronic states in the gap between energy eigenvalues, and in the case of the surface, surface states. Many of the surface states are connected to surface free energy, e.g. surface lattice distortions [12] lead to energy changes [13] and to surface electronic states [15—17] as well.

Surface free energy, through the surface energy states and enrichment, is connected to the state of charge of the surface.

It was shown by our calculations too, that consideration of surface free energy led to surface enrichment of vacancies as well [18].

II. Survey of literature data, experimental and calculation methods

4. *General description of experimental methods*

A direct method is the measurement of the force needed to stop the shrinkage of thin metal sheets or rods at high temperatures [21], giving the most reliable data.

A number of indirect methods was worked out, the application of Kelvin's equation [9], measurement of grinding energy [9], measurement of cleavage work [22, 23], and extrapolation of the surface tension of liquid to temperatures where the solid is stable [9] are the most commonly used procedures. The first two give values far too high, while the other two are rather reliable.

In using experimental data the following should be borne in mind: 1. Generally $\gamma_s{}^*$ is an anistropic quantity. This anisotropy causes changes of some per cent on the different crystal planes of metals [8], but it is much higher in materials such diamond [14]. 2. Value of γ_s is generally dependent on state of tension [24] and of imperfections [8], so that results have to be extrapolated to zero tension and perfect surface. 3. Surface adsorption causes a great change [22, 25] and results have to be extrapolated to vacuum state of gaseous phase. 4. Impurities often tend to accumulate on the surface and to diminish the value of γ_s. Extrapolation to the pure state is needed. 5. Irreversible effects should be avoided.

5. *Theoretical and semi-empirical macrophysical methods*

These methods are based on the use of exact thermodynamic relations, hence in principle, the values of γ are given by them exactly, but in most cases they cannot be used because of the difficulties of experiments mentioned in the previous chapter.

Kelvin's equation gives too high values, as it was, too, mentioned earlier. Another formula, modified by LOTHE and POUND [26] uses the critical radius of nucleation. The Gibbs—Wulff relations [8] may be used to calculate relative areas of different crystal faces on the surface if anisotropy of γ_s is known. Another possibility for obtaining γ_s is the field emission method [27], used mostly for the determination of the surface diffusion coefficient. In some cases, contact angle measurements and Neumann's equation may be used. In connection with this, γ_s may be computed from spreading pressure as well. A closely related method is the use of the condition of stable film formation. The effect of surface contaminations may be calculated by the Gibbs adsorption isotherm. Dupre's formula of the angle of contact of three phases was used succesfully for the determination of interface free energies of crystallites in polycrystalline copper [28]. Measurements of the force needed to break solid rodes were used to compute γ_s, here GILMAN's relation [29] was further developed by MECIK [30].

* Denotion γ_s is used when statements refer only to solids

On the base of DEMCHENKO's work [31] and under rather restrictive conditions, formula

$$\gamma = \beta V^{-2/3} N^{-1/3} L_V \tag{13}$$

was deduced by BAYDOV and KUNIN [19], where V is the molar volume, N is Avogadro's number and L_V is the heat of evaporation, while β is an empirical constant. A similar relationship with $\beta = (2\pi)^{-1}$ was deduced by Byelogurov [32] using the cohesive energy instead of L_V. From this latter under further assumptions a formula [19] using $(C_p - R)\,T$ instead of L_V was developed, C_p being the isobaric heat capacity. All these methods are based on the fact that development of surface and evaporation has the common feature of breaking bonds with neighbouring particles.

Another method connects γ with Young's modulus E [14]:

$$\gamma = \frac{E}{d_0} \left(\frac{a}{\pi}\right)^2 \tag{14}$$

where d_0 is the distance between the atomic layers in the crystal and a is the mean radius of surface atoms (ions).

A rather fair agreement with most of cited experimental data was reported in each cases.

6. The macrophysical empirical relations

Formulae similar to (13) were published for solid metals [33, 34] and for liquid metals at their melting points [35]. This fact was used to connect γ_s to the surface tension of liquid at the melting point [34, 36] such as:

$$\gamma_s = \gamma_L \left(\frac{D_s}{D_L}\right)^{2/3} \frac{L_s}{L_V} \tag{15}$$

where D is the density and L_s is the heat of sublimation at the melting point. Empirical mean value of the multiplier after γ_L is given as 1.07 [36], a rather interesting result.

In a first approximation, according to experiments,

$$\frac{d\gamma}{dT} = 0 \tag{16}$$

with $\gamma = u^s$ from the Gibbs—Helmoltz relation where u^s is the surface internal energy. A better approximation is

$$\frac{d\gamma}{dT} = -\,0.5 \text{ erg cm}^{-2}\,{}^\circ K^{-1} \tag{17}$$

claimed to be valid for most metals by its authors [37]. Relationships (16—17) may be used to compute γ_s from $u^s(0)$, the value of the surface internal energy at $0\,^\circ K$ by the Gibbs—Helmholtz equation at $0\,^\circ K$:

$$\gamma(0) = u^s(0) \tag{18}$$

This is a useful procedure, since value of $u^s(0)$ may be obtained from quantum mechanical approximations.

7. *Microphysical approximate theoretical calculations*

These methods divide the energy of a particle between bonds with its neighbours and then count the number of broken bonds upon forming the surface. A nice example is given by ERDEY-GRÚZ and SCHAY [1] where relationship

$$u^s = \frac{9}{26}\, V^{-2/3} N^{-1/3}(L_V - RT) \tag{19}$$

was obtained from rather simple considerations. Here $9/26$ is the relative number of missing close neighbours (not only nearest neighbours are counted !) of a particle on the surface. A similar formula was published by POPEL Jesin and *et al.* [38], replacing of L_V-RT (the "internal" heat of evaporation) by

$$-F_e = -RT \ln\left(\frac{pV}{RT} - 1\right) \tag{20}$$

and $9/26$ by a number α denoting the fraction of missing nearest neighbours was used. Here F_e is the excess free energy over a perfect gas with the same volume and temperature. This is a negative quantity, measuring the strength of the intermolecular interactions.

The latter relationship was found to be correct for molecular, ionic and metallic liquids as well. Value of α was given by ORIANI [39] as $1/6$.

Further theories connect γ with other quantities, such as with electronic work function [40], sound velocity [41] and lattice energy and atomic radii [42]. These methods were developed by DEMCHENKO, and, as it was pointed out by ZADUMKIN, they may lead to wrong results, taking only the electronic subsystem of a metallic structure into consideration [7]. This was improved in ZADUMKIN's works, where the ionic subsystem and its interaction with the electronic one was included, in a theory based on the Gombás model of the metals leading to much better agreement (within 20—30%) with experimental results.

Values of $d\gamma/dT$ contained errors as high as -30 to $+75\%$ for eight metals [7]. A variant was published earlier [43]. These relations contain the

Table I

Surface free energies of elements and alkali haloids
(Elements are ordered according to atomic numbers. Experimental data are
denoted by*, the others are theoretical ones)

Name	Temperature	ergcm^{-2}	Source
Li	180	397	[54]
	180	398	[56]
	180	890	[55]
Be	700	800	[57]
	700	810*	[54]
C	25	3064 (100)	[14]
	25	2170 (110)	[14]
	25	1770 (111)	[14]
Na	−273	290	[9]
	25	170	[9]
	100	186*	[54]
	100	440	[55]
Mg	660	583	[54]
	681	563	[56]
	894	502	[58]
Al	125±75	1140±200*	[8]
	659	865*	[54]
	700	860	[61]
Si	25	2513 (100)	[14]
	25	1781 (110)	[14]
	25	1451 (111)	[14]
	1410	1230*	[60]
K	64	104	[54]
	64	180	[55]
Ca	850	360	[54]
	850	360	[59]
Cr	1547	1590*	[14]
Fe	1410	2320	[14]
	1427	2150*	[14]
	1477	1950*	[57]
Co	1354	1970*	[8]
Ni	1220	1850	[57]
	1250	1850*	[14]
Cu	967±50	1405±25*	[8]
	1047	1670*	[14]
	1050	1670	[57]

Table I (continued)

Name	Temperature	ergcm^{-2}	Source
	1050	1740*	[8]
	1083	1820	[55]
Zn	377	830*	[14]
	420	768*	[54]
Ge	1937	1060	[60]
Rb	39	79	[54]
	39	140	[55]
Sr	770	304*	[54]
	770	304	[59]
Nb	2247	2100*	[14]
	2250	2100	[57]
Mo	2350	1960*	[14]
Ag	25	800	[9]
	702±25	1073±27*	[8]
	907	1140*	[17]
	930	1140	[57]
	960	1140	[55]
Sn	215	680	[57]
Cs	29	65	[54]
	29	110	[55]
Ba	24	710*	[54]
	24	710	[59]
W	1727	2900*	[14]
	1730	2900	[57]
Re	1947±500	2200*	[8]
Pt	1097±200	2340*	[14]
Au	1027	1410*	[7]
	1030± 13	1400±65	[13]
	1040	1370	[62]
	1063	1250	[56]
Hg (liquid)	25	474	[62]
Th	1850	1100	[63]
U	1129	1200	[63]
Alkali haloids (at 25 °C)			
NaCl		114*	[19]
		150*	[9]
		163	[19]
		189	[9]
		124 (100)	[9]

Table I *(continued)*

Name	Temperature	ergcm^{-2}	Source
KCl		98*	[19]
		118	[14]
		145	[19]
		173	[9]
		163 (100)	[9]
KBr		89*	[19]
		126	[19]
KI		85*	[19]
		108	[19]
RbCl		96*	[19]
		125	[19]
RbBr		88*	[19]
		111	[19]
RbI		55*	[19]
		87	[19]

quantities of equation (19) and some others, too. The number of missing nearest neighbours on a unit surface of a polycrystalline material was computed according to earlier works by ZADUMKIN [43—45] as: 1,055 · 10^{16} cm^{-2} (fcc), 0,972 · 10^{16} cm^{-2} (bcc) and 1,640 · 10^{16} cm^{-2} (hcp). These final relationships for γ and $d\gamma/dT$ of liquid metals gave the most perfect agreement with experimental data from all the known theoretical, semi-empirical and empirical formulae [43]. A variation of this method [46], two new quantum mechanical methods [47, 48, 49] a microphysical theory of nucleation [50] and statistical mechanical theories [53—55] should also be mentioned here.

8. *Tabulated literature data for elements and alkali haloids*

A lot of experimental and theoretical methods for the determination of the surface free energy of solids was developed, but there are only relatively few numerical data. A relatively complete collection of data is given in Table I, where experimental and theoretical data of most elements and of alkali haloids is given. Experimental data include those obtained directly and indirectly.

III. Calculation of the surface free energy
from the cohesional pressure

The particles on the boundary of a condensed and a gaseous phase are attracted by the particles inside the condensed phase [1]. This attraction is the result of interaction forces. On the other hand, these forces are in close relation with the heat of sublimation or the heat of evaporation and with other physical characteristics of the condensed phase, namely with cubic expansion α and isothermal compressibility χ [1, 64].

The aim of the present work is to deduce on thermodynamic basis a relationship in good agrement with experiments and connecting the surface free energy of the boundary surface condensed phase/gaseous phase with characteristics of the condensed phase, by measuring the effect of the intermolecular forces. For such a quantity the relatively unknown, so-called "cohesional pressure" was chosen [1] which is a measure of the total effect of the intermolecular forces.

9. *A macrophysical theory of the surface free energy*

Let us consider a condensed phase in whose neighborhood a gaseous phase at pressure P exists, where P is e.g. 1 atm according to the usual experimental conditions. Let us further suppose that the boundary layer is a perfectly homogeneous plain layer of thickness t.

The pressure acting on the boundary layer from the side of the condensed phase is the so-called internal pressure of the condensed phase:

$$B \equiv \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \equiv K - P \qquad (21)$$

where K is the so-called cohesional pressure [1]. According to Maxwell's relationship:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

hence:

$$\left(\frac{\partial S}{\partial V}\right)_T - P = T\frac{\alpha}{\varkappa} - P \qquad (22)$$

where α is the isobar thermal expansion, $\varkappa$ the isothermal compressibility.

The gaseous phase exerts a pressure P on the boundary layer.

It is well known from basic thermodynamics that for a boundary of a body acted upon by pressures P_1 and P_2 a volume change by dV of this body will lead to a free energy change of the system containing this body given by:

$$dF = -(P_1 - P_2)dV. \qquad (23)$$

In the special case $P_1 = P_2$, $dF = 0$ is valid. This condition is fulfilled e.g. if the system investigated is a homogeneous one. From equation (23) if $P_1 - P_2$ is independent of V integrating between $V = 0$ and $V = V_0$ yields:

$$\Delta F = -(P_1 - P_2)V_0. \tag{24}$$

The quantity V_0 in (24) is the volume of the body. For the model discussed in this paper V_0 is the volume of the surface layer:

$$V_0 = \Omega t \tag{25}$$

where Ω is the area of the surface, t being its thickness. From (24) and (25) one obtains

$$\frac{\Delta F}{\Omega} = \gamma = -(P_1 - P_2)t. \tag{26}$$

In the present model $P_1 = B \cong K$ (since $K \gg P$), and $P_2 = 0$ (the internal pressure of the gas is taken as 0):

$$P_1 - P_2 = T\frac{\alpha}{\varkappa} \equiv K. \tag{27}$$

Finally:

$$\gamma = T\frac{\alpha}{\varkappa}t \equiv Kt. \tag{28}$$

In practical applications of formula (28) the thickness t of the boundary layer is needed. In lack of a general theoretical expression as a first approximation the assumption of a monomolecular boundary layer seems to be satisfactory, so that its thickness would be the distance of the lattice layers in the crystal. For body-centered and face-centered cubic crystals this latter value equals lattice constant a, while in crystals with a more complicated structure it is a quantity easy to obtain from geometrical data of the unit cell.

Consequently, in this approximation the surface free energy of crystals is obtained from formula

$$\gamma = K \cdot a = T\frac{\alpha}{\varkappa}a \tag{29}$$

where a is the distance between the lattice layers.

In the case of liquids more complicated considerations are needed to obtain the t values.

10. *Calculation of surface free energies at* 25 °C

On the basis of the approximation (29) of relationship (28) the surface free energy of some materials was calculated restricted to materials whose relevant data (α, $\varkappa$, a) have already been collected or may be calculated from the literature reviewed [62, 64—68]. The calculations are compiled in Table II, Chapter 16.

The solid materials in the table have cubic symmetry. In fcc ionic crystals the distance between two consecutive (hoo), (oko), (ool) planes is half the lattice constant, so that in equation (28) the half of the lattice constant a was taken for the value of t in ionic crystals, while in other cases the lattice constant itself was taken into account. For liquid mercury assuming a simple cubic structure the relationship

$$a = \left(\frac{V}{N}\right)^{1/3} \tag{30}$$

was used. (Here V is the molar volume and N is the Avogadro number.)

The surface free energies obtained from relationship (29) are seen (in spite of the simplicity of the consideration applied) to be in relatively good agreement with the literature data, irrespective of the nature of forces holding the crystal lattice together.

Except the case of ionic crystals, theoretical values of γ by assuming $t = a$ are generally too low. This fact suggests that t is larger than "a", that is, the surface is not a simple monomolecular layer, but has a more complicated structure.

In ionic crystals the distortion of the lattice near the surface is probably of the opposite nature. Value "a" for NaCl is 2,81 Å, which, because of the polarization of the large Cl^- ions, sinks to 2,66 Å for Na^+ ions and grows to 2,86 Å for Cl^- ions in the vicinity of the surface [9], so that in average, value of "a" diminishes by 0,05 Å, i.e., by some 2%. This fact may be connected with our too high values obtained by assuming $t = a/2$.

11. *Discussion of the relation for homogenous surface layer*

Relationship (29) is formally the same as the BAYDOV and KUNIN equation [19] deduced by the authors to describe the surface tension of liquids on the base of assumptions made for liquids (existence of critical point, disappearance of surface tension at the critical point) further, on others of a rather limiting nature (e.g. α an d β are independent of pressure and temperature). Also the DEMCHENKO relation is of similar nature, there the pressure of the electron gas of metals is substituted for the cohesional pressure [31].

These facts show that the validity of (29) was already known for special cases (liquids with special properties and electronic motion in metals).

12. *The sublayer model*

Upon approximating the crystal surface from inside, a crystal particle (atom, ion, electron) in a plane with a given distance from the surface is in interaction with ever less particles above its layer, so that its binding properties will differ more and more from the binding properties of the same particles on the surface (assuming it to be an ideal plane), where only the gas phase is in connection with the crystal. Thus it follows that the surface layer of the crystal, whose properties differ from the bulk, is much thicker than the atomic layer made up of the particles on the surface.

Let us decompose the surface layer of the crystal (of thickness t) into a finite number of sublayers inside of which the matter is a homogenous one. Let us denote the thickness of such a sublayer by t_i.

If the surface layer consists of sublayers, then, according to the additivity of free energy, γ value can be obtained by addition from the γ_i values of the sublayers. Accordingly, from (26) we have

$$\gamma = \sum_{i=1}^{n} (P_i - P_{i-1})t_i \tag{31}$$

where P_i is the pressure acting on sublayer i from upside while P_{i-1} is the pressure from downside. Substituting relationship (27) in (31) the value of γ can be calculated in principle exactly from the data characterizing the bulk material

$$\gamma = K_1 t_1 + \sum_{i=2}^{n} (K_i - K_{i-1})t_i . \tag{32}$$

The model described is a direct generalization of the model previously used in this paper, where the surface layer was considered to consist of a single sublayer.

13. *The continuum model*

According to the model described in the previous chapter, if the surface layer is a continuum, and z the co-ordinate perpendicular to the surface, the contribution to the free energy by layers bounded by planes spaced at z and $z + dz$ from the surface is

$$d\gamma(z) = \left(\frac{\partial P}{\partial z} dz \right) t . \tag{33}$$

Integrating from $z = 0$ to $z = \infty$ one has

$$\gamma = \left[\int_0^\infty \frac{\partial P}{\partial z} dz \right] t = [P(d) - P(0)]t = (B + p)t = Kt \tag{34}$$

where

$$P(o) = -P \tag{35}$$

$$P(\infty) = B. \tag{36}$$

Relationship (34) agrees with (31) for continua, and results from it by the limit

$$t_i \to 0, \quad n \to \infty.$$

14. *Relative displacement and the change of the internal pressure in the neighbourhood of the surface (assumptions)*

According to those told earlier the distances t_i between atomic layers rapidly converge to the value t in the bulk of the crystals, so that the relative displacement δ_i, defined by the relationship

$$\frac{t_i}{t} = 1 + \delta_i \tag{37}$$

is a numerical series of monotonically and rather fast decreasing nature, tending to zero for $i \to \infty$.

The value of internal pressure B_i pulling the sublayers inside is similarly a changing quantity. Clearly the B_i values consist of a numerical sequence of monotonically increasing nature tending to value B characteristic of the bulk crystal. This is seen from the fact that the layers made up of the particles in the neighbourhood of the surface are farther from the plane made up of the particles immediately below them than the layer inside the crystal from the layer immediately below it because the value of the internal pressure pulling inside the crystal layers is smaller in the vicinity of the surface than deep in the crystal. This way, the change of B_i is opposite to that of t_i.

Quantities t_i and B_i would need rather lengthy calculations on structural basis. Instead, however, an approximate functional relationship described below may be applied.

The conditions mentioned for the numerical sequence δ_i are satisfied by the assumption

$$\delta_i = q^{i-1} \cdot \delta_1 \tag{38}$$

where the value of q is in any case much below 1.

For sequence B_i, using the widespread exponent approximation and taking reasons of computational technics relation into account:

$$B_i = B \left(\frac{t}{t_i} \right)^n \tag{39}$$

where n is a positive number not specified as yet.

Assumptions (38—39) make possible to calculate δ_i and B_1 in relationship (32).

Neglecting details of deduction the final result is:

$$\gamma_i = Bd^n \, \frac{1}{(1 + \delta_1 q^{i-1})^{n-1}} \left[1 - \left(\frac{1 + \delta_1 q^{i-1}}{1 + \delta_1 q^{i-2}} \right)^n \right]. \tag{40}$$

15. *Approximate solution of the sublayer model*

From relation (40) using MacLaurin's expansion

$$(1 + x)^m \cong 1 + mx + \frac{m(m - 1)}{2} x^2 + \dots \tag{41}$$

and taking only linear members into account:

$$\gamma_i = Bt_n(1 - q)\delta_1 q^{i-2} \tag{42}$$

hence:

$$\sum_{i=2}^{\infty} \frac{\gamma}{B_i} = n\delta_1. \tag{43}$$

Since according to (42):

$$\frac{\gamma}{Bt} = \frac{1}{(1 + \delta_1)^{n-1}} \cong 1 - (n - 1)\delta_1 = 1 - n\delta_1 + \delta_2 \tag{44}$$

the final expression from (44) and (43) will be:

$$\gamma = Bt(1 + \delta_1) = Bt_1. \tag{45}$$

In relationship (45) the exponent "n" vanishes. In this approximation the sublayer model will give a relatively higher γ value than calculated in the first part for cases where surface cells expand. So, if $\delta_1 = 0{,}11$ [13, 69—70]:

$$\gamma = 1{,}11 \, Bt \tag{46}$$

For the ionic crystals, on the contrary, $\delta_1 = -0{,}02$ [9], so

$$\gamma = 0{,}98 \, Bt \tag{47}$$

16. *Control by experimental data*

Calculation results according to Eqs (29) and (46—47) are given in the following Table II. In the last column of the table the arithmetical averages of values collected in Table I are given.

<div align="center">

Table II

Surface free energies of some cubic materials at 25 °C

</div>

Symbol	According to (29) ergcm⁻²	According to (46) and (47) ergcm⁻²	Average of literature data ergcm⁻²
Na	175	204	230
Al	606	673	1140±200 (40—150 °C)
C (diamond)	1640	1920	2335
Si	1158	1286	1915
NaCl	243	238	148
KCl	197	193	140
KBr	190	186	108
KI	121	119	97
RbCl	126	124	111
RbBr	141	138	100
RbI	111	109	72
Hg (liquid)	427	474	474

IV. Calculation of the surface free energy of the solid from the surface free energy of the liquid

Another way for calculating the surface free energy of solids is to connect this quantity to the experimentally easily accessible surface tension of the liquid [9].

One of the best of these methods is the theory of ZADUMKIN and KARASHEV [71] making possible the approximate evaluation of the surface free energy of the solid at its melting point. As far as it is known, this theory has not been applied for practical computations so far. One of the main reasons for this is possibly the fact that not all the quantities connected by this theory to the surface free energy of the solid are easy compute.

The aim of the present work is to eliminate this difficulty and to perform concrete calculations to show that this modified theorem is in agreement with the experimental data.

17. The Sherbakov and the Zadumkin—Karashev theories

The surface free energy of a solid is given, according to MACLACLAN [33] by the relationship:

$$\gamma = \frac{L_s}{KN^{1/3}} \left(\frac{D}{A}\right)^{2/3} = \frac{L_s}{KN^{1/3}} V^{-2/3} \tag{48}$$

4*

where the heat of sublimation is L_s, the density D, the atomic weight A, Avogadro's number N, the molar volume V, and K is a factor characteristic of the structure of a value between 4.4 and 9. Then in the case of a cubic solid, the molar surface free energy $\gamma V^{2/3} N^{1/3}$ that belongs to the surface occupied by mole of matter in the form of a monolayer is $(1/K)$ times the molar heat of sublimation:

$$\gamma V^{2/3} N^{1/3} = \frac{1}{K} L_s . \tag{48a}$$

If the formula (48) is assumed to be valid for liquids as well, further if in the place of L_s the heat of evaporation L_v is written, and if the value of K is the same in the liquid and solid states, the relationship

$$\gamma_s = \gamma_L \left(\frac{V_s}{V_L} \right)^{-2/3} \left(\frac{L_s}{L_v} \right) \tag{49}$$

will be obtained from (48) [36]. Here V_s and V_L are the molar volumes in the solid and liquid states, respectively.

Beyond this theory of structural character a theory applicable for the characterization of the solid-liquid surface was developed by ZADUMKIN and KARASHEV [71] too. This will be outlined below in a reviewed form.

Let us assume that all the particles of bodies 1 and 2 in contact interact only with their nearest neighbours. Let the number of these particles denoted by f_1 in body 1 and the number of the nearest neighbours of a particle on the surface of body 1, which neighbours are on the surface of body 2 be denoted by f_{12} and finally the difference between the number of the nearest neighbours inside body 1 and on its surface denoted by Δf_1. (Similar notations are used for the body 2.)

Let us assume, further, that the heat of sublimation L_s for a particle is uniformly distributed between its f bonds with its nearest neighbours (local co-ordination approximation) so that the amount of energy for such a bond is $2L_s/f$. (Factor 2 accounts for the fact, that all bonds are taken twice into consideration.)

If the number of the particles for unit area on surfaces of bodies 1 and 2 are n_1 and n_2 respectively, than in this approximation relations

$$\gamma_1 = \frac{\Delta f_1}{f_1} L_1 n_1 \tag{50}$$

$$\gamma_2 = \frac{\Delta f_2}{f_2} L_2 n_2 \tag{51}$$

will be obtained for surface free energies of bodies 1 and 2.

We note, too, that according to relationships

$$n_1 = K_1 V_1^{-2/3} \tag{52}$$

$$n_2 = K_2 V_2^{-2/3} \tag{53}$$

where the values of constants K_1 and K_2 are determined by the structure, and assuming

$$\frac{\Delta f_1}{f_1} K_1 = \frac{\Delta f_2}{f_2} K_2 \tag{54}$$

(50) and (51) lead just to equation (49).

Further, in the local co-ordination approximation according to relationship

$$K = \frac{L_s}{\gamma N^{1/3}} V^{2/3} \tag{55}$$

value of K can be calculated.

Let us denote the distance between the nearest neighbours in solid body 1 by r_1 and in liquid 2 by r_2, and the distance between particles on the surface of body 1 and their nearest neighbours in body 2 by r_{12}. All the bonds between the nearest neighbours may be regarded as harmonic oscillators with certain energies, averagely spaced from the particle under consideration at r_1, r_2 and r_{12}, their circular frequencies being ω_1, ω_2, ω_{12} respectively.

Then, according to the well-known relationship of Mott:

$$\omega_1 = \omega_2 \, e^{\frac{L_0}{3RT_0}} \tag{56}$$

where L_0 is the heat of melting, T_0 is the temperature of melting. Further, according to the theory of Frenkel, the heat of melting is uniformly distributed between the bonds upon increasing their energies, so that

$$\frac{1}{2} m\omega_2^2 (r_2 - r_1)^2 \equiv u(r_2) = \frac{L_0}{(f_2/2)} \tag{57}$$

becomes valid. Relationships (56) and (57) yield ω_1 and ω_2.

ZADUMKIN and KARASHEV have postulated the validity of relationship

$$\omega_{12} = (\omega_1 \omega_2)^{1/2} \tag{58}$$

Introducing the notation

$$\delta \equiv \frac{r_{12} - r_1}{r_2 - r_1} \tag{59}$$

and taking into consideration

$$u(r_{12}) = \frac{1}{2} m\omega_{12}(r_{12} - r_1)^2 \qquad (60)$$

equation (60) leads to:

$$u(r_{12}) = \frac{2L_0}{f_2} \delta^2 e^{-\frac{L_0}{3RT_0}}. \qquad (61)$$

On the basis of the Dupré equation for the work of adhesion (W_a):

$$Wa = [u_{12} + u(r_{12})]\bar{\Delta f}\bar{n} \qquad (62)$$

on the other hand, obviously:

$$Wa = \gamma_1 + \gamma_2 - \gamma_{12}. \qquad (63)$$

These equations are valid in the local-co-ordination approximation, where the average number of missing bonds per particle is $\bar{\Delta f}$ and the average number of particles is $\bar{n}$ on 1 cm^2 of surface.

Beyond approximations (56) and (58) also the following ones were used:

$$\bar{n} = (\bar{n}_1\bar{n}_2)^{1/2} \qquad (64)$$

$$\bar{\Delta f} = (\Delta f_1 \Delta f_2)^{1/2} \qquad (65)$$

$$f_{12} = (f_1 f_2)^{1/2} \qquad (66)$$

Quantity u_{12} in relationship (62) is the basic energy connected with the interaction between particles 1 and 2 at a distance r_1. This is the arithmetic average of interaction energies. Using these relationships the following formula may be deduced:

$$\gamma_1 + \gamma_2 - \gamma_{12} = \left[\left(\frac{L_1}{f_1} + \frac{L_2}{f_2}\right) + 2\frac{L_0}{(f_1 f_2)^{1/2}} \delta^2 e^{\frac{L_0}{3RT_0}}\right]\left(\gamma_1 \frac{f_1}{L_1} \gamma_2 \frac{f_2}{L_2}\right)^{1/2} =$$
$$= \left[\left(\frac{L_1}{f_1}\right)^{1/2} \bigg/ \left(\frac{L_2}{f_2}\right)^{1/2} + \left(\frac{L_2}{f_2}\right)^{1/2} \bigg/ \left(\frac{L_1}{f_1}\right)^{1/2} + 2\frac{L_0}{(L_1 L_2^{1/2})} \delta^2 e^{\frac{L_0}{3RT_0}}\right](\gamma_1\gamma_2)^{1/2}. \qquad (67)$$

From this formula a quadratic equation is obtained for (γ_1/γ_2) and from its solution, upon using notations

$$b = -\left[\frac{(L_1/f_1)^{1/2}}{(L_2/f_2)^{1/2}} + \frac{(L_2/f_2)^{1/2}}{(L_1/f_1)^{1/2}} + 2\frac{L_0}{(L_1 L_2)^{1/2}} \delta^2 e^{\frac{L_0}{3RT_0}}\right] \qquad (68)$$

$$c = 1 - \frac{\gamma_{12}}{\gamma_2} \qquad (69)$$

we get:

$$\frac{\gamma_1}{\gamma_2} = \left[-\frac{b}{2} + \sqrt{\left(\frac{b}{2}\right)^2 - c} \right]^2. \qquad (70)$$

Equations (68—70) are the general solutions of the problem stated, that is they are suitable for the calculation of the ratio of the surface free energies of two bodies containing the same material. Alternatively, knowing these latter quantities they may be used for the calculation of their interface energy γ_{12}.

18. *Calculation formulae of the Zadumkin—Karashev theory*

For relating surface free energies γ_1 and γ_2 of a solid and a liquid, it was assumed:

$$\frac{L_1}{f_1} = \frac{L_2}{f_2}; \;\; (L_1 L_2)^{1/2} \simeq L_1; \;\; \delta^2 = \left(\sqrt{\frac{1}{2}} \cdot 1\right)^2 = \frac{1}{2}. \qquad (71)$$

Relation (71) simplifies "b" into:

$$b = -2\left(1 + \frac{1}{2}\frac{L_0}{L_v} e^{\frac{L_0}{3RT_0}}\right) \qquad (72)$$

and, on this basis, from (70) we get:

$$\frac{\gamma_1}{\gamma_2} = \left[\left(1 + \frac{1}{2}\frac{L_0}{L_v} e^{\frac{L_0}{3RT_0}}\right) + \sqrt{\frac{L_0}{L_v} e^{\frac{L_0}{3RT_0}} + \frac{1}{4}\left(\frac{L_0}{L_v}\right)^2 e^{\frac{2L_0}{3RT_0}} + \frac{\gamma_{12}}{\gamma_2}} \right]^2. \qquad (73)$$

Denoting:

$$x \equiv \frac{1}{2}\frac{L_0}{L_v} e^{\frac{L_0}{3RT_0}} \qquad (74)$$

and, quantity x being small we have:

$$x^2 \cong 0 \qquad (75)$$

hence:

$$\frac{\gamma_1}{\gamma_2} = \left[(1 + x) + \sqrt{+ 2x + \frac{\gamma_{12}}{\gamma_2}} \right]. \qquad (76)$$

Applying (68) for the grain boundaries of a polycrystalline material, the equation $L_1 = L_2$ will be satisfied, in addition to (71), further $L_s = 0$, so that

$$b = -2 \qquad (77)$$

Replacing it into (70) we have:

$$\frac{\gamma_1}{\gamma_2} = \left[1 + \sqrt{\frac{\gamma_{12}}{\gamma_2}}\right]^2 \tag{78}$$

In using (76) it is necessary to know the value of the free energy of the boundary surface (that is, the free energy on the border of two condensed phases), which may be obtained only by experiment, and its determination is as difficult as that of γ_1.

This difficulty has been lifted by the authors by taking for γ_{12}/γ_2 of the solid-liquid surface an average value 0,075 on the basis of the experimental data scattering between 0,05 and 0,10. Using further $L_0/L_v = 0,04$ and $Q_0/3RT_0 = 0,45$ we have $x = 0,0314$ so that on the basis of (76):

$$\frac{\gamma_1}{\gamma_2} = (1,0691)^2 \simeq 1,15. \tag{79}$$

19. First modification of the Zadumkin—Karashev theory

Perhaps the greatest disadvantage of this theory is to need for the calculation of the surface free energy of a solid the surface free energy of the solid-liquid interface, equally difficult to determine.

This problem may be resolved in several ways.

The simplest method is to replace (76) by (50) and (51) serving as bases of the theory and used in the course of the deduction. Then using (50—53) leads to the formula:

$$\frac{\gamma_1}{\gamma_2} = \left(\frac{\Delta f_1}{f_1} n_1\right) \Big/ \left(\frac{\Delta f_2}{f_2} n_2\right) \tag{80}$$

which is more general than the Sherbakov equation (49). It only involves quantities easy to determine from the knowledge of the structure, further no approximations are made in deduction.

Values of $\Delta f/f$ have been published by ZADUMKIN for the three more common metallic structures [7].

20. Second modification of the Zadumkin—Karashev theory

The estimation of quantity γ_{12} by a relationship (44) valid for a liquid wetting the surface of the solid is a method of a somewhat more complicated nature. This basic formula may be written in the form:

$$0 < \frac{\gamma_{12}}{\gamma_2} \leq \frac{\gamma_1}{\gamma_2} - 1 \, . \tag{81}$$

It is of no use for calculating the value of γ_{12} from values of γ_1 and γ_2, knowing these latter, however, the limits of γ_{12} can be established. Further it appears that using the sign of equality in (81) is a most plausible approximation. According to the statement of ZADUMKIN and KARASHEV, as already discussed, γ_{12}/γ_2 is between 0,05 and 0,10, and its average is roughly 0,075. At the same time γ_1/γ_2 has generally a value approximately 1,07, so that the upper limit of γ_{12}/γ_2 is, according to (81) equal to 0,07. From these it is clear that γ_{12}/γ_2 hits in fact, its upper limit.

On this basis the solid–liquid interface is described by

$$\frac{\gamma_{12}}{\gamma_2} = \frac{\gamma_1}{\gamma_2} - 1 \; . \tag{82}$$

Using approximation (82) in (70) and notations in (68):

$$\frac{\gamma_1}{\gamma_2} = \frac{4}{b^2} \tag{83}$$

Using only (71) from the approximation of ZADUMKIN and KARASHEV on the basis of (72) we get

$$\frac{\gamma_1}{\gamma_2} = \frac{1}{(1-y)^2} \tag{84}$$

where

$$y = \frac{L_0}{(L_s L_v)^{1/2}} \, \delta^2 e^{\frac{L_0}{3RT_0}} \; . \tag{85}$$

The quantity δ^2 is expressed by experimental data of the distance between the nearest neighbours.

With notations

$$r_1 = 2R_1 \tag{86}$$

$$r_2 = 2R_2 \tag{87}$$

$$r_{12} = R_1 + R_2 \tag{88}$$

in definition (59), where R_1 and R_2 are the values of the metallic radii in the solid and liquid phases, respectively, formulae

$$\delta = \frac{R_2 - R_1}{2(R_2 - R_1)} = \frac{1}{2} \qquad (R_2 \neq R_1) \tag{89}$$

and

$$\delta = 1 \qquad (R_2 = R_1) \tag{90}$$

are valid. Using the geometrical average of the two values:

$$y = \frac{1}{2} \frac{L_0}{(L_s L_v)^{1/2}} e^{\frac{L_0}{3RT_0}}$$ (90a)

To check relationship (84) let us use the average value 0,0314 already used for x. With this, from (84)

$$\frac{\gamma_1}{\gamma_2} = 1,0658$$ (91)

in good agreement with the average values used in (79).

Another problem was to obtain values of γ at lower temperature than the melting point. The solution of this question will be attempted in the manner described in DEGRAS's lecture [8], namely that the graph of function $\gamma(T)$ of copper, as it can be seen from the figure published there, has a similar shape in the solid and in the liquid phases. In both cases γ decreases with the temperature approximately in a linear way, and the direction tangent to this line is essentially the same in both phases, that is, as a good approximation

$$\frac{d\gamma_1}{dT}(T_0) = \frac{d\gamma_2}{dT}.$$ (92)

The validity of this equation will be assumed in the case of other materials, too. This involves a relative small error, since, in general, the whole correction from the temperature dependence is, at most, ten to twenty per cent of the value of γ. Value of γ may then be calculated at arbitrary temperatures from relationship

$$\gamma_1(T) = \gamma_1(T_0) + \frac{d\gamma_2}{dT}(T_0)(T - T_0).$$ (93)

Applying relationships (79), (93) and (84), (90a) (93) values of γ have been calculated for a number of solids at temperatures mentioned in the references. Results of these calculations have been compiled in Table III.

From the data of this table it can be concluded that the agreement with the literature data is, in general, more exact on the basis of (84) than in using formula (79).

21. *Standard values of the surface free energies*

Standard values of the surface free energies have been calculated for most elements in the periodical system according to formula (93). Results are given in Table IV.

Table III

Calculated and published values of the surface free energies of metals

Name	Data				Surface free energy (ergcm^{-2})			
	t_0 °C	L_o	L_s	t °C	According to		Literature	
		(Kcal/mole)			(79)	(84)	data	reference
		[72]	[72]					
Li	180	0,723	38,25	180	458	408	397	[54]
Na	99,7	0,622	25,79	99,7	220	197	186	[54]
K	63,6	0,544	21,34	63,6	116	105	104	[54]
Rb	39	0,560.	19,54	39	90	81	79	[54]
Cs	28,5	0,510	18,66	28,5	71	64	65	[54]
Be	1278	2,800	76,24	700	1327	1248	810	[54]
Mg	650	2,140	34,43	650	647,5	616	583	[54]
Ca	850	2,07	39,48	650	387,5	364	360	[54]
Sr	770	2,200	36,89	770	321,2	316	304	[54]
Ba	710	1,830	39,90	710	257,8	239	267	[54]
Nb	1950	6,40	175,33	1950	2247	2146	2100	[7]
Cr	2000	3,30	89,16	1547	1892	1734	1590	[7]
Mo	2600	6,60	150,63	2350	2437	2255	1690	[7]
W	3390	8,42	201,99	1727	2928	2727	2900	[7]
Re	3170	7,9	177,21	1947	3072	2867	2200	[14]
Fe	1530	3,67	94,18	1477	2097	1931	1950	[7]
Co	1492	3,64	97,72	1354	2197	2019	1970	[14]
Ni	1452	4,21	98,24	1250	2252	2112	1850	[14]
Pt	1771	4,7	131,97	1247	2067	1903	2340	[14]
Cu	1083	3,12	79,34	1097	2082	1958	2200	[14]
Ag	960	2,7	66,74	960	1069	988	1140	[7]
Au	1063	2,955	82,94	1063	1173	1076	1250	[7]
Zn	419	1,765	30,57	377	873	870	830	[7]
Al	660	2,55	76,27	125	1048	973	1140	[7]
Th	1850	3,74	133,74	1850	1357	1227	1100	[63]
U	1129	3,7	111,83	1129	1725	1582	1200	[63]

Table IV

Standard values of the surface free energy of elements at 25 °C

Atomic number	Element	Surface free energy ergcm^{-2}	Atomic number	Element	Surface free energy ergcm^{-2}
3	Li	430	44	Ru	3153
4	Be	1354	45	Rh	3222
11	Na	205	46	Pd	1784
12	Mg	832	47	Ag	1110
13	Al	1043	48	Cd	659
14	Si	1182	49	In	593
19	K	109	50	Sn	566
20	Ca	420	51	Sb	536
21	Sc	1273	52	Te	256
22	Ti	1546	55	Cs	65
23	V	2104	56	Ba	304
24	Cr	1854	57	La	758
25	Mn	1341	60	Nd	982
26	Fe	2558	63	Eu	307
27	Co	2248	71	Lu	1144
28	Ni	2297	72	Hf	1785
29	Cu	1623	74	W	2918
30	Zn	900	75	Re	3222
31	Ga	758	76	Os	3064
32	Ge	912	77	Ir	2833
33	As	242	78	Pt	2057
34	Se	126	79	Au	1180
37	Rb	82	81	Tl	513
38	Sr	360	82	Pb	501
39	Y	1150	83	Bi	456
40	Zr	1653	90	Th	1320
41	Nb	2566	92	U	1822
42	Mo	2690			

Summary

New calculation methods of the surface free energy γ_s of solids have been developed. A new presentation is given of basic concepts and literature data. A formula has been derived from thermodynamic, and another from structural considerations. Both give results in fair agreement with test data. These have been used to calculate surface free energies for most elements of the periodic system, shown here in a tabulated form.

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