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# MATHEMATICAL MODELING OF PROCESSES IN THE SURFACE LAYERS OF SOLIDS FOR INTERFACIAL INTERACTIONS

The mathematical model to determine the physical constants on the boundary of the metal and inert gas environment developed based on the basic equations of surface physics and thermodynamics of nonequilibrium processes. These physical constants are included into the state equation, taking into account internal mechanical stresses caused by redistribution of conduction electrons. Using the experimental values of surface tension and energy of the contracted media, we determined physical characteristics of the surface layer, in particular on the boundary of the aluminium (germanium) and the inert gas environment.

Keywords: modeling, mechanical stress, mechanoelectric processes, surface layer.

# МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ ПРОЦЕСІВ У ПРИПОВЕРХНЕВИХ ШАРАХ ТВЕРДИХ ТІЛ ЗА МІЖФАЗНОЇ ВЗАЄМОДІЇ

На основі базових рівнянь фізики поверхні та термодинаміки нерівноважних процесів розроблено математичну модель для визначення фізичних постійних на границі металу з інертним газовим середовищем, що входять у рівняння стану, з урахуванням внутрішніх механічних напружень, зумовлених перерозподілом електронів провідності. З використанням експериментальних значень поверхневих натягу та енергії для контактуючих середовищ визначено фізичні характеристики поверхневого шару, зокрема на межах алюміній(германій) – інертне газове середовище.

Ключові слова: моделювання,механічні напруження, механоелектричні процеси, приповерхневий шар.

## Introduction

The traditional approach of quantitative description of the interfacial interactions usually involves finding energy options of the interfacial interaction and calculation physical characteristics of surface layers. These physical characteristics are characterize the spatial (coordinate) distribution of charges, mechanical stress inside double layer, thickness of interacting phases, surface charge, etc. Also they interconnect state parameters in the relevant state equations. It is clear that adequate values of the such type of characteristics should match the main real energy characteristics of the surface layers, such as the surface tension $\sigma_h$ and the surface energy $\gamma$.

For the solution this problem is usually used algorithmic approach of imitative simulation. The disadvantage of this approach is the some ambiguity of the values of the obtained physical parameters of materials with reliable values of energy characteristics ($\sigma$, $\gamma_h$).

We use a slightly different approach and solve the problem of determining the energy characteristics $\sigma$ and $\gamma_h$ **formally**.

The aim of this work is to develop a mathematical model to determine the physical constants of materials in state equations, taking into account internal mechanical stresses caused by the redistribution of

the conduction electrons. This model based on the principles of surface physics and thermodynamics of nonequilibrium processes without the use of cumbersome approaches of statistical physics.

## 1. Theoretical preconditions for mathematical modeling
## of charges distribution and mechanical stress

**Research object.** As the model object of research we choose a defect-free uniform metallic deformed elastic sphere of radius *R*. The research subject is the macroscopic correlations of surface physics and thermodynamics of nonequilibrium processes, which used to determine surface tension and energy.

We formulate one-dimensional correlations for modeling mechanical stress and redistribution of electric charges (free for metals and related to semiconductor or insulator) with r coordinate, where r – radius vector of a point in a spherical coordinate system. The sphere ($V_m$ area, r < R) is placed in a uniform inert gas environment ($V_c$ area, r > R), which pressure is equal p = 100 kPa. The electric double layer generated conduction electrons and metal ions and located on the sphere surface on the spherical ring, which thickness *h* (*R > r > R-h*) [1].

We simulate the metal sphere using two-component homogeneous solid environment consisting of two continuous continuums: the conduction electrons and grid ions, for which carried out the hypothesis of continuity and local thermodynamic equilibrium [2,3].

The electric double layer is formed on the border of metal (the sphere) and external inert environment. This layer corresponds to the gradient of the electron density in the small border layer (thickness is less than 20 nm) [1]. During this process the electric shells of the thin border atoms are deformed. These deformations are manifested in the change of grid parameters. Based general ideas surface physics and continuum mechanics we put the deformations of atoms in correspondence to the mechanical stresses. Also we consider the distribution of electrical charges and mechanical stress are interrelated. To find the distribution of electrical charges and mechanical stress in a thin surface layer of metal we use Poisson's equation (for electrical charges) of the balance of items of solids and determination of surface tension and energy.

*Selecting state parameters.* To describe mechanoelectric distributions in the sphere we consider two pairs of parameters of the thermodynamic state : a) for redistribution of electrical charges – concentration of electrons $C_e$, ions $C_{ion}$ and the chemical potentials Me, $M_{ion}$ corresponding them (concentrations are dimensionless, dimension of chemical potentials – J / kg); b) for the stressed state – tensors of deformation $\hat{e}$ and mechanical stresses $\hat{\sigma}$ [2–5].

These settings we substitute in the extended Gibbs equation for state function *U* - is internal energy ([U] = J / kg) $\hat{\sigma}$ [2–4]:

$$dU = TdS + \frac{1}{\rho} \sum_{i,j=1}^{3} \sigma_{ij} \cdot de_{ij} + M_e dC_e + M_{ion} dC_{ion}. \qquad (1)$$

Where S, T-entropy and temperature of the local element respectively ([S] = J • (kg*K)$^{-1}$, [T] = K); $\rho$ – specific density of material ([$\rho$] = kg • m$^{-3}$); $e_{ij}$, $\rho_{ij}$ – components tensors of stresses $\hat{\sigma}$ and deformations $\hat{e}$ (*i, j* = 1, 2, 3; [$\sigma_{ij}$] = Pa). Given that the mass of the electron by three orders less than the mass of the ion, we can take $dC_{ion} \approx 0$.

Then we multiply and divide expression $M_e \cdot dC_e$ by a constant $z_e$, where $z_e$ – electric charge of unit mass of conduction electrons ([$z_e$] = Cl • kg$^{-1}$). Result of multiplication is $C_e \cdot z_e = \omega = \omega_V/\rho$; where $\omega$, $\omega_V$ – specific electric charges of local element calculated per unit mass and unit volume respectively: ([$\omega$] = Cl • • kg$^{-1}$, [$\omega_V$] = Cl • m$^{-3}$). The relation $M_e/z_e = \Phi = \Phi_0 + \varphi$ is called modified chemical potential of the conduction electrons (MCPCE) ([$\Phi$] = [$\varphi$] = B).

In this case, the Gibbs equation (1) can be written (including replacement of multiplication result $M_e \cdot dC_e = \Phi \cdot d\omega$) for the free energy $F = U - TS - \omega\Phi$) in the form of [2–4]:

$$dF = -SdT + \frac{1}{\rho} \sum_{i,j=1}^{3} \sigma_{ij} \cdot de_{ij} + \omega d\Phi. \qquad (2)$$

From (2) follow the state equation in general form:

$$S = -\left(\frac{\partial F}{dT}\right)\Bigg|_{e_{ij},\Phi=const} \quad ; \quad \sigma_{ij} = \rho\left(\frac{\partial F}{de_{ij}}\right)\Bigg|_{T,\Phi=const} \quad ; \quad \omega = \rho\left(\frac{\partial F}{d\Phi}\right)\Bigg|_{e_{ij},T=const} . \quad (3)$$

In the next we confine the isothermal case and we aren't considering the state equation for the entropy. Methods for formulating state equations based on relations (2), (3) are shown, for example, in [2–4]. With this purpose usually functional for free energy F is decomposed in the Taylor series on the state parameters in the neighbourhood of the specified equilibrium state. After that decomposition of the functional limited of second component of decomposition is substituted in (3). Then we are get the linear state equations.

Using the principles of the explained technique, according to (2) and (3), we are obtain linear state equations for tensor components of mechanical stress $\sigma_{ij}$ and density of electric charge $\omega$ [3-5]:

$$\sigma_{ij} = \left(\left(K - \frac{2}{3}G\right)e - \alpha_t K \cdot \Delta T - Kb\phi\right)\delta_{ij} + 2Ge_{ij}, \quad (4)$$

$$\omega_V = \rho\omega = \rho C_\phi(\phi - \gamma_t \cdot \Delta T) + bKe. \quad (5)$$

Where $\delta_{ij}$ – Kronecker symbols; $e = e_{ii}/3$ – the first invariant of deformations tensor; $\varphi = \Phi - \Phi_0$ – rejections of the modified chemical potential $\Phi$ of conduction electrons from its equilibrium value $\Phi_0$ in the volume of the body away from the surface; $\Delta T = T - T_0$ – temperature changes ($T_0$ – temperature values in the initial equilibrium state); K, G – factors of the comprehensive compression and shear; $C_\varphi$ – specific capacitance; $b$ – electrostrictive coefficient of volume expansion; $\alpha_t$ – temperature coefficient of volume expansion; $\gamma_t$ – temperature coefficient of changes MCPCE.

***Galvani potential.*** To analyze the redistribution of the conduction electrons of the neighbourhood of the metal surface we are considering Galvani potential (difference of internal electrical potentials - $\Delta\psi$). This potential defines difference of the electrical potentials between two points in different phases [6]. These phases can be two different solids (eg, two mechanically connected metals, metal and semiconductor, etc.).

Electrochemical potential $\bar{\mu}_e$ for conduction electrons in the metal including definition of $\Phi$ can be represented as [6,7]:

$$\bar{\mu}_e = z_e(\Phi + \Psi), \quad (6)$$

where $\Psi$ – the potential of the electric-field intensity (scalar electric potential). $\psi = \Psi - \Psi_0$ - deviations of potential $\Psi$ from its original equilibrium value $\Psi_0$ (potential $\Psi$ is defined up to a constant [6]).

If two phases $\alpha$ and $\alpha$ have the one common charged particle (for example, electron), then their electrochemical potentials $\bar{\mu}_{e\alpha}$ and $\bar{\mu}_{e\beta}$ are aligned [6] and as the result we get the ratio:

$$\bar{\mu}_{e\alpha} = z_e(\Phi_\alpha + \Psi_\alpha), \quad \bar{\mu}_{e\beta} = z_e(\Phi_\beta + \Psi_\beta), \quad \bar{\mu}_{e\alpha} = \bar{\mu}_{e\beta}, \quad \Phi_\alpha + \Psi_\alpha = \Phi_\beta + \Psi_\beta,$$

$$\Delta\psi = \Psi_\beta - \Psi_\alpha = \Phi_\alpha - \Phi_\beta = -\Delta\phi, \quad \Delta\psi + \Delta\phi = 0, \quad \Delta(\psi + \phi) = 0,$$

$$\Delta(\psi + \phi + \Phi_0) = 0, \quad \psi + \phi + \Phi_0 = const. \quad (7)$$

As in this case, the Galvani potential is determined using difference of chemical potentials $\Delta\psi = \Delta\Psi = \Phi_\alpha - \Phi_\beta$ (6). This similar to definition of potential difference of MCPCE. Therefore in the further transformations we use $\Delta\psi = -\Delta\varphi$ (symbol $\Delta$ means the deviation of potential).

Using last relations (6.7) $\psi+\varphi+\Phi_0=A=const$ we provide analysis of particular case, when phase $\alpha$ is metal and phase $\beta$ is not electroconductive inert gas environment, which we take $A = 0$ (because the electrochemical potential is determined up to a constant).

In the external inert environment (outside sphere in volume $V_c$) for electric potential [2, 3] is:

$$\Delta\Psi_c = 0, \quad (8)$$

from which follows that $Y_c=A_c$, where $A_c$ is constant. Taking the electric potential at infinity equal to zero, we obtain $Y_c=A_c=0$ in the volume $V_c$.

Since the electric potential $\Psi$ on the border of arbitrary medium is continuous, then for the boundaries of the phase $\alpha$ (on the surface $\Gamma$) from (7) follows the limit relation:

$$\phi + \Phi_0 = 0, \quad \phi = -\Phi_0. \tag{9}$$

## 2. Determining distributions of electrical charges and mechanical stress
### 2.1. Basic equations of mechanoelectrics for metal

In accordance with the fundamentals of electrostatics and nonequilibrium thermodynamics [4, 5, 7, 8] we can show the electric potential Y using Poisson's equation (10) and the stress tensor we can show as part of the equilibrium equation (11):

$$\varepsilon\varepsilon_0\Delta\Psi = \varepsilon\varepsilon_0\Delta\phi = -\rho\omega = -\omega_V , \tag{10}$$

$$Div\hat{\sigma} + \rho \cdot \omega \cdot \vec{E} = 0, \tag{11}$$

$$\hat{e} = Def\vec{u} , \tag{12}$$

where $\vec{u}$ – is the movement vector in spherical coordinates $\vec{u} = (u_r, 0, 0))$, which is associated with the tensor of deformations $\hat{e}$ by the geometric equation (12) [9].

Boundary conditions on the surface $G$ of the distribution of the electroconductive body and inert gas environment, taking into account (8) [2.3, 8] can be represented as:

$$\vec{\sigma}_n = \vec{p}_c + \frac{1}{2}\Omega\left(\vec{E} + \vec{E}_c\right); \quad \Omega = \varepsilon\varepsilon_0\left(|\vec{E}_n| - |\vec{E}_{cn}|\right); \quad \Psi = \Psi_c; \quad \phi = -\Phi_0. \tag{13}$$

where $\vec{p}_c$ – the environment pressure to the normal $\vec{n}$ to the surface $G$; W – surface charge; e – permittivity material; $\vec{E}_{cn}$, $\vec{E}_n$ – components of the electric-field intensity of environment and metal to the normal to the surface $G$.

The problem of the distribution of electrical charges and the mechanical stresses corresponding them in double electrical layer (4), (5) (10)–(13) we can formulate in a spherical coordinate system (r, q, a). For this we move the origin of coordinates in the geometric center of the sphere. Then we obtain:

$$\frac{d}{dr}\left[\frac{1}{r^2} \cdot \frac{d}{dr}\left(r^2 u_r\right)\right] = \frac{3}{3K + 4G}\left(\beta K\frac{d\phi}{dr} - \omega_V E_r\right); \tag{14}$$

$$\frac{d^2\phi}{dr^2} + \frac{2}{r} \cdot \frac{d\phi}{dr} - k^2 \cdot \phi = \frac{bK}{\varepsilon_0}e, \quad \left(k = \sqrt{\frac{\rho \cdot C_\phi}{\varepsilon_0}}\right); \tag{15}$$

$$\omega_V = \rho\omega = \varepsilon_0 k^2\phi + bKe ; \tag{16}$$

$$\sigma_{ii} = \left(K - \frac{2}{3}G\right)e - bK\varphi + 2Ge_{ii} \quad (i = r, \alpha, \theta); \tag{17}$$

$$e = e_{rr} + 2e_{\theta\theta}; \quad e_{rr} = \frac{du_r}{dr}; \quad e_{\alpha\alpha} = e_{\theta\theta} = \frac{u_r}{r}; \quad \phi + \psi + \Phi_0 = const;$$

$$E_r = -\frac{d\psi}{dr} = \frac{d\phi}{dr}; \quad \Omega = -\varepsilon_o E_r = \varepsilon_o\frac{d\psi}{dr} = -\varepsilon_o\frac{d\phi}{dr} ; \tag{18}$$

$$\phi = -\Phi_0; \quad \sigma_{rr} = -\frac{\varepsilon_0}{2} \cdot \left(\frac{\partial\psi}{\partial r}\right)^2 = \frac{\varepsilon_0}{2} \cdot \left(\frac{\partial\phi}{\partial r}\right)^2 \text{ at r = R.} \tag{19}$$

### 2.2. Method of determining distributions $\varphi$, $\sigma_x$, $\sigma_y$

Since the expression (14) is nonlinear (expression $\omega_V \cdot E_r$ is the ponderomotive component), then we are solving the system of equations (14), (15) taking into account (16)–(19) for finding the distributions of potential $\varphi$ and mechanical stresses $\sigma_r$, $\sigma_\theta$, analytically using the method of small parameter $b_{?*}=b \cdot \Phi_0$, limiting of the four approximations of the decomposition. Methodics of using the small parameter method for solving problems of mathematical physics is described in [10].

We represent the components $u_r$ of movements and φ (deviation of MCPCE) as series of the small parameter:

$$u_r = u_0 + (b \cdot \Phi_0) \cdot u_1 + (b \cdot \Phi_0)^2 \cdot u_2 + (b \cdot \Phi_0)^3 \cdot u_3 + (b \cdot \Phi_0)^4 \cdot u_4 \qquad (20)$$

$$\phi = \phi_0 + (b \cdot \Phi_0) \cdot \phi_1 + (b \cdot \Phi_0)^2 \cdot \phi_2 + (b \cdot \Phi_0)^3 \cdot \phi_3 + (b \cdot \Phi_0)^4 \cdot \phi_4 \qquad (21)$$

Relation for the potential j and mechanical stress $s_r$, $s_q$ we get from (14)–(19) for the area "$V_m$" taking into account the shift $Z_b$ of double electric layer relatively border of the body [11]. The results of the solution (14)–(19) we write in the abbreviated form:

$$\sigma_r = f_r(r,b,k,R,\Phi_0); \qquad \sigma_\theta \approx f_\theta(r,b,k,R,\Phi_0); \qquad (22)$$

$$\phi = f_{\phi r}(r,k,R,\Phi_0) = -\Phi_0 \frac{R}{r} \frac{sh(kr)}{sh(kR)} \; ; \quad \Phi_0 = \frac{q_0 W_e}{2\varepsilon_0 k^2} \cdot \left(2 - \exp(-kZ_b)\right); \qquad (23)$$

$$Z_b = \frac{3}{4k_F}\left(\frac{\pi}{2} + \left(\frac{5E_V}{3E_F} - 1\right) \arcsin\sqrt{\frac{3E_F}{3E_F + 5E_V}} - \sqrt{\frac{5E_V}{3E_F}}\right), \qquad (24)$$

where $f_r$, $f_\theta$ – are symbolizing complex relations which considered four approximations of the small parameter $b \cdot \Phi_{0?}$; $E_F$ – Fermi energy; $E_V$ – electronic work from metal; $k_F$ – Fermi wave vector; $W_e$ – the volume density of the conduction electrons of the metal far from the surface (at a distance of more than 30 nm) ($[W_e] = $ m$^{-3}$); $q_0$ – electron charge.

Shifting $Z_b$ of the double electric layer (24) corresponds to the relationship equations (14) and (15). Note that represented above expression (.23) for $F_0$ is similar to the expression from work [11] derived using the methods of statistical physics. The formula for φ (23) obtained from the solution of (14)–(21) (including four approximations (21)), and similar to the first relation (23) for φ including $Z_b$ (24) (for sphere with a large radius R), given in work [11] virtually identical to within corrections, the magnitude of which less than 4 %. This indicates that the result of four approximations (φ$_1$, φ$_2$, φ$_3$, φ$_4$) for φ manifested in shifting $Z_b$. Therefore we can replace the complex expression like (21) using compact relation for φ (23).

### 2.3 Limiting transition to the flat border

In relations (22), (23) make sense move to the flat distribution border of environments, because effective thicknesses of the double electric layer (surface area) not more than 18 nm [1.11].

In expressions (22), (23) we carry the limiting transition $R \Rightarrow \infty$, where $\sigma_{rr} \Rightarrow \sigma_x$, $\sigma_{\theta\theta} \Rightarrow \sigma_y$, and coordinate r corresponds to x. Then the resulting relations in abbreviated form become:

$$\phi = f_\phi(x,k,\Phi_0) = -\Phi_0 \cdot \exp(-kx); \qquad \sigma_y \approx f_y(x,b,k,\Phi_0);$$

$$\sigma_x \approx f_x(x,b,k,\Phi_0) = -\frac{1}{2}\varepsilon_0 \cdot k^2 \cdot \Phi_o^2 \cdot e^{-2kx} - \frac{1}{2}b \cdot \Phi_0 \cdot K \cdot \Phi_* \cdot e^{-3kx} -$$

$$-(b \cdot \Phi_0)^2 \cdot \frac{3K^2 e^{-2kx}}{2(3K+4G)}\left(1 + \frac{\Phi_*}{4}e^{-2kx}\right) - (b \cdot \Phi_0)^3 \cdot \frac{9K^3 e^{-3kx}}{2(3K+4G)^2}\left(\frac{1}{3} + \frac{\Phi_*}{20}e^{-2kx}\right) -$$

$$-(b \cdot \Phi_0)^4 \cdot \frac{9K^4}{8(3K+4G)^3}e^{-4kx}\left(1 + \frac{1}{10}\Phi_* e^{-2kx}\right) + C_x, \qquad (25)$$

where $f_y$ – is the complex relations; $\Phi_* = \dfrac{\varepsilon_0 \cdot k^2 \cdot \Phi_o^2}{3K + 4G}$

### 3. The method of determining the physical characteristics of the material
### 3.1. Representing systems of nonlinear equations

Traditional approaches to assess of the physical k, b characteristics of the surface layer of metal in the state equations (16), (17) are providing usage approaches of statistical physics or quantum mechanics,

which often lead to ambiguous results. The proposed approach uses a method of the decomposition of displacement variables and potential φ to the small parameter. Also this approach isn't expect explicit usage of theories of statistical physics or quantum mechanics.

Formal expressions for solution of previous problem (25) we are substitute in the system of the four equations [1, 4, 5], in which the surface tension $s_h$ and energy g are defined as:

$$\int_0^h \sigma_y dx = \sigma_h, \quad \sigma_y = \sigma_z, \tag{26}$$

$$\gamma_e + \xi\gamma_M = \gamma, \tag{27}$$

$$\frac{\partial \gamma}{\partial k} = \frac{\partial(\gamma_e + \xi\gamma_M)}{\partial k} = 0, \quad \left( k = \sqrt{\frac{\rho C_\phi}{\varepsilon_0}} \right) \tag{28}$$

$$s_y + p = 0 \text{ (for } x = h) \text{ (}p = 100 \text{ kPa} - \text{atmospheric pressure).} \tag{29}$$

where $\gamma_e = \int_0^h w_e dx$ – the electrical component of the surface energy (SE); $\gamma_M = \int_0^h w_M dx$ – mechanical

component of SE; $w_e = \frac{\varepsilon_0}{2}\left(\frac{\partial \Psi}{\partial x}\right)^2$ and $w_M = \frac{\sigma_x(\sigma_x - 4\nu\sigma_y)}{2E} + \frac{(1-\nu)\sigma_y^2}{E}$ – densities electrical and

mechanical components SE; $h$ – effective thickness of the surface layer; $E$, $\nu$ – Young's modulus and Poisson's ratio, respectively;.

Expressions (26), (27) describing the determination of energy characteristics of surface layers. Relation (28) is a condition of dynamic quasiequilibrium of particles (electrons and ions) that form the double electric layer on the surface of the body. Expression (29) is the condition of the effective thickness of the surface layer. The stresses $s_y$ are stretch (positive) in the boundaries of the surface layer, and $p = 100$ kPa (atmospheric pressure) corresponds to compressive (negative) stresses. Expression $|s_y|=|p|$ is at some distance from the surface $h$, therefore the resulting stress will be zero ($|\sigma_y|-|p|=0$).

The system of equations (26)–(29) is applied to the physical characteristics of the material x, $k$, $b$, $h$ for the first time. In other works [4.5] relations (26)–(29) were, but in there them are used for determine the change of surface tension and energy, and a x, $k$, $b$, $h$ are considered constants (defined using methods of statistical physics or quantum mechanics [1, 11, 12]).

### 3.2. Features of the method of calculation of physical quantities x, k, b, h

Relations (26)–(29) are a system of equations to determine the physical x, $k$, $b$, $F_0$ and geometric $h$ characteristics of the surface layer. The corresponding algorithm for determining x, $k$, $b$, $F_0$, $h$ we present in three stages. First step, using the equation of equilibrium of $\hat{\sigma}$ (14) and (15) for j, which follows from the Poisson equations, state equation (16), (17) and also boundary conditions (19), we find five approximations of distributions normal mechanical stresses $s_r$, $s_q$ from coordinate $r$ (in particular, (22)–(24)) using the technique of [4, 10] and using method of decomposition φ and displacements $u_r$ in the ranks by the small parameter $b_? = bF_0$ (20), (21) . At the second step, we direct radius $R$ to infinity and obtain analytical expressions for j, $s_x$, $s_y$ (25) depending on the x and the parameter $k$, not specifying numeric constants for the material. At the third step, we substitute expressions for $_{???}$ φ, $\sigma_x$ $\sigma_y$ in the relations σ (26)–(29). For the system (26)–(29) we must set only numeric values $\sigma_h$, $\gamma$, $E$, $\nu$, $\rho$, $E_V$, which are known from experiment [13–19] and $E_F$, $W_e$, are obtained from reliable results modeling methods of solid state physics ρ [20] ($\sigma_h$ is determined on the basis of the experiment, and for $\gamma$ is known partial results of experimental studies and theoretical models [19, 20]).

Thus, at the third stage as a result of calculations (simulation modeling), we get four important physical properties of metal – $\xi$, $k$, $b$, $h$. On these basis we can determine the size and $\Phi_0$ (23), through which we are formulating the boundary condition (19) for the modified chemical potential $\varphi$ of conduction electrons.

Electric component of surface energy $\gamma_e$ we are submit through capacitance of the surface electrical capacitor C and potential (Galvani potential) $\Delta\Psi$ using relations of electrostatics [8]:

$$\gamma_{_M} = \Omega^2/(2\cdot C) \quad = C\cdot\Delta\Psi^2/2, \qquad C = \varepsilon_0\cdot k/2, \qquad d = 2/k, \tag{30}$$

where $d$ – the effective distance between the plates of the capacitor surface (within the double electric layer).

### 3.3. The results of calculation of physical quantities. Checking of convergence.

The presented algorithm for estimation characteristics of the material $\xi$, $k$, $b$, $h$ tested for aluminium and germanium (at 20 $^0$C). Values of $\sigma_h$, $\gamma$, $E$, $\nu$, $\rho$, $E_V$ were determined by the results of theoretical and experimental studies (mostly known tabular data) [5, 13–20] (Table 1).

*Table 1*

**Physical characteristics of aluminium and germanium**

| Physical characteristics | Al | Ge | Physical characteristics | Al | Ge |
|---|---|---|---|---|---|
| $E$, GPa | 140 | 108 | $E_F$, eV | 7,50 | – |
| $\nu$ | 0,30 | 0,30 | $E_V$, eV | 4,12÷4,38 | – |
| $\rho$, kg·m$^{-3}$ | 7860 | 2159 | $W_e$, m$^{-3}$ | 7,98·10$^{28}$ | 4,0·10$^{28}$ |
| $K$, GPa | 110 | 110 | $\sigma_h$, H·m$^{-1\cdot}$ | 1,68÷2,35 | 1,117 |
| $G$, GPa | 39 | 49 | $\gamma$, J·m$^{-2}$ | 1,60÷2,01 | 1,231 |

E – Young's modulus; E – Poisson's ratio; $\rho$ – density; $K$ – module of volume compression; $G$ – shear modulus; $E_F$ – Fermi energy; $E_V$ – electron work function; $W_e$ – concentration of conduction electrons in the metal and particle density which correspond of bound charges in the semiconductor; $\sigma_h$ – surface tension; $\gamma$ – surface energy.

It should be noted that the proposed approach for finding $\xi$, $k$, $b$, $h$ can also be applied to semiconductors and dielectrics, but instead the potential $\Phi$ (MCPCE) should be considered potential chemical $Z_c$, which correspond to the particles that form the bound electric charge (in this paper for silicon atoms) [8, 21]. In addition, a shift of the double electric layer on the surface is not taken into account for these materials.

*Table 2*

**Physical properties of the surface layers of materials**

| № z/n | Physical characteristics | Material | |
|---|---|---|---|
| | | aluminium | germanium |
| 1 | $F_0$, H·m$^{-1}$ | 4,114 | — |
| 2 | $Z_0$, N·m$^{-1}$ | — | 5,210 |
| 3 | $\xi$ | 0,201 | 0,581 |
| 4 | $b$, B$^{-1}$ | 0,203 | 0,117 |
| 5 | $k$, m$^{-1}$ | 1,19·10$^{10}$ | 1,68·10$^{10}$ |
| 6 | $\gamma_e$, J·m$^{-2}$ | 1,117 | 0,697 |
| 7 | $\xi\cdot\gamma_m$, J·m$^{-2}$ | 0,695 | 0,405 |
| 8 | $\Omega$, Cl·m$^{-2}$ | 0,406 | 0,313 |
| 9 | $h$, nm | 0,822 | 0,961 |
| 10 | $C$, F·m$^{-2}$ | 69,5 | 53,5 |
| 11 | $\Delta\psi$, in | 6,04 | — |
| 12 | $\Delta Z$, V | — | 5,21 |
| 13 | $d=2k$, нм | 0,138 | — |

Where $F_0$ – equilibrium chemical potential of the electrons in the volume of solids; $Z_0$ – the chemical potential of particles that correspond bound electrical charge in a semiconductor; $\xi$ – dimensionless coefficient that describes change in surface energy by changing the mechanical component of surface energy $\left( \gamma_e + \xi\gamma_{\text{м}} = \gamma \Rightarrow \left. \dfrac{\partial\gamma}{\partial\gamma_{\text{м}}}\right|_{\gamma_e = const} = \xi \right)$; $b$ – electrostrictive coefficient of volume expansion; $k$ – value, which inverse to distance at which space charge in the surface layer varies in $e$ – times. The components of surface energy: $\gamma_e$ – electrical component, $\xi \cdot \gamma_m$ – mechanical component; $\Omega$ – surface charge; $h$ – the thickness of the surface layer; C – the capacity of the double surface layer; $\Delta\psi$ – Galvani potential; $\varDelta Z$ – difference of the potentials of double electric layer on the semiconductor surface (corresponds to related charges); $d=2/k$ – the distance between plates of the surface capacitor.

The resulting physical quantities received during calculations using (31) are given in Table 2. These data correspond to aluminium and germanium without impurities at a temperature $T=20\,°C$ and atmospheric pressure $p = 100$ kPa in the external gas environment. Very important is the significant difference in the values of the electrical and mechanical components of the surface energy of the metal (Al) and a semiconductor (Ge), which is caused by the different nature of the formation of a are double electric layer (free and bound charges, respectively).

As a result of calculations for aluminium received $b_? = bF_0 = 0{,}9 < 1$; $F_* = 0{,}066$. Condition $b_? < 1$ provides the ability to use the method of small parameter [10.22].

Estimation of convergence of calculations of physical quantities we produce for the expression $\sigma_x$ (25) for copper. Analysis $\sigma_x$ (25) allows to confirm the convergence of $\sigma_x$, if the series was formed by the coefficients of approximations

$$1,\ \frac{3K}{\left(3K+4G\right)},\ \frac{3K^2}{\left(3K+4G\right)^2},\ \frac{9K^3}{4\left(3K+4G\right)^3},\ \frac{27K^4}{20\left(3K+4G\right)^4},\ \frac{27K^5}{40\left(3K+4G\right)^5}, \tag{32}$$

ie, 1; 0.686; 0.157; 0,108; 0.0037; 0.00042 ..., the same.

We can compare the series (32) with Dirichlet series $\sum\limits_{n=1}^{\infty}\dfrac{1}{n^s}$ (majorizing in respect to (32), which responds to the Riemann zeta function), where $n = 1, 2, 3 ...$ – natural numbers, Re (s)$> 1$. Dirichlet series for $s > 1$ is converged. Taking, for example, $s = 1{,}2$, we obtain numerical values for Dirichlet series: 1; 0.435; 0.268; 0.189; 0.145; 0.116 …

In accordance with the feature for compare of the series (32) with Dirichlet series, we can argue that a number (32) is also converged, and fractionals $bF_0$, $(bF_0)^2$, $(bF_0)^3$, ... in (25) are reinforcing convergence.

## Conclusions

1. Using basic equations of surface physics and thermodynamics of nonequilibrium processes we developed a mathematical model to determine the physical quantities characterizing the redistribution of conduction electrons (related charges) and mechanical stress in the surface layer of metal (semiconductor) which correspond them. The presented model takes into account the condition of the dynamic quasiequilibrium of conduction electrons (related charges) in the double electric layer on the metal surface (semiconductor).

2. On the basis of the proposed model we developed the method of determining the physical characteristics of the material which including in the linear state equation (physical equation), the boundary conditions for the chemical potential $F_0(Z_c)$ and mechanical stress $\sigma_x$.

3. Also we determined the most important physical quantities for metal surface – capacitance of the double layer C and the Galvani potential $\Delta\Psi$, which can be used to diagnose structural

elements in aggressive environments, as well as to determine the energy characteristics of the surface and interphase layers.

*1. Партенский М. Б. Самосогласованная электронная теория металлической поверхности // УФН. – 1979. – Т. 128, Вып. 1. – С. 69–106. 2. С. де Гроот, П. Мазур. Неравновесная термодинамика. М.: Мир, (1964). – 456 с. 3. Wolff P. A., Albano A. M. Non-eguilibrium thermodynamics of interfacesincluding electromagnetic effect. Physica A. 98A, 491 ( 1979). 4. Юзевич В. Н. Термодинамическое описание поверхностных механоэлектротермодиффузионных процессов и соотношение Антонова. Поверхность. Физика, химия, механика 9, 135 (1988).5. Коман Б. П., Юзевич В. Н. Собственные механические напряжения, термодинамические и адгезионные параметры в системе металлический конденсат – монокристаллический кремний Физ. тверд. тела. – 2012. – Т. 54. – В. 7. – С. 1335–1341. 6. Дамаскин Б. Б., Петрий О. А.. Введение в электрохимическую кинетику. 2-е изд. перераб. и доп. – М.: Высшая школа, 1983. – 400 с. 7. Киреев П. С. Физика полупроводников. – М.: Высшая школа, 1975. – 584 с. 8. Тамм И. Е. Основы теории электричества. – М.: Наука, 1976. – 616 с. 9. Тимошенко С. П., Гудьер Дж. Теория упругости. – М.: Наука, 1975. – 576 с. 10. Боголюбов Н. Н., Митропольский Ю. А. Асимптотические методы в теории нелинейных колебаний. – М.: Наука, 1974. – 504 с. 11. Хориути Д., Тоя Т. Хемосорбция водорода // Поверхностные свойства твердых тел: под ред. М. Грина. – М.: Мир, 1972. – С. 11–103. 12. Lang N. C., Kohn W. Theory of metal surfaces Cyarge density and surface rnergy // Physical Reviev. B 1, 3555 (1970) 13. http://en.wikipedia.org/wiki/Copper. 14. Энциклопедический словарь: http://dic.academic.ru/dic.nsf/es/35532/ 15. http://www.calc.ru/601.html. 16. Климов Ю., Коженков А. С. Поверхностное натяжение твердой меди и межфазное натяжение медь- висмут // Известия высших учебных заведений. Цветная металлургия. – 2006. – 3, – 64. 17. https://en.wikipedia.org/wiki/ Silicon 18. Розенфельд И. Л. Атмосферная коррозия металлов. – М., Изд-сво АН СССР, 1960. – 372 с. 19. Дохов М. П. О межфазной энергии твердое тело-расплав разнородных металлов // Письма в ЖТФ. – 22, 25. – 1996. 20. Киттель Ч. Введение в физику твердого тела. – М.: Наука, 1978. – 792 с. 21. Юзевич В. Н. Термодинамическое описание механоэлектротермодиффузионных процессов в деформируемых диэлектриках с точечными дефектами и соотношение Антонова // Термодинамика необратимых процессов / под. ред. А. И. Лопушанской. – М.: Наука, 1992. – С. 163–168. 22. Бронштейн И. Н., Семендяев К. А. Справочник по математике для инженеров и учащихся втузов. – М.: Наука, 1986. – 544 с.*