

Mathematical modeling of changes in density of near-surface ionic layers in semi-infinite metals. Equations for displacements of ionic layers

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In this work, we propose a mathematical model for describing the change in the ion density of the near-surface ionic layers of a semi-infinite metal. Through averaging over the subsystem of conduction electrons, we obtain in the adiabatic approximation an effective Hamiltonian of the ionic subsystem of a semi-infinite metal, which models the effect of the “metal–vacuum” separation surface on the structure of the near-surface ionic layers. We calculate the free energy of such a model and, by its minimization, obtain an equation for finding the displacements ξ_m of the ionic layer m . We show that in the absence of an inhomogeneous distribution of the electronic subsystem $\xi_m \equiv 0$.

Keywords: *semi-infinite metals; mathematical modeling; lattice ionic structure.*

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1. Introduction

The rapid development of nanotechnologies (especially in the last decade) led to a sharp increase in research aimed both at the search for new nanomaterials for nanosystems and at experimental work focused on clarifying the influence of the dimensions of nanosystems on their physical and mechanical properties [1].

It led to an increase in the number of works aimed at constructing and investigating mathematical models that allow adequate description of the obtained experimental results. These models, in turn, must take into account one essential feature of nanosystems (metallic nanofilms, graphene-like 2D structures, etc.). Since the geometric dimensions of such nanosystems are proportional to the de Broglie wavelength [1] of electrons, the physical and mechanical properties strongly depend on the size of the nanostructure and differ sharply from those found in bulk structures, especially in the near-surface regions (the so-called “size effects”) [2, 3].

The special attention of researchers today is directed to the study of mechanical characteristics of nanosystems accounting for the size effect [4].

In the work [5], the authors present one of the approaches to describing the mechanical characteristics (the Young’s modulus, Poisson’s ratios, etc.) of nanosystems, which is based on the ideas of local mass perturbation related to the method of surface formation. Such, generally speaking, hypothetical idea is associated with an attempt (see [5]) to describe dimensional effects within the framework of a continuum approach, in which the discreteness of the ionic subsystem of a nanostructure is neglected. It is quite clear that for nanostructures with dimensions of the order of 10 – 100 nm, the discreteness of the ionic subsystem is important, because the geometric dimensions of the nanosystem are proportional to the parameter d of the lattice structure [6].

Work [7] proposes an approach to describing nanoscale (especially metallic) structures that takes into account the discreteness of the ionic subsystem. With such a description, the problem of the existence of a “near-surface mass defect” [5] disappears, and the change in the density of the ionic subsystem in the near-surface region is due to a physically justified change in the volume of the unit cell (that is, a change in the parameter d of the lattice structure), which is the main element of a discrete ionic subsystem.

In this work, we propose and investigate a model of a semi-infinite metallic system using the quantum-statistical model of metallic nanostructures proposed in [7–9].

We obtain an effective Hamiltonian of the discrete ionic subsystem and then use it to calculate the change in the volume of a unit cell. This change, in turn, leads to a change in the ion density in the near-surface layer.

2. Mathematical model for describing the lattice ionic subsystem of a semi-infinite metal

We consider a semi-infinite metallic system consisting of N positively charged ions with a charge $\mathcal{Z}|e|$ (e is the electron charge) and $N\mathcal{Z}$ conduction electrons. The ions are placed in the nodes $\mathbf{R}_n = (X_1^{(n)}, X_2^{(n)}, X_3^{(n)})$, $n = \overline{1, N}$, $X_i^{(n)}$ are the Cartesian coordinates ($i = \overline{1, 3}$) of the Cartesian coordinate system (X_1, X_2, X_3) , the axis OX_3 of which is directed perpendicular to the flat “metal–vacuum” separation surface with the equation $X_3 = z_0$. The lattice structure of ions is periodic with a period $\mathbf{d} = (d_1, d_2)$ in planes parallel to the separation plane. The conduction electrons have coordinates $\mathbf{r}_i = (x_i, y_i, z_i)$, $i = \overline{1, N\mathcal{Z}}$.

The Hamiltonian of such a model is as follows [7]:

$$H = H_e + H_i + V_{ei},$$

where

$$H_e = -\frac{\hbar^2}{2m} \sum_{i=1}^{N\mathcal{Z}} \Delta_i + \frac{1}{2} \sum_{i \neq j=1}^{N\mathcal{Z}} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1}$$

is the Hamiltonian of the interacting subsystem of conduction electrons ($\hbar = h/(2\pi)$, h is the Planck constant, m is the electron mass, Δ is the Laplace operator);

$$H_i = \sum_{i=1}^N \frac{P_n^2}{2M} + \frac{1}{2} \sum_{n \neq n'=1}^N \frac{(\mathcal{Z}e)^2}{|\mathbf{R}_n - \mathbf{R}_{n'}|} \tag{2}$$

is the Hamiltonian of the ionic subsystem, which will be considered classical (\mathbf{P}_n is the ion momentum and M is its mass);

$$V_{ei} = \sum_{i=1}^{N\mathcal{Z}} \sum_{n=1}^N w(\mathbf{R}_n - \mathbf{r}_i)$$

is the term describing the interaction of ionic and electronic subsystems.

In equation (2) $P_n^2 = (\mathbf{P}_n, \mathbf{P}_n)$, $\forall n$, $P_n^2 < +\infty$, (\cdot, \cdot) is the scalar product.

As in [7], let us transform (1), highlighting in it the term that describes the behavior of the electronic subsystem in the field of a homogeneous positive jellium with the density

$$\rho_{\text{jell}}(\mathbf{R}) = \rho_{\text{jell}}(\mathcal{Z}) = \rho_0 \theta(-a - z_0), \quad \rho_0 = \frac{2eN}{V}.$$

The parameter a , which ensures the electroneutrality of the model, as shown in [8], is equal

$$a = \frac{3\pi}{8k_F}, \quad k_F = \frac{2m\mu}{\hbar},$$

μ is the chemical potential of the electronic subsystem. We have (see [7]):

$$H = H_{\text{jell}} + \sum_{i=1}^{N\mathcal{Z}} \sum_{n=1}^N V_{ie}(|\mathbf{R}_n - \mathbf{r}_i|) + \tilde{H}_{ii}, \tag{3}$$

where

$$\tilde{H}_{ii} = H_i - \frac{1}{2} \iint_V d\mathbf{R} d\mathbf{R}' \frac{\rho_{\text{jell}}(\mathbf{R}) \rho_{\text{jell}}(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|}, \tag{4}$$

$$V_{ie}(|\mathbf{R}_n - \mathbf{r}_i|) = w(|\mathbf{R}_n - \mathbf{r}_i|) + \frac{1}{N} \int_V d\mathbf{R} \frac{e\rho_{\text{jell}}(\mathbf{R})}{|\mathbf{r}_i - \mathbf{R}|},$$

and H_{jell} , the expression for which is given in [8,9], is the Hamiltonian of the electronic subsystem in

the field of homogeneous jellium. $V = SL$ is the volume of the system, S is the surface area ($S \rightarrow +\infty$), and L is the region of change in the normal to the surface z coordinate of the electron ($z \in [-\frac{L}{2}, \frac{L}{2}]$, $L \rightarrow +\infty$). Representation of the Hamiltonian H in the form (3) allows, using the “reference system” method [10], to calculate (in the adiabatic approximation [11]) the thermodynamic potential

$$\Omega = -\frac{1}{\beta} \ln \text{Sp} \exp \{-\beta(H - \mu N \mathcal{Z})\}$$

for the proposed model of a semi-infinite metal.

Choosing as the “reference system” the system of electrons in the field of positive jellium, for the thermodynamic potential Ω we obtain [7]

$$\Omega = \Omega_{\text{jell}} + \Omega_{\text{ie}} + \tilde{H}_{\text{ii}}, \tag{5}$$

where Ω_{jell} is the thermodynamic potential of the semi-infinite jellium [7], and

$$\Omega_{\text{ie}} = -\frac{1}{\beta} \ln \exp \left\{ -\beta(\delta E^{(1)} + \delta E^{(2)} + \dots) \right\}, \tag{6}$$

where $\delta E^{(i)} \equiv \delta E^{(i)}(\mathbf{R}_1, \dots, \mathbf{R}_n)$ is the energy of the electronic subsystem of a semi-infinite metal of the i th order in the potential V_{ie} . Limiting in (6) to energies $\delta E^{(1)}$ and $\delta E^{(2)}$ (the approximation of paired ion-ion interactions), from (4), (5) and (6) we obtain the effective Hamiltonian of the ionic subsystem of a semi-infinite metal:

$$\mathcal{H} = \sum_{n=1}^N \frac{P_n^2}{2M} + \sum_{n=1}^N \Phi_1(\mathbf{R}_n) + \frac{1}{2} \sum_{n \neq n'=1}^N \Phi_2(\mathbf{R}_n, \mathbf{R}_{n'}),$$

where according to [7]

$$\sum_{n=1}^N \Phi_1(\mathbf{R}_n) = -i \frac{N}{SL} \sum_{\mathbf{q}} \sum_k S_k(\mathbf{q}) \delta w_k(\mathbf{q}) \mathfrak{M}_k^{(1)}(\mathbf{q}),$$

and $\delta w_k(\mathbf{q})$ is defined by the relationship

$$\delta w(\mathbf{R}) = \frac{1}{V} \sum_{\mathbf{q}, k} \delta w_k(\mathbf{q}) \exp \{ -i(\mathbf{q}, \mathbf{R}'') - ikX_3 \}, \tag{7}$$

$\mathbf{R} = (\mathbf{R}^{\parallel}, X_3)$, $\mathbf{R}^{\parallel} = (X_1, X_2)$, and

$$S_k(\mathbf{q}) = \frac{1}{N} \sum_{n=1}^N \exp \{ -i(\mathbf{q}, \mathbf{R}^{\parallel}) - ikX_3 \}$$

is the geometric structure factor of the ionic subsystem of a semi-infinite metal. The term

$$\frac{1}{2} \sum_{n \neq n'=1}^N \Phi_2(\mathbf{R}_n, \mathbf{R}_{n'}) = \frac{N^2}{V^2} \sum_{\mathbf{q}_1, \mathbf{q}_2} \sum_{k_1, k_2} S_{k_1}(\mathbf{q}_1) \delta w_{k_1}(\mathbf{q}_1) \delta w_{k_2}(\mathbf{q}_2) S_{k_2}(\mathbf{q}_2) \mathfrak{M}_{k_1, k_2}^{(2)}(\mathbf{q}_1, \mathbf{q}_2). \tag{8}$$

The correlation functions $\mathfrak{M}_k^{(1)}(\mathbf{q})$ and $\mathfrak{M}_{k_1, k_2}^{(2)}(\mathbf{q}_1, \mathbf{q}_2)$ are defined in [7].

For the considered model of a semi-infinite metal (the model is periodic in a plane parallel to the separation plane) (7) and (8) are simplified. Namely [7]:

$$\mathfrak{M}_k^{(1)}(\mathbf{q}) = i S \delta_{\mathbf{q}, 0} \int_{-\frac{L}{2}}^{\frac{L}{2}} dz e^{ikz} n(z), \tag{9}$$

and

$$\begin{aligned} \mathfrak{M}_{k_1, k_2}^{(2)}(\mathbf{q}_1, \mathbf{q}_2) &= i^2 \frac{N(N-1)}{V^2} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 e^{i[(\mathbf{q}_1, \mathbf{r}_1'') + (\mathbf{q}_2, \mathbf{r}_2'') + (k_1 z_1 + k_2 z_2)]} F_2(\mathbf{r}_1, \mathbf{r}_2) \\ &- i^2 S \delta_{\mathbf{q}_1 + \mathbf{q}_2, 0} \int_{-\frac{L}{2}}^{\frac{L}{2}} dz e^{i(k_1 + k_2)z} n(z) - i^2 S^2 \delta_{\mathbf{q}_1, 0} \delta_{\mathbf{q}_2, 0} \int_{-\frac{L}{2}}^{\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{\frac{L}{2}} dz_2 e^{i(k_1 z_1 + k_2 z_2)} n(z_1) n(z_2). \end{aligned} \tag{10}$$

In (9) and (10)

$$n(z) = \frac{N\mathcal{Z}}{V} F_1(z)$$

is the electron density distribution function in the jellium model, $F_2(\mathbf{r}_1, \mathbf{r}_2)$ and $F_1(z)$ are, respectively, the binary and unary Bogolyubov distribution functions of the semi-infinite jellium [7], $\delta_{\mathbf{q},0}$ is the Kronecker delta [11], i is the imaginary unit.

Now we can finally write the effective Hamiltonian of the ionic subsystem as follows:

$$H = \sum_{n=1}^N \frac{P_n^2}{2M} + \frac{1}{2} \sum_{n=1}^N \Phi_1(\mathbf{R}_n) + \frac{1}{2} \sum_{n \neq n'=1}^N \Phi_2(\mathbf{R}_n, \mathbf{R}_{n'}), \tag{11}$$

where

$$\Phi_1(\mathbf{R}_n) = \int_{-\frac{L}{2}}^{\frac{L}{2}} dz \delta w(\mathbf{q} = 0 | z - X_3^{(n)}) n(z),$$

$n(z) = \frac{N\mathcal{Z}}{V} F_1(z)$ is the electron density for the jellium model, and

$$\Phi_2(\mathbf{R}_n, \mathbf{R}_{n'}) = \frac{1}{2\pi} \int_0^\infty q J_0(q, \mathbf{R}'') V(\mathbf{q} | X_3^{(n)}, X_3^{(n')}) dq. \tag{12}$$

In (12) $V(\mathbf{q} | X_3^{(n)}, X_3^{(n')})$ is defined as [7]:

$$\begin{aligned} V(\mathbf{q} | X_3^{(n)}, X_3^{(n')}) &= \mathcal{Z}^2 \nu(\mathbf{q} | X_3^{(n)} - X_3^{(n')}) \\ &+ \frac{\beta}{VL} \int_{-\frac{L}{2}}^{\frac{L}{2}} dz_1 \int_{-\frac{L}{2}}^{\frac{L}{2}} dz_2 \delta w(\mathbf{q} | X_3^{(n)} - z_1) \mathfrak{M}_2(\mathbf{q}, -\mathbf{q} | z_1, z_2) \delta w(-\mathbf{q} | X_3^{(n)} - z_2), \end{aligned}$$

$J_0(\mathbf{q}, R^{\parallel})$ is the Bessel function of zero order [12], $R^{\parallel} = |\mathbf{R}^{\parallel}|$.

$$\nu(\mathbf{q} | X_3^{(n)} - X_3^{(n')}) = -\frac{2\pi e^2}{q} e^{-q | X_3^{(n)} - X_3^{(n')} |}.$$

For further calculations, the pseudopotential of electron–ion interaction is modeled by the Gursky–Krasko pseudopotential [13], for which

$$\delta w(\mathbf{q} | z) = 2\pi e^2 r_c \left\{ \frac{a|z|}{r_c} \frac{1}{1 + (qr_c)^2} + \frac{1 + a + (qr_c)^2}{(1 + (qr_c)^2)^{\frac{3}{2}}} \right\} \exp \left\{ -\frac{|z|}{r_c} \sqrt{1 + (qr_c)^2} \right\}.$$

a, r_c are the parameters of the Gursky–Krasko pseudopotential [13].

3. Equation for displacement of the lattice ionic subsystem

In semi-infinite metallic systems, a negatively charged layer of electrons with a thickness of $(1 \div 2)d$ is formed above the metal surface (d is the lattice period of an ideal metal) [7, 14]. The interaction of the ionic lattice subsystem of a metal with such a layer leads to displacements ξ_n of ions' positions relative to their positions \mathbf{R}_n^0 in the ideal metal. These displacements must minimize the free energy F of the semi-infinite metal, i.e. ξ_n should be sought from the condition

$$\text{grad}_{\xi_n} F \equiv \nabla_{\xi} F = 0, \tag{13}$$

where $\xi_n = \mathbf{R}_n - \mathbf{R}_n^0$.

The free energy

$$F = -\beta^{-1} \ln \text{Sp} e^{-\beta \mathcal{H}}, \tag{14}$$

where \mathcal{H} is the Hamiltonian of the ionic subsystem (see the formula (11)) of a semi-infinite metal, and

$$\text{Sp}[\dots] = \int d\mathbf{P} \sum_{\{\mathbf{R}_n\}} [\dots],$$

$d\mathbf{P} = d\mathbf{P}_1 \dots d\mathbf{P}_n$, and $\{\mathbf{R}_n\}$ is the set of all values of \mathbf{R}_n .

Let us use the model Hamiltonian H (11) as \mathcal{H} and write it as follows:

$$\mathcal{H} = H_0 + H_1,$$

where H_0 is the Hamiltonian of an ideal ionic subsystem (for it $\mathbf{R}_n = \mathbf{R}_n^0$), and $H_1 = \mathcal{H} - H_0$. Let us transform the expression (14) or the free energy F as follows:

$$\text{Sp} e^{-\beta\mathcal{H}} = \text{Sp}\{e^{-\beta H_0} e^{-\beta H_1}\} = \{\text{Sp} e^{-\beta H_0}\} \cdot \langle e^{-\beta H_1} \rangle,$$

where

$$\langle e^{-\beta H_1} \rangle = \frac{\text{Sp} e^{-\beta H_0} e^{-\beta H_1}}{\text{Sp} e^{-\beta H_0}}.$$

This is possible because $[H_0, H_1] = 0$ ($[b, c]$ is the commutator [11]) due to the classical description of the ionic subsystem. Therefore

$$F = F_0 + F_1,$$

where $F_0 = -\beta^{-1} \ln \text{Sp} e^{-\beta H_0}$ is the free energy of the ionic subsystem of an ideal metal, and

$$F_1 = -\beta^{-1} \ln \langle e^{-\beta H_1} \rangle.$$

Since F_0 does not depend on $\boldsymbol{\xi}$ (according to the definition of H_0), the equation (13) for finding the displacements $\boldsymbol{\xi}_n$ will be as follows

$$\nabla_{\boldsymbol{\xi}} F_1 = 0. \tag{15}$$

Henceforth, we will assume that the displacements $\boldsymbol{\xi}_n$ are small ($|\boldsymbol{\xi}_n| \ll d$, d is the lattice period of an ideal metal [6]). Let us expand the term F_1 into a power series of $\boldsymbol{\xi}_n$ (limiting contributions not higher than the second order of $\boldsymbol{\xi}_n$) and give F_1 like this:

$$F_1 = \mathcal{F}_1 + \mathcal{F}_2,$$

where

$$\begin{aligned} \mathcal{F}_1 = \langle H_1 \rangle = \sum_{n=1}^N \left(\boldsymbol{\xi}_n, \left\langle \nabla_{\boldsymbol{\xi}} \left[\Phi_1(\mathbf{R}_n) + \sum_{n'=1}^N \Phi_2(\mathbf{R}_n, \mathbf{R}_{n'}) \right] \right\rangle_0 \right) \\ + \frac{1}{2} \sum_{n=1}^N (\boldsymbol{\xi}_n, \hat{A} \boldsymbol{\xi}_n) + \sum_{n=1}^N \sum_{n'=1}^N (\boldsymbol{\xi}_n, \hat{D} \boldsymbol{\xi}_{n'}). \end{aligned} \tag{16}$$

Here

$$\hat{A} = \langle (\nabla_{\boldsymbol{\xi}}, \nabla_{\boldsymbol{\xi}} \Phi_1(\mathbf{R}_n) | _0) \rangle, \tag{17}$$

and

$$\hat{D} = \langle (\nabla_{\boldsymbol{\xi}}, \nabla_{\boldsymbol{\xi}'} \Phi_2(\mathbf{R}_n, \mathbf{R}_{n'}) | _0) \rangle, \tag{18}$$

and $\boldsymbol{\xi}' = \boldsymbol{\xi}_{n'}$.

Similarly, for \mathcal{F}_2 we have:

$$\begin{aligned} \mathcal{F}_2 = \frac{\beta}{2} (\langle H_1 \cdot H_1 \rangle - \langle H_1 \rangle \langle H_1 \rangle) = \frac{\beta}{2} \sum_{n=1}^N \left(\boldsymbol{\xi}_n, \left\langle \nabla_{\boldsymbol{\xi}} \left[\Phi_1(\mathbf{R}_n) + \sum_{n'=1}^N \Phi_2(\mathbf{R}_n, \mathbf{R}_{n'}) \right] \right\rangle_0 \right) \\ \cdot \left(\boldsymbol{\xi}_n, \left\langle \nabla_{\boldsymbol{\xi}} \left[\Phi_1(\mathbf{R}_n) + \sum_{n'=1}^N \Phi_2(\mathbf{R}_n, \mathbf{R}_{n'}) \right] \right\rangle_0 \right). \end{aligned} \tag{19}$$

The index “0” in (16)–(19) means that the corresponding gradients are calculated at the points \mathbf{R}_n^0 .

Substituting (16)–(19) into (15) and taking into account the symmetry of the \hat{A} and \hat{D} matrices, we obtain the following equation for finding $\boldsymbol{\xi}_m$:

$$\begin{aligned} \left\langle \nabla_{\boldsymbol{\xi}} \left[\Phi_1(\mathbf{R}_m) + \sum_{n'=1}^N \Phi_2(\mathbf{R}_m, \mathbf{R}_{n'}) \right] \right\rangle_0 + \beta \left(\boldsymbol{\xi}_m, \left\langle \nabla_{\boldsymbol{\xi}} \left[\Phi_1(\mathbf{R}_m) + \sum_{n'=1}^N \Phi_2(\mathbf{R}_m, \mathbf{R}_{n'}) \right] \right\rangle_0 \right) \\ + \hat{A} \boldsymbol{\xi}_m + \sum_{n'=1}^N 2 \hat{D} \boldsymbol{\xi}_{n'} = 0. \end{aligned} \tag{20}$$

The sum of $\hat{A} + \hat{D}$ gives the known in modeling of the lattice ionic subsystem dynamic matrix [15], which is positively defined. This provides a minimum of the free energy F for the values of ξ_m that are solutions of (20).

We should note that in the case of $n(z) = \frac{Nz}{V}$ ($F_1(z) \equiv 1$) the expression for $\Phi_1(\mathbf{R}_n) = 0$, and therefore using the conditions of local equilibrium [13] ($\nabla_\xi \sum_{n'=1}^N \Phi_2(\mathbf{R}_n, \mathbf{R}_{n'})|_0 = 0$), we get that equation (20) has only a trivial solution: $\xi_m \equiv 0$. This allows us to state that it is the inhomogeneity of the electron density $n(z)$ that leads to the displacement of the near-surface ionic layers, and thus to the change in the ion density near the surface. Indeed, in the case when $\xi_m \neq 0$, finding the solutions of the equation (20) and substituting them into the expression for the free energy F_1 , we can calculate the diagonal elements of the stress tensor σ [16], and from the condition

$$\text{Sp } \sigma = \frac{\Delta V}{V}$$

(taking into account the boundary condition $\sum_{k=1}^3 \sigma_{ik} n_k = P_i$, $i = 1, 2, 3$, where n_k are the components of the normal vector to the surface, and P_i are the components of the force vector acting from the side of the electron layer) we can find the change ΔV of the volume, and thereby calculate the change in the density of the ionic system in the near-surface region.

4. Conclusions

In this work, we propose a mathematical model for describing the change in the density of the ionic subsystem in the near-surface region of a semi-infinite metal.

Through averaging over the electronic subsystem, we obtain an effective Hamiltonian of the discrete ionic subsystem, which we use to calculate the free energy of the lattice ion structure of a semi-infinite metal in the quadratic approximation of the ion displacement.

By minimizing the free energy, we obtain the equation for ions' displacements in the near-surface region and show that this equation has a trivial solution for a homogeneous distribution of the electronic subsystem.

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Математичне моделювання зміни густини приповерхневих іонних шарів в напівобмежених металах. Рівняння для зміщень іонних шарів

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У цій роботі запропоновано математичну модель опису зміни іонної густини приповерхневих іонних шарів напівобмеженого металу. Через усереднення по підсистемі електронів провідності отримано в адіабатичному наближенні ефективний гамільтоніан іонної підсистеми напівобмеженого металу, який моделює вплив поверхні поділу “метал–вакуум” на структуру приповерхневих шарів іонів. Проведено розрахунок вільної енергії такої моделі і шляхом її мінімізації отримано рівняння для знаходження зміщень ξ_m іонного шару m . Показано, що у випадку відсутності неоднорідного розподілу електронної підсистеми $\xi_m \equiv 0$.

Keywords: *напівобмежені метали, математичне моделювання, ґраткова іонна структура.*