

# Interface influence on the structure of ion lattice subsystem of semi-infinite metals

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## Introduction

Modern experimentally obtained and studied metallic nanosystems are characterized by  $\sim 10 \div 100$  nm. Due to the "quantum-size effect", the physical and mechanical properties of such nanosystems are significantly different from bulk ones. The presence near the "metal-vacuum" interface of a near-surface electron layer, the thickness of which reaches the order of two lattice periods of an ideal metal (without "metal-vacuum" interface), leads to a change in the mechanical characteristics (Young's modulus, Poisson's ratios, force constants, etc.) of such nanosystems. The works [1, 2] consider models for describing such changes within framework of solid media mechanics, which doesn't take into account the discreteness of the ion subsystem and therefore requires some unreasonable assumptions (in particular, the presence of a mass flow). In works [3, 4] proposed a quantum statistical approach to the description of the thermodynamic characteristics of nanoscale metal systems, that takes into account, on the contrary to [1, 2], discreteness of the ion subsystem. In such approach the change of the ion density in the near-surface area is caused by the change of the volume of the elementary lattice due to the deformation.

## 1. Model

Let's consider semi-infinite metal system, that consists of  $N$  positively charged ions with a charge value  $\mathcal{Z}|e|$  (where  $e$  - is the electron charge) and of  $N\mathcal{Z}$  of conduction electrons. Ions are placed in the nodes  $\vec{R}_n = (x_1^{(n)}, x_2^{(n)}, x_3^{(n)})$  where  $x_i^{(n)}$  - the Cartesian coordinates ( $i = 1 \div 3, n = 1 \div N$ ), in the coordinate system  $(x_1, x_2, x_3)$ , axis  $Ox_3$  of which is perpendicular to the "metal-vacuum" interface. The lattice structure of ions is periodic in the areas parallel to the interface.

Conduction electrons have coordinates  $\vec{r}_i = (x_i^{(1)}, x_i^{(2)}, x_i^{(3)})$ ,  $i = 1 \div N\mathcal{Z}$ .

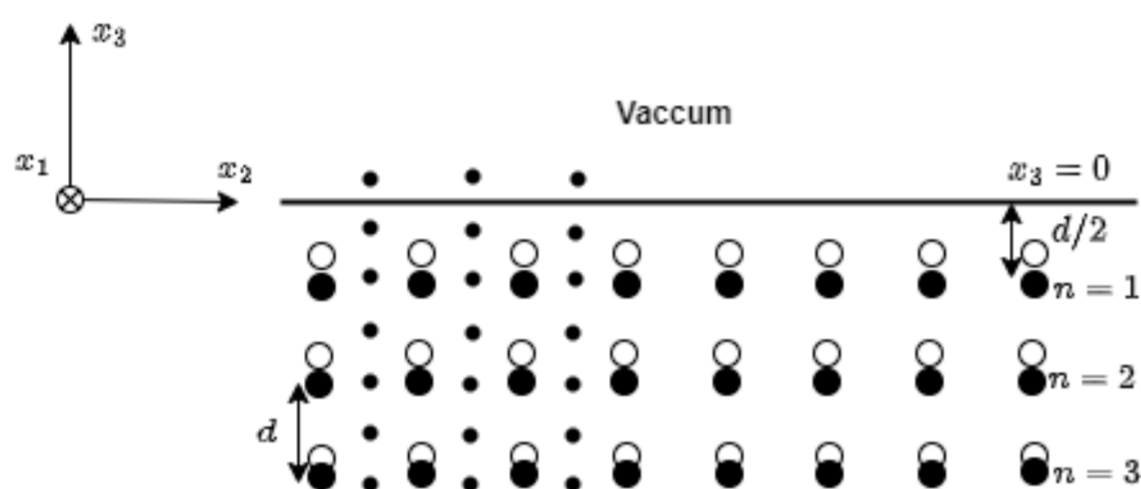


Figure 1: The model scheme.  $\circ$  - ions of a real lattice;  $\bullet$  - ions of an ideal (without interface) lattice;  $\bullet$  - conduction electrons.

The Hamiltonian of a such model is:

$$H = H_e + V + V_{ei}, \quad (1)$$

where

$$H_e = -\frac{\hbar^2}{2m} \sum_{i=1}^{N\mathcal{Z}} \Delta_i + \frac{1}{2} \sum_{i < j}^{N\mathcal{Z}} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} \quad (2)$$

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

$$H_i = \sum_{i=1}^N \frac{\vec{P}_n^2}{2M} + \frac{1}{2} \sum_{n < n'}^N \frac{\mathcal{Z}e^2}{|\vec{R}_n - \vec{R}_{n'}|} \quad (3)$$

is the Hamiltonian of the ion subsystem which further we will consider as classical ( $\vec{P}_n$  - impulse of ion and  $M$  - is its mass);

$$V_{ei} = \sum_{i=1}^{N\mathcal{Z}} \sum_{n=1}^N \omega(\vec{R}_n - \vec{r}_i) \quad (4)$$

is a summand that describes electron-ion interaction.

Choosing as a "reference-system" a system of electrons in the field of a positive "jellium" [3] for a thermodynamic potential  $\Omega$  (in the adiabatic approximation) of proposed model (1)-(4) we obtain

$$\Omega = \Omega_{jell} + \Omega_{ie} + H_{ii}, \quad (5)$$

where  $\Omega_{jell}$  - a thermodynamic potential of a semi-infinite "jellium" [3, 4] and.

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

where  $\delta E^{(j)} \equiv \delta E^{(j)}(\vec{R}_i, \vec{R}_n)$  - an energy of subsystem of semi-infinite metal (model (1)-(4)) of  $j$ -th order by potential  $V_{ie}$ . In the approximation of ion-pairing ( $j = 1, 2$ ) we have the effective Hamiltonian of the ion subsystem for the model (1)-(4):

$$H = \sum_{n=1}^N \frac{P_n^2}{2M} + \sum_{n=1}^N \Phi_1(\vec{R}_n) + \sum_{n, n'=1}^N \Phi_2(\vec{R}_n, \vec{R}_{n'}), \quad (7)$$

where according to [4]:

$$\sum_{n=1}^N \Phi_1(\vec{R}_n) = -i \frac{N}{V} \sum_{\vec{q}} \sum_k S_k(\vec{q}) \delta \omega_k(\vec{q}) \mathfrak{W}_k^{(1)}(\vec{q}), \quad (8)$$

and  $\delta \omega_k(\vec{q})$  is defined by a relationship

$$\begin{aligned} \delta \omega(\vec{R}) &= \frac{1}{V} \sum_{\vec{q}} \sum_k \delta \omega_k(\vec{q}) \exp \left\{ -i(\vec{q}, \vec{R}^{\parallel}) - ikx_3 \right\}, \\ \vec{R}^{\parallel} &= (x_1, x_2), \quad \vec{R} = (\vec{R}^{\parallel}, x_3), \\ S_k(\vec{q}) &= \frac{1}{N} \sum_{n=1}^N \exp \left\{ -i(\vec{q}, \vec{R}_n^{\parallel}) - ikx_3 \right\}. \end{aligned}$$

is a geometrical structural factor of the ion subsystem,

$$\begin{aligned} \frac{1}{2} \sum_{n, n'=1}^N \Phi_2(\vec{R}_n, \vec{R}_{n'}) &= \frac{N^2}{V^2} \sum_{\vec{q}_1, \vec{q}_2} \sum_{k_1, k_2} S_{k_1}(\vec{q}_1) \delta \omega_{k_1}(\vec{q}_1) \delta \omega_{k_2}(\vec{q}_2) \times \\ &\times S_{k_2}(\vec{q}_2) \mathfrak{W}_{k_1, k_2}^{(2)}(\vec{q}_1, \vec{q}_2). \end{aligned} \quad (9)$$

Correlation functions  $\mathfrak{W}_k^{(1)}(\vec{q})$  and  $\mathfrak{W}_{k_1, k_2}^{(2)}(\vec{q}_1, \vec{q}_2)$  are defined in [4].  $V = SL$  is a volume of the system,  $S$  is an area of a surface ( $S \rightarrow +\infty$ ) and  $L$  - area of the change of normal to the surface of coordinate  $x_3$  of electron ( $x_3 \in [-L/2, L/2]$ ,  $L \rightarrow +\infty$ ). Particularly, for the model (1)-(4)

$$\mathfrak{W}_k^{(1)}(\vec{q}) = iS \delta_{\vec{q}, 0} \int dx_3 e^{ikx_3} n_1(x_3),$$

where  $n(x_3) = \frac{N\mathcal{Z}}{V} F_1(x_3)$  is a function of the density distribution of electrons in the "jellium" model.  $F_1(x_3)$  is the Boholubov's unary distribution function;  $\delta_{\vec{q}, 0}$  is the Kronecker symbol.

For a plane interface surface "metal-vacuum"

$$\Phi_1(\vec{R}_n) = \int \delta \omega(\vec{q} = 0 | x_3 - X_3^{(n)}) n(x_3), \quad (10)$$

$$\Phi_2(\vec{R}_n, \vec{R}_{n'}) = \frac{1}{2\pi} \int_0^\infty q v(q | X_3^{(n)}, X_3^{(n')}) J_0(q, \vec{R}^{\parallel}) dq, \quad (11)$$

and

$$\begin{aligned} v(q | X_3^{(n)}, X_3^{(n')}) &= \mathcal{Z}^2 v(q | X_3^{(n)} - X_3^{(n')}) + \\ &+ \frac{\beta}{VL} \int_V dz_1 dz_2 \omega(q | X_3^{(n)} - z_1) \mathfrak{W}^{(2)}(q | z_1, z_2) \delta \omega(-q | X_3^{(n)} - z_2), \\ v(q | X_3^{(n)} - X_3^{(n')}) &= -\frac{2\pi e^2}{q} e^{-q | X_3^{(n)} - X_3^{(n')} |}, \end{aligned} \quad (12)$$

$J_0(q, \vec{R}^{\parallel})$  is the zero-order Bessel function,  $R^{\parallel} = |\vec{R}^{\parallel}|$ .

## 2. Calculation of the volume change for an elementary lattice

In the spatially limited metal systems over the surface emerging a negatively-charged layer of electrons with a thickness  $(1 \div 2)d$ , where  $\alpha$  is a period of the lattice without the interface (see [4]). Interaction of ion lattice subsystem with such layer leads to the displacement  $vec \xi_n$  of ions positions, this displacement is relative to positions  $\vec{R}_n^0$  in the ideal (without the interface surface) metal. Displacement  $\xi_n$  can be found from condition:

$$\nabla_{\xi_n} F = 0, \quad (13)$$

where free energy

$$F = -\frac{1}{\beta} \ln Sp e^{-\beta H},$$

and

$$Sp[\dots] = \int d\vec{p} \sum_{\vec{R}_n} \{\dots\}, \quad \xi_n = \vec{R}_n - \vec{R}_n^0.$$

Deriving the Hamiltonian of the ideal system  $H$  from (7) (for it  $\vec{R}_n = \vec{R}_n^0$ ) in the quadratic approximation for a small ( $|\xi_n| \ll \alpha$ ) displacements we obtain for (13):

$$\begin{aligned} \langle \vec{\nabla}_{\xi} [\Phi_1(\vec{R}_m) + \sum_{n=1}^N \Phi_2(\vec{R}_m, \vec{R}_{n'})]_0 \rangle + \\ + \beta \langle \xi_m, \vec{\nabla}_{\xi} [\Phi_1(\vec{R}_m) + \sum_{n=1}^N \Phi_2(\vec{R}_m, \vec{R}_{n'})]_0 \rangle + \\ + \hat{A} \xi_m + \sum_{n'=1}^N (\hat{D}_{mn'} + \hat{D}_{n'm}) \xi_{n'} = 0. \end{aligned} \quad (14)$$

Here

$$\begin{aligned} \hat{A} &= \langle (\vec{\nabla}_{\xi_n}, \vec{\nabla}_{\xi_n} \Phi_1(\vec{R}_n)) | 0 \rangle \\ \hat{D} &= \langle (\vec{\nabla}_{\xi_n}, \vec{\nabla}_{\xi_{n'}} \Phi_2(\vec{R}_n, \vec{R}_{n'})) | 0 \rangle \end{aligned}$$

In (14)

$$\langle \dots \rangle = \frac{Sp e^{-\beta H_0} e^{-\beta H_1}}{Sp e^{-\beta H_0}}, \quad H = H_0 + H_1,$$

$H_0$  is a Hamiltonian in (7) in which  $\vec{R}_n = \vec{R}_n^0$ ,  $(\dots, \dots)$  is a dot product and  $[\dots]_0$  means that after the calculations we put  $\vec{R}_n = \vec{R}_n^0$ .

Equation (14) in the case when  $n(x_3) = N\mathcal{Z}/V$  has only a trivial solution  $\xi_m \equiv 0$ .

In the case if the simple cubical lattice ( $\xi_m = (0, 0, \xi)$ ) when the condition of a local equilibrium  $\vec{\nabla}_{\xi} \sum_{n=1}^N \sum_{n'=1}^N \Phi_2(\vec{R}_m, \vec{R}_{n'}) = 0$  [5], (14) become simplified and allow a numerical solution. Calculating diagonal elements of a stress tensor  $\sigma_{ii} = \partial F / \partial \xi_m^{(i)}$ , ( $i = 1, 2, 3$ ) when taking into account conditions  $\sigma_{33} = P_3$ , where  $P_3$  is a normal to a interface surface of the force component that affects from the side of the electrons layer from condition

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

We calculated a relative change  $\frac{\Delta V}{V}$ :

$n$	1	2	3	4	5
$\Delta V/V$	0.21	0.15	0.10	0.05	0.001

Knowing  $\frac{\Delta V}{V}$  it is easy to calculate the change of the ion density.

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