On Optimization Problem Arising in Computer Simulation of Crystal Structures

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Abstract— Gradient optimization methods are often used to solve problems of computer simulation of the crystal structures of materials. In this case it becomes necessary to calculate the partial derivatives of the total atoms' system energy according to different parameters. Frequently the calculation of these derivatives is an extremely time-consuming and difficult problem. In this paper we present an algorithm for calculation of the second derivatives of the atoms' system energy with respect to the coordinates of the atoms in the case when the interaction of atoms is described by the Tersoff Potential.

Keywords— potentials, energy, gradients, Hessian, fast automatic differentiation

I. Introduction

When describing and modelling the crystal structure of a material characterized by chemical composition, geometry, and type of chemical bond, interatomic interaction potentials are used. The properties of crystals with a covalent connection (for example, carbon, silicon, germanium, etc.) are often described by the Tersoff Potential (see [1]). It is an example of a multiparticle potential based on the concept of the order of connections: binding force between two atoms is not constant, but depends on the local environment.

One of the important stages of modelling the crystal structure of the material under study is the optimization according to the coordinates of the particles, which arranges particles in positions corresponding to the minimum of the total atoms' system energy. To solve this problem gradient optimization methods are often used (see [2]-[4]). At this stage it becomes necessary to calculate the partial derivatives and the Hessian of the energy of atoms' system according to the coordinates of the atoms. In the case when the energy is determined using the Tersoff Potential, the calculation of the indicated first and second derivatives is an extremely time-consuming and difficult problem.

First, as the results of the performed studies showed (see [5]), the use of the finite difference method does not allow to calculate the derivatives of the energy with acceptable accuracy. In addition, in the case of using this method it is necessary to carry out researches related to the choice of the suitable increment of atoms' coordinates at each stage of the optimization problem.

Second, the use of standard software packages for calculation of second derivatives can be associated with large restrictions on the dimension of the problem and this fact must be taken into account when a fragment of the material under study contains an enormous number of atoms.

In this paper a special multi-step process is constructed to calculate the energy of the atoms' system. This makes it possible to substantially simplify and increase the reliability of the calculation of the second derivatives of energy. On the basis of the constructed multi-step process, an algorithm of calculation of the exact values of the Hessian of considered cost function is proposed.

II. Algorithm for Computing Hessian of the Cost Function

The Tersoff Potential makes it possible to calculate the bond energy of the atoms' system by the following formula:

$$E = \sum_{i=1}^{I} \sum_{\substack{j=1 \\ j \neq i}}^{I} V_{ij}, \quad V_{ij} = f_c(r_{ij})\big(V_R(r_{ij}) - b_{ij} V_A(r_{ij})\big),$$

$$f_c(r) = \begin{cases} 1, & r < R - R_{cut} = R^-, \\ \frac{1}{2}\left(1 - \sin\left(\frac{\pi(r-R)}{2R_{cut}}\right)\right), & R^- < r < R^+, \\ 0, & r > R + R_{cut} = R^+, \end{cases}$$

$$V_{ij}^R = V_R(r_{ij}) = \frac{D_e}{S-1} \exp\left(-\beta\sqrt{2S}\,(r_{ij} - r_e)\right),$$

$$V_{ij}^A = V_A(r_{ij}) = \frac{SD_e}{S-1} \exp\left(-\beta\sqrt{\frac{2}{S}}(r_{ij} - r_e)\right),$$

$$b_{ij} = \left(1 + \left(\gamma\varsigma_{ij}\right)^{\eta}\right)^{-\frac{1}{2\eta}},$$

$$\varsigma_{ij} = \sum_{\substack{k=1 \\ k\neq i,j}}^{I} f_c(r_{ik}) g_{ijk}\omega_{ijk} ,$$

$$\omega_{ijk} = \exp\left(\lambda^3 \tau_{ijk}\right), \qquad \tau_{ijk} = \left(r_{ij} - r_{ik}\right)^3 ,$$

$$g_{ijk} = g(\theta_{ijk}) = 1 + \left(\frac{c}{d}\right)^2 - \frac{c^2}{d^2 + (h - \cos\theta_{ijk})^2} .$$

Here I is the number of atoms in the group under consideration; r_{ij} are the distances between atoms with numbers i and j; θ_{ijk} is the angle formed by the vectors connecting the atom i with the atoms j and k respectively; R and R_{cut} are known parameters, identified from experimental properties of substance. The Tersoff Potential depends on ten parameters, specific to modelled substances: D_e, r_e, β, S, η, γ, λ, c, d, h.

The distance between atoms with numbers i and j ($i, j = \overline{1, I}$) is determined by the relationship:

$$r_{ij} = \sqrt{\left(x_{1i} - x_{1j}\right)^2 + \left(x_{2i} - x_{2j}\right)^2 + \left(x_{3i} - x_{3j}\right)^2} ,$$

(x_{1i}, x_{2i}, x_{3i}) are the coordinates of the i-th atom, $\cos(\theta_{ijk}) = \left(r_{ij}^2 + r_{ik}^2 - r_{jk}^2\right) / \left(2 r_{ij} r_{ik}\right)$.

We represent the calculation of the energy of atoms' system (the interaction of atoms is described by the Tersoff Potential) in the form of a multi-step process. Let $\bar{u}$ and $\bar{z}$ be vectors having coordinates:

$$\bar{u}^T = [u_1, u_2, ..., u_{10}]^T \qquad \bar{z}^T = [z_1, z_2, ..., z_{17}]^T .$$

where

$$u_1 = D_e, \quad u_2 = r_e, \quad u_3 = \beta, \quad u_4 = S, \quad u_5 = \eta,$$

$$u_6 = \gamma, \quad u_7 = \lambda, \quad u_8 = c, \quad u_9 = d, \quad u_{10} = h .$$

Then

$$z_1 = \left\{ z_1^{ijk} = \sqrt{\left(x_{1i} - x_{1k}\right)^2 + \left(x_{2i} - x_{2k}\right)^2 + \left(x_{3i} - x_{3k}\right)^2} \right\},$$

$$z_2 = \left\{ z_2^{ijk} = \sqrt{\left(x_{1j} - x_{1k}\right)^2 + \left(x_{2j} - x_{2k}\right)^2 + \left(x_{3j} - x_{3k}\right)^2} \right\},$$

$$z_3 = \left\{ z_3^{ijk} = q_{ijk} = \frac{(z_{13}^{ij})^2 + (z_1^{ijk})^2 - (z_2^{ijk})^2}{2 z_{13}^{ij} z_1^{ijk}} \right\},$$

$$z_4 = \left\{ z_4^{ijk} = f_c(z_1^{ijk}) \right\},$$

$$z_5 = \left\{ z_5^{ijk} = g_{ijk} = 1 + \left(\frac{u_8}{u_9}\right)^2 - \frac{(u_8)^2}{(u_9)^2 + (u_{10} - z_3^{ijk})^2} \right\},$$

$$z_6 = \left\{ z_6^{ijk} = \tau_{ijk} = \left(z_{13}^{ij} - z_1^{ijk}\right)^3 \right\},$$

$$z_7 = \left\{ z_7^{ijk} = \omega_{ijk} = \exp\left((u_7)^3 z_6^{ijk}\right) \right\},$$

$$z_8 = \left\{ z_8^{ijk} = f_c(r_{ik}) g_{ijk}\omega_{ijk} = z_4^{ijk} z_5^{ijk} z_7^{ijk} \right\},$$

$$z_9 = \left\{ z_9^{ij} = \varsigma_{ij} = \sum_{\substack{k=1, \\ k\neq i,j}}^{I} z_8^{ijk} \right\},$$

$$z_{10} = \left\{ z_{10}^{ij} = \gamma\varsigma_{ij} = u_6 z_9^{ij} \right\},$$

$$z_{11} = \left\{ z_{11}^{ij} = (\gamma\varsigma_{ij})^{\eta} = (z_{10}^{ij})^{u_5} \right\},$$

$$z_{12} = \left\{ z_{12}^{ij} = b_{ij} = (1 + z_{11}^{ij})^{-\frac{1}{2u_5}} \right\},$$

$$z_{13} = \left\{ z_{13}^{ij} = \sqrt{\left(x_{1i} - x_{1j}\right)^2 + \left(x_{2i} - x_{2j}\right)^2 + \left(x_{3i} - x_{3j}\right)^2} \right\},$$

$$z_{14} = \left\{ z_{14}^{ij} = V_{ij}^R = \frac{u_1}{u_4 - 1} \exp\left(-u_3\sqrt{2u_4}(z_{13}^{ij} - u_2)\right) \right\},$$

$$z_{15} = \left\{ z_{15}^{ij} = V_{ij}^A = \frac{u_1 u_4}{u_4 - 1} \exp\left(-u_3\sqrt{\frac{2}{u_4}}(z_{13}^{ij} - u_2)\right) \right\},$$

$$z_{16} = \left\{ z_{16}^{ij} = f_c(z_{13}^{ij}) \right\},$$

$$z_{17} = \left\{ z_{17}^{ij} = V_{ij} = z_{16}^{ij}(z_{14}^{ij} - z_{12}^{ij} z_{15}^{ij}) \right\},$$

$$\left(i = \overline{1, I},\ j = \overline{i, I},\ j \neq i,\ k = \overline{1, I},\ k \neq i,\ j\right).$$

Thus, the energy of the atoms' system is calculated by the formula:

$$E = E(x_{11}, x_{21}, x_{31}^1, \ldots, x_{1I}, x_{2I}, x_{3I}) = \sum_{i=1}^{I} \sum_{\substack{j=i \\ j\neq i}}^{I} z_{17}^{ij} .$$

Note that each z_l component consists of a set of other components.

The derivatives with respect to the coordinates of atoms is a vector with the components:

$$\nabla E = \left(\frac{\partial E}{\partial x_{11}}, \frac{\partial E}{\partial x_{21}}, \frac{\partial E}{\partial x_{31}}, \ldots, \frac{\partial E}{\partial x_{1I}}, \frac{\partial E}{\partial x_{2I}}, \frac{\partial E}{\partial x_{3I}} \right).$$

The matrix of second derivatives has components:

$$\left\{ \frac{\partial^2 E}{\partial x_{lm} \partial x_{np}} \right\}, \quad l, n = \overline{1,3}, \quad m, p = \overline{1, I}.$$

To calculate the Hessian of a function E the need of smoothing of the function $f_c(r)$ appears. It is proposed to replace the function $f_c(r)$ with the following:

$$f_c(r) = \begin{cases} 0, & r \geq R^+, \\ 1, & r \leq R^-, \\ C \cdot (f_*)^{\varphi(r)}, & R \leq r < R^+, \\ C \cdot \left(2 f_* - (f_*)^{\psi(r)} \right), & R^- < r \leq R, \end{cases}$$

where $f_* = \exp(-1.5)$, $C = 1/(2 f_*)$,

$$\varphi(r) = \frac{R_{cut}^2}{(r - R - R_{cut})^2}, \quad \psi(r) = \frac{R_{cut}^2}{(r - R + R_{cut})^2}.$$

The derivative of function $f_c(r)$ with respect to r is calculated by the formula:

$$\frac{df_c(r)}{dr} = \begin{cases} 0, & r \geq R^+, \\ 0, & r \leq R^-, \\ C \cdot (f_*)^{\varphi(r)} \ln(f_*) \cdot \tilde{\varphi}(r), & R \leq r < R^+, \\ -C \cdot (f_*)^{\psi(r)} \ln(f_*) \cdot \tilde{\psi}(r), & R^- < r \leq R, \end{cases}$$

where

$$\tilde{\varphi}(r) = \frac{-2R_{cut}^2}{(r - R - R_{cut})^3}, \quad \tilde{\psi}(r) = \frac{-2R_{cut}^2}{(r - R + R_{cut})^3}.$$

We introduce the following notation: $\tilde{z}_1, \tilde{z}_2, \ldots, \tilde{z}_{17}$ and $\tilde{\tilde{z}}_1, \tilde{\tilde{z}}_2, \ldots, \tilde{\tilde{z}}_{17}$, where

$$\tilde{z}_s = \left\{ \tilde{z}_s^{ijk} : \tilde{z}_s^{ijk} = \frac{\partial z_s^{ijk}}{\partial x_{lm}} \right\}, \quad s = \overline{1,8},$$

$$\tilde{z}_s = \left\{ \tilde{z}_s^{ij} : \tilde{z}_s^{ij} = \frac{\partial z_s^{ij}}{\partial x_{lm}} \right\}, \quad s = \overline{9,17},$$

$$\tilde{\tilde{z}}_s = \left\{ \tilde{\tilde{z}}_s^{ijk} : \tilde{\tilde{z}}_s^{ijk} = \frac{\partial^2 z_s^{ijk}}{\partial x_{lm} \partial x_{np}} \right\}, \quad s = \overline{1,8},$$

$$\tilde{\tilde{z}}_s = \left\{ \tilde{\tilde{z}}_s^{ij} : \tilde{\tilde{z}}_s^{ij} = \frac{\partial^2 z_s^{ij}}{\partial x_{lm} \partial x_{np}} \right\}, \quad s = \overline{9,17}.$$

The above-indicated values are calculated by the formulas (for all $l = 1,2,3; \quad i, j, k, m = \overline{1, I}$):

$$\tilde{z}_1^{ijk} = \frac{\partial z_1^{ijk}}{\partial x_{lm}} = \begin{cases} \frac{x_{lm} - x_{lk}}{z_1^{mjk}}, & m = i, k \neq m \\ \frac{x_{lm} - x_{li}}{z_1^{ijm}}, & m = k, i \neq m \\ 0, & \text{in other cases;} \end{cases}$$

$$\tilde{z}_2^{ijk} = \frac{\partial z_2^{ijk}}{\partial x_{lm}} = \begin{cases} \frac{x_{lm} - x_{lk}}{z_2^{imk}}, & m = j, k \neq m \\ \frac{x_{lm} - x_{lj}}{z_2^{ijm}}, & m = k, j \neq m \\ 0, & \text{in other cases;} \end{cases}$$

$$\tilde{z}_3^{ijk} = \frac{z_1^{ijk} \left(z_{13}^{ij} \right)^2 \tilde{z}_{13}^{ij} + z_{13}^{ij} \left(z_1^{ijk} \right)^2 \tilde{z}_1^{ijk} - 2 z_1^{ijk} z_{13}^{ij} z_2^{ijk} \tilde{z}_2^{ijk}}{2 \left(z_{13}^{ij} \right)^2 \left(z_1^{ijk} \right)^2} +$$

$$+ \frac{-\left(z_1^{ijk} \right)^3 \tilde{z}_{13}^{ij} + z_1^{ijk} \left(z_2^{ijk} \right)^2 \tilde{z}_{13}^{ij} - \left(z_{13}^{ij} \right)^3 \tilde{z}_1^{ijk} + z_{13}^{ij} \left(z_2^{ijk} \right)^2 \tilde{z}_1^{ijk}}{2 \left(z_{13}^{ij} \right)^2 \left(z_1^{ijk} \right)^2};$$

$$\tilde{z}_4^{ijk} = \begin{cases} 0, & z_1^{ijk} \geq R^+, \\ 0, & z_1^{ijk} \leq R^-, \\ -\Pi \cdot (f_*)^{\varphi\left(z_1^{ijk}\right)} / \left(z_1^{ijk} - R^+ \right)^3, & R \leq z_1^{ijk} < R^+, \\ \Pi \cdot (f_*)^{\psi\left(z_1^{ijk}\right)} / \left(z_1^{ijk} - R^- \right)^3, & R^- < z_1^{ijk} \leq R, \end{cases}$$

where $\Pi = 2CR_{cut}^2 \ln(f_*) \cdot \tilde{z}_1^{ijk}$;

$$\tilde{z}_5^{ijk} = \frac{-2 (u_8)^2 \left(u_{10} - z_3^{ijk} \right) \cdot \tilde{z}_3^{ijk}}{\left((u_9)^2 + \left(u_{10} - z_3^{ijk} \right)^2 \right)^2};$$

$$\tilde{z}_6^{ijk} = 3 \left(z_{13}^{ij} - z_1^{ijk} \right)^2 \left(\tilde{z}_{13}^{ij} - \tilde{z}_1^{ijk} \right);$$

$$\tilde{z}_7^{ijk} = (u_7)^3 \exp\left((u_7)^3 z_6^{ijk} \right) \tilde{z}_6^{ijk};$$

$$\tilde{z}_8^{ijk} = \tilde{z}_4^{ijk} z_5^{ijk} z_7^{ijk} + z_4^{ijk} \tilde{z}_5^{ijk} z_7^{ijk} + z_4^{ijk} z_5^{ijk} \tilde{z}_7^{ijk};$$

$$\tilde{z}_9^{ij} = \sum_{\substack{k=1,\\ k\neq i,j}}^{I} \tilde{z}_8^{ijk};$$

$$\tilde{z}_{10}^{ij} = \tilde{z}_9^{ij} \cdot u_6;$$

$$\tilde{z}_{11}^{ij} = \tilde{z}_{10}^{ij} \cdot u_5 \cdot \left(z_{10}^{ij}\right)^{u_5-1};$$

$$\tilde{z}_{12}^{ij} = -\tilde{z}_{11}^{ij} \cdot \left(1+z_{11}^{ij}\right)^{-\frac{1}{2u_5}-1} / (2u_5);$$

$$\tilde{z}_{13}^{ij} = \frac{\partial z_{13}^{ij}}{\partial x_{lm}} = \begin{cases} \dfrac{x_{lm}-x_{lj}}{z_{13}^{mj}}, & m=i,\ j\neq m \\ \dfrac{x_{lm}-x_{li}}{z_{13}^{im}}, & m=j,\ i\neq m \\ 0, & \text{in other cases;} \end{cases}$$

$$\tilde{z}_{14}^{ij} = -u_3\sqrt{2u_4} \cdot z_{14}^{ij} \cdot \tilde{z}_{13}^{ij};$$

$$\tilde{z}_{15}^{ij} = -u_3\sqrt{2/u_4} \cdot z_{15}^{ij} \cdot \tilde{z}_{13}^{ij};$$

$$\tilde{z}_{16}^{ij} = \begin{cases} 0, & z_{13}^{ij} \geq R^+, \\ 0, & z_{13}^{ij} \leq R - R_{cut}, \\ -\Lambda \cdot (f_*)^{\varphi\left(z_{13}^{ij}\right)} / \left(z_{13}^{ij} - R^+\right)^3, & R \leq z_{13}^{ij} < R^+, \\ \Lambda \cdot (f_*)^{\psi\left(z_{13}^{ij}\right)} / \left(z_{13}^{ij} - R^-\right)^3, & R^- < z_{13}^{ij} \leq R, \end{cases}$$

where $\Lambda = 2C \cdot R_{cut}^2 \cdot \ln(f_*) \cdot \tilde{z}_{13}^{ij}$;

$$\tilde{z}_{17}^{ij} = \tilde{z}_{16}^{ij} \cdot z_{14}^{ij} - \tilde{z}_{16}^{ij} \cdot z_{12}^{ij} \cdot z_{15}^{ij} + z_{16}^{ij} \cdot \tilde{z}_{14}^{ij} - $$
$$ - z_{16}^{ij} \cdot \tilde{z}_{12}^{ij} \cdot z_{15}^{ij} - z_{16}^{ij} \cdot z_{12}^{ij} \cdot \tilde{z}_{15}^{ij}.$$

Thus, $$\frac{\partial E(z(u))}{\partial x_{lm}} = \sum_{i=1}^{I} \sum_{\substack{j=i\\ j\neq i}}^{I} \tilde{z}_{17}^{ij}.$$

In order to write the formulas for the second derivatives of the total atoms' system energy with respect to the coordinates of the atoms, we introduce a number of notations:

$$z'_s = \left\{ z'^{ijk}_s : z'^{ijk}_s = \frac{\partial z_s^{ijk}}{\partial x_{np}} \right\}, \qquad s = \overline{1,8},$$

$$z'_s = \left\{ z'^{ij}_s : z'^{ij}_s = \frac{\partial z_s^{ij}}{\partial x_{np}} \right\}, \qquad s = \overline{9,17}.$$

These derivatives are calculated using the same formulas as the derivatives $\tilde{z}_1, \tilde{z}_2, ..., \tilde{z}_{17}$, only here the index l changes to n, and the index m to p.

For more effective calculation of the above mentioned gradient, the Fast Automatic Differentiation technique may be used (see [5]).

The second derivatives of the variables $z_1, z_2, ..., z_{17}$ with respect to the coordinates of the atoms (for all $l,n = 1,2,3;\quad i,j,k = \overline{1,I};\quad m,p = \overline{1,I}$) are calculated by the formulas:

$$\tilde{\tilde{z}}_1^{ijk} = \frac{\partial \tilde{z}_1^{ijk}}{\partial x_{np}} = \frac{\partial^2 z_1^{ijk}}{\partial x_{lm}\partial x_{np}} =$$

$$= \begin{cases} \dfrac{\left(z_1^{pjk}\right)^2 - \left(x_{np}-x_{nk}\right)^2}{\left(z_1^{pjk}\right)^3}, & m=i;\quad n=l;\quad p=m;\quad m\neq k, \\ \dfrac{-\left(z_1^{mjp}\right)^2 + \left(x_{nm}-x_{np}\right)^2}{\left(z_1^{mjp}\right)^3}, & m=i;\quad n=l;\quad p=k;\quad m\neq k, \\ \dfrac{\left(z_1^{ijp}\right)^2 - \left(x_{np}-x_{ni}\right)^2}{\left(z_1^{ijp}\right)^3}, & m=k;\quad n=l;\quad p=m;\quad m\neq i, \\ \dfrac{-\left(z_1^{pjm}\right)^2 + \left(x_{np}-x_{nm}\right)^2}{\left(z_1^{pjm}\right)^3}, & m=k;\quad n=l;\quad p=i;\quad m\neq i, \\ \dfrac{\left(x_{lk}-x_{lm}\right)\left(x_{np}-x_{nk}\right)}{\left(z_1^{pjk}\right)^3}, & m=i;\quad n\neq l;\quad p=m;\quad m\neq k, \\ \dfrac{\left(x_{lm}-x_{lk}\right)\left(x_{nm}-x_{np}\right)}{\left(z_1^{mjp}\right)^3}, & m=i;\quad n\neq l;\quad p=k;\quad m\neq k, \\ \dfrac{\left(x_{li}-x_{lm}\right)\left(x_{np}-x_{nm}\right)}{\left(z_1^{ijp}\right)^3}, & m=k;\quad n\neq l;\quad p=i;\quad m\neq i, \\ \dfrac{\left(x_{lm}-x_{li}\right)\left(x_{ni}-x_{np}\right)}{\left(z_1^{pjm}\right)^3}, & m=k;\quad n\neq l;\quad p=m;\quad m\neq i, \\ 0, & \text{in other cases;} \end{cases}$$

$$\tilde{\tilde{z}}_2^{ijk} = \frac{\partial \tilde{z}_2^{ijk}}{\partial x_{np}} = \frac{\partial^2 z_2^{ijk}}{\partial x_{lm}\partial x_{np}};$$

$$\tilde{\tilde{z}}_3^{ijk} = \Big(z_1^{ijk} z_{13}^{ij} \cdot \Big(z'^{ijk}_1 \left(z_{13}^{ij}\right)^2 \tilde{z}_{13}^{ij} +$$
$$+ 2z_1^{ijk} z_{13}^{ij} \tilde{z}_{13}^{ij} z'^{ij}_{13} + \left(z_{13}^{ij}\right)^2 z_1^{ijk} \tilde{\tilde{z}}_{13}^{ij} +$$
$$+ \left(z_1^{ijk}\right)^2 \tilde{z}_1^{ijk} z'^{ij}_{13} + 2z'^{ijk}_1 z_{13}^{ij} \tilde{z}_1^{ijk} z_1^{ijk} + \tilde{\tilde{z}}_1^{ijk} \left(z_1^{ijk}\right)^2 z_{13}^{ij} -$$
$$- 2(z_2^{ijk} z'^{ijk}_1 \tilde{z}_2^{ijk} z_{13}^{ij} + z_2^{ijk} z_1^{ijk} \tilde{z}_2^{ijk} z'^{ij}_{13} + z'^{ijk}_2 z_1^{ijk} \tilde{z}_2^{ijk} z_{13}^{ij} +$$
$$+ z_2^{ijk} z_1^{ijk} \tilde{\tilde{z}}_2^{ijk} z_{13}^{ij}) - 3\left(z_1^{ijk}\right)^2 \tilde{z}_{13}^{ij} z'^{ijk}_1 -$$

$$-\left(z_1^{ijk}\right)^3 \tilde{\tilde{z}}_{13}^{ij} + z_1'^{ijk}\left(z_2^{ijk}\right)^2 \tilde{z}_{13}^{ij} +$$

$$+ 2z_1^{ijk} z_2^{ijk} z_2'^{ijk}\tilde{z}_{13}^{ij} + z_1^{ijk}\left(z_2^{ijk}\right)^2 \tilde{\tilde{z}}_{13}^{ij} + \tilde{z}_1^{ijk}\left(z_2^{ijk}\right)^2 z_{13}'^{ij} +$$

$$-\left(z_{13}^{ij}\right)^3 \tilde{\tilde{z}}_1^{ijk}\Big) - 2\left(z_1^{ijk} z_{13}'^{ij} + z_{13}^{ij} z_1'^{ijk}\right)\times\Big(z_1^{ijk}\left(z_{13}^{ij}\right)^2\tilde{z}_{13}^{ij} +$$

$$+ z_{13}^{ij}\left(z_1^{ijk}\right)^2 \tilde{z}_1^{ijk} - 2 z_1^{ijk} z_{13}^{ij} z_2^{ijk}\tilde{z}_2^{ijk} -$$

$$-\left(z_1^{ijk}\right)^3 \tilde{z}_{13}^{ij} + z_1^{ijk}\left(z_2^{ijk}\right)^2\tilde{z}_{13}^{ij} -$$

$$-\left(z_{13}^{ij}\right)^3\tilde{z}_1^{ijk} + z_{13}^{ij}\left(z_2^{ijk}\right)^2\Big)\Big)\Big/\left(2\left(z_1^{ijk}\right)^2\left(z_{13}^{ij}\right)^2\right);$$

$$\tilde{\tilde{z}}_4^{ijk} = \begin{cases} 0, & z_1^{ijk} \ge R^+, \\ 0, & z_1^{ijk} \le R^-, \\ -\mathrm{H}\cdot C\cdot\left(f_*\right)^{\varphi\left(z_1^{ijk}\right)}\times \\ \times\Big[-\mathrm{H}\cdot z_1'^{ijk}\tilde{z}_1^{ijk}/\left(z_1^{ijk}-R^+\right)^6 + \\ \tilde{\tilde{z}}_1^{ijk}\left(z_1^{ijk}-R-R_{cut}\right)/\left(z_1^{ijk}-R^+\right)^4 - & R \le z_1^{ijk} < R^+, \\ -3z_1'^{ijk}\tilde{z}_1^{ijk}/\left(z_1^{ijk}-R^+\right)^4\Big], \\ \mathrm{H}\cdot C\cdot\left(f_*\right)^{\psi\left(z_1^{ijk}\right)}\times \\ \times\Big[-\mathrm{H}\cdot z_1'^{ijk}\tilde{z}_1^{ijk}/\left(z_1^{ijk}-R^-\right)^6 + \\ +\tilde{\tilde{z}}_1^{ijk}\left(z_1^{ijk}-R+R_{cut}\right)/\left(z_1^{ijk}-R^-\right)^4 - & R^- < z_1^{ijk} \le R, \\ -3z_1'^{ijk}\tilde{z}_1^{ijk}/\left(z_1^{ijk}-R^-\right)^4\Big], \end{cases}$$

where $\mathrm{H} = 2R_{cut}^2\ln\left(f_*\right)$;

$$\tilde{\tilde{z}}_5^{ijk} = \frac{-2(u_8)^2\left(\left(u_{10}-z_3^{ijk}\right)\tilde{\tilde{z}}_3^{ijk} - z_3'^{ijk}\tilde{z}_3^{ijk}\right)\left((u_9)^2 + \left(u_{10}-z_3^{ijk}\right)^2\right)}{\left((u_9)^2+\left(u_{10}-z_3^{ijk}\right)^2\right)^3} -$$

$$-\frac{8(u_8)^2\left(u_{10}-z_3^{ijk}\right)^2 z_3'^{ijk}\tilde{z}_3^{ijk}}{\left((u_9)^2+\left(u_{10}-z_3^{ijk}\right)^2\right)^3};$$

$$\tilde{\tilde{z}}_6^{ijk} = 6\left(z_{13}^{ij}-z_1^{ijk}\right)\left(z_{13}'^{ij}-z_1'^{ijk}\right)\left(\tilde{z}_{13}^{ij}-\tilde{z}_1^{ijk}\right) +$$

$$+3\left(z_{13}^{ij}-z_1^{ijk}\right)^2\left(z_{13}'^{ij}-z_1'^{ijk}\right);$$

$$\tilde{\tilde{z}}_7^{ijk} = (u_7)^3\exp\left((u_7)^3 z_6^{ijk}\right)\left((u_7)^3 z_6'^{ijk}\tilde{z}_6^{ijk} + \tilde{\tilde{z}}_6^{ijk}\right);$$

$$\tilde{\tilde{z}}_8^{ijk} = \tilde{\tilde{z}}_4^{ijk} z_5^{ijk} z_7^{ijk} + \tilde{z}_4^{ijk} z_5'^{ijk} z_7^{ijk} + \tilde{z}_4^{ijk} z_5^{ijk} z_7'^{ijk} +$$

$$+ z_4^{ijk}\tilde{\tilde{z}}_5^{ijk} z_7^{ijk} + z_4'^{ijk}\tilde{z}_5^{ijk} z_7^{ijk} + z_4^{ijk} z_5^{ijk}\tilde{\tilde{z}}_7^{ijk} +$$

$$+ z_4'^{ijk} z_5^{ijk}\tilde{z}_7^{ijk} + z_4^{ijk}\tilde{z}_5^{ijk} z_7'^{ijk} + z_4^{ijk} z_5'^{ijk}\tilde{z}_7^{ijk};$$

$$\tilde{\tilde{z}}_9^{ij} = \sum_{\substack{k=1 \\ k\ne i,j}}^{I}\tilde{\tilde{z}}_8^{ijk}; \qquad \tilde{\tilde{z}}_{10}^{ij} = \tilde{\tilde{z}}_9^{ij}\cdot u_6;$$

$$\tilde{\tilde{z}}_{11}^{ij} = u_5\left(\tilde{\tilde{z}}_{10}^{ij}\cdot\left(z_{10}^{ij}\right)^{u_5-1} + \left(u_5-1\right)\cdot\left(z_{10}^{ij}\right)^{u_5-2}\cdot z_{10}'^{ij}\tilde{z}_{10}^{ij}\right);$$

$$\tilde{\tilde{z}}_{12}^{ij} = -\frac{1}{2u_5}\left(\tilde{\tilde{z}}_{11}^{ij}\left(1+z_{11}^{ij}\right)^{-\frac{1}{2u_5}-1} - \left(\frac{1}{2u_5}+1\right)\left(1+z_{11}^{ij}\right)^{-\frac{1}{2u_5}-2} z_{11}'^{ij}\tilde{z}_{11}^{ij}\right);$$

$$\tilde{\tilde{z}}_{13}^{ij} = \frac{\partial\tilde{z}_{13}^{ij}}{\partial x_{np}} = \frac{\partial^2 z_{13}^{ij}}{\partial x_{lm}\partial x_{np}};$$

$$\tilde{\tilde{z}}_{14}^{ij} = -u_3\sqrt{2u_4}\cdot\left(z_{14}'^{ij}\cdot\tilde{z}_{13}^{ij} + z_{14}^{ij}\cdot\tilde{\tilde{z}}_{13}^{ij}\right);$$

$$\tilde{\tilde{z}}_{15}^{ij} = -u_3\sqrt{2/u_4}\cdot\left(z_{15}'^{ij}\cdot\tilde{z}_{13}^{ij} + z_{15}^{ij}\cdot\tilde{\tilde{z}}_{13}^{ij}\right);$$

$$\tilde{\tilde{z}}_{16}^{ij} = \begin{cases} 0, & z_{13}^{ij} \ge R^+, \\ 0, & z_{13}^{ij} \le R^-, \\ -\mathrm{H}\cdot C\cdot\left(f_*\right)^{\varphi\left(z_{13}^{ij}\right)}\times \\ \times\Big[-\mathrm{H}\cdot z_{13}'^{ij}\tilde{z}_{13}^{ij}/\left(z_{13}^{ij}-R^+\right)^6 + \\ +(\tilde{\tilde{z}}_{13}^{ij}(z_{13}^{ij}-R^+) - & R \le z_{13}^{ij} < R^+, \\ -3z_{13}'^{ij}\tilde{z}_{13}^{ij})/\left(z_{13}^{ij}-R^+\right)^4\Big], \\ \mathrm{H}\cdot C\cdot\left(f_*\right)^{\psi\left(z_{13}^{ij}\right)}\times \\ \times\Big[-\mathrm{H}\cdot z_{13}'^{ij}\tilde{z}_{13}^{ij}/\left(z_{13}^{ij}-R^-\right)^6 + & R^- < z_{13}^{ij} \le R; \\ +(\tilde{\tilde{z}}_{13}^{ij}\left(z_{13}^{ij}-R^-\right) - \\ -3z_{13}'^{ij}\tilde{z}_{13}^{ij})/\left(z_{13}^{ij}-R^-\right)^4\Big] \end{cases}$$

$$\tilde{\tilde{z}}_{17}^{ij} = \tilde{\tilde{z}}_{16}^{ij}\cdot z_{14}^{ij} + \tilde{z}_{16}^{ij}\cdot z_{14}'^{ij} - \tilde{\tilde{z}}_{16}^{ij}\cdot z_{12}^{ij}\cdot z_{15}^{ij} + z_{16}'^{ij}\cdot\tilde{z}_{14}^{ij} -$$

$$-\tilde{z}_{16}^{ij}\cdot z_{12}'^{ij}\cdot z_{15}^{ij} - \tilde{z}_{16}^{ij}\cdot z_{12}^{ij}\cdot z_{15}'^{ij} + z_{16}^{ij}\cdot\tilde{\tilde{z}}_{14}^{ij} -$$

$$-z_{16}'^{ij}\cdot\tilde{z}_{12}^{ij}\cdot z_{15}^{ij} - z_{16}^{ij}\cdot\tilde{\tilde{z}}_{12}^{ij}\cdot z_{15}^{ij} - z_{16}^{ij}\cdot\tilde{z}_{12}^{ij}\cdot z_{15}'^{ij} -$$

$$-z_{16}'^{ij}\cdot z_{12}^{ij}\cdot\tilde{z}_{15}^{ij} - z_{16}^{ij}\cdot z_{12}'^{ij}\cdot\tilde{z}_{15}^{ij} - z_{16}^{ij}\cdot z_{12}^{ij}\cdot\tilde{\tilde{z}}_{15}^{ij}.$$

Formulas for calculating derivatives $\tilde{\tilde{z}}_2^{ijk}$ and $\tilde{\tilde{z}}_{13}^{ijk}$ are written in the same way as the formula for $\tilde{\tilde{z}}_1^{ijk}$.

Finally, the components of the Hessian of function E are calculated by the formula:

$$\frac{\partial^2 E(z(u))}{\partial x_{lm}\partial x_{np}} = \sum_{i=1}^{I}\sum_{\substack{j=i\\ j\neq i}}^{I} \tilde{\tilde{z}}_{17}^{ij}. \qquad (1)$$

In the case when a two-dimensional material model is considered, the indices l and n take only the values 1 and 2.

III. Calculation the Hessian of the Energy for a Two-Dimensional Material Model with the Unloaded Condition

The two-dimensional model of a multilayer piecewise-homogeneous material proposed in [2] and [3] is considered. In this model the material is represented as a periodic piecewise homogeneous multilayer structure in which the types of atoms in different layers may be different. This model imposes the following constraints on the structure of the layers:

1. Each layer consists of identical atoms, but different layers may consist of different atoms.

2. The distances between adjacent atoms in the same level are identical, but they may be different in different layers.

3. There is a group of K parallel layers that are periodically repeated in the direction of the axis y.

4. The number of atoms in each layer and the total number of layers are potentially unbounded.

Figure 1 gives an example of the model in which a group of three layers is repeated. Each layer consists of atoms of a specific type.

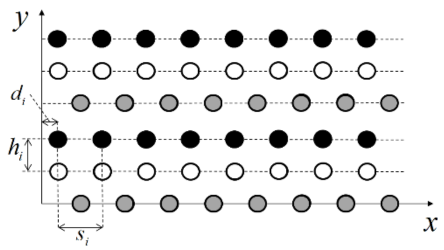

Fig. 1. Two-dimensional model of substance.

In this model, the position of the atoms is determined by the following parameters:

$h_k, k = 1,\ldots,K$ – the distance between the layer with the number k and the previous layer;

d_k, $k = 1,\ldots,K$ – the displacement of the first atom in the layer k with a positive abscissa relative to the zero mark;

s_k, $k = 1,\ldots,K$ – the interatomic distance in the layer k.

The parameters of the optimization problem are the variables $x = (h_1, d_1, s_1, \ldots, h_K, d_K, s_K)$ that make up the vector, which has dimension $n = 3K$.

Let x_i be the first coordinate of the i-th atom of a two-dimensional structure; y_i - its second coordinate. If the i-th atom is an atom with a sequence number j on the k-th layer, then:

$$x_i = d_k + (j-1)s_k;$$

$$y_i = 0, \quad if \quad k = 1; \qquad y_i = \sum_{m=2}^{k} h_k, \ if \quad k = 2,\ldots,K.$$

The first and second derivatives of the energy of atoms' system with the respect to parameters of the optimization problem are calculated by formulas:

$$\frac{\partial E(z)}{\partial h_k} = \sum_{i=1}^{I}\frac{\partial E(z)}{\partial y_i}\frac{\partial y_i}{\partial h_k}; \qquad \frac{\partial E(z)}{\partial d_k} = \sum_{i=1}^{I}\frac{\partial E(z)}{\partial x_i}\frac{\partial x_i}{\partial d_k};$$

$$\frac{\partial E(z)}{\partial s_k} = \sum_{i=1}^{I}\frac{\partial E(z)}{\partial x_i}\frac{\partial x_i}{\partial s_k};$$

$$\frac{\partial^2 E(z)}{\partial h_l \partial h_k} = \sum_{i=1}^{I}\left(\sum_{p=1}^{I}\frac{\partial^2 E(z)}{\partial y_i \partial y_p}\frac{\partial y_p}{\partial h_l}\right)\frac{\partial y_i}{\partial h_k};$$

$$\frac{\partial^2 E(z)}{\partial d_l \partial d_k} = \sum_{i=1}^{I}\left(\sum_{p=1}^{I}\frac{\partial^2 E(z)}{\partial x_i \partial x_p}\frac{\partial x_p}{\partial d_l}\right)\frac{\partial x_i}{\partial d_k};$$

$$\frac{\partial^2 E(z)}{\partial s_l \partial s_k} = \sum_{i=1}^{I}\left(\sum_{p=1}^{I}\frac{\partial^2 E(z)}{\partial x_i \partial x_p}\frac{\partial x_p}{\partial s_l}\right)\frac{\partial x_i}{\partial s_k};$$

$$\frac{\partial^2 E(z)}{\partial d_l \partial s_k} = \sum_{i=1}^{I}\left(\sum_{p=1}^{I}\frac{\partial^2 E(z)}{\partial x_i \partial x_p}\frac{\partial x_p}{\partial d_l}\right)\frac{\partial x_i}{\partial s_k};$$

$$\frac{\partial^2 E(z)}{\partial h_l \partial d_k} = 0; \qquad \frac{\partial^2 E(z)}{\partial h_l \partial s_k} = 0.$$

The second derivatives $\frac{\partial^2 E(z)}{\partial x_i \partial x_p}$ and $\frac{\partial^2 E(z)}{\partial y_i \partial y_p}$, which are used here, are calculated by the formula (1).

As the carried out calculations have shown, the use of the proposed formulas for calculation the second derivatives leads to a noticeable acceleration of the convergence of methods for solving the optimization problem.

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