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# Математическое моделирование

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## Mathematical Modeling of Thermal Restructuring of the Platinum Surface

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The article presents a mathematical model of the thermal rearrangement of the platinum surface (100)Pt. Earlier, the author would developed a termogeometric mathematical model of the dynamics of finite crystal sample. Unlike previous papers, this paper presents more advanced results of computational experiment.

**Key words and phrases:** mathematical model, numerical experiment, thermal rearrangement, reconstruction, molecular dynamics, thermodynamics, averaging over an ensemble.

Mathematical modeling of thermal rearrangement of the platinum surface is based on a model termogeometrical dynamics of finite crystal model, developed earlier by the author [1–3]. The results of simulation are important in connection with the description the so-called thermal reconstruction of the surface of some metals. The phenomenon of thermal reconstruction of clean single crystal surface has a solid experimental basis (reconstruction of some surfaces of noble metals [4,5], tungsten [6,7], silicon [8,9] etc.). For example, in [4,5] found that the clean surface (100)Pt when heated above a certain critical temperature is rearranged into a hexagonal phase.

For the termogeometric dynamics model of the final crystal sample key methodological components were: molecular dynamics method [10,11], as well as the adiabatic Born-Oppenheimer approximation [10–12], in which the interaction potential between atoms in the sample is represented as a decreasing number of many-particle potentials.

In [13–15] based on thermodynamic concepts the reconstruction related to phase transition on the surface. Molecular dynamics method is used to describe the reconstruction of such surfaces, as (100)Au [16–18], (100)Si [19–22], (100)W [23,24] etc.

In the Born-Oppenheimer approximation of potential  $U = U(r_1, \dots, r_N)$  interaction of  $N$  identical atoms of a crystal sample with a radiusvectors  $\mathbf{r}_1, \dots, \mathbf{r}_N$  can be represented as an expansion of many-particle potentials, that is

$$U = \sum_{1 \leq i < j \leq N} \varphi^{(2)}(ij) + \sum_{1 \leq i < j < k \leq N} \varphi^{(3)}(ijk) + \dots + \varphi^{(N)}, \quad (1)$$

where  $\varphi^{(2)}$ ,  $\varphi^{(3)}$ ,  $\dots$ , two-, three-particle, etc. potentials.

In [1] presented an algorithm for constructing many contributions to the potential (1) for a priori given the geometry of the lattice of atoms of the crystal sample. Consequence of the above builds is the conclusion of what non-trivial many-body potentials in a simple lattice of cubic symmetry. Thus, for the face-centered (fcc) lattice, which is typical for platinum, three- and four-particle potentials cannot be regarded as three- and four configurations of nearest neighbors — the equilateral triangle and the tetrahedron — respectively recorded in the binary interaction.

Recall the basic position the termogeometric dynamics model of the final crystal sample [2,3]. Model allows us to move from the ordinary equations of molecular dynamics to the equation to find a local minimum, and we can talk about transitions from one local minimum to another when the temperature parameter change.

Consider an arbitrary pair of local minima of the potential energy of  $N$  atoms. Different local minima will be considered in the case where their potential energies

are different from each other. At zero temperature, taking into account the smallness of the contribution of the effect of thermal expansion of the sample, we say that the system is either in first or second states or phases. In other words, if at zero temperature there are two local minima, then the nonzero — two states (two phases) of the sample.

Let us formulate the purpose of the simulation. For any pair of states to establish the possibility of transitions between them when the temperature changes from a certain range  $[T_1 T_2]$ , where  $T_1 < T_2$  and  $T_2$  less than the melting temperature of the sample. If such a transition is possible, then we will talk about the phase transition at some temperature  $T_f$ ,  $T_f \in [T_1 T_2]$ . If the configuration of the system changes a jump when the temperature changes, we will speak about the irreversible phase transition. If the configuration of the system continuously depends on the temperature of the transition between the states, in this case, such a transition is called reversible. In the last case, back sign of temperature change, we can return to its original state.

Define two local minimum of potential energy  $U$ :  $r^{(1)} = (r_1^{(1)}, \dots, r_N^{(1)})$ ,  $r^{(2)} = (r_1^{(2)}, \dots, r_N^{(2)})$ . In [2, 3] obtained the following equations describing the irreversible phase shift  $r^{(1)} \rightarrow r^{(2)}$ :

$$\dot{r}_i = -\mu \frac{\partial}{\partial r_i} \left[ U(r) + \frac{1}{2} T A_2^{-1} B_1 \cdot r \right], \quad (2)$$

where  $i = 1, \dots, N$ ,  $r = (r_1, \dots, r_N)$ ,  $\mu$  — some nonnegative parameter,  $T$  — temperature parameter In (2) includes the second and third derivatives of potential energy, taken in the local minima of  $r^{(2)}$  and  $r^{(1)}$ , respectively:

$$A_2 = A_{\alpha i, \beta j}^{(2)} = \frac{\partial^2 U(r)}{\partial r_{\alpha, i} \partial r_{\beta, j}} \Big|_{r=r^{(2)}}, \quad B_1 = B_{\alpha i, \beta j, \gamma k}^{(1)} = \frac{\partial^3 U(r)}{\partial r_{\alpha, i} \partial r_{\beta, j} \partial r_{\gamma, k}} \Big|_{r=r^{(1)}}.$$

Equation (2) use for numerical simulation of the thermal reconstruction of the surface of Pt. In this case the phase transition is modeled as follows. The potential  $U$  is chosen so that the growth temperature  $T$  to a certain value little temperature addition in (2) becomes sufficient to “push” system of atoms from the first to the second local minimum potential energy which is lower than the first ( $U_1 > U_2$ ). It is clear that such a phase transition is irreversible, because it goes with decreasing potential energy and with discontinuity in the  $r$  from  $T$ . According to experimental data [4, 5], platinum admits an irreversible phase transition of the surface temperature increases from zero to transition temperature  $T_f = 400$  K.

Usually choice of binary potential based on three conditions [25, 26]: the equilibrium of the lattice of atoms in terms of homogeneous deformation, the correspondence model of the sublimation energy and bulk compressibility of the sample experimentally observed values.

We assume that at distances in the vicinity of the first neighbors in the binary potential is chosen the Mi potential, that is

$$\varphi_1(R) = \frac{m}{n-m} R^{-n} - \frac{n}{n-m} R^{-m}. \quad (3)$$

In (3) considered that the length and energy are expressed at units of  $R$ ,  $\varepsilon$ , where  $R$  and  $\varepsilon$  — the minimum distance and the potential energy of a pair of atoms, in addition,  $\varphi_1(1) = -1$ ,  $\varphi_1'(1) = 0$ ,  $\varphi_1''(1) > 0$  and  $n > m$ . Satisfy the above three conditions, whereas  $\sum_i R_i \varphi_1'(R_i) = 0$ ,  $-E_{\text{sub}} = \frac{1}{2} \sum_i \varphi_1(R_i)$ ,  $K^{-1} = \frac{1}{18\omega} \sum_i R_i^2 \varphi_1''(R_i)$ , where  $E_{\text{sub}}$  — sublimation energy per one atom;  $4\omega$  — unit cell volume Pt,  $K^{-1}$  — coefficient of volume compressibility of the sample. In the last sum fixed atom is placed at origin of coordinates, while on the remaining atoms it is summation with index  $i$



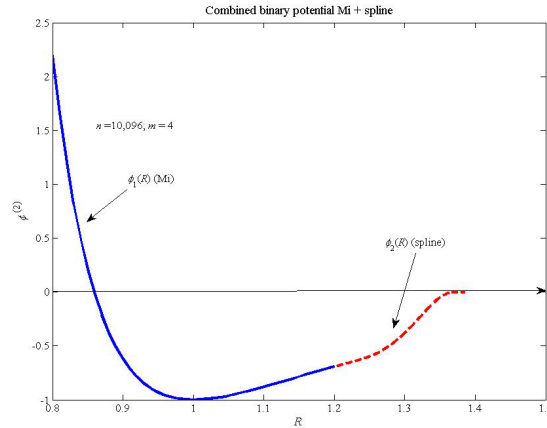


Figure 1. **Combined Binary Potential Mi + Spline**

our sample. To simulate the termogeometric dynamics need to find a solution to (2) when  $t \rightarrow \infty$  at each temperature, gradually approaching the point of irreversible phases transition

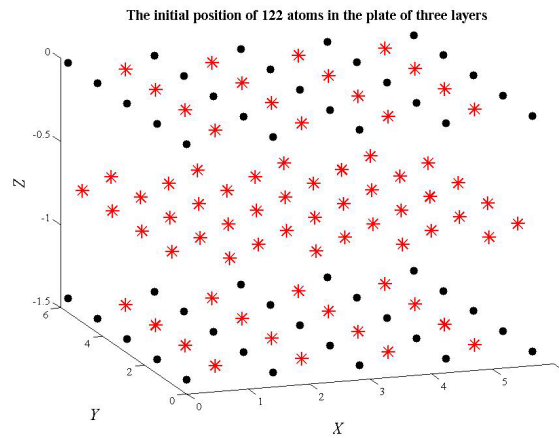


Figure 2. **Three-Dimensional Graph of the Fragment of the fcc Lattice in the Form of a Plate Square**

Figure 2 shows a three-dimensional graph of a fragment of the fcc lattice in the form of a plate of square shape, consisting of three layers of atoms in each of them 41, 40, 41, that is a total of 122 atoms. Markers as dots denote Pt atoms in the nodes of the cubic lattice, and the stars of the atoms in the center of the faces of the crystal cells. Selected number of atoms of 122 were limited resources available for the computation of the vector  $(A_2^{-1}B_1)_\alpha = \sum_{\beta\gamma} (A_2^{-1})_{\beta\gamma} (B_1)_{\alpha\beta\gamma}$ ,  $\alpha\beta\gamma = 1, \dots, 366$  ( $366 = 122 \times 3$ ) in (2). All three layers of atoms are based on a substrate consisting of four atoms of the same type. The presence of the substrate modifies the potential, that is  $U \rightarrow U^* = U + U_b$ , where

$$U_b = \sum_{i=1}^N \sum_{j=1}^4 \varphi^{(2)} (|R_i - R_{b_j}|), \tag{7}$$

$R_{b_1}, \dots, R_{b_4}$  — radiusvectors of the substrate. Note that the number of atoms of the substrate (7) is chosen minimal so that, on the one hand, remove the degeneracy of the matrix of second derivatives of the potential, on the other — to keep the symmetry characteristic of the selected fragment.

Construct two local minimum of the potential energy of atoms  $U^*$  which are included in the equation (2). The first local minimum of  $r^{(1)}$  corresponds to a state Pt at zero temperature is  $(1 \times 1)$ -phase surface Pt. Second  $r^{(2)}$  — corresponds the reconstructed or hexagonal phase (hex-phase) surface of Pt. In addition, it is necessary to  $U_1 > U_2$ .

With the construction of  $r^{(1)}$  the situation is simple. It's enough to the cutoff radius  $R_c$  in (4) was less than the distance to the nearest neighbors, that is  $R_c < \sqrt{2}$ . In this case, the final fragment of the fcc lattice (taking into account of the substrate) is an exact local minimum  $U^*$ . Taking into account that  $n = 10096$ ,  $m = 4, 0$ ,  $R_{c_1} = 1, 2$ ,  $R_{c_2} = 1, 25$ ,  $R_{c_3} = 1, 3$ ,  $R_{c_4} = 1, 35$ ,  $R_{c_5} = 1, 3675$ ,  $R_{c_6} = R_c = 1, 385$ ,  $\lambda = 005$ , numerically found  $U_1 = -496, 0$ .

To construct  $r^{(2)}$  should apply to numerical calculations to find the minimum  $U^*$ . For this purpose, we used a standard MATLAB solver of ordinary differential equations. The calculation was performed by the method of establishing when the Euclidean norm of the gradient of the potential energy of  $\|\text{grad}U^*\|$  becomes sufficiently small, which confirmed the arrival of atoms in a local minimum. Gradient of the potential energy  $U^*$  can be represented as:

$$(\text{grad}U^*)_{\alpha,k} = \frac{\partial U^*}{\partial r_{\alpha,k}} = \sum_{i=1, i \neq k}^N \mu(r_{ik})(r_{\alpha,k} - r_{\alpha,i}) + \sum_{i=1}^4 \mu(|r_k - R_{b_i}|)(r_{\alpha,k} - R_{\alpha,b_i}),$$

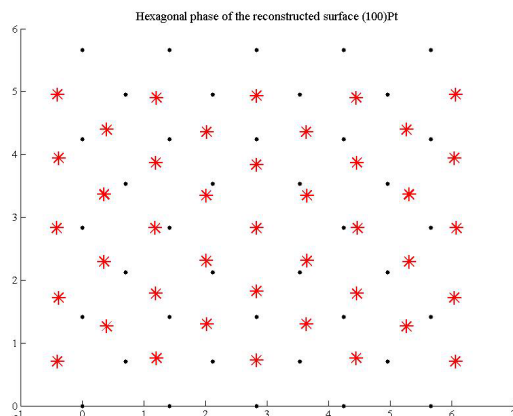
where  $\mu(r) = \varphi^{(2)}(r)/r$ ,  $r_{ik} = |\mathbf{r}_i - \mathbf{r}_k|$ . As a starting configuration chosen configuration  $r^{(1)}$  with a modified first layer of atoms. Atomic positions were chosen symmetrically around the central atom with a slightly elongated along the  $x$  axis and  $y$ -axis compressed first layer atoms with coefficients of expansion and compression —  $\rho$  and  $(2 - \rho^2)^{1/2}$ . The corresponding coordinate's transformation was specified as:

$$\begin{aligned} x'_i &= 2\sqrt{2} + \rho (x_i - 2\sqrt{2}), \\ y'_i &= 2\sqrt{2} + \sqrt{2 - \rho^2} (y_i - 2\sqrt{2}), \end{aligned}$$

where  $\rho = 105$   $i = 1, \dots, 41$ . The value of  $\rho$  is such that  $\rho R_c > \sqrt{2}$ . Last condition means that the initial configuration is chosen so that the sample surface in the interaction of atoms includes second neighbors.

Figure 3 shows the results of calculations of the configuration  $r^{(2)}$  in the part of the first layer (top view). The atomic arrangement of the upper layer (stars in fig3) resembles the hex-reconstructed surface phase of  $(100)\text{Pt}$  [1, 2]. Dots indicate the positions of atoms in the configuration  $r^{(1)}$  while  $U_2 = -545, 065$ .

In the numerical solution of equation (2) believed that  $r = r^{(1)}$  at  $T = 0$ . Further, with increasing temperature for each atom of the sample acts increases with temperature strength, “pushed” the system of atoms is not somewhere, but to the transition in the  $r^{(2)}$ . Since the thermal effect leads to a slight shift, we must to choose  $R_c$  in the vicinity of the second neighbors, that is  $R_c \sim \sqrt{2}$  so that when  $T_f \sim 400\text{K}$  system is irreversibly transferred to the hex-phase. In particular computational experiment  $T_f$  was in the neighborhood of 400K at  $R_c = 1.386$ . The numerical solution of equation (2) was carried out at various temperatures up to  $T_f$ . Figure 3 shows the dots denote the positions of atoms before the surface reconstruction ( $T = 390\text{K}$ ), and the stars — after ( $T = 400\text{K}$ )

Figure 3. **Hexagonal Phase of Reconstructed Surface (100)Pt**

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**Математическое моделирование термической перестройки  
поверхности платины  
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В статье представлена математическая модель термической перестройки поверхности платины (100)Pt. Ранее автором была разработана математическая модель термогеометрической динамики конечного кристаллического образца. В отличие от предыдущих работ автора, в данной статье представлены более продвинутые результаты вычислительного эксперимента.

**Ключевые слова:** математическая модель, вычислительный эксперимент, термическая перестройка, реконструкция, молекулярная динамика, термодинамика, усреднение по ансамблю.