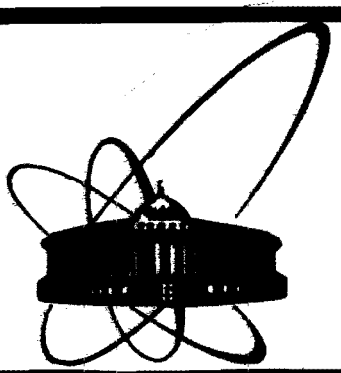

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LINEAR CHAIN MODEL FOR SURFACE RELAXATION IN METALS

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1. INTRODUCTION

Recently, extensive interplaner-spacing data have become available for α-iron [1]. The measurement has been done of several interplanar distances near the surface in 6 different crystal directions. The data stimulated a revived interest in surface relaxation phenomena in metals.

Empirical lattice models based on short-ranged two-body interaction between atoms have been successfully used for defect calculations in bulk crystals [2] or for calculations of concentration dependence of elastic constants in Fe-Si alloys [3]. At present, corresponding calculations for surfaces are beginning to appear [4,5].

The major drawback of present-day surface calculations consists in different treatment of the crystal interior and of the surface layers, where an additional pressure [5] is postulated or some ad hoc modifications of empirical lattice interaction are introduced. The aim of the present communication is to show how the bulk properties of the crystal and the surface interplanar displacements can be treated simultaneously within an empirical lattice model based on short-ranged two-body interaction.

Starting from a given interatomic pair potential and using the continued fraction techniques, we express the interplanar spacing in terms of derivatives of the potential in an analytical way. On the other hand, the elastic constants can be expressed by the same derivatives in the standard manner [7]. Therefore, analytical expressions can be obtained, which combine the bulk characteristics (elastic constants) and surface displacements.

We present here a simplified version of the model just to display the techniques useful in interplanar-spacing calculations and to discuss possible structures created by near the surface planes. Indeed, a detailed comparison with the experiment would require inclusion of density dependent and/or direction dependent terms in the interatomic potential. This will be postponed to the further publication.

The present investigation will be restricted to the relaxation along the main crystal directions only, where the interplanar displacements are perpendicular to the crystal surface. There is simple one-to-one correspondence between the interato-

mic and interplanar potential in this case[6]. Since all the displacements have the same direction, the surface relaxation in the main crystal directions of cubic lattice is equivalent to the relaxation in linear chian. The topic is analyzed in detail in section 2. Various structures, which can occur near the surface are discussed in section 3. Conclusions are drawn in sect.4.

2. SURFACE RELAXATION

Let as assume a linear chain of N points (each of which corresponds to a crystal plane) located at positions $x_j, j=1,2,...N$. The points interact via the pair potential $\Phi(x_i - x_j)$. The later is assumed to be short-ranged, thus the nearest neighbour and the next to the nearest neighbour interplanar interactions are taken into account only. The assumption corresponds literally to the case of surface relaxation of [100] planes in b.c.c. crystals[6]. We remind the reader that the induced interplanar interactions are of different range for different crystal planes, even if the nearest neighbour and next to the nearest neighbour interatomic interactions are postulated in the crystal[4-6].

The potential energy of the crystal reads as

$$U_N = \sum_{j=1}^{N-1} \Phi(x_{j+1} - x_j) + \sum_{j=1}^{N-2} \Phi(x_{j+2} - x_j). \qquad (1)$$

As a reference configuration $\bar{x}_j$ we chose the equidistant one, $\bar{x}_j = ja$, where a is to be determined from the equilibrium condition for a infinite chain

$$\lim_{N\to\infty} \frac{1}{N} \frac{dU_N}{da} \Big|_{x_j = \bar{x}_j} = 0. \qquad (2)$$

Introducing the notation

$$V_1 = \frac{\partial \Phi(x)}{\partial x}\Big|_{x=a} \qquad V_2 = \frac{\partial \Phi(x)}{\partial x}\Big|_{x=2a} \qquad (3a)$$

$$W_1 = \frac{\partial^2 \Phi(x)}{\partial x^2}\Big|_{x=a} \qquad W_2 = \frac{\partial^2 \Phi(x)}{\partial x^2}\Big|_{x=2a}, \qquad (3b)$$

the condition (2) reads as

$$V_1 + 2V_2 = 0. \qquad (4)$$

The reference configuration corresponds to minimum of the potential energy U_∞ per point, i.e.,

$$W_1 + 4W_2 > 0. \qquad (5)$$

The actual positions $x_j = ja + \epsilon_j$ of the points in a finite chain are shifted by the amount ϵ_j from the equilibrium positions

due to the unresolved forces that act at the two ends of the finite chain. The forces arise due to the removal of first and second neighbour interaction during creation of free ends of the chain (or of free crystal surface).

2.1. Relaxation in a Chain of Finite Length

Now the shifts ϵ_j will be determined from the requirement that the forces acting on all the points in their relaxed positions are equal to zero. Since the displacements in actual crystals are small, $\epsilon_j \lesssim 0.1a$, the linearized expression for forces $f_j = -\partial U_N / \partial \epsilon_j$ are used:

$$\begin{aligned}
f_1 &= V_1 + V_2 + W_1(\epsilon_2 - \epsilon_1) + W_2(\epsilon_3 - \epsilon_1) = 0 \\
f_2 &= V_2 + W_1(\epsilon_1 - \epsilon_2) + W_1(\epsilon_3 - \epsilon_2) + W_2(\epsilon_4 - \epsilon_2) = 0 \\
&\vdots \\
f_j &= W_1(\epsilon_{j-1} - \epsilon_j) + W_1(\epsilon_{j+1} - \epsilon_j) + W_2(\epsilon_{j-2} - \epsilon_j) + W_2(\epsilon_{j+2} - \epsilon_j) = 0 \\
&\vdots \\
f_{N-1} &= -V_2 + W_1(\epsilon_N - \epsilon_{N-1}) + W_1(\epsilon_{N-2} - \epsilon_{N-1}) + W_2(\epsilon_{N-3} - \epsilon_{N-1}) = 0 \\
f_N &= -V_1 - V_2 + W_1(\epsilon_{N-1} - \epsilon_N) + W_2(\epsilon_{N-2} - \epsilon_N) = 0.
\end{aligned} \qquad (6)$$

As expected, the unresolved forces V_1 and V_2 act in the reference configuration on the points j = 1,2,N-1 and N only. The resulting system of linear equations (6) for ϵ_j is linearly dependent because of its symmetry with respect to the substitution

$$\epsilon_j = -\epsilon_{N-j+1}, \quad j = 1, 2, \ldots, N, \qquad (7)$$

i.e., the shifts have to be symmetric with respect to the center of the chain. Particularly, eq.(7) indicates

$$\sum_{j=1}^{N} \epsilon_j = 0. \qquad (8)$$

Therefore, the solutions chosen according to (7) do not contain the motion of the chain as a whole.

Using (7) and choosing N = 2n+1 for the sake of definitness, the system (6) can be reduced to the system of n linearly independent equations

$$\omega E = \theta, \qquad (9)$$

where $v^T = (V_1/(2W_1), -V_1/(2W_1), 0, \ldots, 0)$, $E^T = (\epsilon_1, \epsilon_2, \ldots, \epsilon_N)$ and ω is symmetric band matrix with nonzero elements $\omega_{j+2,j} = \omega_{j,j+2} = -Z$, $\omega_{j+1,j} = \omega_{j,j+1} = -1$ and the diagonal matrix elements ω_{jj} are 1+Z, 2+Z, 2+2Z, ..., 2+2Z, 2+3Z for j = 1,2,3,...n-1, n, respectively. In obtaining eq.(9) we introduced $Z = W_2/W_1$ and used the equilibrium condition (4).

Further, the similarity transformation

$$(B^T \omega B)(B^{-1}E) = B^T \theta, \tag{10}$$

where B is the upperdiagonal matrix with elements $b_{i,i+j} = 1$, $i = 1,\ldots,n$ and $j = 0,1,\ldots,n-i$, brings the matrix $\omega' = B^T \omega B$ to symmetric tridiagonal form. The diagonal matrix elements ω'_{jj} are $1+Z$, $1+2Z,\ldots,1+2Z$, $1+3Z$ for $j = 1,2,\ldots,n-1,n$, respectively, and the off diagonal ones $\omega'_{j,j+1} = \omega'_{j+1,j} = Z$. The vector $E'^T = (B^{-1}E)^T = (\eta_1, \eta_2, \ldots \eta_n)$ contains now the relative displacements

$$\eta_j = \epsilon_j - \epsilon_{j+1}, \quad (\epsilon_{n+1} = 0). \tag{11}$$

Finally, the matrix $v'^T = (B^T v)^T = (V_1/2W_1), 0, \ldots, 0)$ has only one nonzero element. This enables one to express the solution of the system (10) in a particularly simple form. Introducing the j-rows x j-columns determinants

$$d_j = \begin{vmatrix} 1+2Z & Z & 0 & \ldots & 0 & 0 & 0 \\ Z & 1+2Z & Z & \ldots & 0 & 0 & 0 \\ 0 & Z & 1+2Z & \ldots & 0 & 0 & 0 \\ \cdot & \cdot & \cdot & \ldots & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & \ldots & Z & 1+2Z & Z \\ 0 & 0 & 0 & \ldots & 0 & Z & 1+3Z \end{vmatrix}, \quad j = 2,3,\ldots,n, \tag{12}$$

and $d_1 = 1+3Z$, the relative displacements are

$$\eta_j = \frac{V_1}{2W_1}(-Z)^{j-1} \frac{d_{n-j}}{d_n - Z d_{n-1}}, \quad \text{for } j = 1,2,\ldots,n. \tag{13}$$

The three-term recurrence relation ($d_0 \equiv 1$)

$$d_{j+1} = (1+2Z)d_j - Z^2 d_{j-1}, \quad j = 1,2,\ldots,n-1 \tag{14}$$

facilitates the evaluation of η_j from eq.(13) for any point of the linear chain of arbitrary finite length.

Before concluding this subsection, one remark is in order. Provided that we were considered the nearest neighbour interaction only, i.e., $Z = V_2 = W_2 = 0$ and $d_j = 1$ for only j, zero relative displacements would be obtained from (13) as a consequence of the equilibrium condition (4) ($V_1 = 0$). Therefore the model, which takes into account the nearest neighbour and the next nearest neighbour interactions is a minimal one in the sence that it yields nontrivial surface relaxation.

2.2. Relaxation in a Chain of Semiinfinite Length

Actual crystals contain large number of parallel planes, which may take part in the relaxation. Therefore, the asymptotic values ($n \gg 1$) of the displacements η_j are relevant in this case. To investigate the asymptotic behaviour of the later, we introduce the quantities

$$A_j = \frac{Z d_{j-1}}{d_j} \quad \text{for } j = 1,2,\ldots,n \tag{15}$$

in terms of which the displacements turn out to be

$$\eta_j = \frac{V_1}{2W_2} \frac{(-1)^{j-1}}{1 - A_{n-1}} \prod_{k=1}^{j} A_{n-k}. \tag{16}$$

The three-term recurrence relation (14) yields the recursion

$$A_{j+1} = \frac{Z}{1+2Z-ZA_j}, \qquad A_1 = \frac{Z}{1+3Z}, \tag{17}$$

for the quantities A_j, $j = 1,2,\ldots,n$, which are of the continued fraction type.

The recursion (17) can be viewed as a sort of mapping $A_j \to A_{j+1}$, which has two fixed points $A_{(+)}$ and $A_{(-)}$

$$A_{(\pm)} = \frac{1}{2Z}[1+2Z \pm \sqrt{1+4Z}]. \tag{18}$$

The latter were obtained assuming $A_{j+1} \approx A_j \approx A$ and solving (17) as a quadratic equation for A. It is interesting to note that $A_{(\pm)} = 1/A_{(\mp)}$ holds.

Real fixed points exist, of course, only for $Z \geq -0.25$. The value $Z = -1/4$ is critical for the bulk stability of the chain (c.f.(5)). Let us discuss now in some detail the properties of the fixed points. It can easily be shown that inequalities

$$A_{(+)} > 1 \qquad A_{(-)} < 1 \tag{19}$$

always hold for $Z > -1/4$. Further, it can be verified that $A_{(-)}$ is stable and $A_{(+)}$ is unstable fixed point for any $Z > -1/4$. The proof of the last statement is based on the following observation. If $A_j \approx A_{(\pm)} + \delta$ lies in the vicinity of one of the fixed points $A_{(\pm)}$ (i.e. $|\delta| \to 0$). Then

$$A_{j+1} = A_{(\pm)} + A^2_{(\pm)}\delta + 0(\delta^2) \tag{20}$$

follows from (17). Because of (19), the value A_{j+1} moves towards (outwards) the fixed point $A_{(-)}$ ($A_{(+)}$).

It can be concluded that asymptotically $A_j \approx A_{(-)}$ and the displacements of the points at the end of a semiinfinite chain are given by

$$\eta_j = -\frac{V_1}{2W_2} \frac{[-A_{(-)}]^j}{1 - A_{(-)}}. \tag{21}$$

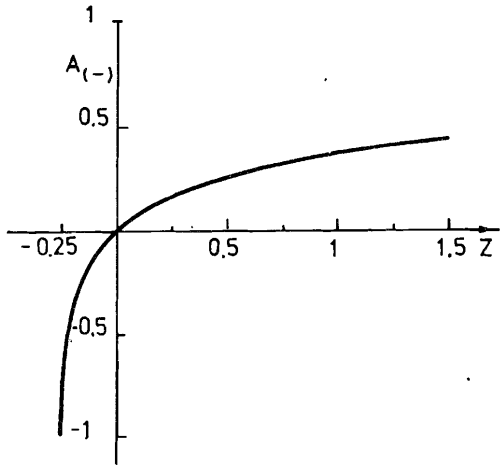

Fig.1. Fixed point $A_{(-)}$.

Therefore, the relative displacements decrease as a geometrical sequence towards the interior of the chain. The quocient of the sequence is always smaller than unity and its dependence on Z is displayed in Fig.1. Eq.(21) represents our final result for the semifinite chain and expresses in a very simple way the relationship between the derivatives of interatomic potential and relative interplanar displacements. For the sake of completeness, we give also the expression for absolute displacements

$$\epsilon_j = -\frac{V_1}{2W_2}\,\frac{[-A_{(-)}]^j}{1-A_{(-)}^2}\,. \tag{22}$$

Except for regions, where $A_{(+)}$ and $A_{(-)}$ have almost the same magnitude (i.e., $Z \to -1/4$ and $Z \to \infty$), the convergence $A_j \to A_{(-)}$ is very fast. Three examples are shown in the Table.

Table

Z	A_1	A_2	A_3	A_4	A_5	$A_{(-)}$
-3/16	-0.42857	-0.34426	-0.33455	-0.33346	-0.33335	-0.33333
0.5	0.26316	0.26761	0.26792	0.26795	0.26795	0.26795
5.5	0.31428	0.53546	0.60740	0.63516	0.64655	0.65492

The value Z = 5.5 in the last row of the Table is close to W_1/W_2 ratio in α-Fe. The conclusion can be drawn that the relaxation typical for a semifinite chain even at the ends of very short chains for almost all values Z.

Since there is only one stable fixed point, the result of the iterative procedure (17) does not depend on the starting value A_1 unless $A_1 = A_{(+)}$. Therefore, the relaxation at the ends of a long chain remains unchanged, even if the equidistant location of points in the interior of the chain is somehow disturbed.

2.3. Surface Stability

By the construction, the resulting force acting on each point in its relaxed position is zero. We investigate now the stability of our solution (21) with respect to small perturbations. Put it in other words, the potential energy of a stable relaxed configuration should be smaller than that of the reference configuration. The requirement of surface stability reads as

$$\lim_{N\to\infty}\frac{1}{N}(U_{refer}-U_{relax}) \sim \frac{1}{2}[V_1\eta_1 - W_1\sum_{j=1}^{\infty}\eta_j^2 - W_2\sum_{j=1}^{\infty}(\eta_j+\eta_{j+1})^2] > 0. \tag{23}$$

Substituting in (23) for η_j (see eq.21) and performing some formal manipulations, we arrive at

$$\frac{1}{4}V_1\eta_1 > 0. \tag{24}$$

The sign of $V_1\eta_1$ is controlled by the sign of W_1. Therefore,

$$W_1 > 0 \tag{25}$$

is our resulting condition of surface stability.

3. SURFACE STRUCTURES

Having obtained the displacements η_j (21) in terms of derivatives of the interplanar potential $\Phi(x)$, we could relate them to the derivatives of the interatomic potential and to the elastic constants. The detailed analysis of surface relaxations in α-Fe along this lines will be given in further publication. Here, we discuss in some detail various structures, that can occur near the surface in the dependence on the sign and magnitude of the derivatives V_1($V_2 = -V_1/2$), W_1 and W_2. Five different orderings are compatible with our model.

(i) $V_1 < 0$, $W_1 > 0$, $W_2 > 0$. In this case the displacements change sign and a sort of "antipairing" develops near the surface. The outermost point moves outwards the chain and the remaining points create pairs. The relaxed distance within each pair is smaller than the reference one (see Fig.2). The simplest interplanar potential leading to this configuration is depicted in Fig.3a, where the reference positions of the nearest neighbour and the next to the nearest neighbour are denoted by 1 and 2, respectively.

(ii) $V_1 < 0$, $W_1 > 0$, $W_2 > 0$. The displacements are negative and a nonuniform dilatation takes place near the surface. All points move outwards the chain. The situation is visualized in Fig.2 and Fig.3a (points 1' and 2').

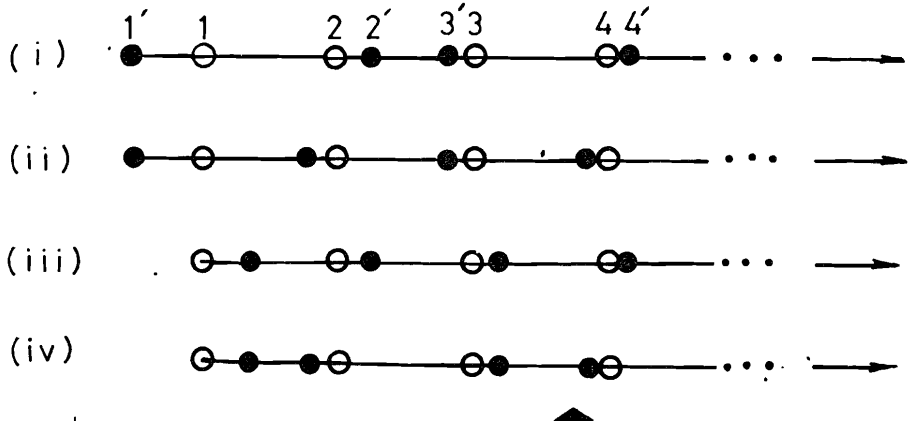

Fig.2. Four structures, which can occur near the end of semiinfinite chain.
● – relaxed configuration
○ – reference configuration.

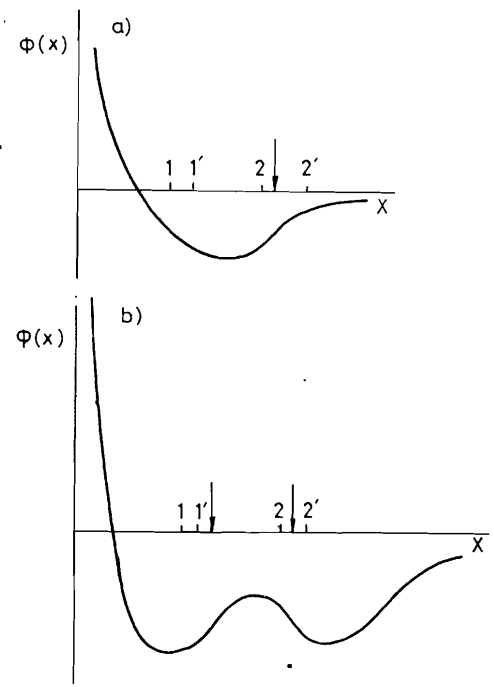

Fig.3. Simple interplanar potentials leading to the structures shown in Fig.2. Arrows indicate the points, where $d^2\Phi/dx^2 = 0$

(iii) $V_1 > 0$, $W_1 > 0$, $W_2 < 0$. The displacements are positive and an over-all compression occurs near the surface. All points move towards the chain (see Fig.2). The simplest interplanar potential accounting for this structure has a two-dip shape shown in Fig.3b. The reference positions are marked by 1 and 2.
(iv) $V_1 > 0$, $W_1 > 0$, $W_2 > 0$. The displacements change the sign and sort of "pairing" takes place. The structure is displayed in Fig.2 and Fig.3b (points 1' and 2').

In the cases (ii) and (iii), the value of W_2 is restricted by the bulk stability condition $W_2 > -W_1/4$ (5).

Up to now we assumed $W_1 > 0$. The opposite case is more delicate. If $W_1 < 0$, the surface stability condition (24) is violated. However, the bulk stability condition requires $Z < -1/4$ in this case. Therefore, the mapping (17) has no fixed points for $W_1 < 0$ and chaotic interplanar spacing occurs near the surface. We have proved numerically that the displacements of the outermost points in the chain depend substantially on its length. If $W_1 < 0$ occurs in real crystal, the creation of free surface is likely to be impossible for corresponding system of crystal planes.

4. CONCLUSIONS

First and second neighbours are assumed to interact in a linear chain with two-body forces. The analytical expressions were obtained for stable configurations of a finite or semiinfinite linear chain using continued fraction techniques. The solutions we obtained for the displacements of the points of a semiinfinite chain with respect to their equilibrium positions in an infinite chain correspond to the surface relaxation of [100] planes in b.c.c. metals.

Five different structures of near the surface planes can exist according to our model. Appart from compression or dilatation, two types of pairing can take places among the planes lying in the surface layer. In some instances, a chaotic interplanar spacing can occur near the surface.

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Мах Р. E14-86-680

Модель линейной цепочки для поверхностных релаксаций в металлах

Изучается релаксация концов конечной и полубесконечной линейной цепочки. Предполагается парное взаимодействие первых и вторых соседей. Получены аналитические выражения для сдвигов точек цепочки относительно их равновесных положений в бесконечной цепи. При этом используется метод цепных дробей. Имеется прямая связь между релаксацией конца полубесконечной цепочки и поверхностных [100] плоскостей в о.ц.к. кристаллах. В соответствии с прилагаемой моделью может произойти сжатие, растяжение или два типа спаривания кристаллических плоскостей около поверхности. Модель предсказывает хаотическое распределение плоскостей около поверхности для некоторых случаев.

Работа выполнена в Лаборатории теоретической физики ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна 1986

Mach R. E14-86-680

Linear Chain Model for Surface Relaxation in Metals

The relaxation at the ends of a finite and semiinfinite linear chain was calculated assuming that first and second neighbours interact via pair forces. Analytical expressions we obtained for displacements of the points from their equilibrium positions in an infinite chain are relevant also for the surface relaxation of [100] planes in b.c.c. metals. Appart from compression or dilatation, two types of pairing can take place among the planes lying in the surface layer according to our model. The model predicts also chaotic ordering of near the surface planes in some cases.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1986