# MANY-BODY KINETIC SEMIPHENOMENOLOGICAL APPROACH TO THE PHENOMENA CAUSED BY ION BOMBARDMENT IN SOLIDS.

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ABSTRACT
The new collective treatment of the behaviour of low energy particles (LEPs) in the bulk and on the surface of solids is considered. Threshold energies $\mathcal{E}_t$ for sputtering and particle displacements in the bulk are calculated. The novel expression for the probability exponentially depending on LEP energy $\mathcal{E} \geqslant \mathcal{E}_t$ of different processes in short-lived hot spots caused by the LEPs in and on solids is discussed.

## I. INTRODUCTION

The phenomena caused in solids and liquids by ion bombardment are not quite understood, especially in the case of low energy impinging particles (LEIP) /I-7/. The applicability of the binary collision grounded theory /5,6/ to the phenomena caused by the LEIP, meets with objections (e.g. see /3/). This theory cannot take into consideration short-lived collective LEIP-induced processes in small volumes of the material /I2/. The earlier attempts /8-II/ to consider short-lived hot spots (SLHS) with the help of the equilibrium statistical mechanics have failed, as the latter is not applicable to the SLHS, that was mentioned in /I2/; these attempts did not take into account momentum-transfer phenomena taking an essential role in considered processes. The suggested non-equilibrium kinetic treatment uses the non-equilibrium statistical thermodynamic and kinetic theories /I3-I5/ to consider collective phenomena in the SLHS and also to take into account momentum-transfer processes. For this purpose we have modified some ideas used earlier for the many-body non equilibrium treatment of the phenomena caused in and on solids by short-lived large energy fluctuations (SLEFs) /I5-I9/, by high energy radiation /20/ and by recoils /2I/. In our earlier work /I2/ we mainly consider the phenomena caused by ions with moderate energies $\mathcal{E} = Mv^2/2$, e.g. with $\mathcal{E} \approx 10^2 - 10^3$ ev, in this paper we concentrate mainly on the phenomena caused in and on the materials by LEIP with energies near (lower and above) the threshold ones.

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## 2. THE KINETIC BEHAVIOUR AND PROPAGATION OF LOW ENERGY PARTICLES IN SOLIDS.

Consider a monoatomic solid consisting of particles with mass m at temperatures $T > \Theta$ with effective coordination number $\varkappa$ and with volume per particle $\Omega_o = d^3 = Q/\gamma_o$, where $\Theta$ is the Debye temperature, Q is the elementary cell volume with $\gamma_o$ particles. Every particle suffers $\varkappa$ collisions with its $\varkappa$ neighbours for the time $\nu_D^{-1} = h/k\Theta$ and the effective time between two subsequent collisions is $\delta t = h/\varkappa k\Theta$. Now consider a low energy particle (LEP) of the solid, which suddenly, at moment $t_o$ gets kinetic energy $U_o(t_o) = mv_o^2/2$ of a few ev. This energy can be transmitted to the LEP by a glancing collision with high-energy particle (HEP) whose velocity v and energy $\mathcal{E} = Mv^2/2$ satisfy the conditions

$$\Delta t \approx d/v \ll \delta t; \quad \text{or } v \gg \eta\, d \varkappa c_o/\lambda_D; \quad \mathcal{E} \geqslant \eta^2 M d^2 c_o^2 \varkappa_o^2 / 2\lambda_D^2; \ \eta \gg 1 \qquad ,(I)$$

where $\lambda_D = hc_o/k\Theta$ is the Debye wave length, $c_o$ is the sound velocity, $\Delta t$ is the time of interaction of the HEP with the particle of the solid. The LEP has the great short-lived initial deviation $\Delta U_o(t_o) \approx U_o(t) - 3kT \approx U_o(t_o)$ from equilibrium thermal excitation $3kT \ll U_o(t_o)$. It interacts with the $\varkappa$ surrounding particles with energy $\Phi_{o1}(q_{(o)}, q_{(1)}) \approx \varkappa \varphi_{o1}$, which is not very small comparatively with $U_o(t_o)$, where $q_{(o)}$ is the coordinates of the LEP, $q_{(1)} = \{q_j\}$ are the coordinates of the surrounding particles, $\varphi_{o1}$ is the pair interaction energy. Therefore, relaxation of the LEP energy is a many-body non-equilibrium non-stationary phenomenon involving many surrounding particles. Consider the following cases: <u>I. The LEP energy $U_o(t_o)$ is not sufficient to leave its initial site and to propagate in the solid.</u> In this case the LEP performs a short-term non-linear non-steady motion with a large amplitude $a_f \approx d$ in volume $V_o = 4\pi\rho_o^3/3$, during time $\tau$ of relaxation and redistribution of the energy $U_o(t_o)$ among $\Delta N_1 = N_1 - 1$ surrounding particles in the LEP vicinity with volume $\Omega_1 = V_1 - V_o$, where

$$V_1 \approx 4l^3 \ (1 + \rho_o/l)^3 \approx 4(\lambda_1/\varkappa)^3 \cdot \left[U_o(t_o)/k\Theta_1\right]^{3/2} \gg V_o \ , \qquad (2)$$

$N_1 = \gamma_o V_1/Q$, $l \approx c_o\tau$ and values $\tau$, l and $V_1$ can be calculated by the method similar to that used in the kinetic many-body SLEF theory /I7/. Then one can obtain the expressions

$$\tau \approx \frac{\left[mU_o(t_o)\right]^{\frac{1}{2}}}{\varkappa \cdot |p_{ef}|} \approx (h/\varkappa k\Theta_1) \cdot \left[U_o(t_o)/k\Theta_1\right]^{\frac{1}{2}} \ ; \ l \approx c_1 \cdot \tau \ , \qquad (3)$$

leading to Eq (2), where $\Theta_1$ and $c_1$ are local values of $\Theta$ and $c_o$ in the LEP vicinity, $|\tilde{p}_{ef}|$ is the effective pair force acting between the LEP and one of the surrounding particles, where $|\tilde{p}_{ef}| \approx |F_{o1}|/\varkappa$ and $F_{o1}$ is given by the equation analogous to that introduced in the SLEF theory /I5,I6/

$$F_{o1} = -\int (1 + Y_{o1}) \cdot \Delta_1(q_{(1)}, p_{(1)}, t) \cdot (\partial \Phi_{o1}/\partial q_{(o)})\, d\cdot\Gamma_{(1)} \qquad , \qquad (4)$$

where

$$D_1(q_{(0)},p_{(0)};q_{(1)},p_{(1)};t) = D_0(q_{(0)},p_{(0)},t)\cdot(1+Y_{01})\cdot\Delta_1(q_{(1)},p_{(1)},t), \quad (5)$$

$D_0$ is the one-particle distribution function of the LEP with phase coordinates $q_{(0)}$ and $p_{(0)}$, $\Delta_1(q_{(1)},p_{(1)},t)$ is the $(N_1-1)$-particle distribution function of $(N_1-1)$ particles with phase coordinates, $q_{(1)}=\{q_j\}$, $p_{(1)}=\{p_j\}$, $j=1,2,\dots,N_1-1$; $d\Gamma_1=dq_{(1)}\cdot dp_{(1)}$, $(1+Y_{01})$ is the factor of short-term statistical coupling between the LEP and the surroundings. The LEP motion and the accompanying motion of the surrounding particles in the phase space, during the LEP energy relaxation are described by the system of coupled kinetic equations analogous to those used for the dynamic SLEF treatment /I5,I6/

$$\frac{d\chi_0}{dt} = \frac{\partial\chi_0}{\partial t} + \{\chi_0,h_0\} + F_{01}\frac{\partial\chi_0}{\partial p_{(0)}} = \frac{\partial F_{01}}{\partial p_{(0)}} \quad (6)$$

$$\frac{d\chi_1}{dt} = \frac{\partial\chi_1}{\partial t} + \{\chi_1,H_1\} + F_{12}\left(A\cdot\frac{\partial\chi_1}{\partial p_0} + \frac{\partial\chi_1}{\partial p_{(1)}}\right) = A\frac{\partial F_{12}}{\partial p_{(0)}} + \frac{\partial F_{12}}{\partial p_{(1)}} \quad (7)$$

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The two first Eqs (6) and (7) of the hierarchy describe the short-termed motion of the LEP and the surrounding correlative cluster of $\Delta N_1=N_1-1$ particles in volume $\Omega_1=V_1-V_0$. The initial conditions in the considered case are different from those taking place in the SLEF /I5,I6/, where the initial conditions include short-term advanced fluxes directed to the fluctuating particle and transferring the fluctuational energy to it from the surroundings. In the LEP case the initial conditions are

$$U_0(t_0) = mv^2(t_0)/2, \ln D_{N-1}(t_0) = \alpha_{N-1} - \beta H_{N-1} \quad (8)$$

and they include $U_0(t_0)$ and the initial equilibrium distribution of the other N-1 particles of the system with Hamiltonian $H_{N-1}$, where $\chi_0=-\ln D_0$, $\chi_1=-\ln D_1$, $H_1$ is the Hamiltonian of $N_1$ particles, $h_0$ is the LEP Hamiltonian, $\{\dots\}$ is the Poisson brackets, $F_{12}$ is the effective force acting on $N_1$ particles from the surroundings and is equal to

$$F_{12} = -\int(1+Y_{12})\cdot\Delta_2\cdot\frac{\partial\varphi_{12}}{\partial q_{(1)}}d\Gamma_2; \quad |A| = \left|\frac{\partial\varphi_{12}}{\partial q_0}\right|\cdot\left|\frac{\partial\varphi_{12}}{\partial q_{(1)}}\right|^{-1} \ll 1 \quad (9)$$

$$D_N(q_{(0)},p_{(0)};q_{(1)},p_{(1)};q_{(2)},p_{(2)};t) = D_1\cdot(1+Y_{12})\cdot G(q_{(2)}p_{(2)}t) \quad (I0)$$

G is the distribution function of the external surroundings of the $N_1$ particles that acts on these particles with the effective force $F_{12}$ given by Eq (9); $q_{(2)}$ and $p_{(2)}$ are the phase coordinates of $N-N_1$ particles of the external surroundings; $d\Gamma_2=dq_{(2)}dp_{(2)}$, $(1+Y_{12})$ is the factor describing the statistical coupling between the $N_1$ particles and the rest of the system. The first stage of relaxation described by Eqs (6),(7),etc. ,may not be described in local "macroscopic" terms:by heat conductivity,temperature,etc.The second stage of the relaxation at $t>\tau$ and for volumes $V_2> V_1$ can be approximately described in such terms.The first two Eqs (6) and (7) can be approximately decoupled from the other equations of the hierarchy with the help of the procedure analogous to that suggested for the SLEF treatment /I5,I6/ and using the following conditions

$$N_1 \gg 1 , Y_{12} \ll 1 , \varphi_{12} < H_1 < H_2 \ ; \ \delta t \approx (h/\varkappa k\Theta) \ll \tau \qquad \text{(II)}$$

<u>2. The LEP has energy $\Delta U_o'(t_o)$,which satisfies the condition $E_1<U_o'(t_o)<$ $<E_2$</u> and which is sufficient for the LEP to propagate from the inicial site to a neighbouring one at a distance $R_1 \approx d$,but is not enough to pass a way $R_2 \approx 2d$ to the next site.Since $d<1$,the energy $U'(t_o)>$ $>U(t_o)$ is released in approximately the same volume $V_1' \approx V_1$ and heats this volume to the larger local short-term temperature $T+\delta T_1$, where

$$\delta T_2 \approx \left[U_o'(t_o) - \Delta E\right] /3kN_1 > \delta T_o \approx U_o(t_o)/3kN_1 \qquad \text{(I2)}$$

here $\Delta E$ is the difference between binding energies in the original LEP site (e.g. a lattice one) and the final one (e.g. an interstitial site).In this case the LEP behaviour can also be described by the system of equations of the type of Eqs (6),(7),etc.Leaving alone this problem here,we shall consider some related problems semiquantatively. The LEP with higher $U_o(t_o)$ (e.g.$U_o(t_o) \approx 20$ev) can pass a way $R_j \approx jd$ along the traectory similar to a random walk one,and such a LEP stops at a distance $\Delta L \approx j^{1/2}d$ from the initial point,here $j=2,3,\ldots$Then $U_o(t_o)$ is released in volume $\Delta V \approx \Delta L^3 \approx j^{3/2}d^3$ with $\Delta N = \Delta V \gamma_o/Q$ particles and the SLHS with local short-term temperature $T+\delta T(U_o)$ is formed,where

$$\delta T(U_o) \approx \frac{U_o(t_o)}{3k\,\Delta N} \approx \frac{U_o(t_o)}{3k\cdot z\cdot j^{3/2}} \sim U_o^{(2-3\alpha)/2} \quad \text{with } \alpha \leqslant 2/3 \ , \qquad \text{(I3)}$$

when $j \sim U_o^{\alpha}$ ,where $\alpha$ can increase with $U_o$,for low $U_o$.Hence,$\delta T$ increases with $U_o$,when $\alpha < 2/3$,and $\delta T$ does not depend on $U_o$,when $\alpha = 2/3$.It can be expected that $\alpha < 2/3$,when $U_o < \widetilde{U}_o$; here $\widetilde{U}_o$ is the LEP energy equal to several tens of ev,when particle displacement caused by the LEP begins to play an essential role.This means that the mechanism of the LEP energy dissipation is changed,when $U_o > \widetilde{U}_o$.However, the behaviour of secondary particles displaced by the LEP with $U_o > \widetilde{U}_o$ can be described through the treatment discussed above,when the secondary particles have energies $U_o' < \widetilde{U}_o$.Since the LEP with $U_o < \widetilde{U}_o$ forms the SLHS with the effective local temperature $T+\delta T(U_o)$,one can expect that the short-term probability of thermally activated processes in the SLHS is given by

$$\varphi(U_o) \sim \exp\left(\frac{\delta S}{k}\right)\cdot \exp\left\{-\frac{\delta W}{k\left[T+\delta T(U_o)\right]}\right\} \ , \qquad \text{(I4)}$$

where $\delta W \gg kT$ and $\delta S$ is the entropy change associated with the

SLHS processes which can also include short-lived phase and polymorphic transformations, electron transitions, etc., analogous to those caused by short-term fluctuations in small volumes of solids /I8/. Hence, one can see that $\varphi(U_o)$ is the exponential function of $U_o$ when $U_o < \widetilde{U}_o$. If $U_o > \widetilde{U}_o$ (eg. when $U_o \approx (1\ to\ 5)\cdot 10^2$ ev) new kinds of collective phenomena can be developed in the SLHS /I2/. The considered approach can also be applied to the LEP on the surface and near it and can help to understand the sharp increase in sputtering yields with a change of energies $\mathcal{E}$ of impinging ions near the threshold values $\mathcal{E}_{ts}$. Such sputtering can be considered as the evaporation of a surface particle from the surface SLHS having a high "temperature", e.g. when energy $\mathcal{E} \approx (20\ to\ 30)$ev is transmitted to a near-surface volume with $\Delta N \lesssim 10^2$ particles and $T=500^oK$, one can get $\delta T > (6.6\ to\ 10)10^3\ ^oK$ and $(T+\delta T) > (1.1\ to\ 1.6)\cdot 10^3\ ^oK$. A similar approach can be applied to liquids.

## 3. On Sputtering Threshold Energies.

A surface particle (SP) can be sputtered (or sublimated) when it gets kinetic energy $U_{sr} = \widetilde{U}_{\perp r} + \widetilde{U}_{\parallel}$ satisfying the conditions

$$\widetilde{U}_{\perp r} = P_{\perp r}^2/2m > E_s = \varkappa_s E_{ABS}; \quad \widetilde{U}_{\parallel} = P_{\parallel}^2/2m < E_{ms} = \varkappa_s E_{MBS} \quad , \qquad (I5)$$

where $P_{\perp r}$ is the SP momentum component directed toward the vacuum, $P_{\parallel}$ is the one parallel to the surface; $\varkappa_s$, $E_s$ and $E_{ms}$ are the SP coordination number, binding and migration energies respectively, depending on the SP position, etc. The SP gets energy $\widetilde{U}_{sr} \approx E_s + E_{ms}$ from the low energy impinging particle (LEIP), not fitting Eqs (I), during collision time $\Delta t_s \approx d_s/v$, which is so long that $\varkappa_s$ neighbours come into play before the collision is over, and they can get energy $\Delta E_s = \xi_s \varkappa_s \cdot \widetilde{U}_{sr}$, where $\xi \lesssim 1$. Therefore, the threshold energy $\mathcal{E}_{ts}$ is determined by the minimal total energy transfer from the LEIP to the SP and $\varkappa_s$ surrounding particles during the collision, allowing conditions (I5) to be satisfied for one of the particles involved. Then one can obtain

$$\mathcal{E}_{ts} \approx U_{sr} + \Delta E_s \quad or \quad \mathcal{E}_{ts} = A(\xi_s \cdot \varkappa_s + 1)(E_s + E_{sm}), \qquad (I6)$$

where $A \approx 1$, $E_{sm} < E_s$. When $\varkappa_s$ is averaged over different SP positions, one can get for many cases $\overline{\varkappa}_s \approx 2$ to 4 and $\overline{\mathcal{E}}_{ts} \approx (3\ to\ 5)E_s$, in agreement with observations. For some special cases, when $\varkappa_s$ is small, $\mathcal{E}_{ts}$ can be less. A similar approach can be applied to estimate threshold energies $\mathcal{E}_{tb}$ for displacement of bulk particles from the lattice site into neighbouring void, where $E \quad E_d - E_v$

$$\mathcal{E}_{tb} \approx \widetilde{\Delta U}_b + \Delta E_b \quad or \quad \mathcal{E}_{tb} = B(\xi_b \cdot \varkappa + 1)\cdot E, \ B \approx 1; \ \xi_b \lesssim 1 \qquad (I7)$$

$E_d$ is the energy of self-diffusion, $E_v$ is vacancy formation energy $\Delta E_b = \xi_b \varkappa \cdot \widetilde{U}_b$. Since $\varkappa \approx (2\ to\ 4)\varkappa_s$ and $E_s \approx (2\ to\ 3)E$, one can expect $\overline{\mathcal{E}}_{ts} \lesssim \mathcal{E}_{tb}$, that fits the observations. Essential differences between collisions of material atoms with a high-energy particle satisfying Eqs (I), with the LEIP that does not satisfy Eqs (I), depend on parameters entering Eqs (I). These parameters vary in relatively wide intervals: $\varkappa = 3$ to 12, $c_o = (1\ to\ 5)10^5$ cm/sec, $\Theta \approx (1\ to\ 10)10^{2o}K$ and $M = (2\ to\ 10^2)M_H$. This gives significant variety of materials and of numerical values of M,v and $\mathcal{E}$ satisfying Eqs (I),when the binary collision approximation,at least for head-on collisions,becomes applicable.However,as a rule,it takes place for $\mathcal{E} \geqslant IO^3 \div IO^4$ ev.

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