COLLECTIVE SHORT-TERM NON-EQUILIBRIUM PHENOMENA CAUSED BY A LOW-ENERGY ION IN THE NEAR-TO-SURFACE MATERIAL VOLUME AS FUNDAMENTAL IN PLASMA-MATERIAL INTERACTION.

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ABSTRACT

Further development of the kinetics of non-stationary non-equilibrium collective explosion-like phenomena in a short-lived hot spot (SLHS) initiated in a small near-to-surface material volume by a low energy ion (LEI) and leading to sputtering and changes of local material properties are considered. Equations and estimates of instanteneous parameters of the hot high pressure SLHS fireball formed by the LEI are obtained.

1. INTRODUCTION

The bombardment of solid materials by low-energy ions (LEI's) with energies $\mathcal{E}_o = Mv^2/2$ from a few sputtering thresholds up to $\mathcal{E}_o \approx 10^3$ ev leads to sputtering, changes of material properties and other related phenomena important for tokamak devices, for plasma coating and deposition, for plasma chemical reaction kinetics, etc.[1-9]. The present knowledge about phenomena initiated by a single LEI on the material surface and in the near-to-surface bulk is rather poor and many observed phenomena are not quite understood, in spite of decades of investigation and many attempts to construct theoretical models of sputtering and related phenomena. At the same time many relevant experimental data have been accumulated[1-11] and empirical relations for sputtering phenomena were suggested[1,10,11]. Earlier applications of the equilibrium statistical thermodynamics to the sputtering problem have failed, since the equilibrium philosophy is not applicable in this case[9,13,14]. Theoretical schemes based on transport theory and the binary collision approximation[15] face serious conceptual objections in the case of the LEI bombardment, and they also meet with significant difficulties in the interpretation of many observations[1,5,9-14,16]. The spike model[17-19] and the shock-wave one[16] face the problem which follows from the absence of proper methods to treat very non-stationary non-equilibrium collective non-linear short-term behaviours of small groups of strongly interacting particles with highly excited energies $\mathcal{E} \gg kT$[13,14,20-26]. In the case in question the conventional methods based on the Hamiltonian formalism (which was used to consider ejection of molecular clusters[12]), on the equilibrium statistical mechanics and so on are invalid. In this connection the author has suggested the program[9,13,14] of a semiphenomenological treatment of the LEI-target interaction by combining some ideas and methods of the non-stationary non-equilibrium thermodynamics, kinetics, microgasdynamics and certain modifications of the ideas used in[20-26] and the concept of the LEI-induced short-lived hot spot (SLHS) with short lifetime $\tau_h = \tau_g + \tau_L + \tau_s$ including[9,14,15]: a) quasi-gas stage (QGS) lifetime τ_g, b) quasi-liquid stage (QLS) time $\tau_L > \tau_g$ and c) hot solid stage (HSS) time $\tau_s > \tau_L$. This work presents a further development of the above program.

2. STATEMENT OF THE PROBLEM.

The initial state of the LEI-solid system just before the LEI starts to interact with target particles is determined by the ordered state of material composed of particles of mass m mainly performing small thermal oscillations at temperature T and by the LEI having momentum $p_o = \{p_{o\perp}^{(in)}, p_{o\parallel}\}$ with "inward" component $p_{o\perp}^{(in)}$ perpendicular to the surface and directed towards the material bulk and "sideward" component $p_{o\parallel} = \{p_{ox}, p_{oy}\}$ directed parallel to the surface. Then

$$\mathcal{E}_o = \mathcal{E}_{o\perp}^{(in)} + \mathcal{E}_{o\parallel} = (2M)^{-1}\left[(p_{o\perp}^{(in)})^2 + p_{o\parallel}^2\right] \qquad (1)$$

Immediately after the SLHS decay one can find short-term: a) energy and momentum micro-fluxes directed towards the material bulk and b) mass, electric charge, energy and momentum microfluxes directed towards the vacuum. Sputtered particles (single particles, ions, clusters, etc.) propagating in vacuum with momenta $p_s = \{p_\perp^{(out)}, p_\parallel\}$ and with kinetic energies

$$\mathcal{E}_s = \frac{1}{2m}\left[(p_{s\perp}^{(out)})^2 + p_{s\parallel}^2\right] = \mathcal{E}_{s\perp}^{(out)} + \mathcal{E}_{s\parallel}, \qquad (2)$$

where $p_{s\perp}^{(out)}$ is the "outward" momentum component perpendicular to the surface and directed from it towards vacuum, $p_{s\parallel}$ is the "sideward" momentum component parallel to the surface. Then

$$\mathcal{E}_{o\perp}^{(in)} = \mathcal{E}_o \cos^2\varphi_o,\ \mathcal{E}_{o\parallel} = \mathcal{E}_o \sin^2\varphi_o,\ \mathcal{E}_{s\perp}^{(out)} = \mathcal{E}_s \cos^2\varphi_s \text{ and } \mathcal{E}_{s\parallel} = \mathcal{E}_s \sin^2\varphi_s, \qquad (3)$$

where φ_o and φ_s are angles of LEI incidence and of sputtering. Therefore the LEI - solid interaction leading to sputtering is inevitably associated with the in-to-out conversion of direction of particle momenta, where the kinetic energy of sputtered particles (or clusters) on the surface should satisfy the condition[9,14]

$$\mathcal{E}_{s\perp}^{(out)} = \mathcal{E}_s \cos^2\varphi_s > \Delta E_s \quad , \qquad (4)$$

where ΔE_s is the surface energy barrier of sputtered particles. Various mechanisms of such conversion and related sputtering can be considered: (i) Sputtering of a single particle caused by the direct LEI - target atoms interaction[11]. (ii) The ejection of a single particle by LEI which is reflected in the interior of the target and on its way out again suffers a heavy collision near the surface causing the ejection of a surface atom[11]. The above two mechanisms, (i) and (ii), help to explain some sputtering data, however they do not help to interpret observed cluster and ion sputtering and known changes of material properties which frequently accompany sputtering. (iii) All the above phenomena can be caused by a rapid release of LEI energy $\mathcal{E}_o \approx (10^4 - 10^5)kT$ in small near-to-surface volume V_f containing a not high number $N_f \approx V_f/\Omega_o$ of material particles in the case of heavy LEI's. This energy release can produce the initial hot high pressure SLHS fireball (see the next section of this paper) in a very small volume. Such fireball, in turn, can induce explosion-like phenomena associated with formation of intensive microshock waves, of cumulative microjets and other collective and gasdynamic processes that can lead to: a) ejection of clusters (of various compositions), ions and single particles with wide energy spectra and with various excitations, b) changes of local material properties and so on. In the case of light LEI's such intensive fireballs and related phenomena do not take place. (iv) Possible evaporation of material particles from the SLHS and short-term rearrangements of the local material structure in the SLHS during successive SLHS stages can lead to additional sputtering of low energy particles and changes of local material properties.

Therefore, observed sputtering yields

$$Y = Y_d + Y_r + Y_g + Y_e \qquad (5)$$

which include components Y_d, Y_r, Y_g and Y_e associated with the above four groups of processes, can have different compositions, energy spectra and intencities. Each of these components and related SLHS phenomena deserves the thorough elaboration. In this paper we shall confine ourselves mainly to the discussion of some questions associated with formation of the SLHS fireball by LEI's with $M \approx m$ and $M > m$ which is one of the chief processes in the SLHS kinetics and related phenomena.

3. FORMATION AND INITIAL PARAMETERS OF SHORT-LIVED HOT SPOTS. HEAVY AND LIGHT LOW ENERGY IONS.

Consider the LEI slowing down to energy $\mathcal{E}_{of}$ of a few ev (when it ceases its propagation in the material[14]), during Δt_f which is treated as the duration of formation of the initial SLHS state. During Δt_f the LEI suffers α_{ef} random collisions with target particles, where α_{ef} and Δt_f are

$$\alpha_{ef} \approx \eta^{-1} \ln(\mathcal{E}_o/\mathcal{E}_{of}) \quad \text{and} \quad \Delta t_f \approx \alpha_{ef} \cdot \Delta l/\bar{v}_o \quad , \qquad (6)$$

here $\eta = \beta\gamma$ is the mean fraction of energy of the LEI losses per one collision, $\gamma = 2mM(M+m)^{-2}$, β reflects deviations from the binary collision approximation and can differ markedly from 1 in the case of $M \approx m$ and $M > m$, when the collective character of the LEI - target atom collisions play a more important role; Δl is the LEI mean free path length. During the slowing down the projectile performs a 3-dimensional random walk with the effective "drift velocity" $u_d \ll \bar{v}_o$ directed along the original direction of the LEI motion. This directed drift velocity is more pronounced in the case of heavy LEI, $M \gg m$. Therefore if LEI energy $\mathcal{E}_o \approx (10^3 - 10^5)kT$ is released and rapidly redistributed in rather small volume V_f with low number $N_f \approx V_f/\Omega_o$ (for not too light LEI's), it leads to formations of the initial hot high pressure SLHS fireball in the near-to-surface material matter, Ω_o is the volume per particle. This causes a very rapid and drastic transformation of the material state and properties. To estimate the fireball parameters for various M/m and $\mathcal{E}_o$, introduce diffusion coefficient $D_f \approx \Delta l \cdot \bar{v}_o$ characterizing the LEI random walk during Δt_f. Then the depth of LEI penetration in the material serving as the space fireball scale, volume V_f and number of particles N_f in V_f are

$$\Delta L \approx (D_f \cdot \Delta t_f)^{\frac{1}{2}} \approx \Delta l \left[\eta^{-1} \cdot \ln(\mathcal{E}_o/\mathcal{E}_{of})\right]^{\frac{1}{2}} \qquad (7)$$

$$V_f \approx A \cdot \Delta L^3 = A \cdot \Delta l^3 \cdot \left[\eta^{-1} \cdot \ln(\mathcal{E}_o/\mathcal{E}_{of})\right]^{3/2} \qquad (8)$$

$$N_g = V_f/\Omega_o \approx \left[\eta^{-1} \cdot \ln(\mathcal{E}_o/\mathcal{E}_{of})\right]^{3/2} (\Delta l^3/\Omega_o) \qquad (9)$$

The LEI netway during Δt_f is

$$L_f = \Delta t_f \cdot \bar{v}_o \approx \alpha_{ef} \cdot \Delta l \approx \eta^{-1} \cdot \Delta l \ln(\mathcal{E}_o/\mathcal{E}_{of}) > \Delta L \qquad (10)$$

Since every material particle receiving energy from the LEI strongly interacts with $æ$ rapidly moving neighbours[9,13,14,20], energy $\mathcal{E}_o - \mathcal{E}_{of}$ is quickly redistributed between N_f particles: part W_f of this energy can be consumed to destroy crystal bonds, to ionize fireball material particles, etc.; the other part $\mathcal{E}_o - \mathcal{E}_{of} - W_f$ produces fast and high heating of N_f particles. The SLHS fireball can be characterized by kinetic temperature

$$T_f \approx \partial S_f/\partial U_f \approx (3kN_f)^{-1}\cdot(\mathcal{E}_o - W_f - \mathcal{E}_{of}) \quad (11)$$

associated with high fireball inner energy $U_f \approx U_{of} + \mathcal{E}_o$, where U_{of} is the inner energy of the N_f particles before the LEI - target interaction starts, $\bar{\varepsilon}_f \approx 3kT_f$ is the mean thermal energy of the fireball particle,

$$S_f = k\ \ln \Delta\Gamma_f = kN_f \ln(\Delta p_{fx}\cdot\Delta p_{fy}\cdot\Delta p_{fz}\cdot n_f^{-1}\cdot h^{-3}) \quad (12)$$

is the effective fireball entropy associated with statistical weight

$$\Delta\Gamma_f = (\Delta p_{fx}\cdot \Delta p_{fy}\cdot \Delta p_{fz})^{N_f}\cdot(N_f!\cdot h^{3N_f})^{-1} = (e\cdot \Delta p_{fx}\cdot \Delta p_{fy}\cdot \Delta p_{fz}\cdot n_f^{-1}\cdot h^{-3})^{N_f} \quad (13)$$

of the N_f particles with effective phase space volume $\omega_f = (\Delta p_{fx}\cdot \Delta p_{fy}\cdot \Delta p_{fz}\cdot V_f)^{N_f}$. The fireball pressure can be estimated by

$$P_f \approx B_f(\mathcal{E}_o - \mathcal{E}_{of} - W_f)\cdot(V_f - N_f\cdot V_o)^{-1} \quad \text{with} \quad V_o \approx (4\pi/3)r_M^3 , \quad (14)$$

where B_f is the fitting dimensionless coefficient, r_M is the effective radius of material particles. Besides the initial excited energy $\mathcal{E}_o - \mathcal{E}_{of}$ the SLHS fireball as a whole gains from the LEI a finite initial momentum $\pi_f \approx M\cdot v_o$ and velocity $V_f = \pi_f/N_f\cdot m$ along the original direction of the LEI motion. Values $U_f, T_f, P_f, S_f, \pi_f$ and V_f characterize the initial conditions of the SLHS fireball at moment $\tau_p^f=0$ which is considered the reference point of the local SLHS time scale (similar to the SLEF peak moment $\tau_p=0$ in the SLEF theory[20]). Phenomena associated with SLHS formation at $\tau^A<0$ are treated as fireball advanced ones; processes associated with fireball time evolution and decay at $\tau^R>0$ can be treated as fireball retarded ones.

The obtained equations allow to estimate fireball parameters for different ratios M/m, since

$$T_f \sim N_f^{-1} \sim \eta^{3/2},\ P_f \sim \eta^{3/2} \approx \beta\cdot 2mM(M+m)^{-2} \quad \text{and} \quad v_f \sim \eta^{3/2} \quad (15)$$

Let $M \approx m \approx 50m_H$, $\gamma \approx 0{,}5$, $\mathcal{E}_o \approx 500$ev, $v_o \approx 3\cdot10^6$cm/s, $\mathcal{E}_{of} \approx 5$ev, then, if A =2, $\Delta l \approx 3\cdot10^{-8}$cm, $\bar{v}_o \approx 0{,}3v_o \approx 10^6$cm/s, $\beta \approx 1{,}3$, $V_f - N_f\cdot V_o \approx 0.5V_f$, one finds

$$W_f \approx 0.2\,\mathcal{E}_o,\ \alpha_{ef} \approx 7,\ L_f \approx \alpha_{ef}\cdot d \approx 2\cdot10^{-7}\text{cm},\ \Delta t_f \approx 2\cdot10^{-13}\text{s};\ \Delta L \approx 7\cdot10^{-8}\text{cm},$$

$$V_f \approx 10^{-21}\text{cm}, D_f \approx 3\cdot10^{-2}\text{cm}^2/\text{s}, N_f \approx 30, T_f \approx 5\cdot10^4\text{K} \gg T, P_f \approx 10^6\text{at}, v_f \approx 10^5\text{cm/s} \quad (16)$$

Such initial SLHS hot high pressure fireball can produce very intensive cumulative microjets and microshock waves.

Light LEI, when $M \ll m$ and $\eta_1 \ll 1$. In this case, if $M \approx 0.02m = m_H$, $\Delta l \approx 2d$, other conditions equal, one finds $\gamma_1 \approx 0.05$, $\eta_1/\eta \approx 10$, $v_o \approx 3\cdot10^7$cm/s, $\bar{v}_o \approx 10^7$cm/s, $\alpha_f' \approx 70$, $\Delta t_f' \approx 4.2\cdot10^{-13}$s, $D_f' = 0.6$cm^2/s, $\Delta L \approx 5\cdot10^{-7}$cm, $V_f \approx 2.5\cdot10^{-19}$cm^3,

$N_f' \approx 8\cdot10^3$, $\mathcal{E}_o/N_f \approx 0.05$ev, $T_f' - T' \approx 200^oK$, $v_f' \longrightarrow 0$. Hence one can see that for light LEI's hot high pressure SLHS fireballs are not formed and therefore, one cannot expect formation of cumulative microjets and very intensive shock waves here.

The above differences in formation of the initial SLHS when $M \simeq m$ and $M > m$ can be one of the main reasons of observed higher sputtering yields of the heavy LEI bombardment. A more detailed study of the fireball and related SLHS phenomena will be considered in another article.

4. QUALITATIVE CONSIDERATION OF THE EVOLUTION OF THE HEAVY LEI-INDUCED FIREBALL.

The SLHS evolution from the initial "fireball state" is determined by competition of various factors: (i) The LEI energy $\mathcal{E}_o$ released in the fireball is redistributed between various degrees of freedom of the material particles and the LEI. Energy W_f is consumed for destroying the crystal structure, for ionization and excitation of inner degrees of freedom of the involved particles. This part of energy depends on the structures of the material particles and the LEI, on particular properties of their interaction, on binding energy E_B of material particles, etc. Only energy $\mathcal{E}_o - W_f$ can be converted in the thermal motion of fireball particles. The condition

$$(\mathcal{E}_o - W_f) >> N_f \cdot E_B \approx \left[\eta^{-1} \cdot \ln(\mathcal{E}_o / \mathcal{E}_{of})\right] \cdot (A l^3 / \Omega_o)^{E_B}, \qquad (17)$$

which can be satisfied only for heavy LEI, enables one to expect that all fireball particles can be involved in the motion during the fireball evolution. (ii) When N_f is not large, the fireball as a whole can gain not low initial velocity $v_f \approx M \cdot v_o / N_f \cdot m$ along the original direction of the LEI incidence. This fireball directed motion, which is practically immediately stopped, can initiate a strong cumulative microshock wave in the direction opposite to the original LEI incidence, due to reflection from the cold surrounding media. The directed fireball motion involves material mass $N_f \cdot m$ and is associated with energy

$$\mathcal{E}_1 \approx m \cdot N_f \cdot v_f^2 / 2 \approx (\mathcal{E}_o / N_f) \cdot (M/m) << \mathcal{E}_o \qquad (18)$$

(iii) The fireball having high T_f and P_f, can generate a microshock wave coming to the surface. This wave can carry energy of the order up to $0.5(\mathcal{E}_o - W_f)$ and can produce microcraters (or funnels) and protrusions on the surface by sputtering a small part of the involved particles, of which energy on the surface satisfies condition (4), and by explosion-like spitting on the surface the rest of the involved target matter which cannot overcome the surface energy barrier. (iv) The fireball also generates the microshock wave propagating inside the target material and forming quasi-gas microbulb in small near-to-surface volume V_g. This shockwave can be partially reflected from the compressed cold surrounding target media. Such reflection can initiate the cumulative shock wave directed to the surface. This wave is also associated with rapid explosion-like closing of the quasi-gas microbulb when the above cumulative wave comes to the surface especially during funnel formation. Then this wave can be transformed into a cumulative microjet directed into vacuum. Such cumulative jet can produce high-energy volcano-like splash of material particles into vacuum, similar to that considered in hydrodynamics during formation of liquid or gas "plumes"[27]. The total number ΔN_f of material particles coming to the surface during the above gasdynamic phenomena depending on the fireball parameters, on the depth of the initial fireball, on material parameters, etc., satisfies the conditions

$$\Delta N_f \cdot E_B < N_f \cdot E_B << \mathcal{E}_o - W_f \quad \text{or} \quad b_s \cdot \Delta N_f \cdot E_B \approx \mathcal{E}_o - W_f \quad \text{with} \quad b_s >> 1 \qquad (19)$$

Only part δN_s of the ΔN_f particles coming to the surface, can overcome the surface energy barriers and can be sputtered, i.e. $a_s \cdot \delta N_s = \Delta N_f$, where $a_s > 1$ and b_s should be found from experimental data.

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