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Sputtering Theory.

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1. – Introduction.

When energetic atomic projectiles collide with a solid, the collisional energy loss processes generally result in both bulk and surface radiation damage. The

microscopic process that produces the ejection of target atomic particles during bombardment is called *sputtering*. This process was first observed in 1852 by Grove [1] who noticed that in experiments on electronic discharges in gases a metallic deposit was found on the walls of the discharge tube.

After this first experimental observation we must wait about a century before interest, both experimental and theoretical, for this phenomenon reawakes: the pionier works of Wehner [2, 3] have given a substantial support to this reawakes. An increase in interest has been constant for many years, while during the last decade we have noticed a great improvement. More precise conclusions can be deduced from a recent analysis made by Oliva [4], on scientific production concerning sputtering during the period 1965-1985. His analysis is

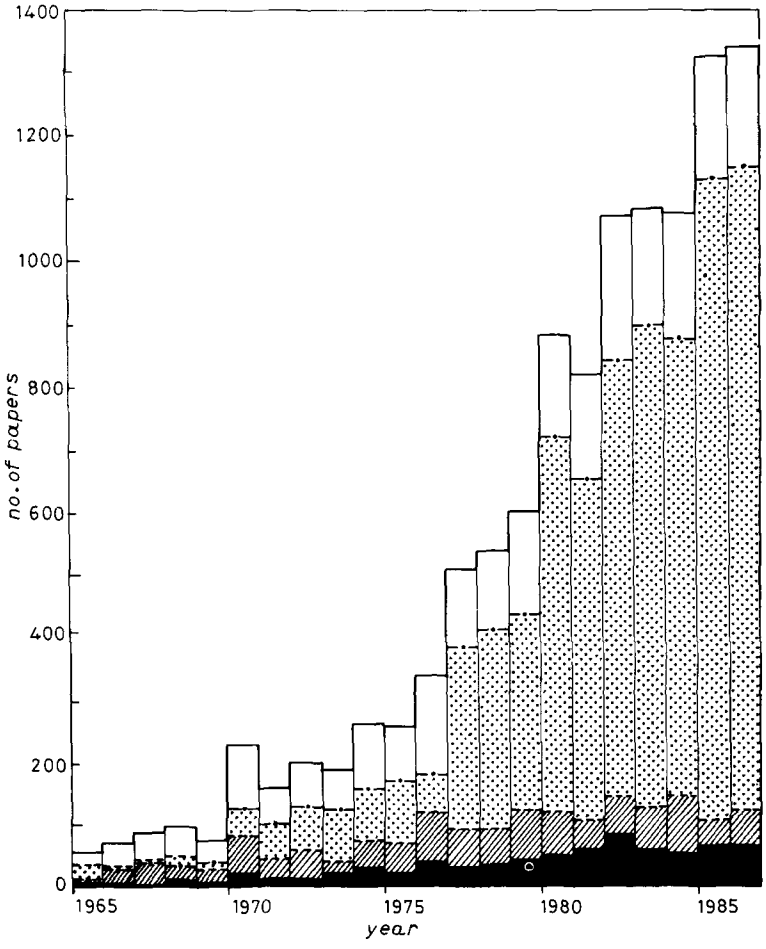

Fig. 1. – Statistics of scientific publications in the field of sputtering covering roughly 20 years. A distinction is made between theoretical, experimental and application oriented works (by courtesy of the author): □ total, □ applications, ▨ experimental, ■ theory.

summarized in fig. 1. He has divided the papers on sputtering into three categories. The first category contains theoretical works and computer simulation studies. The second category contains papers dealing with experimental data and measurements oriented towards the explanation of a model or supporting a theory. In the last category he placed works where the sputtering technique is used as a general application. The most evident result of this analysis is the enormous number of papers on pratical applications of sputtering, whereas the works on basic research seem to be in a stationary state. Moreover, if we gain more insight into the first two categories we notice that, during the last decade, most of published papers in these categories are computer simulation studies. In other words, theoretical works and experimental measurements oriented towards the explanation of a model or supporting a theory have almost disappeared. The reasons for that are, of course, different, but we can also reasonably include a lack of theoretical approaches with a unitary vision of the phenomenon. In reality, in contrast with traditional trends in other fields of physics research, where unified approaches constitute the rule and not the exception, the theoretical sputtering community has produced models or theories oriented towards specific aspects of the phenomenon. At present it is not clear whether this aspect of sputtering production is an intrinsic characteristic of the phenomenon or is a consequence of the relative recentness of research in this field. However, it is evident that a new effort to achieve new theoretical approaches and experiments supporting theories is mandatory.

Starting from these premises, an analysis of the evolution of theoretical models, with a precise attempt to stress conceptual innovations that have stimulated substantial improvements of theoretical approaches, may be very useful. This paper is an attempt, of course partial and subjective, to analyse the evolution of *analytical theories concerning collisional sputtering*. To be precise, the paper is oriented towards theoretical aspects of the sputtering phenomenon produced by ion bombardment of amorphous and polycrystalline monoatomic targets (the size of the physical targets is assumed to be always larger than the mean penetration depth of the incident ion). Moreover, among the different types of sputtered particles (neutral atoms, excited neutral atoms, ions, molecules excited or not, clusters and so on) we shall analyse the most abundant, the neutral atoms. This category of particles has been the most studied, and the general opinion is that other types of sputtered particles can be deduced by an adequate modification of models describing neutral atoms. The choice to restrict our paper to collisional sputtering is motivated by the present theoretical situation, where only this type of sputtering can be included in a unified theory.

It is evident that from our choice we have left out several interesting aspects of the sputtering phenomenon, and the interested reader is referred to several recent review papers or books on the subject [5-13].

In sect. 2 we present the historical development and the evolution of both matematical and physical concepts that have produced the standard transport

theory [14, 15]. The surface aspect of the sputtering and its consequences as originated from the development of the Falcone and Sigmund theory [16] are described in sect. 3. Finally, in sect. 4, a unified sputtering theory [17-20] is presented, and some comments are outlined.

2. – Historical overview and theoretical tools.

The main attempt of this chapter is to describe the theoretical evolution of the basic concepts that are necessary to obtain a modern analytical sputtering theory. We emphasize that, although most of the physical ideas originated long ago, the realization of a modern analytical theory is essentially related to the development of the *Lindhard theoretical apparatus.*

2·1. *The forerunners: Keywell and Harrison.* – From a microscopic point of view, in order for a sputtering event to take place, part of the kinetic energy of the incident particle must be transferred to target particles that *only subsequently* may leave the target as sputtered particles. In other words, we can distinguish in a sputtering event two steps: in the first step the incoming particle transfers, in its slowing-down in the solid, energy and momentum to the target atoms and moving target atoms, called recoils, are generated; in the second step a part of the recoils are able to leave the solid. The description of a sputtering event through two steps can be found, for the first time, in the papers of Keywell [21, 22].

Keywell, starting from a similarity with neutron cooling theory, considers the incident particle as *hard sphere* which loses energy through collisions with the target atoms as moderators: the incident particle can transfer a considerable fraction of its energy to a target atom in one collision; the latter is thus an energetic recoiling atom which can strike other target atoms to produce secondary, tertiary, etc., recoil atoms. Once energetic recoils are produced, according to the above description, one must choose those that leave the surface. Since Keywell recognizes that sputtering is a *radiation damage phenomenon*, he assumes *all displaced particles near the surface* to be sputtered. To be precise, Keywell uses the neutron cooling theory to calculate the energy attenuation of the incident particle in the solid, then he transforms this attenuation in a number of displaced atoms and finally he chooses among the displaced atoms those near the surface by introducing an adequate *escape probability.*

Since it is the opinion of this author that Keywell's sputtering theory contains an almost complete characterization of the basic aspects of the phenomenon we shall describe in detail his formulation.

Let us take an ion with initial energy E and mass M_1 that penetrates into a solid target which atoms have mass M_2. After n collisions, by using the

elementary neutron cooling theory [23], the initial energy will be reduced to

$$E_n = E\exp[-n\xi], \tag{2.1}$$

where

$$\xi = 1 - \frac{(M_1 - M_2)^2}{2M_1M_2}\ln\left(\frac{M_1 + M_2}{M_1 - M_2}\right). \tag{2.2}$$

Since the maximum fraction of projectile's energy that can be transferred to a target atom, *initially at rest*, in a single collision is

$$\gamma = \frac{4M_1M_2}{(M_1 + M_2)^2}, \tag{2.3}$$

the average energy of the $(n+1)$-th recoil atom will be given by

$$\langle E_{n+1}\rangle = \gamma E\exp[-n\xi]. \tag{2.4}$$

If the average number of displaced atoms produced by a recoiling atom of energy $\langle E\rangle$ in a solid, having an atomic displaced energy E_d, is assumed to be [24]

$$n_0 = \left(\frac{\langle E\rangle}{E_d}\right)^{1/2}, \tag{2.5}$$

then, the number of displaced atoms produced by the recoil at the n-th collision of the primary will be

$$n_s = \left(\frac{\langle E_n\rangle}{E_d}\right)^{1/2} = \left(\frac{\gamma E}{E_d}\right)^{1/2}\exp\left[\frac{-(n-1)\xi}{2}\right]. \tag{2.6}$$

Of these n_s displaced atoms, according to Keywell, only the subsequent part will be sputtered

$$n_Y = n_s\exp[-\alpha\sqrt{n}], \tag{2.7}$$

where α is a parameter. Equation (2.7), which represents the ejection function of the model, was derived [22] by assuming that the average depth from which sputtered atoms originate is determined by an atom that progresses by a random walk.

Finally the number of sputtered atoms will be

$$Y = \left(\frac{\gamma E}{E_d}\right)^{1/2}\sum_{n=1}^{n_l}\exp[-\alpha\sqrt{n}]\exp\left[-\frac{(n-1)\xi}{2}\right], \tag{2.8}$$

where

$$n_l \simeq \frac{1}{\xi} \ln\left(\frac{\gamma E}{E_d}\right) \tag{2.9}$$

defines the last collision which produces a displaced atom.

More details and further generalizations of the previous equations can be found in the original paper [22].

The analysis of the above formulation is very instructive. The Keywell theory refers to sputtering produced by the penetration of low-velocity atomic particles through matter. Nevertheless he assumes that a theory, valid for the slowing-down of *fast* neutrons in a moderator, is also adequate to describe the low-velocity atomic slowing-down. It is clear that the analogy between the slowing-down of fast neutrons and low-velocity ions through matter is suspicious and must be given up in a more adequate sputtering theory.

The theory completely neglects the interaction between the incident ion and the electrons of the atomic target: the collisions are of biliard-ball type. This aspect of the penetration of low-velocity atomic particles into matter is shared by other authors contemporary with Keywell and represents a further aspect of the Keywell theory that must be modified.

The results of the theory depend on the *radiation damage model* used to transform the energy lost by the incident particle in displaced atomic target particles (see eq. (2.5)). In this case it is also clear that an improvement of the radiation damage model can improve the theory.

At the time when Keywell presented his theory the experimental data were quite limited and in particular no data were available on the depth of origin of sputtered atoms. Nevertheless, Keywell realized that sputtered atoms originate from a depth very near the surface and used the random walk to obtain an adequate expression. This approach has also been used by almost all subsequent authors and the general philosophy of this approach is that recoiling atoms that will be sputtered will undergo several elastic collisions during the motion from the original position in the solid up to the surface. The recent experimental data on the depth of origin of sputtered atoms (see later) tell us that this vision of the sputtering phenomenon is incorrect.

Finally, we conclude the analysis of the Keywell theory by mentioning that this theory predicts a sputtering threshold, E_{th}, for ions hitting the target at normal incidence, equal to

$$E_{th} = \frac{E_d}{\gamma}, \tag{2.10}$$

which was considered by the author as *upper limit value.*

An attempt to improve the conceptual approach of Keywell was made by Harrison [25]. In fact, Harrison gave up the cooling neutron theory and assumed

that the sputtering mechanism is adequately described by proper linear Boltzmann transport equations. Since this theory has not provided analytical results, we do not discuss this formulation in details, and we mention that the use of Boltzmann's transport equations, when properly carried out (Sigmund's transport theory [15]), turns out to be very adequate to describe several aspect of the sputtering phenomenon. Harrison's is the original intuition of this approach, whereas the lack of analytical result in his formulation is probably related to a lack of adequate development of parallel concepts for particle penetration through matter. In other words, a proper description of the sputtering phenomenon needs the development of new general concepts about the penetration of low-velocity atomic particles through matter, that at the time when Harrison presented his formulation were not yet available. In the subsequent section we shall discuss this new physical and mathematical apparatus in details.

2·2. *The Lindhard theoretical apparatus.* – The penetration of low-velocity atomic particles through matter is in general a very broad field and in this paper we shall limit our discussion to those aspects that are essentially related to the modern analytical formulations of the sputtering phenomenon.

When a particle penetrates a solid target the interaction between the incident particle and the target atoms, according to Lindhard's works [26-28], can be divided, with a good approximation, in two *uncorrelated* contributions: binary elastic collisions between the incident particle and the atomic targets (elastic or nuclear energy loss and scattering) and a separated electronic energy loss which is a continuous slowing-down process that does not affect the direction of the incident particle. While in a high-velocity regime the decoupling between electronic and nuclear processes [29], around the 60 s, was accepted by almost all the scientific community, in the low-velocity regime the decoupling was hardly to share. In fact, difficulty to accept the Lindhard decoupling can be justified by the observation that, in the low-velocity regime, in each collisional event and at the same time, a scattering process takes place as well as electronic and nuclear energy loss. Nevertheless, as Lindhard showed [26, 27], in a penetration theory of low-velocity atomic particles through matter *the electronic processes enter into the theory via a continuous stopping term, whereas the statistics of elastic energy loss and scattering determine the general structure of equations.*

In the subsequent part of this chapter we shall describe the essential characteristics of the Lindhard theoretical apparatus.

2·2.1. The interatomic potential. The interaction between the incident particle and a target atom is a typical many-body problem and a possible description of the interaction can be made by using the Hartree-Fock self-consistent potential method [30, 31]. Since the motion of particles in a self-consistent potential can be assumed to be quasi-classical in most of space, the

quasi-classical (or Thomas-Fermi) approximation of the Hartree-Fock method can be used [32, 33]. In other words, the interaction between two particles of charge $Z_1 e$ and $Z_2 e$, with e the electron charge and Z_1 and Z_2 the atomic numbers of the colliding particles, can be adequately described by the Thomas-Fermi statistical model. Within the accuracy of this model, the interatomic potential between two particles can be described by the following screened Coulomb potential [34, 35]:

$$V(r) = \frac{Z_1 Z_2 e^2}{r} f\left(\frac{r}{a}\right), \tag{2.11}$$

where r is the distance between the two particles, $f(r/a)$ is the Thomas-Fermi function [36] and a is the screening radius. Lindhard and coworkers [28] arrive at the same conclusion and the only difference between the two final expressions of the interatomic potentials is in the expression for the screening radius. The choice between the Firsov or Lindhard screening radius cannot be motivated by any scientific argument. In this paper we adopt the Lindhard screening radius which has the following form:

$$a = \frac{0.8853 a_0}{\sqrt{Z_1^{2/3} + Z_2^{2/3}}}, \tag{2.12}$$

where $a_0 = 0.529$ Å is the Bohr radius.

2·2.2. The power cross-section. Let us analyse the scattering process between two particles in the classical picture. We restrict to the case in which the struck particle (M_2) in the laboratory system is, before the collision, at rest. If φ_1 and φ_2 are the scattering angles of the two particles, in the laboratory system, and θ is the scattering angle in the centre-of-mass system, the relation among these quantities can be written [37] as

$$\operatorname{tg} \varphi_1 = \frac{M_1 \sin\theta}{M_1 + M_2 \cos\theta} \tag{2.13}$$

and

$$\varphi_2 = \frac{\pi - \theta}{2}. \tag{2.14}$$

In the penetration of particles through matter and in particular in the radiation damage field, the energy transferred, T from the incident particle to the struck atom is an important quantity. Simple calculations show that the following relation is valid:

$$T = \gamma E \sin^2 \frac{\theta}{2} = T_m \sin^2 \frac{\theta}{2}. \tag{2.15}$$

It appears clear that all basic quantities involved in a scattering process can be derived if the expression of the scattering angle θ is known. Unfortunately, the general expression [37] of the scattering angle θ, for spherical potential, when screened Coulomb potentials are considered, cannot be calculated analytically [38]. Some improvements can be achieved, if the scattering angle is *small*. In this case we can write [28, 34]

$$\theta = -\frac{1}{\mu v^2}\frac{\partial}{\partial b}\int_{-\infty}^{\infty} V(\sqrt{b^2+z^2})\,\mathrm{d}z\,, \tag{2.16}$$

where μ is the reduced mass, v the velocity of the incident particle, b the impact parameter and z the direction of the incident particle.

If we insert eq. (2.11) in eq. (2.16), we obtain [28]

$$\theta = -d\int_0^{\infty}\mathrm{d}z\left\{\frac{b}{(b^2+z^2)^{3/2}}\left[f\left(\frac{\sqrt{b^2+z^2}}{a}\right)+\frac{\sqrt{b^2+z^2}}{a}f'\left(\frac{\sqrt{b^2+z^2}}{a}\right)\right]\right\}, \tag{2.17}$$

where

$$d = \frac{2Z_1 Z_2 e^2}{\mu v^2} \tag{2.18}$$

is called *collisional diameter* [29]. Moreover f' is the derivative of f with respect to the impact parameter.

If we introduce the new variable

$$\alpha = \arccos\frac{b}{\sqrt{b^2+z^2}}, \tag{2.19}$$

we get

$$\theta = \frac{d}{b}g\left(\frac{b}{a}\right) \tag{2.20}$$

with

$$g\left(\frac{b}{a}\right) = \int_0^{\pi/2}\mathrm{d}\alpha\cos\alpha\left[f\left(\frac{b}{a\cos\alpha}\right)+\frac{b}{a\cos\alpha}f'\left(\frac{b}{a\cos\alpha}\right)\right]. \tag{2.21}$$

Following Lindhard [26-28] we introduce the dimensionless energy variable, ε

$$\varepsilon = \frac{a}{d} = \frac{a}{Z_1 Z_2 e^2}\frac{M_1}{M_1+M_2}E \tag{2.22}$$

and we write eq. (2.20) as follows:

$$\theta\varepsilon = \frac{a}{b} g\left(\frac{b}{a}\right). \tag{2.23}$$

The product of θ and ε is a function of only one variable: b/a. This enables us, by inversion, to obtain a differential cross-section which is a function of only one variable and this result is valid for all screened Coulomb potentials. Numerical calculations of the cross-section can be found in the original paper [28]. Since we are interested in analytical expressions we proceed by choosing the following form for the screening function [28]:

$$f\left(\frac{r}{a}\right) = \frac{k_s}{s}\left(\frac{a}{r}\right)^{s-1}, \tag{2.24}$$

where k_s is a constant and $s = 1, 2, \ldots, \infty$. For this particular choice, we can write the scattering angle in a simple form

$$\theta = k_s \gamma_s \left(\frac{a}{b}\right)^s, \tag{2.25}$$

with

$$\gamma_s = \int_0^{\pi/2} \mathrm{d}\alpha \cos^s \alpha = \frac{\Gamma(1/2)\,\Gamma((s+1)/2)}{2\Gamma(s/2+1)}, \tag{2.26}$$

where $\Gamma(z)$ is the Euler gamma-function [39].

Equation (2.25) enables an analytical differential cross-section, $\mathrm{d}\sigma(\theta)$ to be derived. In fact, by definition [37]

$$\mathrm{d}\sigma(\theta) = 2\pi b \left|\frac{\mathrm{d}b}{\mathrm{d}\theta}\right| \mathrm{d}\theta \tag{2.27}$$

and we obtain, by using, eq. (2.25)

$$\mathrm{d}\sigma(\theta) = \pi a^2 \left(\frac{k_s \gamma_s}{\varepsilon}\right)^{2/s} d\left[\left(\frac{1}{\theta}\right)^{2/s}\right] \tag{2.28}$$

which written in terms of energy transferred T becomes

$$\mathrm{d}\sigma(T) = \frac{\pi}{2} a^2 \lambda_s \varepsilon^{-2/s} T_m^{1/s} T^{-1-1/s} \mathrm{d}T, \tag{2.29}$$

where

$$\lambda_s = \frac{2}{s}\left(\frac{k_s \gamma_s}{2}\right)^{2/s}. \tag{2.30}$$

In deriving eq. (2.29) we have used the expression of eq. (2.15) in the limit of small scattering angle.

Equation (2.29) is called *Lindhard's power cross-section* and, although it has been derived for soft collisions (small scattering angle approximation), it can be shown to be quite accurate even for violent collisions. Usually this power cross-section is used in the form proposed by Sigmund [40]

$$d\sigma(T) = C_m E^{-m} T^{-1-m} dT, \tag{2.31}$$

where

$$C_m = \frac{\pi}{2} \lambda_m a^2 \left(\frac{M_1}{M_2}\right)^m \left(\frac{2Z_1 Z_2 e^2}{a}\right)^{2m}, \tag{2.32}$$

with $m = 1/s$. In table I are shown several used values of the constant λ_m for different m values.

TABLE I. – *Values of λ_m for different values of m.*

m	1	1/2	1/3	1/4	1/5	0
λ_m	0.5	0.327	1.309	1.4	2.92	24

2·2.3. Penetration in random media. In this paper we shall always assume that the motion of particles penetrating a material can be adequately described by classical mechanics [29, 37]. If we also assume that all elastic collisions in the solid are binary, then as in the previous sections we can derive all basic quantities necessary for a description of the scattering process. The subsequent step is the derivation of the theoretical tools describing the nuclear and electronic energy loss. In the slowing-down of particles in materials, particles are point particles that undergo their collisions through specified cross-sections. It is then necessary to specify a statistic of collisions. We shall assume that the probability that a particle, which slows down in a solid, undergo a collision during a small travelled path ΔR is proportional to ΔR and is independent of the past story of the particle. This statistic of collisions is adequate to describe the slowing-down of particles through random media and it is to these materials that we shall refer in this paper. From the last assumption it can then be shown that the probability for a particle to undergo a collision in ΔR is equal to

$$N d\sigma \Delta R, \tag{2.33}$$

where N is the density of target atoms (atoms/cm^3) and $d\sigma$ is the cross-section which characterizes the collisional event.

If the cross-section in eq. (2.33) is the differential cross-section in terms of the energy transferred T, then the average energy loss in elastic collisions can be calculated [29]

$$\langle \Delta E \rangle = N \Delta R \int_0^{T_m} T \, \mathrm{d}\sigma(T) . \tag{2.34}$$

For infinitesimal travelled path, we can write [26, 29, 40]

$$\left(\frac{\mathrm{d}E}{\mathrm{d}R}\right)_{\mathrm{n}} = N S_{\mathrm{n}}(E) \tag{2.35}$$

with

$$S_{\mathrm{n}}(E) = \int_0^{T_m} T \, \mathrm{d}\sigma(T) . \tag{2.36}$$

Expression (2.36) represents the *nuclear stopping cross-section*, whereas eq. (2.35) is the *nuclear stopping power*. Both quantities play a central role in modern theories of penetration of particles in materials and particularly in the low-velocity region. Both quantities refer to the elastic energy loss problem.

If we introduce in eq. (2.35) the power cross-section, eq. (2.31), then we obtain [26, 40]

$$S_{\mathrm{n}}(E) = \frac{1}{1-m} C_m \gamma^{1-m} E^{1-2m} . \tag{2.37}$$

Similar considerations can be developed for the electronic energy loss. In fact, if we indicate with $\mathrm{d}\sigma_{\mathrm{e}}$ the differential cross-section per energy transferred $\sum_i T_{\mathrm{e},i}$ to the electronic system (each electron is labelled by i), then by using the previous procedure we get

$$\left(\frac{\mathrm{d}E}{\mathrm{d}R}\right)_{\mathrm{e}} = N S_{\mathrm{e}}(E) \tag{2.38}$$

with

$$S_{\mathrm{e}}(E) = \int \left(\sum_i T_{\mathrm{e},i} \right) \mathrm{d}\sigma_{\mathrm{e}} . \tag{2.39}$$

Equation (2.39) is the *electronic stopping cross-section* and eq. (2.38) is the *electronic stopping power*.

The precise form of the electronic stopping cross-section depends on the incident velocity region considered [41]. In the low-velocity region, which is

defined by the condition

$$v < v_0 Z_1^{2/3}, \tag{2.40}$$

where v_0 is the Bohr velocity, almost all theories predict [41] the following form for S_e:

$$S_e \propto v^p, \tag{2.41}$$

where p is a number between 1 and 2. The Lindhard-Scharff theory [42], which is that which we shall use in this paper, predicts a value of p equal to 1 and a proportionality constant, K, equal to

$$K = \xi_e 8\pi e^2 \frac{a_0}{v_0} \frac{Z_1 Z_2}{\sqrt{Z_1^{2/3} + Z_2^{2/3}}}, \tag{2.42}$$

with $\xi_e \approx Z_1^{1/6}$. Despite the large use made of the proportionality of the electronic stopping cross-section to the incident velocity, it must be stressed that the experimentally observed dependence of S_e on v only approximately follows this behaviour. The theoretical results will be always affected by this approximation.

Taking together the electronic and nuclear stopping power, we can write

$$\frac{dE}{dR} = N[S_n(E) + S_e(E)] \tag{2.43}$$

which well represents the basic separation of the energy loss in the electronic and nuclear part. As already discussed, the two parts of the energy loss are not equivalent in the Lindhard theoretical apparatus, because the electronic stopping cross-section enters into the theory as an additional term, whereas the choice of the statistic of collisions determines the form and the way that the elastic energy loss enters into a theory. This aspect will be clarified in the subsequent part of this section.

Equation (2.43) also enables the path length, $R(E)$, travelled by a particle before coming to rest in material, to be estimated. In fact, we can write [26, 40]

$$R(E) = \int_0^E \frac{dE'}{N[S_n(E') + S_e(E')]}. \tag{2.44}$$

For $S_e = 0$ and power cross-section eq. (2.44) becomes

$$R(E) = \frac{1-m}{2m} \gamma^{m-1} \frac{E^{2m}}{NC_m}. \tag{2.45}$$

To complete and better clarify the Lindhard apparatus it is mandatory to introduce the reader to his integral-differential equations [26, 27] for the description of the penetration of low-velocity atomic particles into matter. We start with the *path length theory* [26, 40].

According to Lindhard, we introduce the path length distribution $P(E, R)$ such that $P(E, R)\mathrm{d}R$ represents the probability that an ion, with initial energy E, come to rest after travelling a path length $(R, \mathrm{d}R)$. The argument [26, 27] which enables the integro-differential equation for $P(E, R)$ to be derived can be summarized. The energy lost by a particle travelling a path length R can be assumed to take place during n arbitrary collisions; a balance equation can be written by assuming that the n collisions can be obtained in two separated ways: in the first, the n collisional processes all take place as the particle travels the path length $R - \Delta R$; in the second, the particle undergoes $(n-1)$ collisional processes during the path length $R - \Delta R$ and the last one in the remaining ΔR. Since both situations are possible, the balance equation takes the following form [26, 40]:

$$(2.46)\quad P(E,R) = \left(1 - N\,\Delta R \int \mathrm{d}\sigma_{\mathrm{n.e}}\right) P(E, R - \Delta R) + \\ + N\,\Delta R \int \mathrm{d}\sigma_{\mathrm{n,e}} P\left(E - T - \sum_i T_{\mathrm{e},i}, R - \Delta R\right),$$

where $N\,\Delta R\,\mathrm{d}\sigma_{\mathrm{n.e}}$ is the probability of a collisional process specified by energy transfer $\sum_i T_{\mathrm{e},i}$ to electrons and by an energy transfer T to the translational motion of the struck atom.

In the limit of $\Delta R \to 0$, eq. (2.46) becomes

$$(2.47)\quad -\frac{\partial}{\partial R} P(E,R) = N \int \mathrm{d}\sigma_{\mathrm{n,e}} \left[P(E,R) - P\left(E - T - \sum_i T_{\mathrm{e},i}, R\right)\right].$$

If $\mathrm{d}\sigma$ refers to the elastic collisions and $\mathrm{d}\sigma_{\mathrm{e}}$ to the corresponding inelastic collisions, then the assumption of uncorrelated contributions between elastic and inelastic collisions enables eq. (2.47) to be transformed in

$$(2.48)\quad -\frac{\partial}{\partial R} P(E,R) = \\ = N \int \mathrm{d}\sigma [P(E,R) - P(E-T,R)] + N \int \mathrm{d}\sigma_{\mathrm{e}} \left[P(E,R) - P\left(E - \sum_i T_{\mathrm{e},i}, R\right)\right].$$

Finally, if we assume that the electronic energy loss $\sum_i T_{\mathrm{e},i}$ is always small compared with the incident energy and with the elastic energy loss we obtain the

well-known integro-differential equation for P [26, 40]:

$$-\frac{\partial}{\partial R}P(E,R)=N\int \mathrm{d}\sigma[P(E,R)-P(E-T,R)]+NS_{\mathrm{e}}(E)\frac{\partial}{\partial E}P(E,R)\,. \tag{2.49}$$

Equation (2.49) has the announced structure: the electronic processes enter in the equation only via the stopping cross-section, whereas the statistic of elastic energy loss and scattering determines the form of the integral-differential equation.

Equation (2.49) can be analytically solved [26, 40]. Here, we only discuss the relation of this equation with eq. (2.44).

By definition, the distribution $P(E,R)$ is normalized as follows:

$$\int_0^\infty \mathrm{d}R\,P(E,R)=1\,. \tag{2.50}$$

If we introduce the spatial moments of the distribution $P(E,R)$

$$R^n(E)=\int_0^\infty \mathrm{d}R\,R^n P(E,R)\,, \tag{2.51}$$

eq. (2.49) becomes

$$nR^{n-1}(E)=N\int \mathrm{d}\sigma\,[R^n(E)-R^n(E-T)]+NS_{\mathrm{e}}(E)\frac{\mathrm{d}}{\mathrm{d}E}R^n(E)\,. \tag{2.52}$$

For $n=1$, the use of eq. (2.50) enables the following equation to be obtained:

$$1=n\int \mathrm{d}\sigma\,[R^1(E)-R^1(E-T)]+NS_{\mathrm{e}}(E)\frac{\mathrm{d}}{\mathrm{d}E}R^1(E)\,, \tag{2.53}$$

where $R^1(E)=\langle R(E)\rangle$ is the *average path length.*

Finally, if $T\ll E$, we obtain the following solution:

$$\langle R(E)\rangle=\int_0^E \frac{\mathrm{d}E'}{N[S_{\mathrm{n}}(E')+S_{\mathrm{e}}(E')]}\,. \tag{2.54}$$

Since this solution is equal to eq. (2.44), we conclude that in the limit of soft collisions, $R(E)$, defined by eq. (2.44) is equal to the average path length (eq. (2.54)).

Particularly useful for the subsequent discussion is the energy attenuation as a function of the travelled path that can be derived from eq. (2.54), in the case $S_{\mathrm{e}}(E)=0$.

If E_0 is the initial energy of a particle moving in a solid in a straight line along the x-axis, the relation between the travelled path length x and the energy $E(x)$

at x, can be written as

$$x = \int_{E(x)}^{E_0} \frac{\mathrm{d}E}{NS_n(E)}. \tag{2.55}$$

By taking into account eq. (2.45) we obtain

$$E(x) = E_0\left(1 - \frac{x}{R(E)}\right)^{1/2m}. \tag{2.56}$$

In the limit $m \to 0$ we get

$$E(x) = E_0 \exp\left[-NC_0 x\right]. \tag{2.57}$$

In eq. (2.57), the physical meaning of the quantity

$$R_0 = \frac{1}{NC_0} \tag{2.58}$$

is that of average path length for particles moving at very low velocity in materials. In fact, within the Lindhard formulation, for $S_e(E) = 0$ and power cross-section the spatial moments scale with the following law:

$$R^n(E) \propto \left(\frac{E^{2m}}{NC_m}\right)^n, \tag{2.59}$$

where the proportionality constant depends only on the ratio M_2/M_1 and on m. For particles moving at the energies of the order of the energies of sputtered particles (few eV) the adequate value for m is assumed [15] to be $m = 0$.

Two further quantities are necessary for future calculations: the average penetration depth and the projected range.

A substantial improvement in the study of penetration of low-velocity atomic particles through matter can be achieved by introducing a *distribution of end positions* of stopped particles [26, 40]. In particular, we can define [40] the function $F(E, \boldsymbol{e}, x)$ such that $F\mathrm{d}x$ represents the probability that an ion with initial velocity $\boldsymbol{v} = (E, \boldsymbol{e})$ at $x = 0$ comes to rest at depth $(x, \mathrm{d}x)$. If the medium is assumed to be *infinity*, we find [40] by using the balance method and the same procedure described before,

$$-\cos\theta \frac{\partial}{\partial x} F(E, \boldsymbol{e}, x) = N \int \mathrm{d}\sigma(\boldsymbol{v}, \boldsymbol{v}_1)[F(E, \boldsymbol{e}, x) - F(E - T, \boldsymbol{e}_1, x)] + \tag{2.60}$$

$$+ NS_e(E) \frac{\partial}{\partial E} F(E, \boldsymbol{e}, x),$$

where θ is the angle between $\boldsymbol{v}$ and the surface normal, $\boldsymbol{e}_1$ the velocity unit vector of the scattered ion and

$$(2.61) \qquad \mathrm{d}\sigma(\boldsymbol{v}, \boldsymbol{v}_1) = \mathrm{d}\sigma(T)\frac{\mathrm{d}^2 e_1}{2\pi}\delta(\boldsymbol{e}\cdot\boldsymbol{e}_1 - \cos\phi_1)$$

the differential scattering cross-section for scattering from $\boldsymbol{v}$ into $(\boldsymbol{v}_1, \mathrm{d}^3 v_1)$. The normalization condition is now

$$(2.62) \qquad \int_{-\infty}^{\infty} \mathrm{d}x F(E.\boldsymbol{e}, x) = 1\,.$$

When the azimuthal symmetry in scattering processes is assumed, a standard technique to solve eq. (2.60) goes over the Legendre expansion of the angular part and the moment distribution over the depth [43]. From the equation for the first moment

$$(2.63) \qquad \langle x\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\, x F(E, \boldsymbol{e}, x) = F^1(E, \boldsymbol{e})$$

which defines the *average penetration depth*, we can derive the following equation for the *projected range*, $R_p(E)$:

$$(2.64) \qquad 1 = N\int \mathrm{d}\sigma(T)[R_p(E) - \cos\phi_1 R_p(E-T)] + NS_e(E)\frac{\mathrm{d}}{\mathrm{d}E}R_p(E)\,.$$

The relation between the two last quantities is

$$(2.65) \qquad \langle x\rangle = R_p(E)\cos\theta\,.$$

For $S_e(E) = 0$ and power cross-section, the solution for the projected range can be written as

$$(2.66) \qquad R_p(E) = A_p\frac{E^{2m}}{NC_m},$$

where A_p depends only on the ratio M_2/M_1 and on m. The ratio $R_p(E)/\langle R(E)\rangle$, which depends only on the ratio M_2/M_1 and on m is called *path length correction*. In fig. 2 are shown the penetration parameters described in this section. More details of the Lindhard theoretical apparatus can be found in the original papers [26-28] (see also ref. [40, 43, 44].

2·3. *The Brandt and Laubert theory.* – The sputtering theory presented in 1967 by Brandt and Laubert [45] represents the first attempt to introduce part of

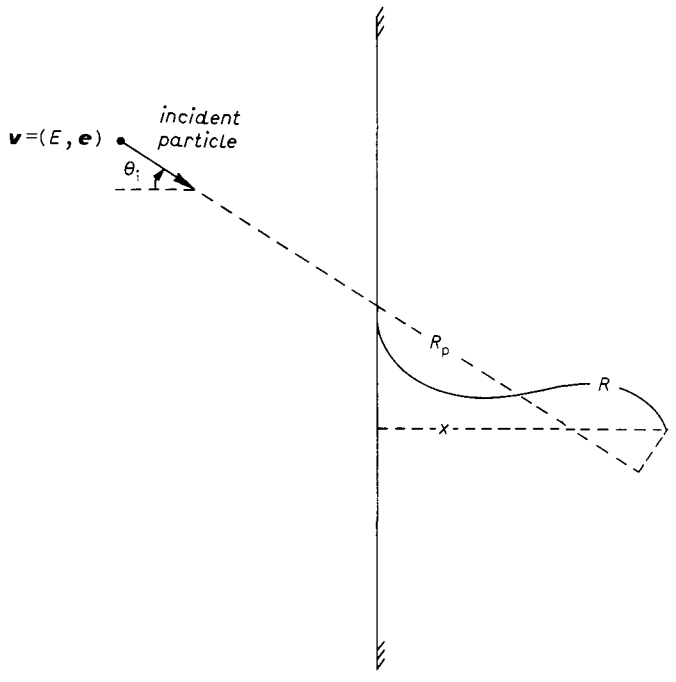

Fig. 2. – Penetration parameters: R is the path length; R_p is the projected range and x the penetration depth.

the Lindhard concepts in a sputtering formulation, where, nevertheless, the basic approach is the same as Keywell (explicit separation between the function describing the displaced atoms and the function describing the escape from the target). The mention of the Brandt and Laubert theory in this paper is due to the following considerations: although their formulation proves to be too simple when compared with subsequent formulations, they have proved that the use, even partial, of the Lindhard concepts may be enough to reproduce some of the basic results of more elaborated theories. In fact, their sputtering yield can be written as

$$Y = \frac{1}{4\cos\theta_i} \frac{l_0 N S_n(E)}{E_d} [f(y) - g(S_e(E))] \tag{2.67}$$

where θ_i is the angle between the incident direction and the outgoing surface normal, l_0 is a constant characteristic of the target material, E_d the displacement energy, g a function which accounts for the energy lost to electronic excitations and f a function of the dimensionless variable

$$y = \frac{E}{l_0 N S_n(E)}. \tag{2.68}$$

The most relevant aspect of the Brandt-Laubert yield is its proportionality to the nuclear stopping power. This result, common to more elaborated theories [15-17], is well proved, under properly physical conditions, by many experiments [46]. In the case of negligible electronic energy loss eq. (2.67) becomes

$$Y = \frac{1}{4\cos\theta_i} \frac{l_0 N S_n(E)}{E_d} f(y). \tag{2.69}$$

In this form, the yield is more suitable for a subsequent comparison, because this general form of yield, when correctly derived, is suitable for many experimental data. Here we stress that, in the low-energy region and for not light incident ions, when the electronic energy loss is negligible, the sputtering yield is proportional to the nuclear stopping power and to a universal function.

2·4. *The Sigmund theory.* – The Sigmund theory [15], like the Harrison theory, is based on a properly linear Boltzmann transport equation. Nevertheless the comparison between the two theories cannot be forced further. In fact, while Harrison has adapted the neutron diffusion theory to the sputtering phenomenon and uses a forward form of linear Boltzmann transport equation, Sigmund directly writes his basic equations in a backward form. Moreover, the Sigmund transport equations have no nonlinear analogue [47] and are suitable for a complete use of the Lindhard theoretical apparatus. This last property enables the theory to give analytical results, as well.

Owing to the central position of the Sigmund theory in the outline of the sputtering theories, many aspects of this theory can be found in several review articles (the study of the original paper may also be a source of useful suggestions about several aspects of the sputtering). In this section we only discuss his sputtering yield in relation to previous authors. Further discussions can be found in the subsequent part of the paper.

The basic quantity of the Sigmund transport theory is the velocity distribution function $G(\boldsymbol{r}, \boldsymbol{v}, \boldsymbol{v}_0, t)$ that specifies the density of moving atoms in the real space $\boldsymbol{r}$ and in the velocity space $\boldsymbol{v}_0$. To be precise, the quantity $G\mathrm{d}^3 v_0 \mathrm{d}x$ represents the average number of atoms moving at time t in a layer $(x, \mathrm{d}x)$ with velocity $(\boldsymbol{v}_0, \mathrm{d}^3 v_0)$ if at time $t = 0$ an atom starts its motion in the plane $x = 0$ (in $x = 0$ it is also assumed to be the surface). Since the number of atoms with velocity $(\boldsymbol{v}_0, \mathrm{d}^3 v_0)$ penetrating the plane x in a time interval $\mathrm{d}t$ is given by

$$G(x, \boldsymbol{v}, \boldsymbol{v}_0, t)\, \mathrm{d}^3 v_0 |v_{0x}|\, \mathrm{d}t, \tag{2.70}$$

where v_{0x} is the x component of the vector $\boldsymbol{v}_0$, the sputtering yield can be written as

$$Y = \int \mathrm{d}^3 v_0 |v_{0x}| \int_0^\infty \mathrm{d}t G(0, \boldsymbol{v}, \boldsymbol{v}_0, t). \tag{2.71}$$

The integration over the recoiling velocity is extended over all values with a negative x component large enough to overcome the surface binding potential. For an *infinite* medium and in the *isotropic* limit the expression of the Sigmund sputtering yield is written as

$$Y_0 = \frac{\Gamma F_D(E, \boldsymbol{e}, x = 0)}{8NC_0U}, \tag{2.72}$$

where Γ is a constant equal to 0.608, $F_D\mathrm{d}x$ is [43] the average energy deposited into recoils at depth $(x, \mathrm{d}x)$ by the incident ion, with initial energy E and direction $\boldsymbol{e}$, and U is the height of a planar surface potential barrier; moreover, C_0 the constant of the power cross-section for $m = 0$ is set equal to 1.808 Å^2 [15].

To make a comparison of eq. (2.72) with previous theories more transparent we write function F_D in the case where the incident ion hits the target at normal incidence and the elastic energy loss is the predominat mechanism:

$$F_D(E) = \alpha N S_n(E), \tag{2.73}$$

where α is a factor that depends only on m and M_2/M_1.

In this case, as for the Brandt-Laubert theory, the sputtering yield is proportional to the nuclear stopping power. Nevertheless, in this case also the comparison cannot be forced any further. To understand the basic differences between these two formulations we shall discuss the dependence of the yield on the incident angle. Within a linear cascade theory of the sputtering phenomenon a simple path length argument, as in the Brandt-Laubert theory, leads to a $1/\cos\theta_i$ angular dependence. This result, valid only for $M_1 \ll M_2$, is based on the assumption that the energy deposited in primary collisions (direct collision between the incident ion and the target atoms) is not transported away from the particle trajectory by energetic recoil atoms. Since recoil atoms may have considerable ranges, it is clear that the substitution of the function F_D with S_n is not possible under general conditions.

The proportionality of the sputtering yield to the function F_D also represents the better proof of the strong connection between transport and collisional approaches to the sputtering phenomenon: F_D although is a typical damage function, has appeared in a transport equation. This means that independently of the starting approach to the sputtering, transport or collisional formulation, under the same physical conditions, must give the same results. And more important for future analysis, within the region of validity of the Sigmund results any future collisional sputtering theory must reproduce the Sigmund transport results.

Possible improvements of the Sigmund theory are of technical aspects and have been discussed by the same author [47, 48]. Where the approach seems *historically* conditioned is in the surface analysis of the phenomenon. The

Sigmund approach reflects the Lindhard structure, which in its turn is oriented only towards *the penetration aspects* of particles moving through matter. Recoil atoms that will be sputtered and recoil atoms moving in the bulk of materials follow the same physics: the depth of origin of sputtered atoms is related, in the Sigmund interpretation, to the range of low-velocity particles in matter. In subsequent chapters we shall show that a correct interpretation of the surface aspects of the sputtering can avoid some misunderstanding of the transport formulation and develop new ideas about the sputtering phenomenon.

2·5. *The Thompson energy spectrum.* – To explain his pioneer experiments on energy spectra of sputtered particles, Thompson developed in 1968 a collisional sputtering theory [14]. Within this formulation, and by using a notation [16] useful for the subsequent discussion, the energy spectrum of sputtered particles can be written [16] as

$$J_0(E_1) = \frac{\Gamma F_D(E, \boldsymbol{e}, x=0)}{4NC_0} \frac{E_1}{(E_1+U)^3}, \tag{2.74}$$

where E_1 is the energy of sputtered particles.

The essential characteristics of this spectrum are easily summarized. The spectrum predicts a position for the peak, E_p, which depends only on the value of the surface binding energy U

$$E_p = \frac{U}{2}. \tag{2.75}$$

For $E_1 \gg U$, the Thompson spectrum gives an energy dependence which is inversely proportional to the square of the energy and this dependence reproduces essentially the energy distribution of recoiling atoms in a linear collisional cascade [40]. Moreover, the form of the surface potential barrier, as in the Sigmund theory, is assumed to be planar.

Finally, the Thompson energy spectrum is related to the Sigmund sputtering yield by the well-known relation

$$Y_0 = \int_0^\infty J_0(E_1)\, \mathrm{d}E_1 . \tag{2.76}$$

On the basis of the last relation we shall refer to the transport theory as the Sigmund-Thompson theory. Nevertheless, we want to stress that the two formulations have been derived by using different approches (transport and collisional approaches), although they refer to identical physical situations.

2·6. *A suspicious lack.* – As mentioned in the introduction the number of papers or review articles concerning the sputtering phenomenon is remarkable.

Nevertheless, except for a Kelly review [12] or more recently by Eckstein [49] the problem of the derivation of the theoretical expression of the average energy of sputtered atoms, $\langle E_1 \rangle$, in the Sigmund-Thompson theory has never been solved [20]. In fact, two decades after the publication of the theory no expression of $\langle E_1 \rangle$ for the transport theory exists. Let us look more closely at the reason for this. In principle there is no difficulty in defining the average energy of sputtered atoms in the Sigmund-Thompson theory. In fact, by using eq. (2.76), we immediately find

$$\langle E_1 \rangle = Y_0^{-1} \int_0^\infty \mathrm{d}E_1 E_1 J_0(E_1) . \tag{2.77}$$

Nevertheless, a rapid inspection of eq. (2.77) shows that this average energy cannot be calculated because the integral is *divergent.*

In the subsequent section we shall show that this problem can be properly solved only with a precise definition of the surface aspect of the sputtering phenomenon.

3. – Sputtering as a surface phenomenon.

In recent years several experiments [50-55] have been aimed at widening our knowledge of the depth of origin of sputtered particles. This subject plays an important role in multiple interaction and binary collision simulations [11, 13, 56-58] and in the angular distribution of atoms sputtered from segregate alloys [59-63]. A theoretical formulation of the sputtering phenomenon which contains explicit information on the depth of origin of sputtered particles was proposed, for the first time, only in 1981 by Falcone and Sigmund [16]. In this chapter we shall discuss this theory and the forced modifications that a correct interpretation of the surface aspect of the sputtering introduces in the same formulation.

3·1. *The Falcone and Sigmund theory.* – In describing the sputtering mechanism we have clearly distinguished two steps. In the first step is described the process that transfers energy and momentum from the incident particle to the target atoms, and that produces the displaced atoms. In the second step a part of the displaced atoms, under suitable conditions, leave the surface. The most general formulation of the sputtering phenomenon, in which the explicit separation of the two described steps is proposed, is in Falcone and Sigmund paper [16].

Following these authors, when an incident particle, starting from the plane $x = 0$ with energy E and direction $\boldsymbol{e}$, penetrates into a solid target, it generates a linear collisional cascade and it is possible to define the function $D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x)$ such that $D\mathrm{d}x\mathrm{d}E_0 d^2 e_0$ represents the average number of target atoms set in

motion, by the incident particle, at depth $(x, \mathrm{d}x)$ with initial energy $(E_0, \mathrm{d}E_0)$ in the solid angle $(\boldsymbol{e}_0, \mathrm{d}^2 e_0)$. We shall call this function *damage function.*

Moreover, if we indicate with $P(E_0, \boldsymbol{e}_0, x; E_1, \boldsymbol{e}_1)\,\mathrm{d}E_1\,\mathrm{d}^2 e_1$ the probability that a recoiling atom $(E_0, \boldsymbol{e}_0, x)$ will be ejected from the surface with energy $(E_1, \mathrm{d}E_1)$ in the solid angle $(\boldsymbol{e}_1, \mathrm{d}^2 e_1)$, then the double differential sputtering yield can be written as

$$J(E_1, \boldsymbol{e}_1) = \int \mathrm{d}x\,\mathrm{d}E_0\,\mathrm{d}^2 e_0 D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x) P(E_0, \boldsymbol{e}_0, x; E_1, \boldsymbol{e}_1)\,. \tag{3.1}$$

We shall call the function P *ejection function.* From eq. (3.1) the sputtering yield can be obtained by further integrations

$$Y = \int \mathrm{d}E_1 d^2 e_1 J(E_1, \boldsymbol{e}_1)\,. \tag{3.2}$$

Since eq. (3.1) is equivalent to a pertinent linear transport eq. [64]; the assumption that eq. (3.1) can describe the sputtering phenomenon is equivalent to the assumption that this phenomenon can be described by a proper linear transport equation. Once eq. (3.1) has been established the subsequent problem is the determination of adequate expressions for both D and P. In ref. [16], to describe the sputtering in the region of validity of the Sigmund-Thompson theory, the authors assumed for D and P the following expressions:

$$D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x) = \frac{\Gamma F_D(E, \boldsymbol{e}, x)}{E_0^2} \tag{3.3}$$

and

$$P(E_0, \theta_0, \chi_0, x; E_1, \theta_1, \chi_1) = \tag{3.4}$$

$$= \delta\left[E_1 - E_0 \exp\left[\frac{-NC_0 x}{\cos\theta_0}\right]\right] \delta(\chi_1 - \chi_0)\,\delta(\cos\theta_1 - \cos\theta_0)\,,$$

where E_0, θ_0 and χ_0 are, respectevely, the energy, polar angle and azimuth with respect to the surface normal of a target atom set in motion at depth $(x, \mathrm{d}x)$, whereas E_1, θ_1, χ_1 are the corresponding quantities at the surface. Moreover δ is the Dirac delta.

The expression of the damage function in the form expressed by eq. (3.3) was derived by Sigmund [15, 44] and represents a well-founded result of linear collisional theory, when the power cross-section is used. The basic technique of its derivation, namely the search for an asymptotic solution of the balance equations, is due to Robinson [65]. In appendix A we have derived a general equation and some solutions for D.

Equation (3.4), on the contrary, is based on the derivation of eq. (2.57),

namely it is based on the assumption that the motion of a recoil to be sputtered is along a straight line and that the recoil suffers a continuous loss of energy during its motion towards the surface.

If the assumption of a planar surface potential barrier is included in the expression of P, then eq. (3.4) becomes

$$P = \mathcal{E}\left[E_1 + U - E_0 \exp\left[\frac{-NC_0 x}{\cos\theta_0}\right]\right] \mathcal{E}(\chi_1 - \chi_0) \cdot \cdot \mathcal{E}\left(\cos\theta_1 - \sqrt{\left(1 - \frac{U}{E_1}\right)\cos^2\theta_0 - \frac{U}{E_1}}\right). \tag{3.5}$$

Equations (3.1)-(3.5) enable the following sputtering yield to be obtained:

$$Y = \frac{\Gamma}{8U} \int_0^\infty \mathrm{d}x F_D(E, \boldsymbol{e}, x)\, 4E_4(NC_0 x), \tag{3.6}$$

where

$$E_n(z) = \int_1^\infty \mathrm{d}t \frac{\exp[-zt]}{t^n} \tag{3.7}$$

is the exponential integral function [39].

To obtain exactly the Sigmund sputtering yield from eq. (3.6) we must disregard the depth dependence in F_D by setting [16]

$$F_D(E, \boldsymbol{e}, x) \simeq F_D(E, \boldsymbol{e}, x = 0). \tag{3.8}$$

This assumption is, of course not essential, for more general expressions of the yield, nevertheless its use and validity are well established in sputtering calculations: the sputtering yield is determined by the energy deposited near the surface.

Within the same approximation the above formulation also enables the Thompson energy spectrum to be obtained [16]. Finally, from eq. (3.6) the average depth of sputtered atoms can be obtained:

$$\langle x \rangle = \frac{\int_0^\infty \mathrm{d}x\, x \frac{\Gamma F_D(0)}{8U} 4E_4(NC_0 x)}{\int_0^\infty \frac{\Gamma F_D(0)}{8U} 4E_4(NC_0)} = \frac{4}{5}\frac{1}{NC_0}. \tag{3.9}$$

Among the several applications of the above theory, we just mention the extension to compound targets [66] and segregation phenomena [67].

3·2. *The surface character of the sputtering phenomenon.* – In the previous section we have mentioned that in deriving the expression of function P we have made the assumption that a recoil to be sputtered loses its energy in a continuous process. Nevertheless, it is well known [26-28] that the elastic energy loss process in the low-velocity regime is essentially a statistical process. Moreover, in the same derivation of P it has been assumed that recoils to be sputtered move along a straight line (the authors [16] supported this assumption by the observation that for a homogeneous and isotropic source, as was the used expression of D, any loss of particles due to scattering from a given direction of motion is compensated by an equivalent gain). The correcteness of both assumptions is hardly to be accepted and more important both assumptions are not present in the standard transport theory [15]. These difficulties can be solved with a correct interpretation of the surface character of the sputtering.

3·2.1. The correct form of the ejection function: The first problem to solve is to show the equivalence between the standard transport theory and the Falcone-Sigmund theory. To do this, we must show that eq. (3.5) can be derived using the same assumptions of the transport theory. This proof has been given in ref. [68] and the key result is that the equivalence is possible if the interpretation of the quantity

$$L_0 = \frac{1}{NC_0} \tag{3.10}$$

is changed from the range of particles moving at low velocity in solids (see eq. 2.58) to the low-velocity *collisional mean free path* [69]. To be precise, it was shown [68] that eq. (3.5) could be derived with the same assumptions of the transport theory (penetration in random media and binary elastic collisions always occur between moving and fixed atoms). Moreover as in the transport formulation, it was assumed that during the ejection motion (the motion from the original position in the solid up to the surface) recoils to be sputtered could loss energy in elastic processes (the energy lost in overcoming the surface potential barrier is always an extra loss).

In fig. 3 is shown a possible sputtering event based on this new interpretation. The picture shows that sputtered particles originate essentially from the first monolayer as also indicated by experiments [50-55] and simulation studies [11, 13, 56, 57] on the depth of origin of sputtered atoms.

Nevertheless a contradiction immediately appears: if particles to be sputtered originate from the first monolayer, how is possible that they lose energy in elastic processes? Within the physical apparatus described in the previous chapter this loss is not possible and we arrive at the conclusion that the most probable ejection motion is in a straight line (no scattering) and without any loss of energy in elastic processes. In other words, *the surface character of the*

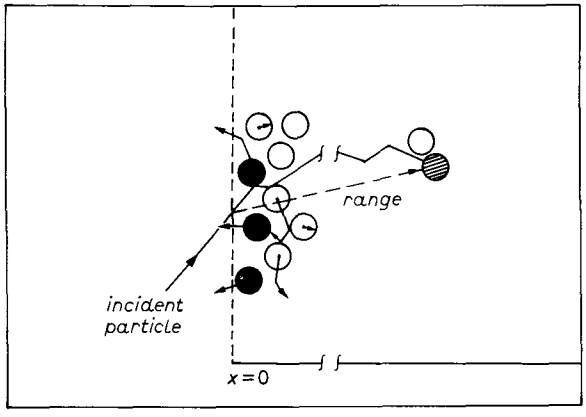

Fig. 3. – Sputtering process in the linear regime. Black balls are recoils partecipating in sputtering.

sputtering phenomenon is only compatible with an ejection function which states the energy conservation for recoiling atoms during the ejection process.

The energy attenuation (see eq. (2.57)) underlying the derivation of eq. (3.5), while compatible with the motion of atoms in the bulk of materials, is not adequate to describe the ejection process in the sputtering phenomenon. The correct expression of the ejection function in the sputtering phenomenon must be [17]

$$(3.11)\qquad P(E_0, \boldsymbol{e}_0, x; E_1, \boldsymbol{e}_1) = \exp\left[-\frac{x}{L_0 \cos\theta_0}\right] \delta(E_1 + U - E_0)\, \delta(\chi_1 - \chi_0) \cdot$$

$$\cdot\, \delta\left(\cos\theta_1 - \sqrt{\left(1 - \frac{U}{E_1}\right)\cos^2\theta_0 - \frac{U}{E_1}}\right),$$

where L_0 is given by eq. (3.10). Numerical differences between L_0 and R_0 will be discussed later. In the subsequent part of the paper for ejection function we always indicate eq. (3.11).

3·2.2. Maximum sputtered energy and threshold for sputtering. Equation (3.11) is the mathematical expression of the surface character of a sputtering theory based on binary elastic collisions and represents a key innovation with respect to all previous theories. This innovation is well characterized by the results that we are going to discuss in this section.

If we indicate with A (we remark that this quantity cannot be confused with γ defined in eq. (2.3) the maximum fraction of the projectile's energy that can be transferred to a recoil to be sputtered in a single collision, *independently of the explicit expression for function D*, the maximum sputtered energy, E_M is always

expresses by the following relation:

$$E_M = AE - U. \tag{3.12}$$

Equation (3.12) is the more general equation for a binary collisional sputtering theory that can be compared with experimental data. This equation states that, with identical initial conditions, except for the incident energy, all couples (E, E_M) must be over the same straight line: the slope of this straight line gives information on the binary collisions between the incident ion and the surface-target atoms and the value of the intersection of this straight line with the E_M axis gives the value of U. In other words, eq. (3.12) contains several spectroscopic information. Moreover, due to its general character, eq. (3.12) can be used to establish the limit of validity of the binary collisional approximation (see next chapter).

Finally, by definition, we derive from eq. (3.12), the general form of the threshold, E_{th} for sputtering:

$$E_{th} = \frac{U}{A}. \tag{3.13}$$

The sputtering threshold, in all theories that are able to derive it, is calculated from the sputtering yield expression and in this sense depends (see also later) on the expression used for D. Here we have shown that the form of the threshold is only a consequence of the binary collision approximation and of the surface character of the sputtering. Further discussion about the two last quantities will be given in the subsequent chapter. The next section will be devoted to the modifications induced by the correct expression of the ejection function in the standard transport theory.

3·3. *Standard transport results: a revision.* – In this section we shall calculate some basic quantities that we shall subsequently compare with the Sigmund-Thompson transport theory. To do this we shall assume, in all calculations, for D the expression given by eq. (3.3) and for P eq. (3.11).

3·3.1. Depth dependence of sputter erosion. If we introduce eqs. (3.3) and (3.11) in eq. (3.1), the double differential sputtering yield, including the spatial distribution, can be written as

$$J(E_1, \theta_1, x) = \frac{\Gamma}{4\pi} \frac{1}{(E_1 + U)^2} \iint \mathrm{d}x \, \mathrm{d}(\cos\theta_0) F_D(x) \exp\left[-\frac{x}{L_0 \cos\theta_0}\right] \cdot \tag{3.14}$$

$$\cdot \delta\left(\cos\theta_1 - \sqrt{\left(1 - \frac{U}{E_1}\right)\cos^2\theta_0 - \frac{U}{E_1}}\right).$$

A further integration over the angular variables gives the depth dependence of the energy spectrum

$$J(E_1, x) = \frac{\Gamma}{2(E_1 + U)^2} \int_0^x \mathrm{d}x F_D(x)\, G(x/L_0, U, E_1) \tag{3.15}$$

with

$$G(x/L_0, U, E_1) = E_2(x/L_0) - \sqrt{\frac{U}{E_1 + U}}\, E_2\left(\frac{x}{L_0}\sqrt{\frac{E_1 + U}{U}}\right), \tag{3.16}$$

where $E_2(z)$ is the exponential integral function (see eq. (3.7)).

A further integration, by taking into account eq. (3.12), gives

$$Y = \frac{\Gamma}{8U} \int_0^\infty \mathrm{d}x F_D(x)\, Y(x/L_0, w), \tag{3.17}$$

where

$$Y(x/L_0, w) = Y_1(x/L_0) + Y_2(x/L_0, w), \tag{3.18}$$

with

$$Y_1(x/L_0) = \frac{4}{3}\left[E_2\left(\frac{x}{L_0}\right) + \frac{x}{L_0}E_1\left(\frac{x}{L_0}\right) - \frac{x}{L_0}E_3\left(\frac{x}{L_0}\right)\right], \tag{3.19}$$

$$Y_2(x/L_0, w) = \tag{3.20}$$

$$= \frac{4}{3w}\left[\frac{x}{L_0}E_3\left(\frac{x}{L_0}\sqrt{w}\right) - 3E_2\left(\frac{x}{L_0}\right) - \frac{x}{L_0}E_1\left(\frac{x}{L_0}\sqrt{w}\right) + \frac{8}{3w^{3/2}}E_2\left(\frac{x}{L_0}\sqrt{w}\right)\right]$$

and

$$w = \frac{AE}{U} = \frac{E}{E_{\mathrm{th}}}. \tag{3.21}$$

If we disregard the spatial dependence in F_D the function $Y(x/L_0, w)$ represents the depth dependence of sputter erosion. With respect to the previous expression of this quantity [16], there is an extra term $Y_2(x/L_0, w)$ which depends also on w. For $E \gg E_{\mathrm{th}}$, $Y_2 = 0$ and $Y(x/L_0, w)$ reduces to $Y_1(x/L_0)$. This latter quantity is equal to $4E_4(x/L_0)$ which is, if we set $L_0 = R_0$, the depth dependence of sputter erosion according to Falcone-Sigmund calculations [16] (see eq. (3.6)). Then, at large incident energies, the average escape depth is

$$\langle x \rangle = \frac{4}{5}L_0. \tag{3.22}$$

It appears from the previous analysis that the standard transport results are strictly valid only at incident energies that are very large when compared with the threshold energy. This result is also confirmed by the yield calculations of the next section.

3·3.2. Generalized sputtering yield. If we disregard the spatial dependence in F_D and we make the approximation used in eq. (3.8), then, after a final integration, we get the following sputtering yield [20, 69]:

$$Y = Y_0\left(1 - \frac{1}{w}\right)^2, \tag{3.23}$$

where Y_0 is the Sigmund sputtering yield (see eq. (2.72)).

Equation (3.23) contains the extension of the standard sputtering yield in the low-energy region [20, 69]. To show this property, we compare in fig. 4 the experimental results [70] of Ni bombarded, at normal incidence, with Ar ions, with the Sigmund sputtering yield and eq. (3.23). The chosen value of E_{th} has been 60 eV and is equal to the lowest ion energy for which sputtering of Ni bombarded, at normal incidence, with Ar ions has been measured [71].

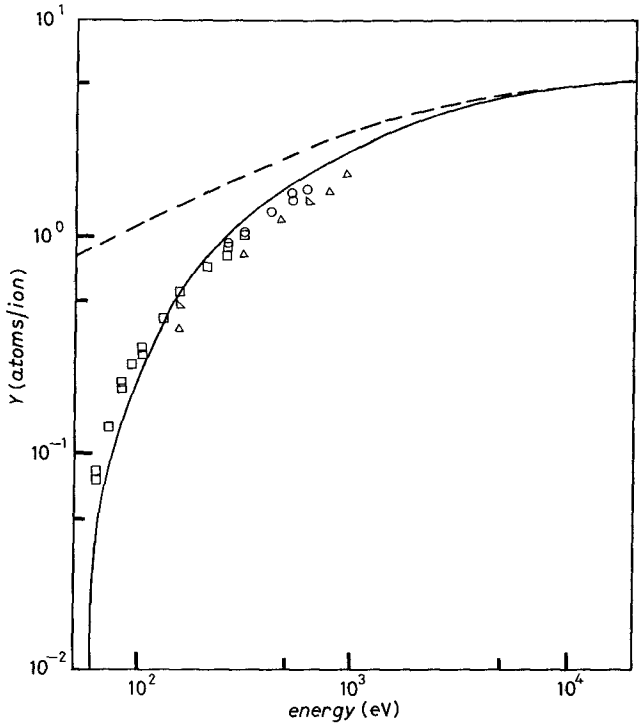

Fig. 4. – Sputtering yield of Ni targets bombarded with Ar ions *vs.* the incident energy. The experimental data are taken from ref. [70]. The dashed line is the Sigmund yield. The solid line is eq. (3.23), with $E_{th} = 60$ eV.

The picture shows a clear improvement of the standard transport theory in the low-energy region. Similar results can be found for other ion-target combinations [20, 69].

At large incident energies ($E \gg E_{th}$) eq. (3.23) reduces to Sigmund's sputtering yield.

3·3.3. Average energy of sputtered atoms. The previous results enable us to derive the expression of the average energy of sputtered atoms for the standard transport theory. In fact, by definition we write

$$\langle E_1 \rangle = Y^{-1} \int_0^{\lambda E - U} \mathrm{d}E_1 E_1 J_0(E_1), \tag{3.24}$$

where Y is given by eq. (3.23) and J_0 is the Thompson energy spectrum. After the substitution of the proper quantities and a simple integration, we get [20]

$$\langle E_1 \rangle = 2Ug(w) \tag{3.25}$$

with

$$g(w) = \left(\ln w + \frac{2}{w} - \frac{1}{2w^2} - \frac{3}{2}\right)\left(1 - \frac{1}{w}\right)^{-2}. \tag{3.26}$$

For $E \gg E_{th}$, eq. (3.25) reduces to

$$\langle E_1 \rangle = 2U\left(\ln w - \frac{3}{2}\right). \tag{3.27}$$

Equation (3.27) is the theoretical expression of the average energy of sputtered atoms associated with the Sigmund-Thompson theory. The result has been a direct consequence of the precise maximum sputtered energy, which in turn, is related to the surface character of the sputtering and with the binary collision approximation.

4. – Unified sputtering theory.

The theory described in the previous chapter has been used to reproduce and extend the results of the Sigmund and Thompson theory. The formalism refers to collisional cascades, generated by the incident ions, that are characterized by two physical conditions (*conditions for linearity*): the first is that the density of moving atoms in a cascade, at any single time, is small compared with the solid density and the second that in each binary collision the struck atom is always at rest before the collision. All theories described in the previous chapters refer to

the assumption that collisional cascades always develop. We shall call this regime the *Sigmund-Thompson regime.* Since this regime verifies the above two properties, this regime is also *linear.*

It is not difficult to convince oneself that there are several physical conditions that cannot be included in the previous description. For example, in the case of sputtering of heavy targets by light-ion bombardment the mass ratio M_2/M_1 is so large that, for low and medium keV incident energy, cascades cannot be generated and only target atoms set in motion by direct collisions with the incident ion (primary recoils) can be sputtered. Even in the case of very low incident energy cascades cannot develop and only primary recoils can be *candidates for sputtering.* We shall call the regime where only primary recoils are candidates for sputtering *the single collisional regime.* It is clear that the single collisional regime is also a linear regime, because the two physical conditions for linearity are still present. In other words, the single collisional regime and the Sigmund-Thompson regime are both part of a more general regime (the linear regime). This connection is very transparent when the equations describing linear regimes are derived (see appendix A).

Different is the situation where one or both conditions of linearity are not present. All physical situations where one or both conditions of linearity are not present will be referred to as *nonlinear regimes.* In this paper we do not discuss these regimes.

We shall now show the extension of the theory presented in the previous section to other linear collisional regimes: the unsolved problems will appear technical rather than basic.

4·1. *General formulation.* – The problem of a sputtering theory valid for all sputtering processes does not seem at the moment to be conceptually practicable. Nevertheless the attempt to formulate a theory which enables all linear regimes to be explained within the same formalism seems realizable. In this chapter we present a generalization of the formalism already discussed that at present appears as a possible unified theory for linear collisional sputtering.

We first state the basic picture of the formalism that we are going to present. Our theory refers to targets whose atoms are randomly distributed and can be represented together with the incident ion as *point-particles.* The motion of each atomic particle can be described by classical mechanics and the elastic collisions among *atomic* particles are assumed to be binary.

If this is the general scheme, which is in common with the standard transport or collisional theories, we shall introduce a first restriction: an atomic target in order to be sputtered must always overcome a surface potential barrier which is planar and of height U. This assumption cannot be proved valid for all physical systems, but it seems adequate to describe the cases discussed in this paper. However, in general this assumption is unnecessary.

The general mathematical apparatus is equivalent to that described in the

previous chapter. In fact, we assume that all sputtering events can be adequately described by the following double differential sputtering yield:

$$J(E_1, \boldsymbol{e}_1) = \int \mathrm{d}x\, \mathrm{d}E_0\, \mathrm{d}^2 e_0 D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x)\, P(E_0, \boldsymbol{e}_0, x; E_1, \boldsymbol{e}_1)\,, \tag{4.1}$$

where the ejection function P is *always* given by eq. (3.11)

$$P(E_0, \boldsymbol{e}_0, x; E_1, \boldsymbol{e}_1) = \exp\left[-\frac{x}{L_0 \cos\theta_0}\right] \delta(E_1 + U - E_0)\, \delta(\chi_1 - \chi_0) \cdot \cdot \delta\left(\cos\theta_1 - \sqrt{\left(1 - \frac{U}{E_1}\right)\cos^2\theta_0 - \frac{U}{E_1}}\right), \tag{4.2}$$

whereas *the expression of the damage function D depends on the regime considered*. Following this formulation, the sputtering phenomenon has a universal characteristic that is its surface aspect, which mathematical representation is given by eq. (4.2). In other words, all recoils to be sputtered follow the same motion: no scattering and no elastic energy loss after they start from the original position in the solid. Sputtered particles originate from the first monolayer. Deviations from this picture are statistical irrelevant or if present depend on the lack in the theory of the evolution and modification of the surface topografy [72].

All possible regimes can be described by using different expressions of D. At present only a limited number of expressions of D are available.

The theory is now ready to obtain the first and more general results. For all collisional regimes where moving particles can only slow down (*cooling collisions*: no gain of energy in collisions), if A is the maximum fraction of the projectile's energy that can by transferred to a target atom to be sputtered in a single collison, then the maximum sputtered energy, E_{M} can be always written as

$$E_{\mathrm{M}} = AE - U\,. \tag{4.3}$$

This result is a consequence of the surface character of the sputtering and of the binary collision approximation used. To understand this result it must be realized that, under the conditions of cooling collisions, the collision with the maximum energy transferred is always between the incident ion and a target particle and this collision is present in all linear regimes. For this category of experiments, since eq. (4.3) is not affected by multiple interaction,the latter equation is a powerful tool for spectroscopic information: eq. (4.3) gives information on both binary collisions at the surface and surface potential barrier. In fact, as announced in sect. 3, within the same initial conditions except for the incident energy, all couples (E, E_{M}) must be over the same straight line. The

slope of the straight line is A and contains information on the binary elastic collisions between the incident ion and the surface target atoms. According to the theory of binary elastic collisions, A must depend on M_1, M_2 and some geometrical variables [37, 38]. By changing the ion-target combination and the geometrical conditions, the functional dependence of A on the different parameters can be studied.

The intersection of the same straight line with the E_M axis gives the value of U. The determination of the correct value of U is an important unsolved problem for the sputtering phenomenon. Usually the sublimation energy [14, 15] is used, but there is no proof for this choice. In recent years several authors [73, 74] have considered the possibility of using alternative values. Since eq. (4.3) is independent of the collisional regime considered, it represents a more adequate tool for studying the precise physical meaning of U. Finally, since from (4.3) we can derive, by definition, the threshold for sputtering

$$E_{th} = \frac{U}{A}, \tag{4.4}$$

the results of the studies of eq. (4.3) can be used to calculate the threshold for sputtering under very different physical conditions.

4·2. *The double differential sputtering yield.* – To proceed further in the analysis of the theory we need expressions of D. The related physical quantities, namely energy spectrum, sputtering yield and so on, can be obtained by relative simple integrations. Nevertheless, to preserve the general structure of the theory, we shall try to obtain, whenever possible, expressions that are independent of the form of D. However, this choice means introducing from the very beginning further assumptions regarding the theory.

Suggested by the surface character of the sputtering and supported by the results of the Sigmund-Thompson regime, we assume to be adequate, in sputtering calculations, the following approximation:

$$D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x) \cong D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x = 0)\,. \tag{4.5}$$

By using this approximation a general expression for the double differential sputtering yield can be obtained from eqs. (1) and (2):

$$J(E_1, \boldsymbol{e}_1) = L_0 \frac{E_1}{E_1 + U} \cos\theta_1 D(E, \boldsymbol{e}; E_0 = E_1 + U, \chi_1 = \chi_0, \cos\theta_0 = g, x = 0)\,, \tag{4.6}$$

where

$$g = g(E_1, \theta_1, U) = \sqrt{\frac{E_1 \cos^2\theta_1 + U}{E_1 + U}}\,. \tag{4.7}$$

Equation (4.6) gives a simple prescription to obtain the distribution of ejected atoms once the distribution of recoils inside the solid is known, and *vice versa*, by means of eq. (4.6) sputtered atoms give direct information about the cascades in the solid. In other words, the sputtering phenomenon *opens a window* on the several properties of the bombarded solid.

4·3. *The isotropic case.* – The most studied expression of D is that describing the isotropic velocity distribution of recoils, namely the case where D can be simplified as follows:

$$D_{is}(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x = 0) = \frac{1}{4\pi} D(E, \boldsymbol{e}; E_0, x = 0) . \tag{4.8}$$

In this case, the double differential sputtering yield reduces to [17]

$$J_{is}(E_1, \boldsymbol{e}_1) = \frac{L_0}{4\pi} \frac{E_1}{E_1 + U} \cos\theta_1 D(E, \boldsymbol{e}; E_0 = E_1 + U, x = 0) , \tag{4.9}$$

whereas the energy spectrum becomes

$$J_{is}(E_1) = \frac{L_0}{4} \frac{E_1}{E_1 + U} D(E, \boldsymbol{e}; E_0 = E_1 + U, x = 0) . \tag{4.10}$$

Moreover, the position of the peak in the energy spectrum is at energy E_1 solution of the following eq. [17]:

$$\frac{D}{D'} = -\frac{E_1(E_1 + U)}{U} , \tag{4.11}$$

where D' is the derivative of D with respect to E_1. Equation (4.11) tell us that, in general, the position of the peak in the energy spectrum depends on the type of damage produced in the materials, namely, depends on function D.

Finally, by using eq. (4.3) we obtain the following form of the sputtering yield [17]:

$$Y_{is}(E_1) = \frac{L_0}{4} \int_{U}^{\lambda E} \mathrm{d}E_0 \left(1 - \frac{U}{E_0}\right) D(E, \boldsymbol{e}; E_0, x = 0) . \tag{4.12}$$

Two applications of the results of this section will be now presented.

4·3.1. The Sigmund-Thompson regime. This regime is characterized by the Sigmund expression of D (cf. eq. (3.3))

$$D = \frac{\Gamma F_D(E, \boldsymbol{e}, x)}{E_0^2} . \tag{4.13}$$

In this case eq. (4.10) reduces to Thompson energy spectrum

$$J_{is}(E_1) = J_0(E_1) = \frac{\Gamma L_0 F_D(E, e, x=0)}{4} \frac{E_1}{(E_1 + U)^3}, \tag{4.14}$$

with the peak in the usual position:

$$E_p = \frac{U}{2}. \tag{4.15}$$

Finally, the sputtering yield eq. (4.12) becomes

$$Y_{is} = Y_0 \left(1 - \frac{1}{w}\right)^2, \tag{4.16}$$

where Y_0 is the Sigmund sputtering yield and w is given by eq. (3.21). The results of this section have been discussed in details in the previous chapter.

4·3.2. Sputtering by light-ion bombardment. When light ions hit heavy solid targets the incident ions loose their energy predominantly by nonelastic electronic excitations, whereas elastic collisional cross-sections are relatively small. The consequence is that cascades cannot develop, or, more precisely, the linear extension of the collisional cascades is always small compared with the range of the incident ions. With a good approximation, sputtering by light-ion bombardment belongs to the category of the single collisional regime.

The first major interst in the sputtering of solids due to low-energy light-ion bombardment arose from the need to study this process in connection with plasma surface interaction in fusion devices [75]. In fact, the solid walls sorrounding a magnetically confined hot plasma are continuously bombarded by low-energy deuterium-tritium and helium ions and neutrals from the plasma. Sputtering caused by such bombardment can be a major source of impurities which contaminate the plasma. Theories and experiments will be useful to establish plasma and surface conditions where sputtering is minimized. Further interest comes from the need to understand the erosion of solid surfaces outside the earth's atmosphere which are bombarded by solar wind predominantly consisting in protons in the energy range of a few keV [76].

Theoretical attempts to explain the sputtering by light-ion bombardment within the framework of the standard transport theory have always failed. On the contrary, the models [77-79] based on the backscattering mechanism have achieved some success. The physical picture underlying this mechanism is the following: after ion bombardment some ions are reflected back, and during their motion towards the surface they can generate primary recoiling target atoms which can be ejected from the surface if they have enough energy to overcome

the surface potential barrier. The above mechanism seems to suggest, for the sputtering by light ions, a formulation that has to be different from that used for other linear regimes.

We shall also show that this type of sputtering can also be described within our formulation and that the only difference between the different linear regimes is the expression for D [18].

An approximate expression for D, at normal incidence and in the case of low-energy light-ion bombardment of heavy targets has been proposed in 1983 by Falcone and Oliva [80, 81] (see also appendix A):

$$D = \frac{C_{1/2}}{4\pi K R(E)} \frac{1}{E_0^{3/2}} \ln\left(\frac{AE}{E_0}\right), \tag{4.17}$$

with (cf. eq. (2.32))

$$C_{12} = \frac{\pi}{2} \lambda_{1/2} a \sqrt{\frac{M_1}{M_2}} 2 Z_1 Z_2 e^2 \tag{4.18}$$

and

$$R(E) = \frac{2E}{N S_e(E)}. \tag{4.19}$$

Moreover, K is given by eq. (2.42) and a by eq. (2.12).

According to eq. (4.10) we get immediately the following energy spectrum [17]:

$$J(E_1) \propto \frac{E_1}{(E_1 + U)^{5/2}} \ln\left(\frac{AE}{E_1 + U}\right). \tag{4.20}$$

To obtain the explicit expression of the sputtering yield, we must specify the expression for A. Since we refer to the normal incidence, there is a general agreement about the following threshold for sputtering [18]:

$$E_{th} = \frac{U}{\gamma(1-\gamma)}, \tag{4.21}$$

where γ is given by eq. (2.3). Then according to eqs. (4.3) and (4.4), we derive the following expression for A:

$$A = \gamma(1-\gamma). \tag{4.22}$$

By using the value of A given by eq. (4.22), the energy integration of eq. (4.20) gives the following sputtering yield:

$$Y = \frac{6.031 \cdot 10^{-3}}{\xi_e} \frac{v_0}{v_U} \frac{M_1}{M_2} \frac{L_0 N S_e(E)}{E} F(w_1) \tag{4.23}$$

with

$$F(w_1) = \ln w_1 + \frac{3}{\sqrt{w_1}} - \frac{1}{3w_1^{3/2}} - \frac{8}{3}. \tag{4.24}$$

Moreover

$$w_1 = \frac{\gamma(1-\gamma)E}{U} \tag{4.25}$$

and

$$v_U = \sqrt{\frac{2U}{M_2}}. \tag{4.26}$$

Figure 5 compares the experimental data [70] of W targets bombarded with He ions and the results obtained from eq. (4.23) with $U = 8.68$ eV. The picture (see also ref. [18]) shows a good matching between theory and experiments.

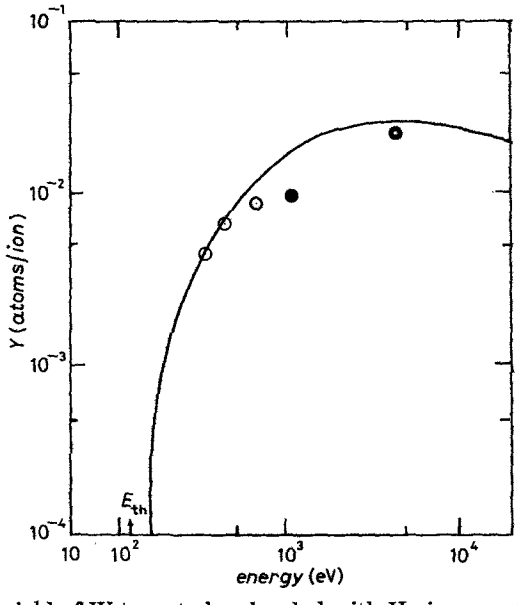

Fig. 5. – Sputtering yield of W targets bombarded with He ions *vs.* the incident energy. The experimental data are taken from ref. [70]. The solid line is eq. (4.23).

Equation (4.23) is proportional to $S_e(E)$ and since the Sigmund yield is proportional to $S_n(E)$, both results seem to indicate that linearity will always reflect in a sputtering yield proportional to the stopping power (nuclear or electronic).

4·4. *Inclusion of anisotropic effects: a simple case.* – As discussed in appendix A, a general equation of the damage function, in the linear regime, can be derived. Unfortunately, the only available analytical solutions are asymptotic and not adequate to describe the low-energy regime. To present analytical results, including anisotropic effects and valid at low energy, we shall assume in this section the following general form of D [19]:

$$D = D_{is} \cos^k \theta_0 , \tag{4.27}$$

where D_{is} represents the isotropic part of D and the power k gives the degree of anisotropy ($k = 0$ is the isotropic case). Equation (4.27) is a generalization of a D expression used [82] with $k = 2$ with success in order to explain recent energy spectra of sputtered particles. Nevertheless, we stress that eq. (4.27) has never been proved to be a solution of eq. (A.31).

According to the general expression of the double differential sputtering yield, eq. (4.6), we obtain

$$J(E_1, \boldsymbol{e}_1) = L_0 \frac{E_1}{E_1 + U} D_{is}(E, \boldsymbol{e}; \chi_1 = \chi_0, x = 0) \cos\theta_1 \left(\frac{E_1 \cos^2\theta_1 + U}{E_1 + U} \right)^{k/2} \tag{4.28}$$

and after further integrations we arrive at the following sputtering yield:

$$Y = \frac{L_0}{4} \int_U^{AE} \mathrm{d}E_0 D_{is}(E_0) \frac{2}{2+k} \left[1 - \left(\frac{U}{E_0} \right)^{1+k/2} \right]. \tag{4.29}$$

To obtain this latter equation, we have taken into account eq. (4.3).

To obtain explicit expressions of physical quantities, we must specify the form of D_{is}. According to ref. [82] we assume for D_{is} eq. (4.13) and we get

$$J(E_1, \boldsymbol{e}_1) = \frac{\Gamma L_0 F_D}{4\pi} \frac{E_1}{(E_1 + U)^3} \cos\theta_1 \left(\frac{E_1 \cos^2\theta_1 + U}{E_1 + U} \right)^{k/2} \tag{4.30}$$

and

$$Y = Y_0 \frac{4}{4+k} \left[1 - \frac{4+k}{2+k} \left(\frac{1}{w} \right) + \frac{2}{2+k} \left(\frac{1}{w} \right)^{2+k/2} \right]. \tag{4.31}$$

In eq. (4.31) Y_0 is the Sigmund sputtering yield and w is given by eq. (3.21).

At large incident energies ($E \gg E_{th}$) eq. (4.31) becomes

$$Y = Y_0 \frac{4}{4+k}. \tag{4.32}$$

Let us discuss in detail the case $k = 2$. For this value of k, the double differential sputtering yield becomes

$$J(E_1, e_1) = \frac{L_0 \Gamma F_D}{4\pi} \frac{E_1}{(E_1 + U)^4} \cos\theta_1 (E_1 \cos^2\theta_1 + U). \tag{4.33}$$

Equation (4.33) is in agreement with the expression derived by Garrison [82] and used to explain some recent experimental data.

The peak position for this expression is given by [82]

$$E_p = \frac{2\cos^2\theta_1 - 3 + \sqrt{4\cos^4\theta_1 - 4\cos^2\theta_1 + 9}}{4\cos^2\theta_1}, \tag{4.34}$$

which reduces to the Thompson peak position for $\theta_1 = 0°$, whereas shifts to lower energy occur as the polar angle increases, and this trend is independent of the choice of U [81].

Integrations of eq. (4.33) over the angular variables enable the following energy spectrum to be obtained:

$$J(E_1) = J_0(E_1) 2\left(1 + \frac{E_1}{E_1 + U}\right), \tag{4.35}$$

where J_0 is the Thompson energy spectrum.

Integration of eq. (4.33) over the energy variable, by taking into account eq. (4.3), gives

$$J(\theta_1) = \frac{L_0 \Gamma F_D}{2U} \cos\theta_1 H(\theta_1, w) \tag{4.36}$$

with

$$H(\theta_1, w) = \tag{4.37}$$

$$= \cos^2\theta_1 \left[\left(1 - \frac{1}{w}\right) - \left(1 - \frac{1}{w^2}\right) + \frac{1}{3}\left(1 - \frac{1}{w^3}\right)\right] + \frac{1}{2}\left(1 - \frac{1}{w^2}\right) - \frac{1}{3}\left(1 - \frac{1}{w^3}\right).$$

At large incident energies, eq. (4.37) can be approximated by the Garrison result [81]

$$J(\theta_1) = \frac{L_0 \Gamma F_D}{4\pi} \cos\theta_1 \left[\frac{2\cos^2\theta_1 + 1}{3}\right]. \tag{4.38}$$

Finally integration of eq. (4.36) over the angular variable gives the following

sputtering yield [19]:

$$Y = Y_0 \frac{4}{6}\left(1 - \frac{3}{2w} + \frac{1}{2w^3}\right), \tag{4.39}$$

where Y_0 is again the Sigmund sputtering yield.

The comparison and discussion of eq. (4.39) with experimental data can be found in ref. [19].

4·5. *Outlook and conclusions.* – At the beginning of my studies on sputtering (around 1980) the current opinion, among colleagues of the sputtering community, was that the standard transport theory was able, for linear regimes, to describe all physics quantities involved in the phenomenon. Some unsolved problems were of a technical nature rather than basic (see Sigmund in ref. [6]), and the success of this theory has been so large that, despite the same authors, the theory has been used with some technical modifications to explain sputtering events clearly out of its field of validity. In contrast, the only intrinsic contradiction of the theory, namely the divergence in the value of the average energy of sputtered atoms, has been completely unnoticed by the scientific community. The elimination of this divergence is not only necessary for a completly consistent theory, but when properly realized enables new ideas on sputtering phenomenon to come to the fire.

The possibility of a consistent formulation was originated by the Falcone and Sigmund theory which made it possible to have direct information on the escape depth of sputtered particles. In other words, this latter theory enables to study the surface aspect of the phenomenon quantitatively. The first step towards a quantitative definition of the surface aspect of the sputtering has been [68] the connection between the collisional mean free path and the depth of origin of sputtered particles. With this interpretation of the escape depth it is established that the most probable motion of a recoiling atom which is to be sputtered is in a straight line without collisions. Subsequently, owing to the surface aspect of the sputtering (atoms are ejected essentially from the first monolayer), recoiling atoms which are to be sputtered cannot lose energy and the general expression of the ejection function becomes eq. (4.2) (the assumption of a planar surface potential barrier is of secondary importance in the theory).

We have already noticed that the quantity R_0 of the Falcone-Sigmund theory is different from the quantity L_0 of eq. (4.2) and the difference between them is also quantitative. Our present aim is to calculate the difference between the two quantities.

Particles moving through a solid are point particles that undergo their elastic collisions through specified cross-sections. Since sputtered particles originate from the first monolayer, the *sputter cross-section*, namely the cross-section between two point-particles that produces as its result a sputtered particle must

be constant and equal to

$$\sigma_0 = N^{-2/3} \tag{4.40}$$

and we can write

$$L_0 = \frac{1}{N\sigma_0} = N^{-1/3}. \tag{4.41}$$

In contrast, the quantity R_0 is (cf. eq. (2.58))

$$R_0 = \frac{1}{NC_0} \tag{2.58}$$

with $C_0 = 1.808\,\text{Å}^2$. Let us calculate L_0 and R_0 for the case of an iron target (the results are similar for all other targets). For Fe, $N = 8.48 \cdot 10^{-2}\,\text{At/Å}^3$ and we find $L_0 = 2.276\,\text{Å}$ and $R_0 = 6.522\,\text{Å}$. The difference between the two values, of order of 3, is relevant for quantitative analysis and it should be important to have the possibility to establish which of the two quantities is the correct one. This check can be done by comparing theoretical and experimental values of the average escape depth of sputtered particles. An analysis of both experiments and computer simulation studies [83] has given

$$\langle x \rangle / \lambda = 0.80 \pm 0.10, \tag{4.42}$$

where λ is the mean atomic spacing. Since, at least in the Sigmund-Thompson regime, we have found (cf. eqs. (3.9) and (3.22))

$$\langle x \rangle = 0.8 R_0 \tag{4.43}$$

and

$$\langle x \rangle = 0.8 L_0, \tag{4.44}$$

we reach the conclusion that the depth of origin of sputtered atoms in terms of the mean free path is the correct physical interpretation.

If L_0 is given by eq. (4.41) all our previous yield calculations are overstimated (we have used the value given by eq. (2.58)) and the general agreement found between the experiments and theoretical results of transport theory, or of its generalization, is less than that claimed. In reality, a definitive conclusion about the agreement of the yield calculations that follows from the transport theory (or from the theory presented by this author) and the experiment is not yet possible. In fact, in the yield expressions there are other quantities, Γ, F_D, U and thresholds that are not yet well calculated [83, 84]. Improvement in the values of

Γ and F_D depends on a better determination of the damage function (we do not have adequate solutions for semi-infinite targets), whereas the precise determination of the surface binding energy and thresholds for sputtering is related to surface properties of the sputtering (in table II are given several used values of U). For these latter quantities we have derived, on the basis of the binary approximation, two general results (cf. eqs. (4.3) and (4.4)) that can be used to have more precise information about both quantities. Most of this work remains to be done. Moreover, owing to their general character, the range of validity of eqs. (4.3) and (4.4) is equivalent to the range of validity of the binary approximation in a sputtering theory.

TABLE II. – *Atomic number Z, atomic weight M, and sublimation energy U* (eV) *of several elements (data from ref.* [70]).

Element	Z	M	U
Na	11	22.990	1.12
Mg	12	24.312	1.54
Al	13	26.982	3.36
Ca	20	40.080	1.83
Ti	22	47.900	4.89
V	23	50.942	5.33
Cr	24	51.996	4.12
Mn	25	54.938	2.92
Fe	26	55.847	4.34
Co	27	58.933	4.43
Ni	28	58.71	4.46
Cu	29	63.546	3.52
Zn	30	65.37	1.35
Ga	31	69.72	2.82
Ge	32	72.59	3.88
As	33	74.922	1.26
Zr	40	91.22	6.33
Nb	41	92.906	7.59
Mo	42	95.94	6.83
Ag	47	107.87	2.97
Ta	73	180.95	8.10
W	74	183.85	8.68
Au	79	196.97	3.80

As regards the extension of the above unified sputtering theory to some nonlinear regime, we remain of the opinion that the question is at present completely open. It is the decided opinion of this author that the surface character of the sputtering is a universal property of the phenomenon, although the mathematical representation of this character may be different from eq. (4.2).

In conclusion, while a general and consistent formulation of the sputtering phenomenon for linear regimes is now available, other interesting surface and bulk properties must be further analysed.

* * *

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APPENDIX

General equations for the damage function.

In this appendix we shall derive the general equation of the damage function D under linear conditions. Some solutions will be also shown.

The formalism that we are going to present is essentially due to the works of Robinson [65], Lindhard [26-28], Sanders [85], Sigmund [40, 44, 86] and Winterbond [43]. In particular, in describing the techniques and the definitions we follow Sigmund [44].

According to this latter author, we can define a function D (the Sigmund recoil density function) such that $D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0)\,\mathrm{d}E_0\,\mathrm{d}^2\boldsymbol{e}_0$ is the average number of atoms set in motion with initial energy $(E_0, \mathrm{d}E_0)$ and direction in the solid angle $(\boldsymbol{e}_0, \mathrm{d}^2\boldsymbol{e}_0)$, in a collisional cascade generated by an incident ion with initial energy E and direction $\boldsymbol{e}$.

Following the Lindhard procedure for balance equations, we can obtain for D the following eq. [87]:

$$\text{(A.1)}\quad \frac{1}{2\pi}\frac{\mathrm{d}\sigma(E, E_0)}{\mathrm{d}E_0}\,\delta\left(\boldsymbol{e}\cdot\boldsymbol{e}_0 - \sqrt{\frac{E_0}{\gamma E}}\right) = S_e(E)\frac{\partial}{\partial E}D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0) +$$

$$+ \int \mathrm{d}\sigma(\boldsymbol{v}, \boldsymbol{v}', \boldsymbol{v}'')[D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0) - D(E - T, \boldsymbol{e}'; E_0, \boldsymbol{e}_0) - H(T, \boldsymbol{e}''; E_0, \boldsymbol{e}_0)]\,,$$

where $\mathrm{d}\sigma(E, E_0)$ is the energy loss cross-section, $\mathrm{d}\sigma(\boldsymbol{v}, \boldsymbol{v}', \boldsymbol{v}'')$ the differential cross-section for elastic collisions between an incident particle with initial velocity $\boldsymbol{v} = (E, \boldsymbol{e})$ and final velocity $\boldsymbol{v}' = (E - T, \boldsymbol{e}')$ and a recoiling particle with zero initial velocity and final velocity $\boldsymbol{v}'' = (T, \boldsymbol{e}'')$; H is a function similar to D, but

referred to a system with equal ion-target mass; the equation for H is

$$\text{(A.2)}\quad \frac{1}{2\pi}\frac{\mathrm{d}\sigma(E,E_0)}{\mathrm{d}E_0}\delta\left(\boldsymbol{e}\cdot\boldsymbol{e}_0-\sqrt{\frac{E_0}{E}}\right)=S_e(E)\frac{\partial}{\partial E}H+\int\mathrm{d}\sigma(\boldsymbol{v},\boldsymbol{v}',\boldsymbol{v}'')[H-H'-H''],$$

where $H=H(E,\boldsymbol{e};E_0,\boldsymbol{e}_0)$, $H'=H(E-T,\boldsymbol{e}';E_0,\boldsymbol{e}_0)$ and $H''=H(T,\boldsymbol{e}'';E_0,\boldsymbol{e}_0)$.

To solve eq. (A.1) we must first solve eq. (A.2). The techniques for solving these types of equations are described in details in ref. [43]. The first step is to expand the angular part in terms of Legendre polynomes

$$\text{(A.3)}\quad H(E,\boldsymbol{e};E_0,\boldsymbol{e}_0)=H(E,E_0;\boldsymbol{e}\cdot\boldsymbol{e}_0)=\sum_{l=0}^{\infty}(2l+1)H_l(E,E_0)P_l(\boldsymbol{e}\cdot\boldsymbol{e}_0).$$

The use of eq. (A.3) in eq. (A.2) enables one to derive the equations for the coefficients. For $S_e(E)=0$, we get

$$\text{(A.4)}\quad \int\mathrm{d}\sigma(E,T)[H_l(E,e_0)-H_l(E-T,e_0)P_l(\cos\phi_1)-H_l(T,E_0)P_l(\cos\phi_2)]=$$

$$=\frac{1}{4\pi}\frac{\mathrm{d}\sigma(E,E_0)}{\mathrm{d}E_0}P_l\left(\sqrt{\frac{E_0}{E}}\right),$$

where ϕ_1 and ϕ_2 are the scattering angles, in the laboratory system, of the incident and recoiling particles, respectively. The expressions of these angles, in terms of the transferred energy T, are [85]

$$\text{(A.5)}\quad \cos\phi_1=A\sqrt{1-t}+\frac{B}{\sqrt{1-t}}$$

and

$$\text{(A.6)}\quad \cos\phi_2=\sqrt{\frac{t}{\gamma}},$$

where

$$\text{(A.7)}\quad A=M_1+\frac{M_2}{2M_1},\qquad B=M_1-\frac{M_2}{2M_1}$$

and

$$\text{(A.8)}\quad t=\frac{T}{E}.$$

To obtain eq. (A.4), we have used eq. (2.61) and a similar equation

$$\text{(A.9)}\quad \mathrm{d}\sigma(\boldsymbol{v},\boldsymbol{v}'')=\mathrm{d}\sigma(E,T\frac{\mathrm{d}^2e_2}{2\pi}\delta\boldsymbol{e}\cdot\boldsymbol{e}_2-\cos\phi_2)$$

together with the following representation of the delta-function:

$$\delta(x-y)=\sum_{l=0}^{\infty}\frac{(2l+1)}{2}P_l(x)P_l(y)\,. \tag{A.10}$$

Equation (A.4) can be now solved for the Lindhard power cross-section (cfr. eq. (2.31)); one obtains

$$k_l(E,E_0)=\int_0^1 \mathrm{d}t\,t^{-1-m}[H_l-H_l'P_l(\cos\phi_1)-H''P_l(\cos\phi_2)]\,, \tag{A.11}$$

where

$$k_l(E,E_0)=\frac{1}{4\pi}\frac{\mathrm{d}\sigma(E,E_0)}{\mathrm{d}E_0}\frac{E^{2m}}{C_m}P_l\left(\sqrt{\frac{E_0}{E}}\right). \tag{A.12}$$

Equation (A.11) can be solved by the Laplace transform. We introduce the variable

$$u=\ln(E/E_0) \tag{A.13}$$

and we take the Laplace transform of both sides of eq. (A.11), according to the following definition:

$$H_l(s)=\int_0^{\infty}\mathrm{d}u\exp[-su]H_l(u)\,. \tag{A.14}$$

We get

$$H_l(s)=\frac{k_l(s)}{-m^{-1}-g_l(s)-f_l(s)}, \tag{A.15}$$

where $g_l(s)$ and $f_l(s)$ are the Laplace Transform of

$$g_l(u)=[1-\exp[-u]]^{-1-m}\exp[-u]P_l(\exp[-u])\,, \tag{A.16}$$

$$f_l(u)=\exp[u]P_l(\exp[-u/2])\,. \tag{A.17}$$

We shall use eq. (A.15) to solve eq. (A.1). By using a procedure similar to that used for eq. (A.2), we find for the Legendre coefficients of D, the following equation:

$$k_l^{\mathrm{d}}(E,E_0)= \tag{A.18}$$

$$=\int_0^T \mathrm{d}t\,t^{-1-m}[D_l(E,E_0)-D_l(E-T,E_0)P_l(\cos\phi_1)-D_l(T,E_0)P_l(\cos\phi_2)]\,,$$

where

$$k_l^{\mathrm{d}}(E,E_0)=\frac{1}{4\pi}\frac{\mathrm{d}\sigma_{\mathrm{d}}(E,E_0)}{\mathrm{d}E_0}\frac{E^{2m}}{C_m}P_l\left(\sqrt{\frac{E_0}{\gamma E}}\right). \tag{A.19}$$

The index d refers to a system where the incident and the target particles are *different*.

Equation (A.18), in terms of the variable u, can be written as

$$k_l^{\mathrm{d}}=-\frac{D_l}{m\gamma^m}-\int_0^u \mathrm{d}v\, g_l^{\mathrm{d}}(u-v)D_l(v)-\int_0^u \mathrm{d}v\, f_l^{\mathrm{d}}(u-v)H_l(v), \tag{A.20}$$

with

$$g_l^{\mathrm{d}}=\exp[-u](1-\exp[-u])^{-1-m}\Theta(\exp[-u]-1+\gamma)\cdot \cdot P_l(A\exp[-u/2]+B\exp[u/2]) \tag{A.21}$$

and

$$f_l^{\mathrm{d}}(u)=\exp[m]\,\Theta(\gamma-\exp[-u])\,P_l\left(\frac{1}{\sqrt{\gamma}}\exp[-u/2]\right), \tag{A.22}$$

where $\Theta(x)$ is the unit step function and $v=\ln T/E_0$. After the use of the Laplace transform, eq. (A.20) becomes

$$D_l(s)=\frac{k_l^{\mathrm{d}}(s)+f_l^{\mathrm{d}}(s)H_l(s)}{-\gamma^{-m}/m-g_l^{\mathrm{d}}(s)}, \tag{A.23}$$

where $H_l(s)$ is given by eq. (A.15).

Evaluation of the inverse Laplace transform of eq. (A.23) in a closed form has never been obtained. Nevertheless, as indicated by Robinson [65] and Sigmund [44, 86], asymptotic solutions for $D_l(E,E_0)$ can be obtained from eq. (A.23). In general, for a function $F(s)$, whose poles are s_n, one can write [88]

$$F(u)=\sum_n \exp[s_n u]\,\mathrm{Res}\{F(s=s_n)\}, \tag{A.24}$$

where Res $\{F\}$ means residues of F calculated at the poles. Moreover, the poles are taken in a decreasing order. An asymptotic expansion of coefficients $D_l(E,E_0)$ can be written as

$$D_l(E,E_0)\approx\left(\frac{E}{E_0}\right)^{s_0}\mathrm{Res}\,\{D_l(s=s_0)\} \tag{A.25}$$

where s_0 is the highest positive pole.

In particular, in eq. (A.23), for $l = 0$ the highest positive pole is at $s = 1$, whereas for $l = 1$ is at $s = 1/2$. The explicit calculations give the following expressions for the first two coefficients:

$$D_0(E, E_0) \approx H_0(E, E_0) = \frac{\Gamma_m}{4\pi} \frac{E}{E_0^2} \tag{A.26}$$

and

$$D_1(E, E_0) \approx \frac{\Gamma_m}{4\pi} \frac{1}{E_0} \sqrt{\frac{M_1 E}{M_2 E_0}}, \tag{A.27}$$

where

$$\Gamma_m = \frac{m}{\psi(1) - \psi(1-m)} \tag{A.28}$$

with $\psi(x)$ the logarithmic derivative of the Eulero gamma-function [39].

Thus, an asymptotic solution of eq. (A.1) can be written as

$$D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0) \approx D_0(E, E_0) + 3\,\boldsymbol{e}_0 \cdot \boldsymbol{e}\, D_1(E, E_0) \approx \tag{A.29}$$

$$\approx \frac{\Gamma_m}{4\pi E_0} \left[\frac{E}{E_0} + \frac{3}{\sqrt{2M_2 E_0}} \boldsymbol{e}_0 \cdot \boldsymbol{e} P \right]$$

with $P = M_1 v$ the linear momentum of the incident particle.

If we also include the electronic stopping cross-section in eq. (A.1), then as shown by Sigmund [44, 48] eq. (A.29) becomes

$$D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0) \approx \frac{\Gamma_m}{4\pi E_0} \left[\frac{\nu(E)}{E_0} + \frac{3}{\sqrt{2M_2 E_0}} \boldsymbol{e}_0 \cdot \boldsymbol{e} P \right], \tag{A.30}$$

where $\nu(E)$ is the *energy deposited in atomic motion* [27].

Equation (A.1) can be further generalized by including the spatial dependence. We define a function $D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x)$ such that $D \mathrm{d}E_0 \mathrm{d}^2 e_0 \mathrm{d}x$ is the average number of atoms set in motion at depth $(x, \mathrm{d}x)$ with initial energy $(E_0, \mathrm{d}E_0)$ and direction in the solid angle $(\boldsymbol{e}_0, d^2 e_0)$, in a collisional cascade generated by an incident ion with initial energy E and direction $\boldsymbol{e}$. The balance method enables the following equation to be derived [87]

$$-\cos\theta_i \frac{\partial}{\partial x} D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x) + \frac{N}{2\pi} \frac{\mathrm{d}\sigma(E, E_0)}{\mathrm{d}E_0} \delta\left(\boldsymbol{e} \cdot \boldsymbol{e}_0 - \sqrt{\frac{E_0}{\gamma E}} \right) \delta(x) = \tag{A.31}$$

$$= N S_e(E) \frac{\partial}{\partial E} D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x) + N \int \mathrm{d}\sigma(\boldsymbol{v}, \boldsymbol{v}', \boldsymbol{v}'') [D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x) -$$

$$- D(E - T, \boldsymbol{e}'; E_0, \boldsymbol{e}_0, x) - H(T, \boldsymbol{e}''; E_0, \boldsymbol{e}_0, x)].$$

By first taking, the momentum distribution over the depth and by using the previous techniques eq. (A.31) can be solved [43, 48] and its ensuing result is

$$(A.32)\quad D(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x) \approx \frac{\Gamma_m}{4\pi E_0}\left[\frac{F_D(E, \boldsymbol{e}, x)}{E_0} + \frac{3}{\sqrt{2M_2 E_0}}\boldsymbol{e}_0 \cdot \boldsymbol{F}_p(E, \boldsymbol{e}, x)\right],$$

where $\boldsymbol{F}_p(E, \boldsymbol{e}, x)\,\mathrm{d}x$ is the mean momentum deposited in $(x, \mathrm{d}x)$ per incoming ion of initial energy E and direction $\boldsymbol{e}$ [89,90]. Equation (A.32) is the only available solution of eq. (A.31).

A.1. *Equation for primary recoils.* – Equation (A.1) with $H = 0$ is the equation for recoiling atoms generated directly by the incident ion, namely for the primary recoils. To be precise, if we indicate with $D_p\,\mathrm{d}E_0\mathrm{d}^2e_0$ the average number of primary recoiling atoms, set in motion with initial energy $(E_0, \mathrm{d}E_0)$ and direction in the solid angle $(\boldsymbol{e}_0, \mathrm{d}^2e_0)$ by an incident ion with initial energy E and direction $\boldsymbol{e}$, the equation for this quantity will be

$$(A.33)\quad \frac{1}{2\pi}\frac{\mathrm{d}\sigma(E, e_0)}{\mathrm{d}E_0}\delta\left(\boldsymbol{e}\cdot\boldsymbol{e}_0 - \sqrt{\frac{E_0}{\gamma E}}\right) = S_e(E)\frac{\partial}{\partial E}D_p(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0) + \\ + \int \mathrm{d}\sigma(\boldsymbol{v}, \boldsymbol{v}', \boldsymbol{v}'')[D_p(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0) - D_p(E, T, \boldsymbol{e}'; E_0, \boldsymbol{e}_0)].$$

By using the same procedure as before, we get the following equation for the Legendre coefficients:

$$(A.34)\quad \frac{1}{4\pi}\frac{\mathrm{d}\sigma(E, E_0)}{\mathrm{d}E_0}P_l\left(\sqrt{\frac{E_0}{\gamma E}}\right) = S_e(E)\frac{\partial}{\partial E}D_{p,l}(E, E_0) + \\ + \int \mathrm{d}\sigma(E, E_0)[D_{p,l}(E, E_0) - P_l(\cos\varphi_1)\,D_{p,l}(E - T, E_0)],$$

where we write $\cos\varphi_1$ as [91]

$$(A.35)\quad \cos\varphi_1 = \left(1 + \frac{1+\mu}{2}t\right)\frac{1}{\sqrt{1-t}}$$

with

$$(A.36)\quad \mu = \frac{M_2}{M_1}.$$

A.2. *Low-energy light ion in heavy targets.* – When light-ions hit heavy targets, the mass ratio μ is so large that the energy transfer in a binary elastic collision is small compared with the energy of the projectile. Then a T-expansion [91] can be used in (A.34)

$$(A.37)\quad D_{p,l}(E - T, E_0) \approx D_{p,l}(E, E_0) - T\frac{\partial}{\partial E}D_{p,l}(E, E_0).$$

In addition, always for low-energy light-ions in heavy targets, the nuclear stopping cross-section $S_n(E)$ can be assumed [91] to be much smaller than the electronic stopping cross-section $S_e(E)$.

This last assumption, together with the expansion (A.37), enables the following solution of eq. (A.34) to be derived:

$$D_{p,l}(E, E_0) = \int_{E_0/\gamma}^{E} dE' \frac{h_l(E')}{S_e(E')} \exp\left[\int_{E}^{E'} dE'' \frac{\sigma_l(E'')}{S_l(E'')}\right], \tag{A.38}$$

where

$$h_l(E, E_0) = \frac{1}{4\pi} \frac{d\sigma(E, E_0)}{dE_0} P_l\left(\sqrt{\frac{E_0}{\gamma E}}\right) \tag{A.39}$$

and

$$\sigma_l(E) = \int d\sigma(E, T)[1 - P_l(\cos\phi_1)]. \tag{A.40}$$

In particular, for $l = 0$, we find

$$D_{p,0}(E, E_0) = \frac{1}{4\pi} \int_{E_0/\gamma}^{E} dE' \frac{d\sigma(E', E_0)}{dE_0} \frac{1}{S_e(E')} \tag{A.41}$$

which is the isotropic solution derived by Sigmund [44].

Explicit expressions of eq. (A.41) depend on the choice of the ion-target elastic cross-section and on the electronic stopping power used.

Following Schiøtt [91], we assume for $S_e(E)$ the Lindhard electronic stopping cross-section (cf. eq. (2.41)) and for $d\sigma$ the Lindhard power cross-section with $m = 1/2$

$$d\sigma(E, E_0) = C_{1/2} \frac{1}{\sqrt{E}} \frac{dE_0}{E_0^{3/2}}. \tag{A.42}$$

With these choices, eq. (A.41) can be written as [44]

$$D_{p,0}(E, E_0) \approx \frac{C_{1/2}}{4\pi k} \frac{1}{E_0^{3/2}} \ln\left(\frac{\gamma E}{E_0}\right). \tag{A.43}$$

According to Falcone-Oliva [80, 81], an approximate solution, including the spatial dependence is

$$D_{p,0}(E, e_0, x) \approx \frac{D_{p,0}(E, E_0)}{X_{max}}, \tag{A.44}$$

where $X_{max} = R_p \cos\theta_i$ is the *maximum damage depth*. Moreover, since eq. (4.44)

includes multiple scattering through the plane $x = 0$ (*the surface*), the solution has been corrected [81] by the path length correction

$$D_{p,0}(E, E_0, x) \approx \frac{R_p}{R} \frac{D_{p,0}(E, E_0)}{X_{\max}}. \tag{A.45}$$

Thus, an approximate solution, in the isotropic limit, for low-energy light-ions in heavy targets, can be written [81] as

$$D_p(E, \boldsymbol{e}; E_0, \boldsymbol{e}_0, x) \approx \frac{C_{12}}{4\pi k} \frac{1}{\cos\theta_i} \frac{1}{R(E)} \frac{1}{E_0^{3/2}} \ln\left(\frac{\gamma E}{E_0}\right). \tag{A.46}$$

Equation (A.46), for candidates for sputtering and referred to normal incidence, reduces to eq. (4.17).

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