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COLLISION CASCADES AND SPUTTERING INDUCED BY LARGER CLUSTER IONS

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Abstract - Recent experimental work on larger cluster impact on solid surfaces suggests large deviations from the standard case of additive sputter yields both in the nuclear and electronic stopping regime. The paper concentrates on elastic collision cascades. In addition to very pronounced spike effects, two phenomena are pointed out that are specific to cluster bombardment. Multiple hits of cluster atoms on one and the same target atom may result in recoil atoms that move faster than the maximum recoil speed for monomer bombardment at the same projectile speed. This effect is important when the atomic mass of a beam atom is less than that of a target atom, $M_1 << M_2$. In the opposite case, $M_1 >> M_2$, collisions between beam particles may accelerate some beam particles and slow down others. Some consequences are mentioned. Remarks on the nuclear stopping power of larger clusters and on electronic sputtering by cluster bombardment conclude the paper.

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1 - INTRODUCTION

Cluster bombardment of solid surfaces is an upcoming field /1-13/. Motivations for studies reach from the needs of surface analysis and biomolecular mass spectrometry to surface modification of materials that are of interest in microtechnology and space research.

Existing experimental facilities provide water clusters of ~ 25-150 molecules in the energy range of ~ 1-10 keV per molecule /3-5/, hydrogen clusters of up to ~ 60 atoms with a total energy of 600 keV /6-8/, CO_2 clusters of unspecified size accelerated to 155 kV /9/, covalent as well as ionic clusters of total energies in the lower keV range /10/, small hydrocarbon clusters in the MeV range /11/, and Al clusters accelerated up to a few kV /12/.

These experimental possibilities cover very different physical situations. At the highest velocities /6-8,11/, energy dissipation of penetrating clusters and/or cluster fragments is predominantly electronic, and damage and sputtering effects observed on <u>insulators</u> are likely to be electronic. At lower energies, clusters may still be expected to penetrate -- although highly fragmented -- but dissipate their energy predominantly via recoil cascades /3-5,9/. When the energy per atom reaches the lower eV range, clusters may still initiate collision cascades although only a minor fraction of the constituents may penetrate /10,12/. At even lower velocities, phenomena may be observed that are not unlike those seen after macro- and micro-meteorite bombardment /2,14-16/.

This brief survey will emphasize some phenomena that are unique to cluster bombardment in the sense that they will not be seen in monomer bombardment at conventional current densities. There will be little specific reference to existing experimental results, but mainly penetrating clusters in the nuclear stopping region will be considered.

2 - THE STANDARD CASE

As a reference standard, take the case where a cluster dissociates right at the surface and all its constituent atoms penetrate independently without mutual interference. This case may be realized with a small cluster of light ions hitting a metallic target at not too low energy. It will manifest itself such that neither the penetration profile nor the sputter yield per cluster atom nor the damage per cluster atom depend on n, the number of atoms per cluster, provided that the comparison is made at constant velocity.

Experiments on cluster bombardment are more often performed at constant energy per cluster. Then, assuming the standard case, the sputter yield Y_n for a homonuclear cluster containing n atoms is

$$Y_n\ (E) = n \cdot Y_1\ (E/n). \qquad (1)$$

for a small, high-energy proton cluster /6/ bombarding a metal, one expects $Y_1\ (E) \propto E^{-1}$ by Rutherford's law /17/ and hence $Y_n \propto n^2$. Conversely, if $Y_1\ (E_1) \propto E$, which is the case at much lower energies /17/, Y_n becomes independent of n. Evidently, care is indicated in this type of comparison: An n^2 dependence of the sputter yield per cluster need by no means be indicative of a nonlinear effect, unless the comparison is done at constant velocity.

From the point of view of ion penetration and collision physics, this standard case does not offer many challenges. However, a target bombarded by cluster ions does differ from a target bombarded by an equivalent beam of cluster fragments or individual atoms. Most of all, craters may be expected to form more easily, hence the surface morphology may develop differently; the primary damage state will be more compact; bubbles and precipitates may form at low fluences where one would not look for such phenomena otherwise.

Whether or not one deals with the standard case may well depend on the type of phenomenon observed. The total sputter yield per cluster atom is notorically sensitive to n, even for very small clusters /18,19/, while the energy reflection coefficient or sputter efficiency, being a small effect governed by high-energy recoils and reflected projectile particles /20/, may be expected to be less sensitive to cluster size.

It may be necessary to include the charge balance in considerations of whether or not one deals with the standard case. A cluster ion typically contains more electrons than an equivalent beam of atomic ions. These additional electrons may contribute to the measured secondary electron yield /21,22/.

3. Elastic-Collision Spikes

It has long been known that a high concentration of deposited energy per volume causes deviations from the standard linear cascade theory of energy dissipation /23/. This shows up in enhanced sputter yields of heavy targets bombarded by heavy atomic ions /17,18/ and, more convincingly, for bombardment with dimers and trimers /18,19/.

The range of energy deposited per volume achievable in larger-cluster bombardment reaches far beyond that for dimers and trimers. Estimates have been performed for water clusters /3/ that indicate energies ~ 100 eV per target atom in the core of the track. These numbers are based on the assumption of independent continuous slowing down of the constituent atoms of the cluster, the latter being smeared out to a monolayer circular disk. Details of the calculation may be questioned. The neglect of angular scattering and recoil transport may overestimate the deposition density in particular in deeper layers, yet approximating the cluster as a disk rather than a sphere has the opposite tendency. Moreover, "evaporation" of atoms at the high temperatures quoted above cannot be an activated process. All this does not affect the main point that a cluster of ~ 100 water molecules of a total energy of 300 keV must generate more dramatic spike phenomena than any atomic ion at a similar energy. Observed sputter yields of up to 10^5 atoms per bombarding cluster provide ample evidence /4/.

From a theoretical point of view, cluster bombardment provides an experimental tool to realize three-dimensional energy deposition profiles gained from standard penetration theory /24/. The latter constitute an average over many bombarding particles, and considerable labor has been invested to arrive at feasible statements about the average energy deposition volume of individual cascades /25-27/. In cluster bombardment, the initial assumption of many bombarding atomic particles is realized with a relative fluctuation $\sim n^{-1/2}$. Hence, that problem has been largely eliminated.

The basic assumption of a randomized elastic-collision spike may be expected to be realized to a higher degree in bombardment with large water clusters than for dimers or trimers of heavy ions because of substantial angular scattering of oxygen atoms, in particular for heavy targets like gold or tantalum /4/ where projectiles scatter frequently and lose their energy in small bits.

There is no unanimous agreement on the detailed mechanism of enhanced sputtering from an elastic-collision spike /28/, where evaporation /29,4/ and shockwaves /30,31/ have been proposed as the main alternatives, and gas flow for the special case of condensed inert gas targets /32/. The relative merits of these models may be of minor significance in the present connection.

4 - MULTIPLE HITS

Consider a cluster containing n atoms of mass M_1 hitting a target consisting of atoms with mass M_2, and assume for a moment that $M_1 << M_2$. Evidently, a target atom C recoiling from a collision with a beam atom A moves slowly enough to have a chance to be hit by another beam atom B (Fig. 1a). If σ_{12} is a pertinent cross section for such a collision, the average number ν_2 of hits on a target atom, caused by atoms of one cluster, is given by

$$\nu_2 \cong N_1 \ell_{av} \sigma_{12} \quad , \tag{2}$$

provided that the target atom lies within the trajectory of the cluster, where N_1 is the number density of atoms in the cluster and ℓ_{av} the average length of a straight line going through the cluster. For a spherical cluster with a radius R,

$$\ell_{av} = \frac{3}{4} R. \tag{3}$$

Equation (2) is most readily found by viewing the interaction from a coordinate system in which the cluster is at rest (Fig. 1b). The simplifying assumption of $M_1 << M_2$ enters in several ways: It justifies the straight line trajectory in Fig. 2b as well as the neglect of the dependence on target speed in σ_{12}.

The net result of a multiple hit is a recoil energy exceeding that achievable by monomer bombardment at the same velocity. In fact, multiple hits can lead to an energy transfer from the projectile to the target as long as the speed of the beam particle exceeds that of the target particle. Hence, an upper limit on the energy E_2 of a target atom is given by

$$E_2 < \frac{M_2}{M_1} E_1 = \frac{M_2}{M_1} \bullet \frac{E}{n} = \frac{M_2}{M} E, \tag{4}$$

where E_1 is the energy per beam atom, and E and M the total energy and mass of the cluster, respectively. Evidently, Eq. (4) is only relevant for clusters with $M > M_2$, otherwise $E_2 < E$.

In practice, Eq. (2) will be of interest for collisions leading to significant energy transfer which, at the same time, are infrequent. Hence, except for very large clusters, double hits may be the most prominent feature to show up in such experiments, resulting in a moderate increase of the maximum energy of a target atom by somewhat less than a factor of two beyond the familiar limit γE_1, with $\gamma = 4M_1M_2 (M_1 + M_2)^{-2}$.

Even such a moderate enhancement may cause a significant increase of damage production and sputtering, in particular under conditions where monomer bombardment would go below the pertinent threshold.

5 - COLLIDING BEAM PARTICLES

Consider now the reverse case of a cluster of heavy atoms hitting a target of light ones, $M_1 >> M_2$ (Fig. 2a). Again, it is convenient to view the penetration from a system moving along with the projectile. In this frame, let a target atom C hit a beam atom A (Fig. 2b). A will receive a recoil velocity while C will be scattered away. The heavy beam atom A has a larger cross section for collision with other beam atoms than the light target atom. Hence, the most likely subsequent event is a collision with another beam atom B (Fig. 2c). As shown in the graph, B may have a velocity component in the positive beam direction. Hence, in the laboratory frame, B has been accelerated to above the initial beam velocity. At the same time, A has been deflected toward the direction opposing the beam, i.e., it may have slowed in the laboratory system.

A significant fraction of accelerated beam particles has been found by computer simulation of argon clusters bombarding carbon targets, and this feature was ascribed to nonlinear effects in the collision cascade /13/. While there is little doubt about the importance of nonlinear effects in this type of cascade, the very occurrence of accelerated beam particles is an entirely linear effect as is evident from Fig. 2b. The only difference from the conventional scheme is the fact that the linear cascade propagates in the projectile rather than the target!

Accelerated beam particles may open up new reaction channels, in particular with regard to electronic excitation and electron emission, as well as enhanced damage production and sputtering near threshold.

Note that for every accelerated beam particle there is another one that has suffered enhanced stopping. Thus, collisions between beam particles affect primarily the straggling rather than the stopping power. Heavy atomic ions hitting a light target have typically a rather narrow range profile /33/. This profile will be spread in case of cluster bombardment by collisions between beam particles, thus allowing some beam atoms to come to rest very close to the surface. The observation of Cs ions in a low-fluence SIMS signal initiated by clusters containing Cs /10/ may be related to this phenomenon.

6 - QUANTITATIVE ESTIMATES?

The range of validity of conventional transport theory /17/ must be considerably narrower in describing cluster bombardment than for monomer bombardment. At the same time, the range of applicability of continuum descriptions /2,3,29-32/ is enhanced. Phenomena involving hard collisions such as those sketched in the previous sections should, however, be accessible to transport theory.

Computer simulation is an obvious alternative, yet, many existing simulation codes do not readily adapt to cluster bombardment. Standard Monte Carlo and binary collision lattice simulation codes do not contain a clock; this feature appears important in case of nearly simultaneous bombardment by several projectiles.

Standard molecular dynamics codes readily allow for cluster bombardment but may run into capacity problems when simulating bombardments with clusters of high total energies such as several hundreds of keV.

Feasible compromises are molecular dynamics codes with a narrow cutoff radius /34/ or a binary collision code with a built-in clock /13/. In a recent comparison between different types of simulation codes /35/, molecular dynamics and binary collision lattice codes turned up to have more in common with each other than accepted conventionally, while Monte Carlo codes showed a less coherent behavior.

It is thus quite feasible to describe the collisional phase with a binary collision code -- as was done in Ref. /13/ -- while the relaxation to equilibrium of a target implanted with a high concentration of impurities, and thus an estimate of a penetration profile in absolute length units, must invoke properties that are beyond the scope of a binary collision simulation.

7 - STOPPING POWER OF A CLUSTER

The question of whether the stopping power per atom of a cluster is higher or lower than that of a monomer appears interesting and important /2/. Only effects due to elastic collisions are considered here.

A target atom hit by a projectile atom tends to move away from the track of the cluster, and hence might leave the track before being hit by another beam particle (Fig. 2b). This paving-the-way effect tends to decrease the effective stopping power of the beam. A similar effect has been analyzed recently on very small collision systems /36/. The effect on the stopping power turned out small there, but the systems analyzed were too small to justify implications on larger cluster penetration. At any rate, paving-the-way should be most pronounced for $M_1 >> M_2$. This shows up clearly in simulations of argon on carbon /13/ where the mean penetration depth was found to increase by more than a factor of four when the cluster size increased from n = 1 to 200.

For $M_1 << M_2$, recoil velocities are too small to allow recoil atoms to escape from the track. It appears unlikely that multiple hits have a pronounced effect on the stopping power.

In Ref. /2/, specific geometries were pointed out leading to an increased collisional energy loss. If, e.g., the trajectory of a target particle in Fig. 1b goes between a "ring" of 2-4 projectile atoms, the simultaneity of the collisions increases the transferred momentum and hence the energy loss per projectile atom /37/. However, the opposite case of a target atom passing by a number of atoms on one side, and hence greater deflection, increased collision distance and smaller momentum transfer per beam particle, would seem statistically more significant. This phase space argument would seem to favor smaller stopping powers.

8 - ELECTRONIC SPUTTERING

In a series of very promising experiments /6-8/, empirical scaling rules have been found which clearly demonstrate that the emission of positive and negative ions from CsI and a biomolecular target induced by hydrogen clusters in the electronic stopping regime ($v \simeq v_o = e^2/\hbar$) does not go under the standard case. The interpretation is complicated due to the fact that negative and positive ions seem to obey different scaling relations, and that the significance of the electronic stopping power in determining erosion yields is subject to debate. Estimates of dimer stopping powers are involved in the analysis /38/, the validity of which is not ascertained for targets that do not contain free electrons and for clusters with a radius significantly larger than the Bohr adiabatic radius, the latter being quite small at the rather low projectile velocities. The major point of uncertainty in the analysis is the lack of an unambiguous description of the laws governing the erosion of these targets by monomer bombardment. Cluster bombardment might well elucidate some aspects of this process. However, the velocity range around $v \sim v_o$ may well be the most complex one to tackle.

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Figure Captions

Fig. 1 Target particle C hit by several beam atoms A, B... The size of the circles reflects the mass of the atoms.

a) Seen from the laboratory frame of reference.

b) Seen from a frame moving with the cluster.

Fig. 2 Collisions between beam atoms A and B, initiated by an interaction between beam atom A and target atom C. The size of the circles reflects the mass of the atoms.

a) Initial configuration seen from the laboratory frame of reference.

b) A colliding with C, seen from a frame moving with the cluster.

c) A colliding with B, same frame as in b).

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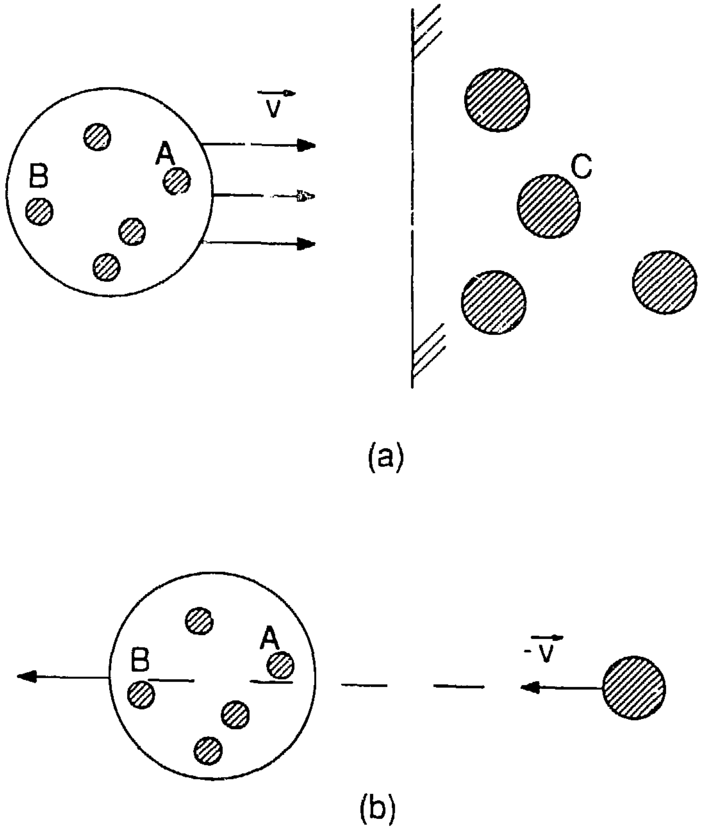

Fig. 1

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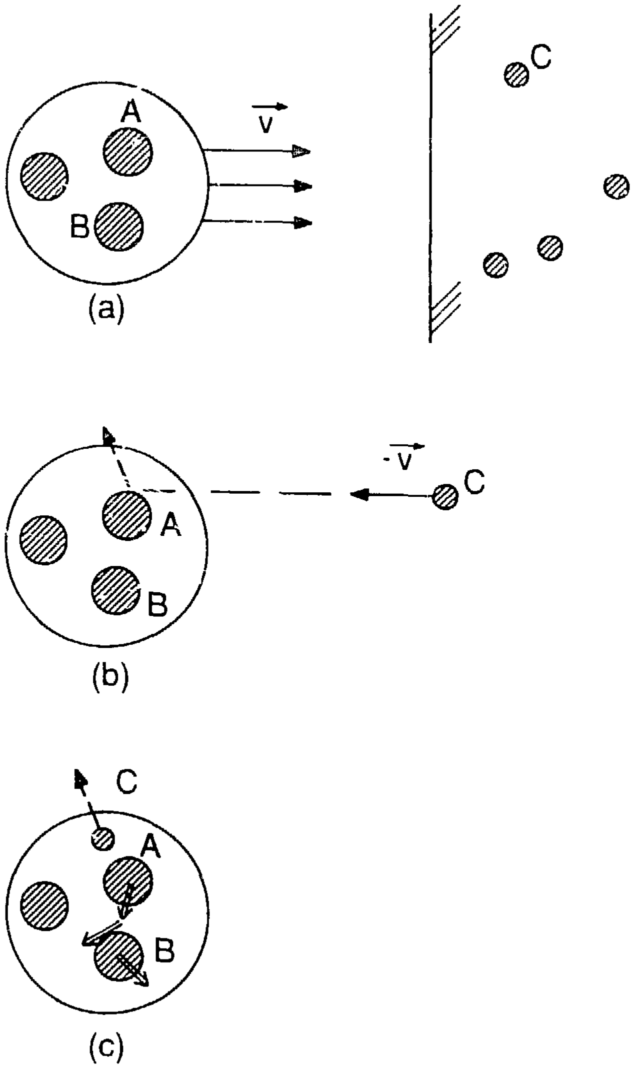

Fig. 2