

COMPUTER SIMULATION OF THE HIID FROM LANGMUIR-BLODGETT FILMS<sup>(1)</sup>

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**Résumé** -

Les processus de désorption en HIID (Heavy Ion Induced Desorption) sont simulés à l'aide d'une évaluation numérique directe des équations de mouvement des molécules. Ceci permet une meilleure comparaison des résultats expérimentaux aux modèles qui décrivent comment les forces effectives sur les molécules sont produites à partir d'une excitation électronique initiale. Nos calculs reproduisent sans ajustement de paramètres quelques aspects caractéristiques de HIID qui ont été trouvés dans des expériences avec des cibles Langmuir-Blodgett, telles que la dépendance des rendements avec les épaisseurs de films et l'énergie électronique perdue.

**Abstract** - The desorption process in HIID is simulated by direct numerical evaluation of the molecular equations of motion. This allows a better comparison of experimental data to models which describe how effective forces on the molecules are produced from an initial electronic excitation. Our calculations reproduce without parameter fitting some characteristic features of HIID which have been found in experiments with Langmuir-Blodgett targets, such as the dependence of yields from layer thickness or from electronic energy loss.

## Introduction

A theoretical description of the processes following the impact of a heavy ion to an insulator surfaces and leading to the desorption of secondary ions, clusters and molecules requires three basic steps:

- It has to provide for an appropriate description of the electronic excitation of different degrees of freedom and of its spatial distribution
- It has to explain how molecular forces can result from an initial configuration of electronic excitation
- It has to describe which molecular motion is finally produced by these forces and how this motion leads to the formation of the different species found in the mass spectra (such as clusters of molecular fragments).

The present situation is that there is little known about the first question while many attempts have been made to solve the second one. This is usually justified by the (reasonable) assumption that the quite well known total electronic energy loss is evenly distributed to many degrees of freedom, which justifies in later steps the use of  $(dE/dx)_e$  and an effective excitation range obtained from secondary electron data. Here we will also share this point of view.

The third question is usually answered by application of continuum models or equivalence considerations, which sometimes serve quite well for a description of overall yields, but usually are not used for the purpose of describing details of the yield structure.

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Another approach, the direct numerical evaluation of the molecular Hamilton equations of motion, should yield more information. In this way laser ablation from organic solid surfaces has yet been investigated [4]. The advantage of this method is obvious: it allows a comparison of different excitation models and the simultaneous calculation of many different properties of the desorbed material such as information about "how many molecules are desorbed from one special depth" etc.. The disadvantage is, of course, that for any experimental situation a large series of iteration steps is required and that (in our case) the method is strictly deterministic without allowing any statistical variation from one impact event to another.

## Model Base of the Calculations

For the description of the electronic excitation we use the same model as in a previous paper [1]: as suggested in the Sternglass model we assume that the half part of the electronic energy loss of the projectile is spent into low-energy excitation of electrons. This portion is fed into short-ranging motion of electrons and its spatial distribution is therefore controlled rather by dissipative processes than by ballistic particle motion. So we use an electron temperature and a temperature dependent diffusion parameter for electron heat.

Molecular forces are assumed to be produced by the same mechanism as described in [1]. In insulators valence electrons cause intermolecular and intramolecular forces, i.e. covalent, polar and V.d.Waals-forces. We use for parametrization Morse-potentials for describing covalent binding potentials and 6/12-potentials for the description of V.d.Waals-potentials. The separation of these empiric potentials into an attractive and a repulsive part is somehow arbitrary, but we assume that the latter one is approximately independent of the outer-shell electron configuration (hard-core repulsion).

The introduction of an electron temperature suggests a statistical description of band population, which is extended to a statistical description of the attractive part of molecular potential. Interatomic potentials thus become dependent of the electron temperature, which thus affects "macroscopic" material properties. In contrast to earlier calculations we use the temperature-dependent equilibrium distance between the atoms in order to obtain molecular forces, i.e. we use here an approach related to the model of Sundqvist and Williams [2], where the "equilibrium length" of molecules is translated in to an effective spring tension, since at zero time the excited molecules still share the same amount of volume.

This allows a test of both models within the same numerical context. The difference between them is:

- By the model of Sundqvist and Williams the elongation of molecules results from the excitation of inner vibrations and from the anharmonicity of the intramolecular potentials (Morse-potentials). The excitation of molecular vibrations is caused by electron scattering, so molecular forces are built up by a rate which should be equivalent (not automatically proportional) to the electronic energy density.
- In our model potential modification and molecule elongation is related directly to electronic excitation.

Calculations were restricted to projectiles hitting the surface by a 90°-angle. In this case the mechanical problem can be treated as approximately cylindrical symmetric. Furthermore we neglect motion parallel to the surface. This can be justified by the anisotropy of the material which is caused by the uniform orientation of long molecules.

## Treatment of the problem

**Electron Heat:** Temperature exchange within the electron system is enhanced by a population of the conduction band. Thus we apply a temperature-dependent diffusion parameter as described in [1]. Heat exchange between large molecules is assumed as proportional to the surface they share; in our case only molecules in the same or in parallel rows can get into a contact close enough.

**Forces due to immediate potential modification:** As described in [1] interatomic potentials are described by composition of a repulsive and an attractive contribution, where the latter one is reduced by a factor  $\{1 - \exp(-G/k_B T)\}$  ( $G$ =band gap) at nonzero electron temperature. Using Morse-Potentials to describe intramolecular forces for each molecule a force contribution  $\exp(-G/K_B T) * F_{rep} * N_{bond}$ , where  $F_{rep}$  is the repulsive part of the forces resulting from the morse potential and  $N_{bond}$  is the number of bonds in the molecule. Usually intermolecular potentials are short-ranged and weak as compared to Morse-type intramolecular potentials. Thus forces resulting from intramolecular bond modification may be strong enough to give rise to molecule separation, while bonds do not have to be broken necessarily.

**Friction:** When we deal with a sample of the Langmuir-Blodgett type forces between the molecules depend strongly from their orientation. In our quasi-two-dimensional approach we account for the interaction between molecules in adjacent rows by setting an empiric friction term which is proportional to the surface they share and to their relative velocity.

## Results

**Absolute yield characteristics:** The calculations show for low energy loss a characteristic threshold behaviour of the total yield (see fig. 1). It results here from the interdependence between spreading out of electron energy and excitation of mechanical motion. For small  $(dE/dx)_e$  the time where a sufficient energy density is present may become too short to give rise for molecular acceleration and breaking up the surface structure.

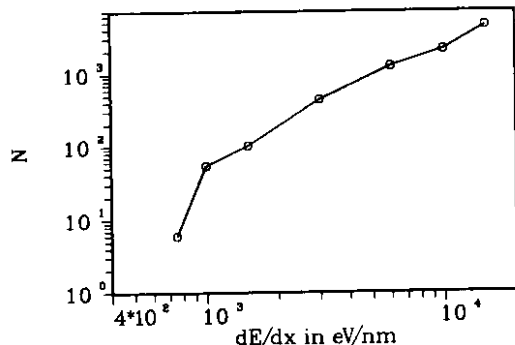


Figure 1: Absolute yield in dependence of the electronic energy loss

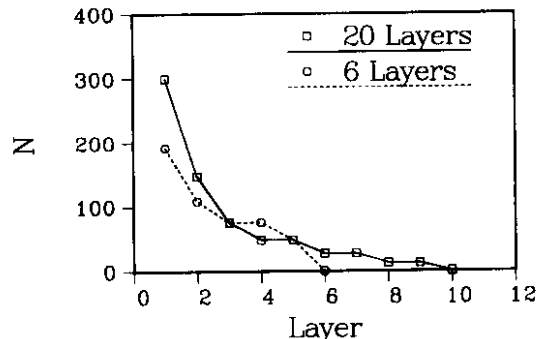


Figure 2: Differential plot of the yield contributions from different layers for samples with 6 and 20 layers.

**Contributions from varying depths:** Our calculations give information about the magnitude of the contribution of different layers to the yield. The results are shown in fig. 2: obviously even for a little number of layers the main contribution is produced from the top layer. The boundary conditions we used in our calculation were "fixed", i.e. the deepest layer was assumed to stick and we assumed that no forces were produced from the base. This should apply to clean metal surfaces, while the situation is probably different for nitrocellulose. The dependence of the contributions from the depth is roughly quadratic, which indicates that some "conical hole" is created when the surface is broken up, but pictures of the configurations show that a lot of rearrangement destroys the geometrical shape. This is in qualitative agreement with measurements from the IPN [3].

**Varying layer thickness:** Although the main contribution to the yield is produced from the top layer, the number of layers makes much effect. This is the consequence of the "collective" property of the desorption process: molecules are pushed out by forces which can be produced in deeper lying layers, which may stay sticking after transferring energy and momentum to the surface. Fig. 3 shows the important difference between the situations given either by a metal surface with few layers or by a bulk of organic matter. The latter is

reached asymptotically for about 20 layers, where some saturation becomes visible.

Figure 3: Dependence of the total desorption yield from the number of layers on the sample for  $(\frac{dE}{dx})_e = 500$  eV/nm

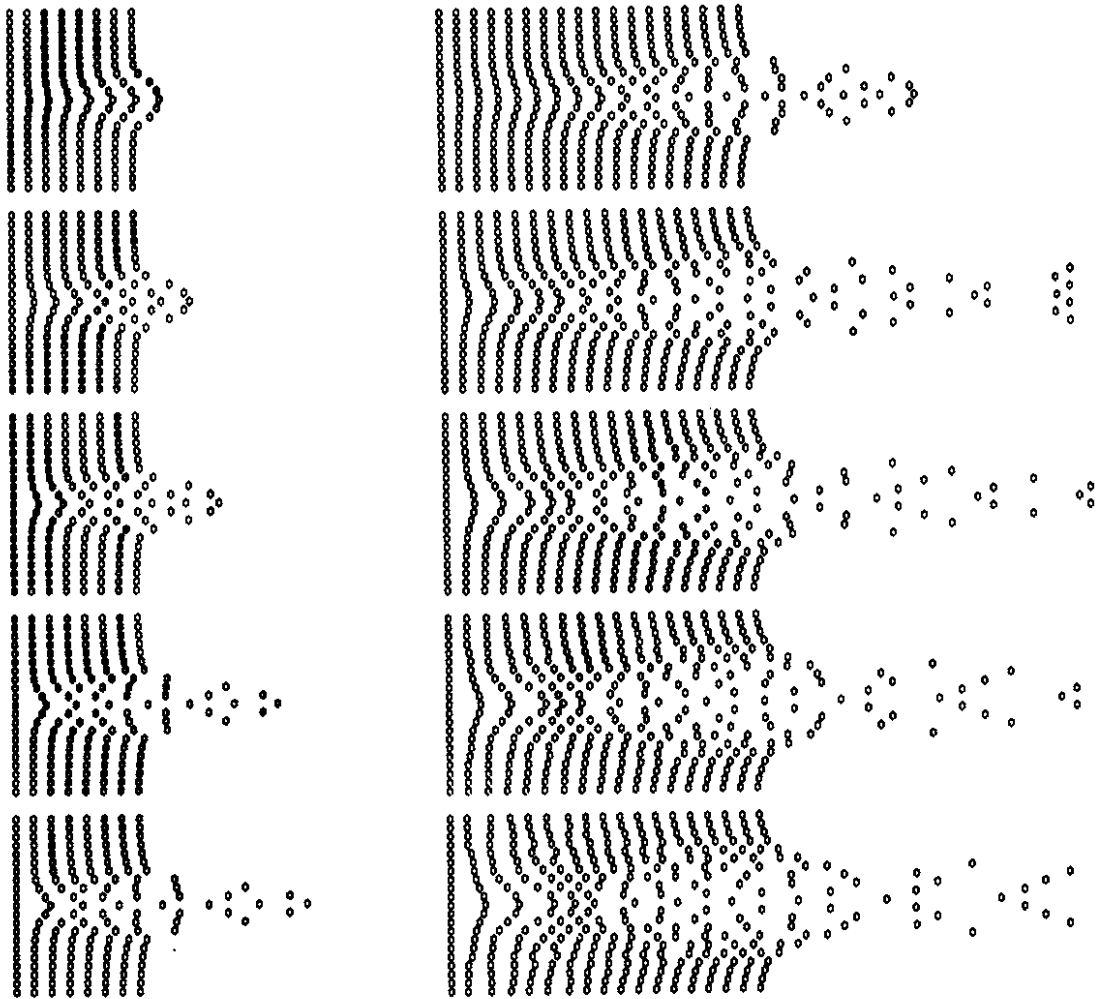
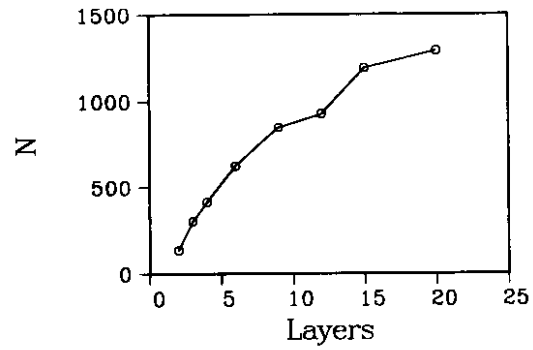


Figure 4: Molecular coordinates calculated for heavy-ion impact with  $(\frac{dE}{dx})_e = 150$  and 7500 eV/nm until 1.5 ns after impact

## References

- [1] H.F.Kammer in *PDMS and Clusters*, Lecture Notes in Physics 269 (1986) 107, Springer-Verlag Berlin, Heidelberg
- [2] B.U.R. Sundqvist, P.Williams, PR Lett. Vol. 58 No. 10 (1987) 1031
- [3] G.Bolbach, S.Della-Negra, C.Deprun, Y.LeBeyec, K.Standing, Rap. Comm. in Mass Spectr. Vol.1, No.2 (1987) 22
- [4] B.J.Garrison, R.Srinivasan, J.Appl.Phys. 57 (1985) 2909