



ELSEVIER

Nuclear Instruments and Methods in Physics Research B 193 (2002) 365–370

---

---

**NIM B**  
Beam Interactions  
with Materials & Atoms

---

---

www.elsevier.com/locate/nimb

# Sputtering of nano-grains by energetic ions

E.M. Bringa<sup>\*</sup>, R.E. Johnson*Material Sciences Department and Astronomy Department, University of Virginia, Charlottesville, VA 22903, USA*

---

## Abstract

Sputtering from grains with a size of tens of nanometers is important in a number of astrophysical environments having a variety of plasma properties and can have applications in nano-technology. Since energy deposition by incident ions or electrons can create ‘hot’ regions in a small grain, thermal spike (TS) models have been applied to estimate the sputtering. The excitations produced by a fast ion are often assumed to form a ‘hot’ cylindrical track. In this paper we use molecular dynamics (MD) calculations to describe the energy transport and sputtering due to the creation of a ‘hot’ track in a grain with one quarter million atoms. We show the enhancement due to grain size and find that TS models work over a limited range of excitation densities. Discrepancies of several orders of magnitude are found when comparing our MD results for sputtering of small dust grains to those obtained by the astrophysical community using spike models. © 2002 Elsevier Science B.V. All rights reserved.

*PACS:* 79.20.R; 95.75.P; 61.80.–x; 79.20.A

*Keywords:* Grains; Sputtering; Inter-stellar medium; Molecular dynamics; Thermal spike

---

## 1. Introduction

With the advent of new experimental techniques, the processing of nanometer size grains can be relevant for material and surface analysis [1]. They are also of interest because such grains form the “dust” in the inter-stellar medium (ISM) [2]. It can exist in a variety of environments, from the hot inter-cloud medium to the cold neutral clouds. This dust contains most of the refractory material in the ISM and accounts for extinction, polariza-

tion, and scattering of light, as well as for certain absorption and emission features. The dust also plays an important role in determining the total energy balance, converting light to infrared emission and heating the clouds through photoelectron emission. It is estimated that approximately 2/3 of the grain mass in the ISM is tied up in grains with radius,  $a$ , less than  $\sim 0.05 \mu\text{m}$ , accounting for the UV extinction, and  $\sim 20\%$  in small grains,  $a < 0.025 \mu\text{m}$ . In dense clouds grains can acquire a mantle of condensed molecules. This environment is not static, since the mantles and the grains are eroded (sputtered) by hot gas atoms or the local plasma, by photons, by grain–grain collisions, and by cosmic ray (CR) ions. These loss processes compete with grain growth by accretion.

The light CR ions penetrating molecular clouds ( $\text{H}^+$ ,  $\text{He}^{++}$ ) primarily produce photons in

---

<sup>\*</sup> Corresponding author. Present address: Lawrence Livermore National Laboratory, Chemistry and Material Sciences Dir. Computational Material Sciences, P.O. Box 808 L-353, 94550 Livermore, CA, USA. Tel.: +1-925-423-5724; fax: +1-925-423-7040.

E-mail address: [ebringa@llnl.gov](mailto:ebringa@llnl.gov) (E.M. Bringa).

the ambient gas, whereas a heavy CR ion efficiently sputters a grain. Here we examine models for sputtering of grains by heavy CR ions. Earlier we used a Monte Carlo particle tracking model to describe the size effect on the sputtering of small refractory grains in a shocked gas [3] and icy grains in a hot plasma trapped in a planetary magnetosphere [4]. We also considered CR ion-induced desorption of large organic molecules [5]. Here we use molecular dynamics (MD) simulations of the effect of a pulse of energy to further examine the effect of grain size and to test models for CR ion erosion of grains and grain mantles.

Whereas low energy ion bombardment erodes a grain by knock-on sputtering [3] fast ions deposit energy by exciting the electrons. A fraction of this energy is released by non-radiative processes leading to electronic sputtering [6,7]. Since energy deposition in the solid eventually manifests itself as atomic motion, thermal spike models (TS) have been popular for interpreting laboratory data [6,8] and for modeling grain erosion in molecular clouds [9,10]. TS models have been used extensively to calculate desorption induced by ion bombardment of a solid [11,12] and recently their limitations have been discussed [13–15]. A model by Hasegawa and Herbst (HH) [10], used often by the astrophysical community, assumes that grains reach a fixed temperature, independent of the energy deposited and grain size, for a time  $t_{\text{HH}}$ , during which loss is calculated as thermal desorption. Leger et al. [9] (LJO) assume a hot cylindrical track is formed.

## 2. MD simulations

Classical MD simulations consists in solving Newton's equations of motion for a collection of  $N$  interacting particles. The two parameter Lennard-Jones (L-J) potential is convenient because the results scale with the energy and length parameters. In addition, a number of condensed gas solids are well described by this pair potential. In our simulations, the L-J potential  $V(r) = 4\epsilon[(r/\sigma)^{-6} - (r/\sigma)^{-12}]$  with parameters  $\epsilon$  and  $\sigma$  and a cut-off radius  $r_{\text{cut}} = 2.5\sigma$ , was used to describe an

amorphous solid. In the following, lengths will be expressed in units of  $\sigma$  and energy in units of  $\epsilon$ . The sample has a binding energy  $U \approx 8\epsilon$ . Because the simulation results scale with the  $L$ - $J$  parameters [14] results for different solids can be obtained using the appropriate  $U$  and  $n$ , the density of the sample. The mass of the simulated particles,  $M$ , changes the time scale, which is given in units of  $t_0 = \sigma\sqrt{M/\epsilon}$  ( $t_0 \approx 1.9$  ps for CO). Simulations of solid  $\text{O}_2$  in which the intra-molecular potential was included are in good agreement with simulations without structure [16].

A CR iron ion deposits most of its energy in electronic excitations, typically  $\sim 10$ – $100$  eV/Å. This energy couples to the lattice by non-radiative repulsive decay events [6]. These are represented by giving an atom or neighboring atoms in the lattice an extra kinetic energy,  $E_{\text{exc}}$ , such that the total energy per unit length is equal to the effective stopping power,  $(dE/dx)_{\text{eff}}$ . Although the events in a track are statistical, it has become customary to consider a cylindrically heated region of radius  $r_{\text{cyl}}$  to approximate the effect of the track core [9].

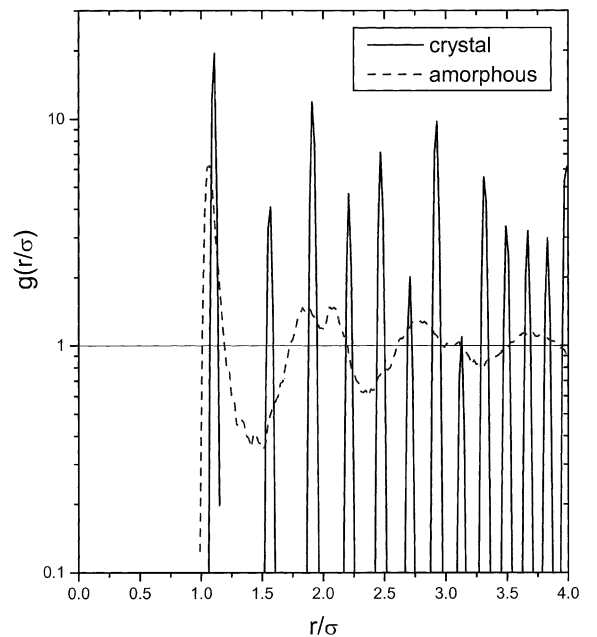


Fig. 1. Pair correlation function of the amorphous sample (---,  $n = 1.02/\sigma^3$ ), and of a crystalline sample (—,  $n = 1.05/\sigma^3$ ) at the same temperature,  $k_{\text{B}}T \approx 0.01U$ .

Although this can be very inaccurate, we make the same assumption in order to test the models typically used in astrophysics. Therefore, we create a heat spike by giving all atoms within  $r_{\text{cyl}}$  an energy  $E_{\text{exc}}$  with their velocities in random directions. The value of  $r_{\text{cyl}}$  depends on the projectile velocity and target properties. We use  $r_{\text{cyl}} \approx 14.7\sigma$  ( $\sim 50 \text{ \AA}$  for CO) as in Ref. [9]. The average kinetic energy of the atoms can be used to calculate a local temperature  $T(r, t)$ , but the velocity distribution is non-Maxwellian at early times when sputtering occurs [13].

MD has several limitations regarding the size of samples and simulation times. To calculate the evolution of a weakly bound L-J solid with a  $0.1 \mu\text{m}$  side and a density of  $0.03 \text{ \AA}^{-3}$  ( $1.26 \times 10^8$  atoms) for 10 ns ( $10^6$  steps for a time step of 0.01 ps) would take two years in a single CPU workstation, since even the most optimized codes have calculation times of roughly  $0.5 \mu\text{s}/\text{atom}/\text{step}/\text{CPU}$ . For

this reason we simulate a small grain of radius  $a = 37.5\sigma$  ( $\sim 0.013 \mu\text{m}$  for a CO grain) with nearly 0.25 million particles. This allows us to extract the main features of the ejection process while keeping the computational time reasonable.

### 2.1. Making the amorphous sample

A slight modification of the method used by Cui et al. [17] was applied to build the amorphous sample. We started with a cubic fcc crystal with 33 cells on each side (143,748 atoms) and a length  $L \approx 51.5\sigma$ . The initial density was the equilibrium density for the solid at low temperature,  $n = 1.05/\sigma^3$ . Using periodic boundary conditions the crystal was suddenly heated to temperatures well above the melting temperature, and it was equilibrated at this high temperature. The velocities of all atoms were then set to zero, and the mean kinetic energy  $\text{KE}(t_1)$  was calculated. Then the system was

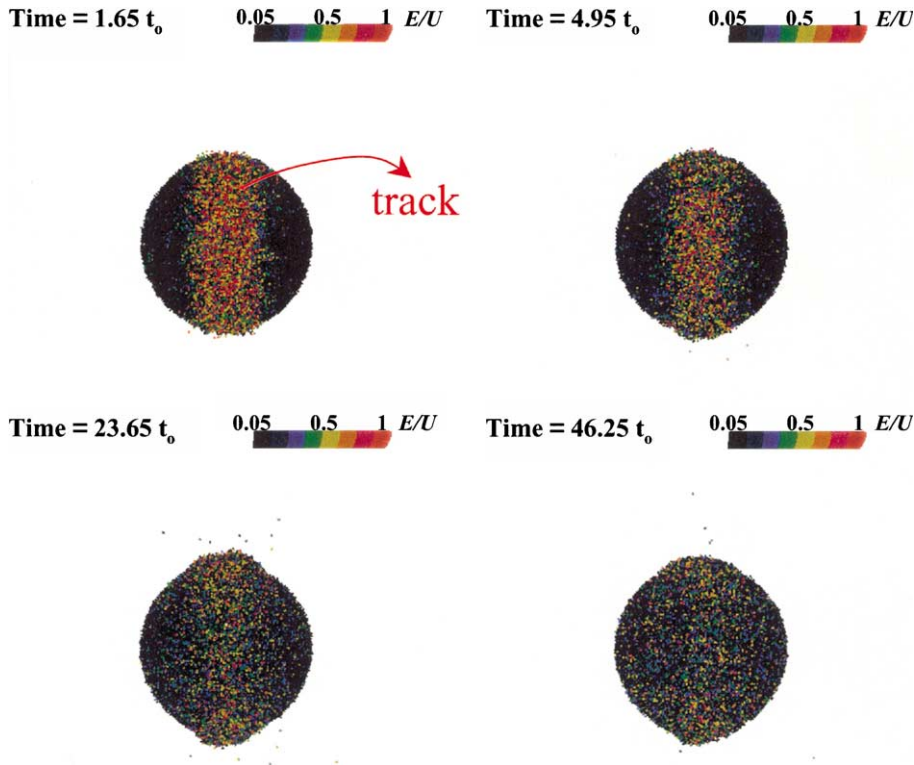


Fig. 2. Snapshot of the grain for  $E_{\text{exc}} = 0.5U$  (a total deposited energy of 2 keV for a CO grain), at different times. Color code indicates kinetic energy.

allowed to relax for few time steps, and now  $KE(t_2)$  was calculated. If  $|1 - KE(t_2)/KE(t_1)| < 0.05$  and  $KE(t_2) < 0.05U$  the simulation was stopped. Otherwise, the velocities were again reset to zero until the previous conditions were reached. This process was repeated until no more velocity scaling was necessary. The pair correlation function of the resulting sample in Fig. 1 is that of an amorphous sample [17]. Some short-range correlation remains. The final amorphous configuration was repeated eight times to obtain a cube with  $L \approx 103\sigma$ . A sphere of radius  $a = 36.7\sigma$ , centered at the center of the cube, was carved out and allowed to relax with free boundary conditions for several ps. This produced the grain used in our

simulations, which had a relaxed radius of  $37.5\sigma$ , and 216,996 particles, with an average density  $n = 1.02/\sigma^3$ . For a CO grain,  $a \approx 130 \text{ \AA}$ .

### 3. Results

Figs. 2 and 3 are snapshots from two simulations [18]. The high temperature of the track leads to early ( $t \lesssim 20t_0$ ) desorption of a large amount of material. Melting and the formation of a pressure pulse (shock) occur as seen in Fig. 3. At times  $\gtrsim 45t_0$  the process resembles thermal desorption. At low  $E_{\text{exc}}$  only few particles are desorbed (Fig. 2), but at large  $E_{\text{exc}}$  the grain can be totally de-

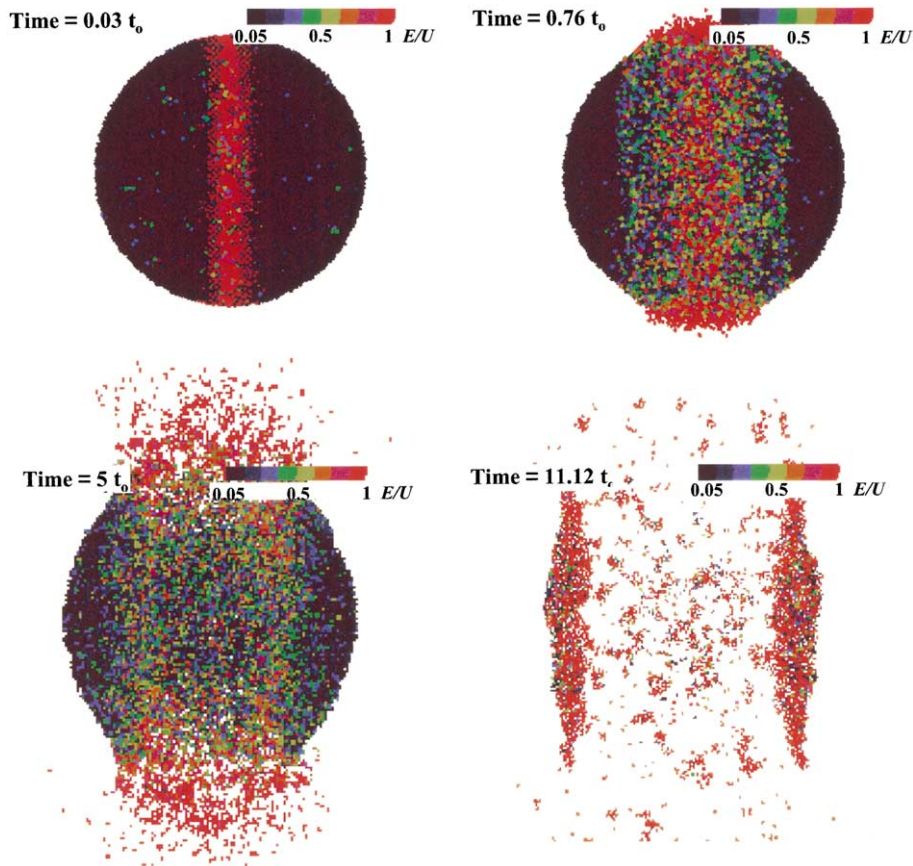


Fig. 3. Same as Fig. 2 for  $E_{\text{exc}} = 2.0U$  (a total deposited energy of 8 keV for a CO grain). The grain is broken into few large clusters plus a number of small clusters and monomers, and destroyed by  $100t_0$ .

stroyed (Fig. 3). At this energy liquid droplets form that will eventually lead to the break up and evaporation of the grain.

The MD simulations were stopped at times of  $28t_0$ – $140t_0$ . The MD yield at  $28t_0$  is shown in Fig. 4, together with the results from the HH model obtained using the simulation time  $t_{\text{HH}} = 28t_0$ , instead of  $t_{\text{HH}} = 10^{-5}$  s as in [10]. This gives a very low yield because the assumed temperature is low so the thermal desorption is close to 1 particle for the whole grain. For the grain size studied, the final surface temperature may be large enough to cause further desorption so that  $Y(28t_0)$  is not the true yield. Subsequent desorption can be treated using spike models.

For large grains, the size becomes irrelevant and we recover the yield for a flat, infinite surface. If the grain diameter is much smaller than the range of the CR, then we need to multiply the sputtering

yield by two, to account for the entrance and exit points. At low energy densities this follows the TS result (Fig. 4) [12] as verified earlier [14]. In this threshold regime, the mean energy per molecule is lower than the binding energy and desorption roughly follows  $Y \propto \exp(-U/E_{\text{exc}})$ . For  $E_{\text{exc}}$  closer to or larger than  $U$  the analytic models are no longer valid. The infinite grain yield in Fig. 4 has been taken from Bringa et al. [14] giving a lower limit to the yield from a grain. It is seen that the finite size enhances desorption since the energy can not dissipate into the semi-infinite material.

#### 4. Summary

Here we used a MD simulation of the transport of energy and desorption from a small grain following a heat pulse in order to test models of spike heating and evaporation by a heavy CR ion [9,10]. For comparison with models the same range of track parameters was used, although these may not describe a CR ion track very well. This will be dealt with in a subsequent paper.

We show the enhancement in the yield for a small grain depends critically on the energy density in the track. The studies here and our earlier work for semi-infinite solids also show the physics of ejection is not well described by the spike models typically used by the astrophysical community. In the HH model the sputtering yield from a more refractory material like ammonia ( $U \sim 0.3$  eV) or water ice ( $U \sim 0.5$  eV) would be essentially zero because of the exponential dependence with binding energy. However, in the regime where  $E_{\text{exc}} \gtrsim U$  it has been shown that the prompt component of the yield scales roughly as  $U^{-1}$  [14] giving larger yields from water ice and ammonia.

There are several caveats in the simulations described here. The track structure is not described, only a single component material and spherical grains were considered, and we have not studied grazing impact. Differences between model and MD results are due to a correct treatment of the high temperatures in the track. Heavy CR ions are also interesting as they not only erode grains, but the pressure pulse produced can cause the ejection of large molecules [19] possibly explaining

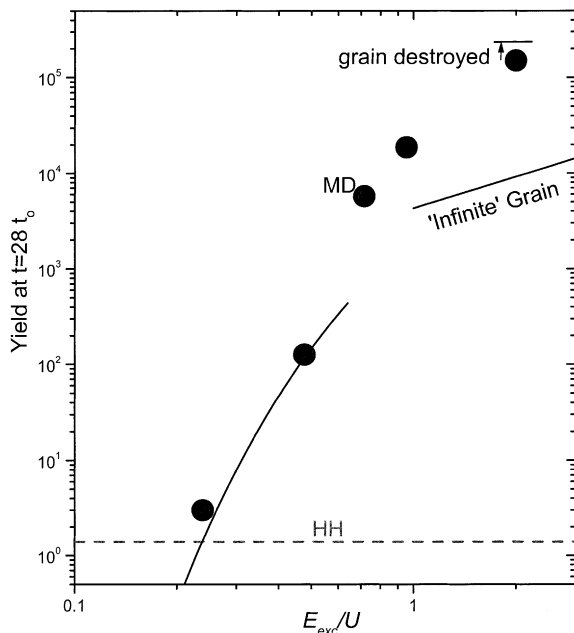


Fig. 4. Sputtering yield at  $28t_0$ , defined as the number of atoms at a radial distance greater than  $5\sigma$  from the surface of the grain. MD result (●), HH model for  $U = 0.08$  eV (---), infinite grain prediction (—). 'Infinite' grain: data for  $E_{\text{exc}} < 1$  calculated as in [12], data for  $E_{\text{exc}} \geq 1$  taken from [14]. The grain is destroyed for  $E_{\text{exc}}/U = 2.0$  and the short line segment and arrow indicate a yield equal to the total number of particles in the grain.

their abundance in the gas phase in the ISM [5]. This heating can also lead to a phase change offering a possible explanation for the crystalline material observed in the ISM [20].

### Acknowledgements

We would like to thank Barry Turner and Eric Herbst for discussions on the paper. This work was supported by the NSF Astronomy Division and NASA's Origins Program.

### References

- [1] M.C. Roco, *J. Nanopart. Res.* 3 (2001) 1.
- [2] J.M. Greenberg, C. Shen, astro-ph/0006337.
- [3] S. Jurac, R.E. Johnson, B. Donn, *Astrophys. J. Lett.* 503 (1998) 247.
- [4] S. Jurac, R.E. Johnson, J.D. Richardson, *Icarus* 149 (2001) 384.
- [5] R.E. Johnson et al., *Astrophys. J.* 379 (1991) L75.
- [6] R.E. Johnson, J. Schou, *Matematisk-fysiske Meddelelser* 43 (1993) 403.
- [7] I.A. Baranov et al., *Sov. Phys. Usp.* 31 (1988) 880.
- [8] A.E. Volkov, V.A. Borodin, *Nucl. Instr. and Meth. B* 146 (1998) 137.
- [9] A. Leger, M. Jura, A. Omont, *Astron. Astrophys.* 144 (1985) 147.
- [10] T. Hasegawa, E. Herbst, *Mon. Not. R. Astron. Soc.* 261 (1993) 83.
- [11] M. Toulemonde et al., *Nucl. Instr. and Meth. B* 166–167 (2000) 903.
- [12] P. Sigmund, C. Claussen, *J. Appl. Phys.* 52 (1981) 2.
- [13] E.M. Bringa, R. Johnson, Ł. Dutkiewicz, *Nucl. Instr. and Meth. B* 152 (1999) 267.
- [14] E.M. Bringa, R.E. Johnson, M. Jakas, *Phys. Rev. B* 60 (1999) 15107.
- [15] M.M. Jakas, E.M. Bringa, *Phys. Rev. B* 62 (2000) 824.
- [16] E.M. Bringa, R.E. Johnson, *Surf. Sci.* 451 (2000) 108.
- [17] S. Cui, P. Cummings, R.E. Johnson, *Surf. Sci.* 222 (1989) 491.
- [18] Movies of the simulations can be found at: <http://dirac.ms.virginia.edu/~emb3t/grains/grains.html>.
- [19] D. Fenyő, R.E. Johnson, *Phys. Rev. B* 46 (1992) 5090.
- [20] F.J. Molster et al., *Nature* 401 (1999) 563.