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COMPUTER SIMULATIONS OF PARTICLE-SURFACE DYNAMICS*

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ABSTRACT

Our simulations of particle-surface dynamics use the molecular dynamics codes that we have developed over the past several years. The initial state of a molecule and the parameters defining the incoming trajectory can be specifically described or randomly selected. Statistical analyses of the states of the particles and their trajectories following wall collisions are carried out by the code. We have carried out calculations at high center-of-mass energies and low incidence angles and have examined the survival fraction of molecules and the dependence upon the incoming trajectory. We report also on preliminary efforts that are being made to simulate sputtering and recombinant desorption processes, since the recombinant desorption of hydrogen from typical wall materials may be an important source for vibrationally-excited hydrogen in volume sources; for surface sources the presence of occluded hydrogen may affect the concentration of atomic species.

INTRODUCTION

Computer molecular dynamics (CMD) is a powerful technique for examining the microscopic details of a wide variety of phenomena. During the past few years we have reported on the successful application of CMD to the study of a number of important technological problems relevant to an understanding of the plasma-wall interaction zone of fusion plasmas. The problems of interest involve particle-surface dynamics, where experimental data is extremely difficult, as well as costly, to obtain. As we have described in more detail elsewhere,¹ CMD involves the numerical solution of Newton's Second Law equations of motion for all the atoms, thus providing a detailed time history of the coordinates and velocities of the particles. The initial positions and velocities of the particles represent the initial conditions on these equations, and it then remains only to define the forces acting on each of the particles. This has been done

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in our present calculations of particle-surface grazing-angle collisions by means of the usual sum-of-pair-potentials approximation (Figure 1). It should be noted that realistic simulations of recombinant desorption and sputtering will require a more general treatment of the forces acting on the particles, and our work in these areas will be briefly described.

Figure 1. Pair potentials for the interactions between atoms (from ref. 1).

For the development of either volume or surface sources of intense negative hydrogen ion beams, it is crucial to understand the possible mechanisms that can affect both the atomic concentrations and the concentrations of vibrationally-excited molecules in the plasmas. In volume sources, several processes are known to form highly-vibrationally-excited molecules which then by means of dissociative attachment with low-energy electrons form H^- ions from the decay of an intermediate H_2^+ state.² Our work to date has emphasized the excitation of H_2 molecules to high vibrational levels by fast-electron collisions or from H_2^+ ions that have been accelerated across the discharge-wall potential, undergoing Auger neutralization immediately before impact with the discharge chamber wall.^{1,3} As we have discussed previously, at high densities and

depending on the discharge parameters, either electronic excitation or H_2^+ Auger neutralization will be the dominant source of vibrational excitation.^{3,4}

In order to examine both the creation and depletion of vibrationally-excited molecular hydrogen, we began our early calculations with the de-excitation and re-excitation of highly-vibrationally-excited H_2 molecules, initially at thermal (500K) velocities, undergoing repeated wall collisions.⁵ By statistically analyzing a large number of trajectories, we obtained qualitative estimates of the average loss of vibrational energy as a function of the number of wall collisions and also obtained qualitative estimates of the rates of energy exchange and the extent of equipartition among the degrees of freedom of the molecular system, as well as estimates of the average transfer of energy between the molecules and the wall. Later, in addition to studying low-energy, thermal wall collisions, we carried out studies of collisions where the translational energies ranged up to 50 to 100 eV.¹ The purpose of these calculations was to determine the survival probability of vibrationally-excited H_2 molecules after undergoing high-energy collisions with a wall composed of metal atoms and to determine as well the fraction of survivors that remain in, or are excited to, high-lying vibrotational states. The results showed that the process of the wall recombination of H_2^+ to form H_2 ($v'' \geq 6$) could make an important contribution to the total vibrationally excited population and to the negative ion yield, comparable to that from the fast-electron process.³

The application of these results to the interpretation of ion-source operation has proven successful and has provided a basis for extrapolation to high-power systems. At the same time because of the unusual nature of the initial conditions defining the state of the molecule, experimental results with which to compare the results of the simulations are for all practical purposes nonexistent. However, as we noted in our earlier study of the generation of vibrationally-excited H_2 molecules by H_2^+ wall collisions, we found a substantial fraction of surviving neutrals for translational kinetic energies ranging from 1 to 20 eV. Subsequently, experimental verification of the prediction of the survival of a large neutral fraction of H_2 for beams of H_2^+ incident on a metal surface has been reported.⁶ These experimental studies and the current interest in molecular-ion scattering have encouraged us to undertake a series of grazing-angle trajectory calculations in which the great advantage of using computer experiments to modify the initial conditions can be utilized. These calculations will be discussed in the following section.

In addition, in order to understand the plasma-wall interaction zone in more detail, we have been designing simulations that can (1) describe the recombinant desorption of hydrogen molecules from metal surfaces containing a partial monolayer of hydrogen atoms upon which a flux of energetic protons is directed and (2) describe the sputtering and possible recombination of hydrogen atoms lying just below a heavy metal surface when a flux of light ions (e.g., H^+) or heavy ions (e.g., Cs^+) is directed toward such a prepared surface.

Our preliminary studies of these processes will be described in the third section.

LOW-ANGLE SCATTERING OF MOLECULAR HYDROGEN FROM METAL SURFACES

In Figure 2, we show schematically a typical starting configuration for an H_2 molecule set in motion with some velocity " v " toward a heavy-atom wall and with an initial phase angle α and an angle θ with respect to the direction perpendicular to the surface. Vibrational states of H_2 have been selected that represent vibrationally-excited species with $v'' = 2, 8, \text{ and } 12$, corresponding

Figure 2. Schematic representation of a typical starting configuration for an H_2 molecule moving at a low incidence angle toward a wall. Initial conditions include the velocity v , the phase angle α , and the angle θ from the normal, as well as the wall temperature T .

to energies ranging from 10,200 cm^{-1} to 35,250 cm^{-1} (1.266 eV to 4.371 eV) above the potential energy minimum (cf. Figure 1). The rotational quantum number J was set equal to 1 in each case, corresponding to a plasma temperature of 500 K where this rotational state predominates. The center-of-mass velocities have been given values so that at each grazing angle the normal component of center-of-mass translational kinetic energy will be 1, 4 or 10 eV. This provides a correspondence with our earlier work¹ where the trajectories were selected to be normal or near-normal with the perpendicular components of the translational energies ranging from 1 to 50 eV. Results from these earlier calculations indicated that survival fractions and excitations were essentially statistically independent of the angle of approach of the incoming trajectory when the normal component of energy was held constant. For the grazing-angle collisions, the mechanism we have previously described for the near-surface neutralization of an energetic beam of H_2^+ ions³ will result in a range of vibrotational states corresponding to those indicated above. For the interatomic potentials, which are shown in Figure 1, we have used a modification of the two-body potential of Scott and Richards⁷ for FeH, where we have reduced the strength of the interaction by a factor of 5, thereby simulating the weaker pair interaction between a hydrogen molecule and a cluster of Fe atoms. (An FeH effective "cluster" two-body potential obtained from ab initio calculations on Fe_4H clusters has also been shown to give statistically very similar results.) The Fe wall potential does not play a significant role in the dynamics, and we have continued to use the two-body potential of Johnson⁸ obtained from elastic constant data. Finally, as shown in Figure 1, a Morse fit to the experimental H_2 potential curve is very accurate up to $v'' = 8$ or 9. The effect of a somewhat more slowly-rising potential for $v'' = 12$ will very likely be subtle and less important than other approximations involved in the calculations.

The results to date of more than a thousand trajectories are summarized in Table I. It can be seen that the percent of surviving neutrals ranges from slightly less than 10 percent to more than 50 percent. As the normal component of beam energy changes from 1 to 10 eV, the fraction of surviving neutrals, taking into account statistical error, remains about the same for initial vibrational excitations $v'' = 2$ and 8; for $v'' = 12$ the neutral fraction appears to increase, although this may be a spurious result because of the relatively small number of trajectories examined so far. Additional computer studies are in progress to decrease the statistical uncertainty. More importantly, the surviving fraction of neutrals with large vibrational excitation (i.e., $f_1 f_2$) remains significant and of the order of 10 to 20 percent throughout the range of v'' and $E_{\perp}$ that we have examined. A comparison with results from our earlier calculations of the survival fraction after normal and near-normal surface collisions,¹ shown in Table II, indicates for both the earlier and the present calculations that the survival rate is consistent with a strong dependence on the normal velocity component of the incoming molecule; however, the dynamic processes leading to vibrational excitation are seen to be enhanced by grazing collisions with the wall. Thus, for $v'' = 2$ and $E_{\perp} = 2$ eV, there is

Table I. Fraction f_1 of molecules surviving a wall collision at high impact energies. The fraction of the surviving molecules with $v'' \geq 6$ is f_2 ; the grazing angle is 85° .

E_{com} (eV)	$E_{\perp}$ (eV)	v''								
		2			8			12		
		f_1	f_2	$f_1 f_2$	f_1	f_2	$f_1 f_2$	f_1	f_2	$f_1 f_2$
131.6	1.0	0.40	0.20	0.08	0.55	0.42	0.23	0.08	0.38	0.03
526.6	4.0	0.29	0.45	0.13	0.29	0.72	0.21	0.19	0.87	0.16
1316.6	10.0	0.33	0.17	0.06	0.22	1.00	0.22	0.28	0.77	0.21

Table II. Fraction f_1 of molecules surviving a wall collision at higher impact energies. The fraction of the surviving molecules with $v'' \geq 6$ is f_2 .

$E_{\perp}$		v''								
		2			8			12		
		f_1	f_2	$f_1 f_2$	f_1	f_2	$f_1 f_2$	f_1	f_2	$f_1 f_2$
1 eV	0°	1.00	0.00	0.00	1.00	0.47	0.47	0.60	0.50	0.30
	15°	1.00	0.00	0.00	1.00	0.38	0.38	0.56	0.54	0.30
4 eV	0°	0.92	0.13	0.12	0.38	0.32	0.12	0.64	0.28	0.18
	15°	0.94	0.16	0.15	0.48	0.54	0.26	0.64	0.22	0.14
10 eV	0°	0.42	0.57	0.24	0.20	0.83	0.17	0.18	0.89	0.16
	10°	0.27	0.73	0.20	0.15	0.67	0.10	0.14	0.86	0.12

now more than sufficient translational energy to excite low-lying vibrational states of the molecule during the grazing collision to high vibrotational levels. In addition to adding many more trajectories to reduce the statistical uncertainty, we are attempting to understand the dynamical events leading either to molecular survival or destruction at these large total energies.

ATOMIC AND RECOMBINANT DESORPTION OF HYDROGEN FROM METAL SURFACES

Other recent simulations have been designed to study the recombinant desorption of hydrogen molecules from metal surfaces

containing a partial monolayer of hydrogen atoms upon which a flux of energetic protons is directed. Computer experiments have also been designed to look at the sputtering and possible recombination of hydrogen atoms lying just below a heavy metal surface when fluxes of light or heavy ions are directed toward such a prepared surface. These are processes affecting both the atomic concentrations and the concentrations of vibrationally-excited molecules in the plasmas. The recombinant desorption of hydrogen could be an important source of vibrationally-excited hydrogen in volume sources; for surface sources, the presence of occluded hydrogen in the wall could affect the concentration of atomic species and provide an additional mechanism for the creation of excited molecular hydrogen.

Figures 3 and 4 show schematic representations of possible initial configurations for the simulations described above. For the calculation of recombinant desorption of hydrogen from surfaces, an Fe surface was formed upon which we placed a partial monolayer of hydrogen atoms. Surface temperatures were set equal to 500 K. Fluxes of atomic hydrogen with a random velocity distribution equivalent to a plasma temperature of 1000 K and with translational velocities ranging from 2-20 eV were directed toward the surface. Within a few picoseconds in these calculations, dynamical events are found to occur leading to the desorption of hydrogen atoms and molecular hydrogen. Although results from these initial calculations seem to indicate that the recombinant desorption of hydrogen from

Figure 3. Schematic representation of an assembly of particles used to study recombinant desorption of hydrogen from a metal surface. Multi-body force terms are included in describing the dynamics of the cluster within the dashed region.

Figure 4. Schematic representation of an assembly of particles used to study sputtering and possible recombination of hydrogen atoms placed at equilibrium positions just below a heavy metal surface. The incoming flux may be composed of either light (as shown) or heavy ions. Multi-body force terms are included in describing the dynamics of the cluster within the dashed region.

typical wall materials can be an important source for vibrationally-excited hydrogen, the statistical analysis of a much larger number of runs is needed, and this work is in progress. Additionally, an improved molecular dynamics code containing multi-body force terms is being written that will provide a more realistic approach to these dynamic processes. Calculations of the sputtering of occluded hydrogen are also currently in progress. We are simulating both heavy and light ion bombardment in order to look for differences in the energy and angular distributions of the sputtered species.

SUMMARY

In the simulations of glancing collisions of H_2 with metallic surfaces, we have found the survival fraction of molecules to be significant and vibrotational excitation during the surface collision to be very likely. When comparison is made with our earlier calculations of the survival fraction after normal surface collisions, the survival rate appears consistent with a strong dependence on the normal velocity component. The survival of a large neutral fraction, as predicted by our calculations, has been verified by experiment. Simulations directed toward studying sputtering and recombination

desorption of H and D atoms from metal surfaces have shown the ready formation of atomic and excited molecular species, thus identifying mechanisms affecting their concentrations in plasmas.

REFERENCES

1. A. M. Karo, J. R. Hiskes, and R. J. Hardy, J. Vac. Sci. Technol. A3(3), 1222 (1985).
2. J. R. Hiskes, A.M. Karo, M. Bacal, A. M. Bruneteau, and W. G. Graham, J. Appl. Phys. 53 (5), 3469 (1982).
3. J. R. Hiskes and A. M. Karo, AIP Conference Proceedings No. 111, (American Institute of Physics, New York, 1984), p. 125.
4. J. R. Hiskes and A. M. Karo, AIP Conference Proceedings No. 111, (American Institute of Physics, New York, 1984), p. 3.
5. A. M. Karo, J. R. Hiskes, K. D. Olwell, T. M. DeBoni, and R. J. Hardy, AIP Conference Proceedings No. 111, (American Institute of Physics, New York, 1984), p. 197.
6. B. Willerding, W. Heiland, and K. J. Snowdon, Phys. Rev. Lett. 53, 2031 (1984).
7. P. R. Scott and W. G. Richards, J. Chem. Phys. 63, 1690 (1975).
8. R. A. Johnson, Phys. Rev. 134A, 1329 (1964).