Velocity distributions of molecules ejected in laser ablation

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Based on the results of molecular dynamics simulations, we propose an analytical expression for the velocity distributions of molecules ejected in laser ablation. The Maxwell-Boltzmann distribution on a stream velocity, commonly used to describe the measured velocity distributions, is modified to account for a range of stream velocities in the ejected plume. The proposed distribution function provides a consistent description of the axial and radial velocity distributions. The function has two parameters that are independent of the desorption angle and have clear physical meaning, namely, the temperature of the plume and the maximum stream velocity or velocity of the plume propagation. © *1997 American Institute of Physics.* [S0003-6951(97)03330-5]

Two important applications of laser ablation are in mass spectrometry and thin film deposition. In mass spectrometry laser ablation of organic material has become an established method for producing intact molecules and molecular ions in the gas phase.[1] Film synthesis by pulsed laser deposition has opened up wide opportunities for producing new and artificially-structured materials and coatings.[2] For both of these applications, the velocity distribution of the ablated molecules is an important characteristic for determining the resolution of the mass spectra or the structural quality of the deposited film. There is no clear understanding, however, of the physical processes leading to the observed velocity distributions and the high maximum kinetic energies of the ejected particles. In particular, confusion persists as to the equation that should be used to describe the experimental data, as well as to the interpretation of the fitting parameters in the equation.

The velocity distributions of the ablated particles are commonly described in terms of a Maxwell-Boltzmann distribution function on a stream velocity, $N(v,T,u)$:[3–9]

$$dN(v,T,u) = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left\{-\frac{m[v_x^2+v_y^2+(v_z-u)^2]}{2kT}\right\} \times dv_x dv_y dv_z, \quad (1)$$

where m denotes the particle mass, v_x, v_y, and v_z are the velocity components and k is Boltzmann's constant. An offset or stream velocity, u, is used to account for the forward emission of ablated material in the z direction. Equilibration in the moving reference frame is assumed to occur and T is the equilibrium temperature of the plume. An additional fitting parameter, namely, the stream velocity u, allows reasonably good fits of experimental distributions observed in laser ablation experiments for a variety of systems, such as molecular solids,[3,5] polymers,[6,10] frozen gases,[7] insulators,[8] and metals.[9]

The problems, however, arise when one wants to correlate the temperatures and stream velocities from the fit with real physical quantities of the system. The association of the spread of translational energy along the direction of flow solely with the thermal motion can be misleading and yields an overestimated value for translational temperature.[3,7,11] Moreover, angular resolved measurements reveal that velocity distributions for off-normal angles could not be fit to Eq. (1) unless the fitting parameters, T and u, are chosen to be dependent on angle.[5,8] In one attempt to account for the angular dependence, an elliptical Maxwell-Boltzmann distribution with three independent parameters (radial and axial temperatures and a stream velocity) has been proposed.[8,12] Since a physical interpretation of the two different temperatures is lacking, the temperatures and stream velocity have to be considered, however, only as fit parameters and cannot be directly correlated with the real physical characteristics of the ablated plume.

A detailed understanding of the elementary processes in the irradiated material leading to ablation, as well as the interactions in the plume occurring after the ejection events, is essential for characterization of the final velocity distribution. Recently, a breathing sphere model for molecular dynamics simulations of laser ablation has laid the foundation for delineating the microscopic and mesoscopic physical mechanisms responsible for the onset of laser ablation.[13] The laser induced pressure and a phase explosion due to overheating of the irradiated material are identified as the key processes that determine the dynamics of laser ablation. In agreement with experimental observations, the model reproduces the strongly forwarded emission and high (500–1500 m s) maximum velocities of the ablated material. In the present letter, we analyze the factors that define the precise shapes of the velocity distributions in the ablated plume. This analysis leads to a new analytical expression for the description of the velocity distributions of the ejected molecules in laser ablation. Moreover, the parameters are angle independent and have clear physical interpretation.

The simulation of laser ablation of a molecular solid is performed using a breathing sphere model that has been described in detail elsewhere.[13] Briefly, the molecules are represented by spherical particles interacting with each other *via* a pair potential. All vibrational modes of a given molecule are approximated by one internal breathing degree of freedom. This approximation permits a significant expansion of the time- and length-scales of the simulation, yet allows one to reproduce a realistic rate of energy relaxation of excited molecules. The results presented in the present letter are ob-

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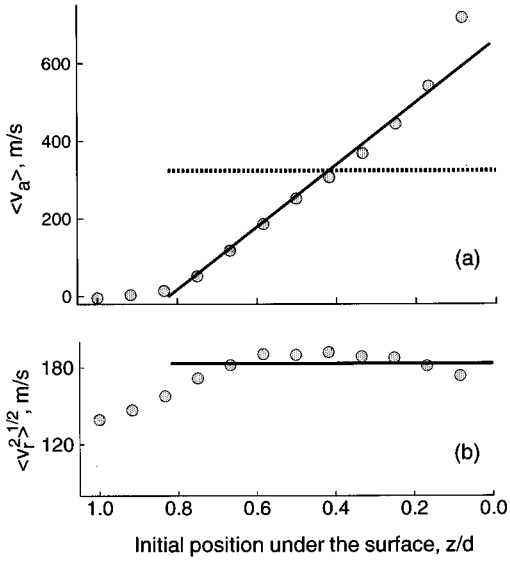

FIG. 1. Mean axial velocity $\langle v_a \rangle$ and root mean square radial velocity $\langle v_r^2 \rangle^{1/2}$ of molecules as a function of their initial position under the surface, z, relative to the laser penetration depth, d. Points represent the velocities at 500 ps after the laser pulse. Solid lines show the approximations used in derivation of Eq. (2). The dashed line shows the approximation of a single stream velocity u assumed in Eq. (1).

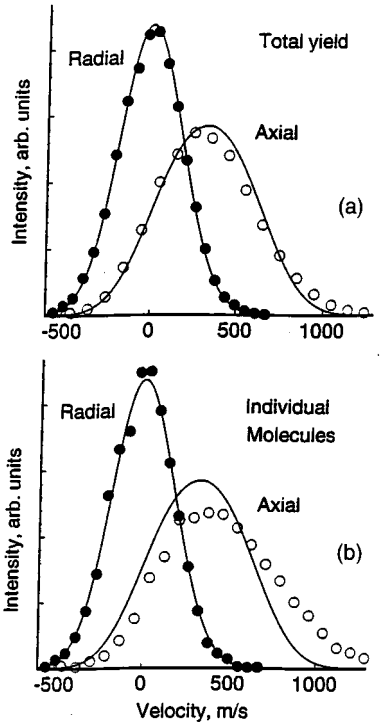

FIG. 2. The distributions of the velocities in the axial and radial directions. The points are data from the simulation and the curves are obtained using Eq. (2) with $T=400$ K and $u_{\max}=650$ m/s. Data points for the total yield (a) and individual molecules only (b) are shown.

tained for the two-dimensional version of the breathing sphere model. The parameters of the intermolecular potential are chosen to represent the van der Waals interaction between the molecules. A mass of 100 Daltons has been attributed to each particle. A computational cell of dimensions 81×210 nm (58 800 molecules) is used. Periodic boundary conditions in the directions parallel to the surface are imposed, thus the effects of the edges of the laser beam are neglected. The laser irradiation is simulated by vibrational excitation of molecules that are randomly chosen during the laser pulse duration. In this case, an implicit assumption is that the laser radiation is absorbed by the molecules and is internally converted to vibrational energy.[14] The vibrational excitations are performed by depositing a quantum of energy equal to the photon energy into the kinetic energy of internal vibration of the molecules to be excited. Laser pulses of 15 ps in duration at a wavelength of 337 nm are used in the simulations. The photon energy is scaled down by a factor of 2 in order to account for the lower cohesive energies in the two-dimensional system, as compared to the three-dimensional case. The simulation used in this work is one with a laser fluence that is $\sim$50% higher than the threshold fluence for ablation.[15]

The simulations clearly show that the dynamics of material ablation provide different ejection conditions for molecules, depending upon their original depth in the substrate. Moreover, there are collisions in the plume that tend to accelerate the motion of the molecules that ablate early, and consequently, slow down the molecules that ablate near the end. This picture hints that correlating average velocities with the original depth in the sample might delineate an appropriate velocity distribution. Figure 1 shows the axial (normal to the surface) and radial (parallel to the surface) velocity components of the ejected molecules as a function of their initial position under the surface. Each point in Fig. 1 represents an average over molecules that belong to a four monolayer thick slab of material located at different depths in the sample. For the entire depth of material ejected, there is nearly a linear dependence of the mean axial velocity on the initial position under the surface, Fig. 1(a). This observation suggests that the single flow velocity as assumed in Eq. (1) is a rather poor approximation. Actually, there is a range of stream velocities from zero up to a maximum value. The total velocity distribution, thus, might be a superposition of Maxwell-Boltzmann distributions with different stream velocities.

In contrast to the axial velocities, the radial velocities of the ejected molecules have no significant correlation with the initial position under the surface, Fig. 1(b). Since the radial component does not contain a contribution from a stream velocity, it appears to be associated with the thermal motion in the ejected plume. A root mean square radial velocity of 182 m/s, denoted by the solid line in Fig. 1(b), corresponds to a temperature of 400 K.[16] As shown in Fig. 2(a), a Maxwell-Boltzmann distribution with $T=400$ K accurately represents the radial velocity distribution of the ejected molecules. Thus, at least in the radial direction a single temperature can be used to describe thermal motion in the ejected plume.[17] As shown in Ref. 13, the final temperature of the ejected plume results from the fast cooling of the ejected material due to an explosive matrix disintegration in the ablation process and a slower gradual cooling during the plume expansion.

The results of molecular dynamics simulations discussed above suggest that the total velocity distribution in laser ablation can be described by one temperature but a range of

stream velocities. This approximation is denoted by the solid lines in Fig. 1.

The Maxwell-Boltzmann distribution, thus, has to be modified to account for the range of stream velocities. We integrate Eq. (1) over a range of stream velocities from zero to $u_{\max}$ and then normalize it to unity. The total velocity distribution of ejected molecules is then given by

$$dN(v,T,u_{\max}) = \frac{m}{4\pi kTu_{\max}} \exp\left\{ -\frac{m(v_x^2+v_y^2)}{2kT} \right\} \times \left\{ \operatorname{erf}\left[\sqrt{\frac{m}{2kT}}\, v_z \right] - \operatorname{erf}\left[\sqrt{\frac{m}{2kT}}\, (v_z - u_{\max}) \right] \right\} dv_x dv_y dv_z , \quad (2)$$

where erf is the standard error function.

The velocity distributions given by Eq. (2) for $T=400$ K and $u_{\max}=650$ m/s are shown in Fig. 2. As discussed above, the radial velocity distribution is well represented by a Maxwell-Boltzmann distribution at $T=400$ K. [Equations (1) and (2) are equivalent for the radial velocities.] The same temperature with a maximum stream velocity of 650 m/s ensures a good representation of the axial velocities as well, Fig. 2(a). A fit of the axial velocity data in Fig. 2(a) to Eq. (1), on the other hand, results in a temperature as high as 1000 K and an average stream velocity of $\sim$325 m/s.

There is a slight discrepancy between Eq. (2) and the data points for the axial velocity shown in Fig. 2(a). Namely, Eq. (2) underestimates the data at high velocities ($\sim$1000 m/s) and overestimates the data at velocities $\sim$500 m/s. These discrepancies are directly correlated with the deviations in Fig. 1(a) of the actual mean axial velocities from the linear approximation at $z/d \approx 0$ and $z/d \approx 0.3$, respectively. These deviations from linearity are due to collisions within the expanding plume that redistribute energy and momentum.[18]

The velocity distributions shown in Fig. 2(a) include all the particles that eject during the ablation event. As shown in Refs. 13 and 15, the plume consists of individual molecules as well as clusters of molecules. The distribution of cluster sizes with depth of origin is not uniform. Namely, individual molecules tend to originate closer to the surface and, thus, tend to have larger stream velocities. The clusters, on the other hand, tend to originate from deeper in the solid and, thus, tend to have smaller stream velocities. The precise fraction of individual molecules versus larger clusters depends on the fluence.[13,15] As an example of how the apparent velocity distributions might change, the axial and radial velocity distributions for individual molecules in this simulation are shown in Fig. 2(b). As stated above, the monomers tend to have larger stream velocities than the total distribution which leads to the high velocity tail[3] observed in axial distribution in Fig. 2(b). Additionally, ionization of a part of the ejecta at high laser fluences and interaction with background gases can lead to additional changes in the velocity profile.[2] In these cases, the analytical velocity distribution given by Eq. (2) should be viewed only as a new starting point in discussing more complex final distributions.

In conclusion, the results of the molecular dynamics simulation show that the average axial velocities of molecules ejected in laser ablation depend nearly linearly on their initial position under the surface. The Maxwell-Boltzmann distribution on a stream velocity has accordingly been modified to account for the range of stream velocities in the ejected plume. We find that both axial and radial total velocity distributions are well represented by the modified distribution, providing a consistent way to describe the complete velocity distribution with a single set of parameters. The two parameters of the proposed equation are independent of angle and have clear physical meaning, namely, the temperature that describes the thermal motion in the plume and the maximum stream velocity or velocity of the plume propagation in the direction normal to the surface.

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[16] The two-dimensional model has only one radial degree of freedom, thus, the root mean square radial velocity of the particles is related to temperature by $\langle v_r^2 \rangle^{1/2} = (kT/m)^{1/2}$.
[17] The equilibration of the plume at $\sim$400 K has been monitored by plotting the radial velocity distributions for the same subsets of particles as used for the points shown in Fig. 1. The individual distributions are, in fact, Maxwell-Boltzmann distributions at 400 K within the limited statistical accuracy of the smaller number of particles.
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