Expansion of Laser-Generated Plumes Near the Plasma Ignition Threshold

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Expansion of laser-produced plumes on a solid–vacuum interface during and after the laser shot was investigated theoretically, incorporating several new features into our previous one-component one-dimensional hydrodynamic model. Time development of density, velocity, temperature, and pressure profiles was calculated at laser irradiances below and above the plasma ignition threshold. The estimated velocity of ions released from the plume was close to the measured values. The fast spreading of the blow-off material under the laser vaporization regime and the long lifetime of the relatively compact plasma core above the ignition threshold were predicted in agreement with experimental observations. Calculated surface recession due to evaporation provided a lower bound to the measured crater depth, whereas the calculated melt depth proved to be a realistic upper limit.

INTRODUCTION

When a high-power laser pulse is focused onto a solid surface, the irradiance in the focal spot can lead to rapid local heating, intense evaporation, and degradation of the material.

In analytical chemistry several exploited and potential uses of such processes exist. Most eminent among them is its application in mass spectrometry as an ion source in a vacuum environment (1–3). Further possibilities lie with the utilization as an optical emission source (4) or as a universal tool for sampling solids (5–8). Laser heating of the solid surface and of the induced plume leads to the generation of different chemical species. Ion–molecule reactions are among the favored reaction channels for producing ions which contribute to the variety of important lines in the mass spectra (12). Protonation and alkalination reactions are often the sources of the most characteristic species in the ion cloud (13).

Increasing the energy deposition into the sample the surface temperature reaches a point where material transfer across the surface is negligible (Figure 1a). In this regime the amount of material transport across the surface becomes significant (Figure 1b). Laser heating of the solid surface and of the induced plume often offer advantages in analysis, like for example the application of time of flight ion analyzers. Easy tuning of the delivered energy amount and the possibility of localized sampling supplement the list of benefits.

The difficulty related to laser excitation is that the sample has to absorb the light at the particular wavelength, a prerequisite often met in the ultraviolet region. Further problems are the high cost and complexity of the laser systems and the poor understanding of laser-induced processes. Both of these shortcomings are likely to improve in the near future. In this paper we will try to unveil some of the underlying processes of laser–target interaction in a vacuum environment.

It is well known from mass spectrometric investigations that the amount and ionization degree of the vaporized material depend on the energy deposited into the target. The different regimes of laser ionization, laser desorption, laser vaporization, and laser plasma ionization are characterized by the amounts of deposited energy. The different regimes require different descriptions, because each has its distinctive features determined by a dominating process or several competing processes.

The most common mechanism of laser desorption is a thermally activated process induced by surface heating of the sample (11). In this regime the amount of material transport across the surface is negligible (Figure 1a). Laser heating of the solid surface and of the induced plume leads to the generation of different chemical species. Ion–molecule reactions are among the favored reaction channels for producing ions which contribute to the variety of important lines in the mass spectra (12). Protonation and alkalination reactions are often the sources of the most characteristic species in the ion cloud (13).

Increasing the energy deposition into the sample the surface temperature reaches a point where material transfer across the surface becomes significant (Figure 1b). In the experiments observable target erosion appears in the form of craters (14). In theoretical terms it means that the energy balance equation has to be supplemented by the balance equations for mass and momentum. The flow, the heating, and the expansion of the evaporated target material are governed by the equations of hydrodynamics (15–17). Solving the coupled partial differential equations of the conservation laws provides
RAPID VAPOR FORMATION AT HIGH TEMPERATURES CAUSES SIGNIFICANT SORBED ENERGY TO BE DEVOTED TO THE HEAT OF VAPORIZATION. ALTHOUGH TIN CASES OF LASER THERMAL ABLATION, THE SURFACE TEMPERATURE CONTINUES TO RISE UNTIL EVAPORATION COMMENCES. PART OF THE AB- LATIONS ARE EXPULSED FROM THE MOLTEN SURFACE LAYER AND EJECTION CONTINUES FOR AS LONG AS SEVERAL HUNDRED MICROSECONDS.

HYDRODYNAMIC EFFECTS IN WHICH DROPLETS AND PARTICU- LATES ARE EXPULSED FROM THE MOLTEN SURFACE LAYER ARE IMPORTANT. EXPANSION OF THE HOT CLOUD OF PARTICLES CONTINUES AFTER LASER HEATING HAS CEASED, AND THE PLUME STARTS TO COOL DOWN, LEADING TO RECOMBINATION. ATOMIC EMISSION SPECTROSCOPY IS BASED ON THE LINE EMISSION EMERGING FROM VARIOUS PHASES OF THE EXPANDING PLUME, INCLUDING PHASES TOWARDS THE END OF THE LASER PULSE.

Figure 1. Different regimes of laser-target interaction under vacuum. In laser desorption (a) material transport across the surface is negligible. Laser volatilization (b) is characterized by considerable transport of mass, momentum, and energy and occasional plasma formation.

METHODOLOGICAL CONSIDERATIONS

METHODS OF CALCULATION

In order to study pulsed-laser heating and evaporation of solids, we constructed a one-dimensional model consisting of two parts: the first dealt with the heating and melting of the target and predicted the temperature, density, and flow velocity of the particles emerging on the liquid-vapor interface, whereas the second followed the expansion of the plume expelled from the surface. In the following sections we present the framework of the calculations.

(a) Heating, Melting, and Vapor Formation. Let us consider a pulsed laser beam impinging perpendicularly on the solid surface. If the beam diameter is much larger than the thermally affected thickness of the solid, the diffusion of the absorbed laser energy can be described by the one-dimensional heat conduction equation with a source term:

\[ \frac{\partial T(x,t)}{\partial t} + \frac{1}{\alpha}(\frac{\partial}{\partial x} + \frac{\partial^2 T(x,t)}{\partial x^2}) = \frac{I(x,t)}{K} \]

where \( T \) denotes the temperature inside the solid, \( x \) is the position measured from the surface, \( t \) is the time, and \( K \), \( \alpha \), \( c_p \), and \( \rho \) stand for the thermal conductivity, heat capacity, absorption coefficient, and mass density, respectively. \( I(x,t) \) is the laser irradiance which, assuming a homogeneous absorbing medium, can be written as

\[ I(x,t) = I_0(t)(1 - R) \exp(-\alpha x) \]

Here \( I_0(t) \) is the incident laser irradiance and \( R \) is the reflectivity of the surface.
Reliable experimental data on the reflectivity of hot surfaces are rather scarce, although there is strong evidence that in the case of metals the infrared reflectivity drops sharply with increasing temperature whereas the change is less pronounced in the UV domain (19, 20, 28). It is usually assumed that for long wavelengths the temperature dependence of reflectivity can be related to that of the dc conductivity, $\sigma(T)$, through the following expression:

$$1 - R(T) = \left[1 - R(T_0)\right] \frac{\sigma(T_0)}{\sigma(T)} \tag{3}$$

where $R(T_0)$ and $\sigma(T_0)$ are the free-electron part of the reflectivity and the dc conductivity of the solid (19).

In order to deal with phase transitions during the heat transfer and to cope with temperature-dependent optical and thermal parameters, eq 1 had to be solved numerically. The finite difference method we employed was similar to the one described by several authors (29-31).

Assuming thermally activated surface vaporization, the flux of atoms crossing the liquid–vapor interface is determined by the actual surface temperature, $T_s$, and can be approximated by

$$j(T_s) = A p v \sqrt{\frac{2}{\pi}} M R T_s \tag{4}$$

where $M$ is the molecular mass of atoms, $R$ is the gas constant, and $p(T_s)$ is the equilibrium vapor pressure (19). The sticking coefficient, $A$, is usually taken to be close to unity in the case of metals. An expression for the temperature dependence of the equilibrium vapor pressure can be obtained by integrating the Clausius-Clapeyron equation:

$$p(T) = p_0 \exp\left(\frac{\Delta H_v}{RT} - \frac{T_0}{T}\right) \tag{5}$$

where $\Delta H_v$ stands for the heat of vaporization and $T_0$ is the boiling point at the ambient pressure $p_0$. The amount of heat devoted to the vaporization and the thickness of the layer evaporated during the time interval, $\Delta t$, are expressed as

$$\Delta Q_{\text{evap}} = j \Delta H_v \Delta t \tag{6}$$

$$\Delta x_{\text{evap}} = \frac{j M \Delta t}{\rho} \tag{7}$$

The initial velocity distribution of particles which come off the surface can be regarded as a half-range Maxwellian; i.e., the velocity component normal to the surface can have non-negative values only (32). The flow velocity of the vapor appearing above the liquid surface can be approximated by the average of the normal velocity component (32):

$$\bar{v}_n = \sqrt{2kT_s/nm} \tag{8}$$

where $k$ is the Boltzmann constant and $m$ is the mass of an atom.

The main source of positive ions at the onset of vaporization is the thermionic emission from the heated surface, generally described by the so-called Langmuir–Saha equation (38):

$$n_1 = \frac{e^{E_1 - \phi}}{kT} \tag{9}$$

where $n_0$ and $n_1$ are the number densities of neutrals and singly charged ions, respectively, $E_1$ is the first ionization potential, and $\phi$ is the electronic work function.

(b) Vapor Expansion and Plasma Generation. As target heating continues and the plume develops with continuously increasing density and temperature, the collisions between particles become frequent enough that the hypothesis of local thermal equilibrium for the individual volume elements can be adopted. This means, that, in a sufficiently small region of the plume, thermal equilibrium is established between electrons, ions, and neutrals; that is, they can be characterized with a common temperature and the Saha–Eggert equation can be utilized for calculating electron, ion, and neutral densities. We consider a quasi-neutral plasma of one chemical element consisting of electrons, atoms, and ions with charge number $z$, ranging from $z = 1$ to $z = z_{\text{max}}$. Only thermal ionization due to energetic collisions in the plasma was considered, other processes like charge exchange, excitation, cluster formation, etc. were not included in the model.

Neglecting the possible depression in ionization potentials and the difference between the partition function of ions and neutrals, we can write for each ionization step an appropriate Saha–Eggert equation:

$$\frac{x_{z-1}}{x_z} = \frac{1}{n} \frac{2 \pi m k T^{3/2}}{h^3} \exp\left(\frac{E_z}{kT}\right) \tag{10}$$

where $h$ stands for the Planck constant and $E_z$ is the ionization energy of the species with a charge number $z - 1$. The local number density, $n$, is given by $n = \mu / m$; $\mu$ is the mass density of the plasma, $m_e$ is the electron mass, and $x_z$ and $x_0$ are defined as $x_z = n_z / n$ and $x_0 = n_0 / n$.

Supplementing eq 10 with the conservation of matter

$$x_0 + x_1 + x_2 + \ldots + x_{z_{\text{max}}} = 1 \tag{11}$$

and with the conservation of charge

$$x_1 + 2x_2 + \ldots + z_{\text{max}} x_{z_{\text{max}}} = x_0 \tag{12}$$

we obtain a complete set of equations from which the local densities of each component can be obtained. The Newton–Raphson method (33) was used to solve this strongly nonlinear system of equations, ensuring fast and reliable convergence during the iteration.

For the sake of simplicity we neglect the radial thinning of the plume, which is a good approximation if the diameter of the laser focal spot is commensurable or especially if it is much larger than the distance left behind by the plume during the time of investigation. To follow the expansion of the vapor, we then have to solve the one-dimensional equations of hydrodynamics expressing the conservation of mass, momentum, and energy, respectively:

$$\frac{\partial \rho}{\partial t} - \frac{\partial (\rho v_n)}{\partial x} = 0 \tag{13}$$

$$\frac{\partial (\rho v_n)}{\partial t} - \frac{\partial (\rho v_n^2)}{\partial x} = -\frac{\partial p}{\partial x} + \rho a_{\text{rad}} \tag{14}$$

$$\frac{\partial}{\partial t}\left[\rho\left(e + \frac{v_n^2}{2}\right)\right] = \frac{\partial}{\partial x}\left[\rho (e + P) + \frac{v_n^2}{2}\right] + \alpha \Phi - e_{\text{rad}} \tag{15}$$

Here $p$ denotes the local pressure, $\rho$ is the local internal energy density, $\Phi$ is the laser irradiance, and $\alpha$ and $e_{\text{rad}}$ are the linear light absorption coefficient and the radiation power loss emitted in the Bremsstrahlung process, respectively. If the electrons have a Maxwellian distribution of velocities, the total amount of energy emitted per unit volume per unit time is (34)

$$e_{\text{rad}} = \left(\frac{2\pi k T}{3m_e}\right)^{1/2} \frac{32\pi e^6}{3m_e^2 c^3} n_e \sum_{z=1}^{z_{\text{max}}} x_z e z \tag{16}$$

where $e$ is the electron charge, $c$ is the velocity of light, and $g_z$ stands for the Gaunt factor, which is usually close and has been taken equal to unity in our calculations. Assuming that the plasma follows the ideal gas rule, the relation of pressure and internal energy density to the state variables can be written in the form

$$p = (1 + x_0) \rho kT/m \tag{17}$$

$$\rho e = \frac{\rho}{m} \left(\frac{3}{2} + (1 + x_0) kT + \sum_{z=1}^{z_{\text{max}}} (E_z \sum_{z=1}^{z_{\text{max}}} x_z)\right) \tag{18}$$
where \( E_g \) is the \( g \)th ionization energy.

As it was mentioned earlier, transition between laser vaporization and plasma ignition shows threshold behavior and drastic differences can be observed in characteristic features of the plumes generated under the two different regimes. This threshold behavior can be explained by the onset of a feedback mechanism in the absorption of the plume which turns the almost completely transparent vapor into a strongly absorbing, opaque plasma.

Absorption of heated gases that have no molecular absorption bands can be attributed mainly to free–free transitions of electrons in the field of neutrals or ions. Photoionization of excited species may have important contribution only in the case of UV lasers and in the presence of species with low ionization potential (35). Preceding plasma ignition, the plume consisting of largely neutral atoms, interacts with the laser mainly through electron–neutral inverse Bremsstrahlung processes. For this process the absorption coefficient is given by

\[
\alpha_{e,n} = \left[ 1 + \exp\left( -\frac{h\nu}{kT} \right) \right] \frac{Q \rho n_e}{n_0} \tag{19}
\]

where \( \nu \) is the laser frequency, \( T \) is the local plume temperature, \( n_e \) and \( n_n \) are the electron and neutral number densities, and \( Q \) is the cross section of the photon absorption (36). As the vapor temperature and hence the number of charged particles increases, the electron–ion inverse Bremsstrahlung process becomes dominant. The absorption coefficient in this case can be written as follows (34, 36):

\[
\alpha_{e,i} = \left[ 1 - \exp\left( -\frac{h\nu}{kT} \right) \right] \frac{4e^2n_e}{3h\nu^2m_e} \left( \frac{2\pi}{3m_e kT} \right)^{1/2} \sum_i z_i^2 n_i g_i \tag{20}
\]

Equations 5 and 8 completed with the assumption that the vapor temperature at the liquid–gas interface is equal to the actual surface temperature served as boundary conditions for the equations of hydrodynamics. Numerical solution of the problem was based on a finite difference approximation of eqs 13–15 utilizing the scheme of Godunov (37). Details of the algorithm were discussed elsewhere (16).

### RESULTS AND DISCUSSION

Calculations were carried out for the ruby laser–copper interaction at 30 J/cm² and at somewhat lower, 36 J/cm², laser energy densities. The temporal intensity profile of the laser pulse, \( I(t) \) in eq 1, was approximated by Gaussian distribution of 30-ns full width at half-maximum (see dashed curve in Figure 4). Although the numerical solution of eq 1 enabled the accurate temperature dependence of the thermophysical parameters to be considered, we made distinction only between the solid and the liquid phase, each characterized by one set of thermal parameters, as it is displayed in Table I.

In eq 15 the absorption coefficient, \( \alpha \), was approximated by the sum of the electron–neutral and electron–ion inverse Bremsstrahlung coefficients given by eqs 19 and 20. Surface reflectivity was calculated according to eq 3 on the basis of dc conductivity and on other data (19, 38–40). In the plasmas, formation of singly and doubly charged copper ions (ionization potentials \( E_{Cu} = 7.726 \text{ ev} \) and \( E_{Cu^+} = 20.29 \text{ ev} \)) was investigated.

Results referring to the trailing edge of the laser pulse (70 ns) are presented in Figures 2 and 3, for 30 and 36 J/cm² laser fluences. The conspicuous difference in the calculated density, velocity, temperature, and pressure profiles points to the difference in the position of energy deposition.

Below the plasma ignition threshold, the blow-off material remains transparent as long as the laser is on. Therefore the laser can reach the metal surface without appreciable attenuation where a fraction of its energy is absorbed while the rest

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**Table I. Thermophysical and Optical Parameters of Copper Used in Our Calculations**

<table>
<thead>
<tr>
<th>Property</th>
<th>Solid</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity, ( W/(m K) )</td>
<td>380</td>
<td>170</td>
</tr>
<tr>
<td>Specific heat, ( J/(kg K) )</td>
<td>420</td>
<td>494</td>
</tr>
<tr>
<td>Density, ( kg/m³ )</td>
<td>8900</td>
<td>7800</td>
</tr>
<tr>
<td>mp, K</td>
<td>1356</td>
<td></td>
</tr>
<tr>
<td>( \Delta H_{fusion} ), ( \text{kJ/mol} )</td>
<td>13.0</td>
<td>304.8</td>
</tr>
<tr>
<td>Reflectivity at 300 K</td>
<td>0.975</td>
<td>7.44 x 10⁷</td>
</tr>
</tbody>
</table>

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**Figure 2.** Calculated density (a), velocity (b), temperature (c), and pressure (d) profiles at 70 ns. The laser energy fluence was 30 J/cm². The dashed curve in b corresponds to the local sound velocity defined by eq 21.

**Figure 3.** Calculated density (a), velocity (b), temperature (c), and pressure (d) profiles at 70 ns. The laser energy fluence was 36 J/cm². The different lines in a correspond to different species: (—) \( Cu \); (— —) \( Cu^+ \); (— — —) \( Cu^{2+} \). The broken line in b represents the local sound velocity defined by eq 21.
is reflected and lost as far as the laser ablation process is concerned. The temperature of the expanding plume never exceeds the surface temperature, and in the vapor thermal ionization is almost completely absent. The plume expands into the vacuum, and its flow becomes supersonic; i.e. the flow velocity exceeds the local velocity of sound, defined as

\[ \nu_s = \sqrt{\gamma kT/m} \]  

where \( \gamma = 5/3 \) for a gas consisting of atomic species.

In the high-fluence case, the energy delivered to the plume through electron-neutral inverse Bremsstrahlung processes was enough to elevate the temperature close to the surface value, giving rise to high electron density as well as intense light absorption.

In Figure 4 the comparison of maximum flow velocities as a function of time indicates that streaming velocities were almost identical for low- and high-energy fluences until the onset of plasma formation.

In the high-fluence case, at about 50 ns a transition period starts leading to the rapid growth of the plasma, which is apparent from the steep rise in the flow velocity. After breakdown, the incident laser energy is completely deposited into the plasma, increasing its velocity to about \( 2.4 \times 10^7 \text{ cm/s} \), whereas at \( 30 \text{ J/cm}^2 \) the expansion velocity remains about one-eighth of this value due to the lack of direct plume heating.

As it is apparent in Figure 3a and c, a highly ionized, hot layer is formed at the plasma front in which the temperature exceeds \( 10^5 \text{ K} \) by the end of the laser pulse. These high temperatures result in the production of multiply charged ions. Depending on the local density and temperature the different regions are dominated by different species. Figure 3b and d illustrate the piling up of waves induced by laser heating in the absorption zone and the development of the shock wave driven by the dense, expanding plasma core.

Expansion of the plasma continues after the laser pulse has ceased, and plume properties change considerably during this additional flow. In order to elucidate some of these variations, we traced the expansion further in time.

Figures 5 and 6 show three selected stages of the evolution of density profiles for \( 30 \text{ and } 36 \text{ J/cm}^2 \) energy fluences, respectively. As time evolves the vapor detaches from the target and a bell-shaped density distribution develops, which drifts towards the vacuum. The motion of the blow-off material can be interpreted as the translation of the center-of-gravity accompanied by the expansion of the cloud.

The fast decay of the density distribution at \( 30 \text{ J/cm}^2 \) and the persistence of a relatively compact core at the higher energy fluence reflect that the relation between the propagation and expansion velocities is different below and above the plasma ignition threshold. Translation velocities are \( 1.5 \times 10^7 \text{ cm/s} \) and \( 1.3 \times 10^6 \text{ cm/s} \) for the low- and high-fluence cases, respectively. The expansion velocities estimated at the half-maxima of the density distribution curves are \( 2 \times 10^5 \text{ cm/s} \) below and above the ignition threshold.

Another feature of the plume formation is that the ratio of propagation and expansion velocities does not change during the postpulse period. It is worth noting that this kind of behavior corresponds to a steadily growing spherical plume in three dimensions drifting along the target normal. The laser blow-off material occupies a conical annular region, and the opening angle is determined by the ratio of the expansion and translation velocities. This observation is justified by laser beam deflection experiments on laser-generated plumes (41).

We indicated in Figures 5 and 6 the angle of a hypothetical cone in which a three-dimensional plume would be confined with the same expansion and translation velocities that were obtained in the calculations: \( \alpha = 100^\circ \) for the subthreshold situation, whereas \( \alpha = 30^\circ \) for the plasma ignition case.

Experimental evidence was adduced that laser-generated plasmas exhibit strong forward peaking; moreover, in certain
behavior resulted in low evaporated thickness, whereas in the higher fluence case the amount of material removed by evaporation was increased significantly due to the exponential dependence of evaporation rate on the surface temperature.

As it was discussed above, in pulsed-laser ablation experiments, the splashing of the melt due to vapor recoil is observed. If we assume that the melt is completely ejected before resolidification, the maximum and the melt depth curve serves as an upper limit for the measured value. This assumption is supported by measurements on copper where a 2.2 μm deep crater was produced by a 44 J/cm² irradiance Q-switched ruby laser pulse (28). Extrapolating our calculated maximum melt front position to this fluence, we obtain 2.6 μm, a fair estimate for the measured crater depth.

**CONCLUSIONS**

The diversity of phenomena occurring during laser ablation and the lack of reliable experimental data on the high-temperature behavior of solids compelled us not to make any pretense of describing laser–solid interaction in detail. We rather tried to find a simple model to account for pulse melting and vaporization of metals as well as for the absorption and ignition of the plume. The fair agreement between the calculated and measured ion velocities and the possible upper and lower limits for the crater depth, as well as the prediction of the plume propagation confined in a conical spatial region, indicate that laser vaporization and plasma ionization can be treated in the framework of the presented model.

Nevertheless, the general formulation of the problem makes it difficult to account for all the events of practical and theoretical interest during the laser–solid interaction. The applicability of the model at high irradiances could be stretched by taking into account more ionization steps, employing a more realistic equation of state, and possibly considering critical phenomena.

**LITERATURE CITED**

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