Back Flux for Pulsed Laser Evaporation into Vacuum

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Abstract. This paper proposes results on calculation of the back flux for the case of pulsed laser evaporation into vacuum. On the basis of the direct Monte Carlo simulation, one-dimensional plane expansion of vapor cloud was calculated for a wide range of the number of evaporated monolayers. A substantial back flux rise is observed if the rotational degrees of freedom are taken into account. Influence of relaxation collision number on the back flux is demonstrated. Computations that combine the laser-induced target heating calculation and the direct Monte Carlo simulation of vapor cloud expansion show an insignificant effect of the time evolution of the surface temperature on the back flux.

INTRODUCTION

Laser ablation of solids with nanosecond pulses of moderate intensity is widely used in modern technologies [1]. A laser pulse produces a cloud of ablation products. The evaporated particles can return back to the evaporation surface due to collisions in the vapor cloud. The intensity of this back flux depends on the amount of the evaporated substance. It can vary from zero for the collisionless expansion at desorption up to a value corresponding to a steady evaporation into vacuum. Molecules continue to return to the surface for a long time upon completion of the pulse, which results in a significant decrease of the evaporated mass.

Knowledge of the back flux value under pulsed evaporation is important for many laser ablation applications. For description of laser-induced heating and evaporation of solid with nanosecond pulses, thermal model is usually used [2, 3]. To correctly consider conditions at the target-cloud interface, the back flux value during evaporation is required. The post-pulse back flux value is important for comparison of calculated and measured mass of evaporated matter [4]. Pulsed laser evaporation is widely used for cleaning of different contaminated surfaces: spacecraft optical systems, astronomical telescope mirrors, painted artworks and antiquities, etc. [5, 6]. To estimate the effectiveness of contamination layer removal, it is important to know the post-pulse back flux value. Data on back flux value can be useful for development of the thin film deposition technique with off-axis configuration, when the target and substrate are located in the same plane [7].

Available data on the back flux value for steady evaporation are obtained on the basis of analytical solution of the Boltzmann equation [8 – 10] and by the direct Monte Carlo simulation [11, 12]. Value of the back flux after evaporation completion was obtained by an analytical solution of one-dimensional equations of ideal gas pulsed expansion into vacuum [13]. These data concern to the continuum regime, when a large amount of substance is evaporated. However, in works on surface laser cleaning, the amount of evaporated matter can be as small as several monolayers, which makes the above results hardly applicable. So the data on the back flux value in dependence on amount of evaporated matter are requisite.

The objective of this work is to determine the back flux on the basis of the direct simulation Monte Carlo (DSMC) method [14]. Since pulsed evaporation of a small quantity of material is accompanied by a non-equilibrium gas state, the DSMC is the most suitable method for this purpose. This work is an extension of earlier researches for monatomic particles modeled as hard spheres [4, 15]. The present paper gives the results about the influence of intermolecular potential on the back flux. Since polyatomic particles are abundant among photoproducts observed in ablation of polymers [16] and molecular solids [17], molecules with internal degrees of freedom should be considered. The probability for vibrational energy transfer is known to be very low compared to the probability for rotational energy transfer [18]. For a small amount of evaporated matter, cloud expansion leads to practically

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collisionless regime, and the molecules have no time for vibrational-translational energy transfer. Therefore the present simulation is limited by rotational freedom degrees only.

In real experiments, the target temperature and the flux of evaporated particles are not constant and depend on the laser pulse shape and the material properties. Several works were devoted to investigation of the influence of the surface temperature time evolution on the laser ablated flow characteristics [19 – 22]. However the obtained results do not allow to judge definitely about importance and necessity to consider this temperature evolution. In the present work, the influence of the surface temperature evolution on the back flux value is considered on the basis of conjugated calculation of laser-induced target heating and vapor cloud expansion.

## BACK FLUX DETERMINATION FROM DSMC CALCULATION

During pulse under the considered conditions of laser ablation (nanosecond pulse duration, laser radiation spot diameter of order of 1 mm) cloud expansion is practically one-dimensional. Later the cloud begins extending transversally, implying two-dimensionality of the problem. Since our interest is limited by determination of the total number of particles returning to the surface, whether to the irradiation spot or beyond it, one dimensional calculation can be used as a rough approximation.

The problem of particle evaporation from a surface with consequent expansion into vacuum is considered in one-dimensional approach. Particles are evaporated according to the diffusive law with energy corresponding to the surface temperature T_S. During time interval τ, particle flux Ψ_{VAP} is constant and equal to $\Psi_{VAP} = n_S u_T /4$, where n_S is the density of the saturated gas corresponding to the temperature T_S, $u_T = \sqrt{8kT_S/(\pi m)}$, m is the molecular mass, k is the Boltzmann constant. All backscattered particles recondense at the surface. To describe particle interaction, the hard sphere model and the Maxwell model [14] are used. Polyatomic particles with rotational degrees of freedom are considered. To account for rotational energy, the Larsen-Borgnakke model is used [14]. In this model, the number of rotational degrees of freedom j for considered molecules is prescribed. All collisions are classified as elastic or inelastic. The relaxation rate is determined by the relaxation collision number Z. The inverse of this number provides a fraction of collisions that are regarded as inelastic. If a collision is considered as inelastic, the total energy is reassigned between the translational and internal modes by sampling from the equilibrium distributions of these modes that are appropriate to the total energy of colliding molecules. The amount of evaporated matter and consequently the evaporation rate is directly connected with the number of evaporated monolayers $\Theta = \Psi \tau \Sigma$, where Σ is an area occupied by one particle at the surface. As a criterion, characterizing flow rarefaction, the Knudsen number $Kn = \lambda_0/(u_T \tau)$ can be used (λ_0 is the mean free path in the saturated vapor). For the hard sphere molecular model, this number is unambiguously connected with the number of evaporated monolayers as $Kn = 1/(16\sqrt{2}\ \Theta)$.

Particular emphasis has been placed on determination of the back flux value during time sufficient for the cloud to reach the substrate, i.e. time that is much longer than pulse duration τ. In the simulation, cloud expansion was followed up during time interval of $10^5 \tau$. During such a prolonged time, cloud expansion is characterized both by a considerable density decrease in the cloud core and by large parameter gradients at the cloud front. Therefore, an adaptive grid was used. The grid was built to make the cell size not exceeding 0.25 of the local mean free path. For construction of such a grid, preliminary calculations with a small number of particles and a large time step were performed. Based on the calculations, the spatial density profiles in different time moments were estimated and used for building the adaptive grid. Number of particles in calculations was up to 5,000,000.

The main considered characteristic of the back flux phenomenon is the back recondensed fraction β. At any time moment, it was defined as $\beta(t) = \dfrac{N_{BACK}(t)}{N_{VAP}(t)}$, where N_{VAP} is the total number of evaporated particles and N_{BACK} is the total number of particles back recondensed at the surface. Time evolution of back flux fraction β for monatomic particles for different values Θ is presented in Fig. 1. Calculations were performed for the number of evaporated monolayers $\Theta = 10^{-2} \div 10^3$. It is seen that for any $\Theta > 1$, β tends to a common limiting value of about 27.5%. It is worth noting that the maximum value of β during pulse corresponds to the back flux at stationary evaporation 16.3% [11]. After termination of evaporation, a sharp increase of β is observed. To demonstrate molecular model influence on the back flux, results both for the hard sphere model and the Maxwell model are presented. It is seen that the molecular model has a small effect on the back flux fraction, with the exception of case $\Theta = 1$. Since laser evaporation of large amount of matter ($\Theta > 1$) is of the most interest for real applications, for simplicity we will use the hard sphere model only in the all following calculations.
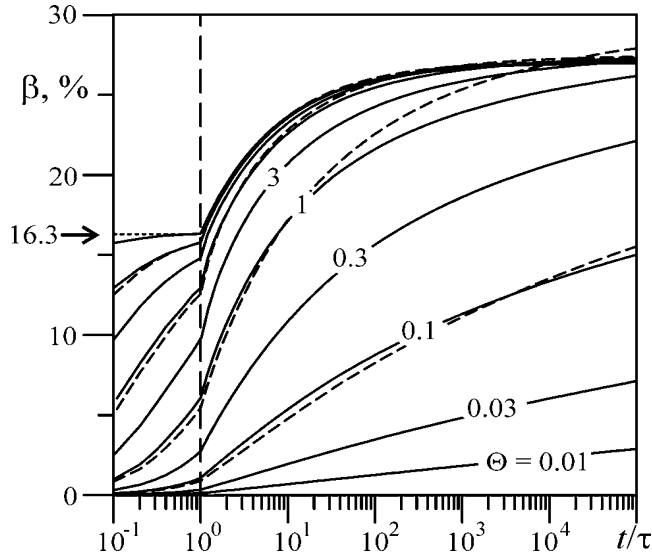
FIGURE 1. Temporal evolution of the back flux fraction β for various values of the number of evaporated monolayers Θ = 0.01, 0.03, 0.1, 0.3, 1, 3, 10, 30, 100, 1000 for monatomic particles for the hard sphere molecular model (*solid lines*) and the Maxwell model (*dashed lines*).
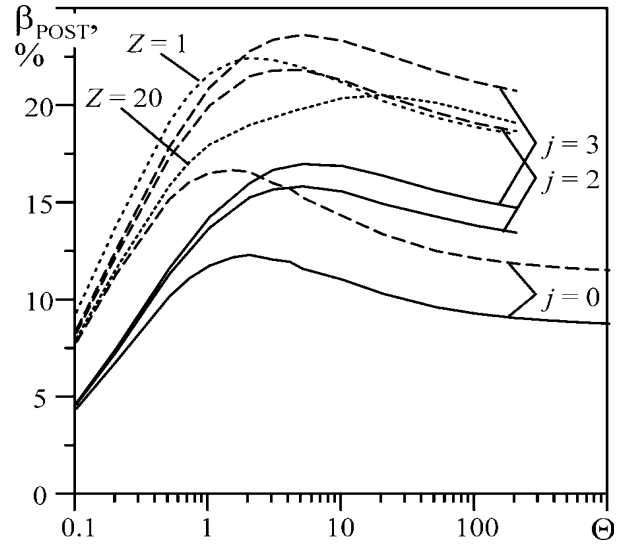
FIGURE 2. Post-pulse back flux fraction β_{POST} as a function of the number of evaporated monolayers Θ for the number of rotational degrees of freedom j = 0, 2, 3 with the relaxation collision number Z = 5 in time moments $t = 10\tau$ (*solid lines*) and $t = 100\tau$ (*dashed lines*). *Dotted lines* correspond to calculation for j = 2 with Z = 1 and Z = 20 in time moment $t = 100\ \tau$.

Particular attention was paid to the post-pulse back flux. The fraction of particles returned to the target after evaporation termination is defined as $\beta_{POST}(t) = \dfrac{N_{BACK}(t) - N_{BACK}(\tau)}{N_{VAP}(\tau) - N_{BACK}(\tau)}$. Dependence of β_{POST} on the number of evaporated monolayers is presented in Figure 2. The figure shows results for molecules with rotational energy (j = 2 and j = 3) for time moments $t = 10\ \tau$ and $t = 100\ \tau$. The time moment choice originates from the fact that difference of one-dimensional and two-dimensional calculations becomes noticeable starting with time moment $t = 10\tau \div 100\tau$, depending on the radiated spot size, the surface temperature, and the evaporated particle mass. For larger time, one-dimensional calculation gives some overestimated value of back flux due to disregard of lateral cloud expansion. So in Figure 2, back flux values are presented for these limiting cases showing bounds of β_{POST} variation, as applied to various laser ablation conditions. The dependence β(Θ) is not monotone with a maximum in the vicinity of Θ = 2. The maximum is obviously caused by a small back flux during evaporation and a large back flux after its termination (Fig. 1). For polyatomic particles, calculations were performed with the relaxation collision number Z = 5, as the representative one for rotational energy relaxation [18]. It is seen that rotational energy consideration leads to back flux increase nearly to double. To ascertain the relaxation collision number Z effect, calculations with Z = 1 and Z = 20 were carried out for the case of j = 2. The largest response is seen for Θ ≈ 2. With the evaporated particles number increase, the effect becomes negligible. It is worth noting that Z rise for Θ < 10 leads to decrease of back flux, whereas for Θ > 10, on the contrary, results in increase of back flux.

Similar results for the post-pulse back flux were obtained on the basis of an analytical approximation under the assumption of continuum cloud expansion [13] and on the basis of numerical solution of the Boltzmann equation for Θ ≈ 20 [23]. For example, in [23] for monatomic gas $\beta_{POST}(20\tau)$ ≈ 10%, and in the present work for Θ = 20 we have

TABLE 1. Values of the post-pulse back flux fraction β_{POST} in time moment t = 20 τ obtained by DSMC calculation (for Θ = 100 and Z = 1) and by an analytical solution of one-dimensional equations for pulsed expansion of ideal gas [13]

Number of internal degrees of freedom j	DSMC calculation	Analytical solution [13]
0	10.4	8.9
2	15.7	14
4	18.4	17

$\beta_{POST}(20\tau) = 11.5\%$. Table I shows good agreement between the back flux value β_{POST} from the DSMC calculations and from the analytical solution [13] for polyatomic gas expansion.

The post-pulse back flux value is particularly important for comparison of the experimental data with numerical results obtained by the thermal model. Often the evaporated mass is used for such a comparison. The model allows determining the mass after evaporation termination only, but in experiments the mass is measured at much longer time after the completion of cloud expansion. The resulted discrepancy of mass removal due to the post-pulse back flux can exceed 20% (Fig. 2), and its taking into account can be important for correct comparison.

COMBINED TARGET/CLOUD CALCULATIONS

To ascertain the influence of the time evolution of surface temperature on the back flux, we performed combined calculations consisting of two parts: description of laser-induced target heating on the basis of the well known thermal model of laser ablation [2, 3] and conjugated DSMC calculation of the forming vapor cloud expansion.

In the thermal model of laser-induced target heating and evaporation, one-dimensional heat conduction equation is solved

$$\left(c\rho + L_m\delta(T - T_m)\right)\left(\frac{\partial T}{\partial t} - u\frac{\partial T}{\partial x}\right) = \frac{\partial}{\partial x}\lambda\frac{\partial T}{\partial x} + (1-R)\alpha I(t)e^{-\alpha x} \qquad (1)$$

with the initial and boundary conditions

$$T(x,0) = T_0, \, T(0,t) = T_S(t), \, \lambda\frac{\partial T}{\partial x}\bigg|_{x=0} = \rho u L_V, \qquad (2)$$

where ρ, c, λ, α are the mass density, the thermal capacity, the thermal conductivity, and the absorption coefficient of the target material; T_m is the melting temperature; $R(T_S)$ is the reflection coefficient of the surface; $I(t)$ is the laser intensity; L_V is the latent heat of evaporation, L_m is the latent heat of fusion. The term $L_m\delta(T - T_m)$ allows to perform calculations of the solid-liquid interface. The velocity of the surface recession u is determined as

$$u(t) = \frac{m}{\rho}\left(\Psi_{VAP} - \Psi_{BACK}\right). \qquad (3)$$

Here Ψ_{VAP} is the flux of evaporated particles determined by the Hertz-Knudsen equation coupled with the Clausius-Clapeyron equation

$$\Psi_{VAP}(t) = \frac{p_B}{\sqrt{2\pi mkT_S(t)}}\exp\left\{\frac{L_V m}{k}\left(\frac{1}{T_B} - \frac{1}{T_S(t)}\right)\right\}, \qquad (4)$$

where T_B is the boiling temperature under pressure p_B. The back flux Ψ_{BACK} is determined directly from the DSMC calculation. It is connected with the back flux ratio β by the relationship $\beta(\tilde{t}) = \int_0^{\tilde{t}}\Psi_{BACK}(t)dt \bigg/ \int_0^{\tilde{t}}\Psi_{VAP}(t)dt$. The heat conduction equation was numerically solved by the finite difference method (details are presented in [24]).

Conjugation of the thermal model and DSMC is that for the heat-conductivity equation solution, the back flux is determined by the DSMC calculation, and, on the other hand, for the DSMC simulation, the surface temperature (which determines the number of evaporated particles and their initial energy) is taken from the thermal model calculation.

As the irradiated substance, graphite was chosen. For the thermal model calculations, thermophysical and optical properties of graphite were taken from [25], except for the latent heat of fusion (1 eV/atom from [26]). Calculations were performed for real Gaussian shape of the laser pulse with duration $\tau = 13$ ns (FWHM) [25]. The evaporated particles were supposed to be monatomic.

Let us consider laser fluence of $E = 2$ J/cm^2. For this case, the combined calculation gives the total amount of evaporated matter (without returned back particles) of $\Theta = 76.7$. To analyze boundary condition effect, calculations with constant flux of evaporated particles for $\Theta = 76.7$ were performed. Figure 3, *a* presents temporal evolution of the evaporation front velocity with separation of the back flux contribution. Figure 3, *b* shows evolution of the back flux fraction β and of the depth of evaporation, expressed in units of evaporated monolayers (ML). For the both calculations after evaporation termination, the surface recession velocity becomes negative. It indicates substantial post-pulse back flux, especially significant for the constant temperature calculation. Temporal evolution of back flux during the whole time of cloud expansion is presented in Figure 4. With time a small difference between back flux
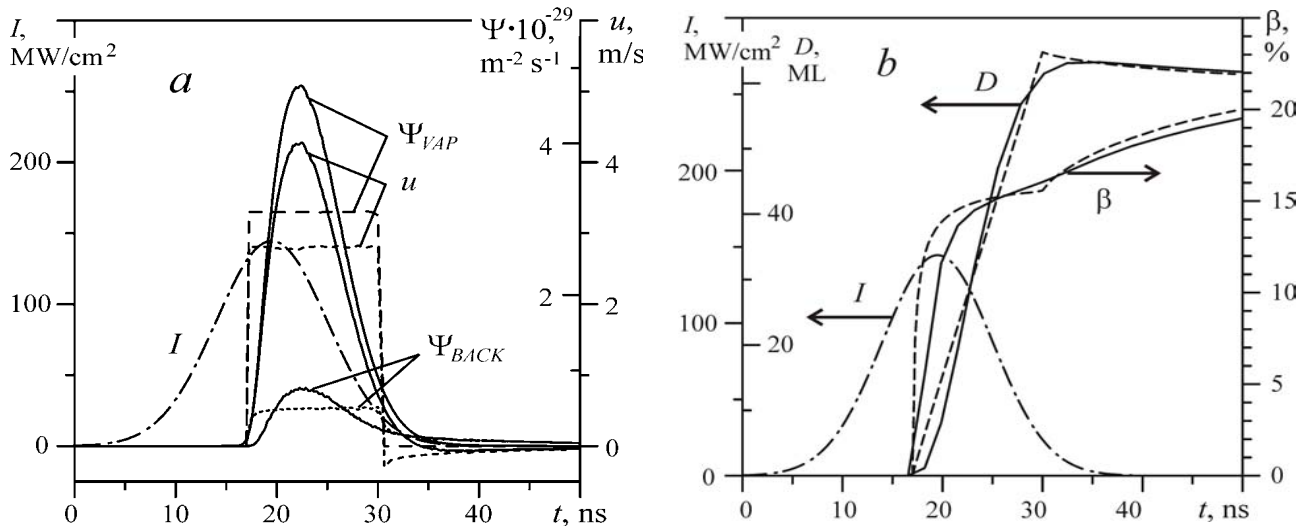
FIGURE 3. Temporal evolution of laser intensity I (*dash-dotted line*), flux of evaporated particles Ψ_{VAP}, back flux of particles Ψ_{BACK}, the velocity of the surface recession u (*a*), depth of evaporation D and back flux fraction β (*b*) for laser evaporation of graphite target with laser fluence $E = 2$ J/cm^2. *Solid lines* correspond to conjugated target/cloud calculation and *dashed lines* correspond to the DSMC calculation with constant flux of evaporated particles ($\Psi_{VAP} = $ const).
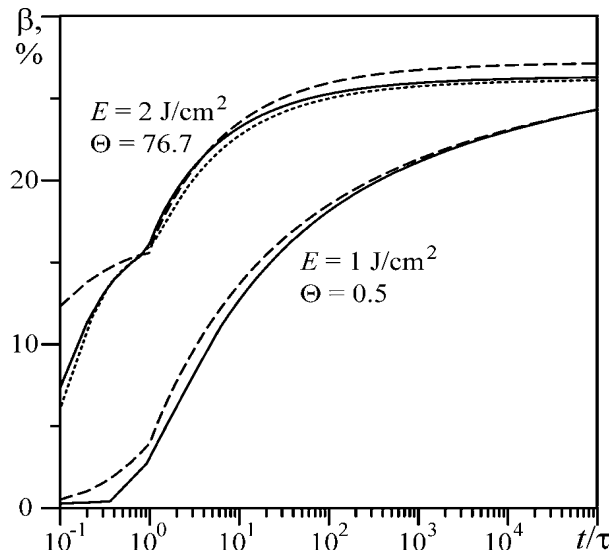
FIGURE 4. Temporal evolution of the back flux fraction β for laser fluence $E = 1$ J/cm^2 and $E = 2$ J/cm^2, obtained by combined calculations (*solid lines*), DSMC calculation with constant (*dashed lines*) and variable (*dotted line*) fluxes of evaporated particles and constant surface temperature.

for the combined calculation and the DSMC calculation appears (about 1% at $t = 10^5$ τ). To comprehend the difference origin, calculation with variable flux of evaporated particles was performed (but the surface temperature taken constant). The temporal evolution of the flux Ψ_{VAP} was set according to the sinusoidal law. For this case, the back flux is nearly identical to the back flux from the combined calculation. When a small amount of matter is evaporated ($\Theta = 0.52$ for $E = 1$J/cm^2), good coincidence of back flux values for constant and variable surface temperature cases was obtained (Fig. 4).

Based on these results, conclusion can be made about insignificant influence of surface temperature on the total amount of backscattered particles. This deduction correlates well with the known result that when simulating evaporation of 5 monolayers with constant and variable surface temperature, similar cloud parameters forms with time due to the interparticle collisions [21].

SUMMARY

On the basis of the direct Monte Carlo simulation, back flux under one-dimensional plane pulsed evaporation into vacuum for a wide range of evaporated matter amount is obtained. Negligible influence of intermolecular collision model is demonstrated. Consideration of rotational degrees of freedom results in almost doubled back flux. Combined calculations of laser-induced target heating with conjugated simulation of vapor cloud expansion demonstrated the insignificant influence of temporary evolution of the surface temperature on the back flux value.

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