Effect of temporal evolution of the evaporation surface temperature on the plume expansion under pulsed laser ablation

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Abstract. The effect of the temporal evolution of the evaporation surface temperature on the neutral plume expansion under pulsed evaporation into vacuum has been studied. Two-dimensional calculations have been performed based on the direct simulation Monte Carlo (DSMC) method. The Gaussian distribution of the temporal evolution of the surface temperature is assumed. The regimes with the constant and varying temperature of the evaporation surface have been compared. It is shown that for evaporation of more than ten monolayers the varying temperature leads to a considerable change in the plume dynamics with up to 9% decrease in the average energy of particles passing through a time-of-flight detector on the normal to the surface.

1. Introduction
Pulse laser ablation has numerous applications, such as thin film deposition, sampling for the analysis of substances, cleaning, processing and structuring of surfaces, synthesis of new nanomaterials, welding, cutting and drilling of substances, etc [1]. The dynamics of the plume expansion under pulsed laser ablation has been the subject of many theoretical works over the past 30 years. Typically, to simulate such flows, the direct simulation Monte Carlo (DSMC) method [2] or the numerical solution of the Boltzmann model equation are used.

In the simplest formulation of the study of gas-dynamic processes during laser ablation, it is assumed that the temperature of the evaporation surface is the same throughout the evaporation spot and does not change in time, and the corresponding particle flux from the surface is constant [3–9]. This approach, despite its simplicity, is quite plausible, since the main flux of the evaporating particles arises from the central part of the irradiated spot with a temperature close to maximum. The advantage of this model is that the number of parameters is only two (the number of evaporated monolayers and the evaporation spot radius), which facilitates the derivation of generalizing regularities of the dynamics of the gas expansion [8, 10].

In reality, the dynamics of evaporation is more complex, since the density of laser radiation, which determines the surface temperature, is unstable both in time and in space. For a theoretical analysis of real experimental data, it is important to correctly compare regimes with constant and variable surface temperatures. Given temporal evolution of the flux of evaporated particles from the heat conductivity equation, one can calculate the average evaporation rate and, knowing the total amount of evaporated matter, obtain the effective duration of evaporation. Recently, analytical models have been developed to determine the effective radius and depth of the evaporation spot [11], as well as the effective duration and temperature of evaporation [12]. The next step is to determine how the consideration of the spatial
nonuniformity of the surface temperature and its temporal evolution effects the dynamics of the plume expansion and the final distribution of particles in the space.

In this paper, we study the influence of the temporal evolution of temperature on the dynamics of the plume expansion during nanosecond laser evaporation into vacuum. Previously, the effect of varying surface temperature on flux of particles was investigated in the work [13] on the basis of the one-dimensional DSMC calculation for a special case of evaporation of 5 monolayers. In contrast to this work, we perform more correct two-dimensional calculations for a wide range of the parameters. It is assumed that the surface temperature linearly depends on the energy of laser radiation. The flow of evaporated particles from the surface is specified in accordance with previously developed analytical formulas under the assumption of the Gaussian distribution of laser radiation energy [12]. This paper analyzes both the dynamics of the plume expansion and the finally formed angular distribution of particles and the energy of particles passing through the time-of-flight detector located on the normal to the evaporation surface.

2. Model

The two-dimensional axisymmetric problem of pulsed evaporation from a spot with radius \( R \) into vacuum is considered. The Gaussian distribution of the laser radiation energy on the target surface is specified. A normal evaporation mechanism is proposed, corresponding to the thermal ablation model [14]. The modes of low-intensity laser radiation are considered when the absorption of laser radiation in the plume can be neglected. For a qualitative study of the effect of varying the surface temperature in time on the dynamics of the gas expansion, a simple model approach is proposed. It is assumed that the surface temperature linearly depends on the energy of laser radiation, i.e. under assumption of the Gaussian distribution of laser radiation energy we have

\[
T_S(t) = T_{\text{max}} \exp \left(-4 \ln 2 \left[ \frac{t-t_{\text{max}}}{\tau_{\text{hot}}} \right]^2 \right),
\]

where \( T_{\text{max}} \) is the maximum temperature of the surface, \( t_{\text{max}} \) is the time moment when \( T_S = T_{\text{max}} \), \( \tau_{\text{hot}} \) is the duration of the high-temperature stage of laser ablation. It was previously shown that this approach allows one to obtain data on the effective duration and temperature of evaporation, which are in good agreement with the results of calculations in the framework of the thermal model of pulsed laser ablation based on the solution of the unsteady heat conduction equation [12]. At each time moment, the temperature is assumed to be the same throughout the evaporation spot.

Alternatively, calculations have been carried out with the constant temperature of the surface \( T_{\text{const}} \). Let us define the dimensionless maximum surface temperature as

\[
D = \frac{kT_{\text{max}}}{mL_V},
\]

where \( k \) is the Boltzmann constant, \( m \) is the molecular mass, \( L_V \) is the latent heat of evaporation. Then the constant temperature \( T_{\text{const}} \) is related with \( T_{\text{max}} \) temperature as

\[
T_{\text{const}} = T_{\text{max}} A_2(D)/A_1(D),
\]

where

\[
A_1(D) = \int_0^\infty \frac{4^{3/2} \, dx}{\exp(16^{3/2}/D)}, \quad A_2(D) = \int_0^\infty \frac{dx}{\exp(16^{3/2}/D)} \quad [12].
\]

Similarly, the duration of evaporation with a constant temperature is determined by the formula

\[
\tau_{\text{const}} = 2\tau_{\text{hot}} A_2^2(D)/A_3(D),
\]

where

\[
A_3(D) = \int_0^\infty \frac{16^{3/2} \, dx}{\exp(16^{3/2} \cdot 2/D)} \quad [12].
\]

To simulate gas expansion, the implementation of the usual DSMC method is used [15]. In each time moment \( t \), molecules are evaporated with the energy corresponding to the surface temperature \( T_S(t) \). The
\[ \Psi = \frac{1}{4} n_S(t) u_T(t) = \frac{p_S(t)}{\sqrt{2kT_S(t)\pi n}} \]

where \( n_S \) and \( p_S \) are the density and pressure of the saturated gas corresponding to the temperature \( T_S \). \( u_T(t) = \sqrt{8kT_S(t) / (\pi n)} \) is the average thermal speed. The molecules are treated in the frames of the hard sphere model. All backscattered molecules which reach the evaporation surface are assumed to recondense on the surface. A monatomic gas is considered.

The problem with the constant temperature \( T_{\text{const}} \) is characterized by the evaporation depth and the evaporation spot radius \( R \). As a generally accepted measure of the evaporation depth, we use the number of evaporated monolayers

\[ \Theta = \Psi \tau \Sigma, \]

where \( \Sigma = \sigma / 4 \) is the area occupied by one molecule at the surface, and \( \sigma \) is the collision cross-section. The normalized spot radius is defined as

\[ b = R / (u_T(T_{\text{const}})\tau_{\text{const}}). \]

If we consider the problem with \( T_S \) changing in time temperature, we have to add the third parameter, \( D \) (2). The typical range of the number of evaporated monolayers is \( \Theta = 0.1 \div 100 \), while the typical normalized spot radius is \( b = 3 \div 30 \) and the normalized surface temperature \( D = 0.1 \).

Figure 1 presents an illustration of the considered model representation of pulsed evaporation. The illustration is based on the analysis of numerical calculation of nanosecond laser ablation of gold (11 ns FWHM, 1.5 J/cm²) in the framework of the thermal model of laser ablation [12]. The calculated surface temperature evolution has been fitted by the Gaussian distribution (1). The calculated temperature is characterized by relatively steep heating and then gentle cooling, while the model Gaussian distribution is symmetrical with respect to the maximum temperature. However, in general, the model distribution agrees relatively well with the calculated one in the range of the effective evaporation, when \( TS > 0.6 \) Tconst. Given the temporal evolution of the surface temperature TS, we can analytically calculate the flux of evaporated particles (figure 1b).
3. Dynamics of plume expansion

Figure 2 shows the density profiles along the normal to the evaporation surface for the number of evaporated monolayers $\Theta = 1$ and 30 for the same spot size $b = 10$. The density is normalized to the density $n_{\text{const}}$ of the saturated gas corresponding to the temperature $T_{\text{const}}$. At the initial stage of expansion, up to time $t = 3 \tau_{\text{const}}$, the dynamics of gas expansion for $\Theta = 1$ and 30 is qualitatively the same. After the completion of evaporation, the density corresponding to the constant surface temperature $T_{\text{const}}$ is higher than with the varying temperature $T_S$ (see $t = 1.5 \tau_{\text{const}}$, figure 2b). Accordingly, gas with constant evaporation expands faster, and by time $t = 3 \tau_{\text{const}}$ the density profiles approach each other.

Then for $\Theta = 1$ and 30 there is a qualitative difference associated with different degrees of rarefaction of the regimes. Indeed, let us estimate the Knudsen number $Kn$ at time $t = 3 \tau_{\text{const}}$. Taking the plume length $\tilde{L} = L / R = 0.5$ and the average density $\tilde{n} = n / n_{\text{const}} = 0.04$, we get the Knudsen number

$$Kn = \frac{\lambda}{L} = \frac{\lambda_0}{\tilde{n} \tilde{L} u_T \tau_{\text{const}} b} = \frac{1}{16 \sqrt{2} \tilde{n} \tilde{L} \Theta b},$$

(7)

where $\lambda$ is the mean free path in the plume, and $\lambda_0$ is the mean free path corresponding to the density $n_{\text{const}}$. For $\Theta = 1$ we have $Kn \approx 0.2$, while for $\Theta = 30$ there is $Kn \approx 0.007$. With further expansion, rarefaction rapidly increases due to the increasing lateral expansion of the gas.

Since the problem is non-stationary, the average number of collisions $N_C$ per molecule during the expansion is a similar, and more correct, measure of rarefaction. Typical data on the number of collisions

![Figure 2](image_url)

**Figure 2.** Density profiles along the normal to the evaporation surface for $\Theta = 1$ and 30 in time $t = 1, 1.5, 3, 10, 100 \tau_{\text{const}}$ (a-e) and the distribution of particles near the normal that move along the normal in time $t = 100 \tau_{\text{const}}$ (f) for the constant surface temperature $T_{\text{const}}$ and temperature $T_S(t)$ varying in time.
during pulsed gas expansion into vacuum can be found in the work [15]. For \( \Theta = 1 \) by time \( t = 5 \tau_{\text{const}} \), there is \( N_C = 6 \), and during the subsequent expansion, the particles experience no more than one collision. The regime of collisionless expansion is actually established, and the density profiles do not change anymore. Therefore, by time \( t = 10 \tau_{\text{const}} \), the density profile calculated for the constant temperature \( T_{\text{const}} \) is practically identical with the profile for the varying temperature \( T_S \).

On the contrary, for \( \Theta = 30 \) starting from the time \( t = 5 \tau_{\text{const}} \), the particles experience 23 collisions on average, which is accompanied by an additional elongation of the plume. In this case, the gas with the constant temperature \( T_{\text{const}} \) continues to expand more intensively, so that at time \( t = 10 \tau_{\text{const}} \) its density becomes lower than for the case with the varying temperature \( T_S \). During further expansion, up to a time \( t = 100 \tau_{\text{const}} \), the difference in profiles increases even more. Thus, as can be seen from figure 2e, if for \( \Theta = 1 \) we have practically the same density profiles, then for \( \Theta = 30 \) the plume with constant temperature \( T_{\text{const}} \) is more extended forward and less dense. It should be noted that the strong difference between the densities for \( \Theta = 1 \) and 30 at time \( t = 100 \tau_{\text{const}} \) is due to the fact that for \( \Theta = 1 \) the lateral expansion of the cloud begins much earlier than for \( \Theta = 30 \) [15].

The distribution of particles that arrive at a detector located normal to the surface is of particular interest. The typical distance to the detector is about \( 100 \div 1000 \) \( R \). At time \( t = 100 \tau_{\text{const}} \), the flow is already collisionless, and only those molecules that move along the normal to the surface will pass through the detector. In the calculation, we selected only those molecules whose velocity vector diverges from the normal by no more than \( 3^\circ \). Choosing smaller angles gives qualitatively similar distributions, but only with noticeably worse statistics. In figure 2f it can be seen that for \( \Theta = 1 \) the profiles are very close, with the distribution with the varying surface temperature being slightly shifted towards higher speeds. For \( \Theta = 30 \), on the contrary, the distribution for the constant temperature is shifted forward, and the difference is quite strong.

![Figure 3](image_url)

**Figure 3.** Density flow fields \( n/n_0 \times 10^5 \) and current stream-lines under gas expansion for \( \Theta = 1 \) (upper part) and \( \Theta = 30 \) (lower part) for the spot size \( b = 10 \) for the constant surface temperature \( T_{\text{const}} \) (solid lines) and temperature \( T_S(t) \) varying in time (dashed lines) in time moment \( t = 100 \tau_{\text{const}} \).
Figure 4. Angular distribution of flux of particles (a) and their mean energy (b) for particles arriving to the detector at an angle $\alpha$ with respect to the surface normal for the spot size $b = 10$ for the number of evaporated monolayers $\Theta = 1$ and $30$ for the constant and varying temperature.

Figure 5. The mean energy of particles passing through the time-of-flight detector for angle $\alpha = 0^\circ$ as a function of the number of evaporated monolayers $\Theta$ for the spot size $b = 3, 10, 30$ and from 1D calculations [13] for the constant and varying surface temperature.

Figure 3 shows the finally formed density field for $\Theta = 1$ and $30$ at time $t = 100 \tau_{\text{const}}$. It can be seen that for $\Theta = 30$ the plume is more elongated forward. Moreover, for $\Theta = 1$ we have almost the same distributions, while for $\Theta = 30$ the distributions are noticeably different.

4. Integral characteristics of the plume
Such a difference in the formed fields leads to various integral flow characteristics that are of interest from the point of view of the analysis of experimental measurements. Figure 4a shows the angular distribution of the flux of particles $Y$ arriving to a far-located detector. The average energy of the particles is shown as well (figure 4b). For the collisionless expansion, there is $Y \sim \cos \alpha$, while the energy ratio is $E/E_0 = 1$ for all angles (here $E_0 = 2kT_{\text{const}}$ is the energy of particles during evaporation). For a larger number of monolayers ($\Theta = 30$), the plume is more extended forward with a corresponding increase in the particle energy near the normal, which is in good agreement with the known data on evaporation into vacuum [3, 4, 8]. Taking into account the temporal evolution of the surface temperature practically does not change the number of particles near the axis. However, varying temperature changes energy near the axis. For $\Theta = 1$, an increase in the energy near the axis by 1.2% is observed, while for $\Theta = 30$, on the contrary, there is a decrease by 5.7%.

Figure 5 shows the average energy of particles passing through the time-of-flight detector located at the normal to the evaporating surface (at $\alpha = 0^\circ$) as a function of the number of evaporated monolayers for different spot sizes $b = 3, 10, 30$. The energy monotonously increases with an increase in the number of monolayers [8]. For the constant temperature for $\Theta > 10$ the curves practically coincide, which is associated with a complex dependence of the energy on the spot size [16]. For $\Theta < 5$, taking into account the time evolution leads to a slight increase in energy, by 1%. However, the subsequent increasing the number of monolayers leads to a qualitative change in the dependence: the varying temperature results in a noticeable decrease in energy, up to 9%. This difference is in agreement with the difference of the distributions of particles which move strictly along the normal to the surface (figure 2f). It should be noted that for a large number of monolayers ($\Theta > 20$), the error in determining the average energy can be about 1%.
Figure 5 also shows the results of the DSMC calculation from work [13]. In this work, a comparison was made of one-dimensional gas expansion for $\Theta = 5.25$ at a constant surface temperature and a variable temperature, which was determined from the solution of the heat conduction equation. An analysis of the velocity distribution functions for particles arriving at the detector yields average energies $E = 1.72E_0$ for constant evaporation and $E = 1.69E_0$ for varying evaporation. As in our work, constant evaporation gives a slightly larger value of the particle energy. Some difference in the absolute values of energy from our results can be explained by the fact that in [13] the one-dimensional approach was used instead of the two-dimensional one. In addition, in our work, to determine the average energy near the normal to the surface, we chose particles moving at an angle of 2º, while in work [13] a larger angle of 5º was chosen, which should lead to an underestimation of the energy value by 1-2% (see figure 4,b).

It should be noted that the authors' choice of the number of monolayers ($\Theta = 5.25$) is inadequate in the sense that it is for this value that the difference between the calculations with constant and varying temperature is minimal, while with the increase in the number of monolayers the difference increases significantly. In this regard, the conclusion of the work [13] that the interparticle collisions in the plume "smear" the difference is valid only for $\Theta < 10$.

**Conclusion**

The effect of the temporal evolution of the evaporation surface temperature on the neutral plume expansion under pulsed evaporation into vacuum has been studied based on the axisymmetric DSMC calculations. The regimes with the constant and varying temperature of the evaporation surface have been compared. It is shown that under evaporation of more than ten monolayers the varying temperature leads to considerable changing the plume dynamics with up to 9% decrease in the average energy of particles passing through a time-of-flight detector.

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