**Dynamics of gas cloud expansion under pulsed laser evaporation into vacuum**

A A Morozov  
Kutateladze Institute of Thermophysics SB RAS, Novosibirsk, Russia

E-mail: morozov@itp.nsc.ru

**Abstract.** Two-dimensional direct Monte Carlo simulation of neutral gas expansion under pulsed evaporation into vacuum has been performed. Analysis of temporal evolution of the spatially-averaged characteristics of the plume has been carried out for a wide range of the problem parameters: the spot radius and the evaporation depth. Special attention has been paid to determination of the limits of applicability of one-dimensional approach for gas dynamic simulation.

**1. Introduction**

Pulsed laser ablation is widely used for thin film deposition, nanoparticle synthesis, surface treatment etc [1, 2]. Analysis of dynamics of laser-induced plume expansion into vacuum is vital for development of analytical models of gas-phase processes during pulsed laser ablation, for example, for correct interpretation of experimentally measured time-of-flight distributions [3-6]. For nanosecond laser ablation the spot radius is typically much greater than the plume length during the pulse action, and therefore the initial stage of the plume expansion can be considered as one-dimensional one. Such an approach is commonly used for simplified theoretical analysis [4-10]. This is very important since for evaporation of a small amount of material (which is a typical case for laser ablation applications) the interparticle collisions within the plume occur only during the one-dimensional expansion. The subsequent three-dimensional expansion can be considered as collisionless one, which greatly simplifies the analysis. However the range of applicability of this approach for analysis of experimental data is not clear, since the duration of this one-dimensional stage strongly depends on the conditions of evaporation.

Previous theoretical analysis of the pulsed laser-induced plume expansion into vacuum is mainly restricted by calculations using the direct simulation Monte Carlo (DSMC) method [11]. NoorBatcha et al [7] and Feil et al [8] studied angular distributions under pulsed desorption of a few monolayers based on one-dimensional calculations. Sibold and Urbassek first performed two-dimensional calculations and considered energetic characteristics of the plume [12]. The structure of the forming laser-induced plume was studied by Bulgakova et al. [13] and Bykov et al. [14]. Dynamics of polyatomic gas cloud expansion under pulsed laser evaporation into vacuum was studied based on one-dimensional calculations for the nearly continuum regime (one hundred monolayers) [10].

This work presents results of numerical analysis of neutral gas cloud expansion under pulsed evaporation into vacuum based on two-dimensional DSMC calculations. The major attention is focused on analysis of temporal evolution of spatially-averaged plume characteristics and on determination of the time of transition from one-dimensional expansion to three-dimensional one.
2. Model
A two-dimensional axially symmetric problem of pulsed evaporation of molecules into vacuum is considered. The laser-induced plume is proposed to be neutral. The classical mechanism of evaporation is supposed (when the Clausius-Clapeyron equation can be used to describe relation between the surface temperature and the saturated gas pressure). This mechanism is commonly considered to be adequate for describing experiments for moderate laser fluences for nanosecond ablation of different materials, e.g. metals, semiconductors, or graphite [15].

Molecules are evaporated with the energy corresponding to a surface temperature $T_0$. It is assumed that during time interval $\tau$ particle flux $\Psi$ is constant and equal to $\Psi = \frac{1}{2} n_0 u_0$, where $n_0$ is the density of the saturated gas corresponding to the temperature $T_0$, $u_0 = \sqrt{\frac{k T_0}{\pi m}}$ is the most probable thermal speed, $k$ is the Boltzmann constant, $m$ is the molecular mass. The molecules are treated in the frames of the hard sphere model. All backscattered molecules which reach the evaporating surface are assumed to recondense on the surface. A polyatomic gas with $j$ internal degrees of freedom is considered. To account for the internal degrees of freedom, the Larsen-Borgnakke model is used [11]. Collisions are classified as elastic for monatomic gases and inelastic for polyatomic gases.

The problem 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 $\Theta = \Psi + \Sigma$, where $\Sigma = \sigma/4$ is an area occupied by one molecule at the surface, $\sigma$ is the collision cross-section. The normalized spot radius is defined as $b = R(u_0 \tau)$. On default we consider monatomic gas, while for some specially mentioned cases we consider polyatomic gas with rotational degrees of freedom ($j = 3$).

3. Results and discussion
A typical dynamics of the change in the cloud during the monatomic gas expansion for a large evaporation spot is shown in figure 1, (a)-(d). To illustrate the effect of collisional processes in the plume, the results of calculations for the collisionless expansion of the same number of particles from the same spot are shown in the same figure as well. Initially in the time moment of evaporation termination ($t = \tau$), the cloud represents as a flat pancake above the surface of evaporation (figure 1 (a)). Then, due to motion of particles and collisions between them, the plume transformed and strongly extended forward. Apparently, this is conditioned by the large pressure gradient along the normal for a relatively large evaporation spots [16, 17]. Starting from the time moment $t = 30 \tau$, there is practically no interparticle collisions due to extremely low density within the plume, and the plume shape does not change any more. After this time the cloud, despite its great elongation, does not fly forward, but rather expands as if from a spherical source (the current stream-lines demonstrate this effect in figure 1 (d)). It should be noted that for collisionless expansion the plume density is much lower than for the expansion considering collisions (e.g., at time $t = 100 \tau$ for collisionless expansion the average density is $n = 1.1 \cdot 10^5 n_0$, while for the collisional one $n = 4.5 \cdot 10^5 n_0$). This great difference is caused by the fact that for the collisionless expansion a considerable part of the particles fly away to the periphery, and near the normal to the evaporation spot only a relatively small number of particles remains. One can see that at time $t = 100 \tau$ for the collisional expansion the region near the normal to the surface (axis $r = 0$) is enriched by high-velocity molecules (figure 1 (d)) in comparison with the collisionless expansion (figure 1 (h)). This axial enrichment clearly illustrates why the kinetic energy of molecules passing through the time-of-flight detector located at the normal to the surface can be much higher than the energy of molecules under thermal evaporation [3].

To analyze the cloud dynamic expansion into vacuum it is convenient to introduce the spatially-averaged values of density, velocity, and temperature in the plume. The average plume density is determined as

$$\bar{n} = \frac{\sum_i n_i N_i}{\sum_i N_i}$$
where $N_i$ is the number of particles in the $i$-th cell, $n_i = N_i/V_i$ is the density in the $i$-th cell, $V_i$ is the volume of the $i$-th cell. The average values of velocity and temperature are determined in a similar way. Such an approach was previously applied for analysis of the laser-induced flow based on one-dimensional calculations for nearly continuum regimes [10].

Figure 2 shows typical temporal dependences of these average plume characteristics obtained from the one-dimensional calculations, which correspond to the limiting case of $b = \infty$. The directed velocity with time tends to a certain maximum value of the velocity $u_{\text{max}}$, which is determined by the initial energy of the particles. Indeed, if the kinetic energy of the particles under evaporation $E_0 = 2kT_0$...
wholly transforms into the energy of the directed motion (with a corresponding drop of the plume temperature to zero), then assuming the conservation of energy, the maximum velocity is $u_{\text{max}} = \sqrt{2E_0/m} = 1.4u_0$, which agrees well with the result of the calculation in figure 2 (b). Let us calculate the minimum directed velocity, for the collisionless expansion ($\Theta = 0$). The distribution function of the thermal velocity component is $f(u) = \exp\left(-u^2 / u_0^2\right) / (u_0\sqrt{\pi})$. Then for the flux of evaporating molecules the average velocity is

$$u_{\text{min}} = \int_0^\infty u f(u) du \int_0^\infty uf(u) du = u_0\sqrt{\pi} / 2 = 0.886 u_0,$$

which can be seen in figure 2 (b) for $\Theta = 0.01$. For most regimes the velocity varies slightly and can be considered as constant, and, accordingly, the density decreases practically linearly, $n \sim t^{-1}$ (see figure 2 (a)). The drop of the plume temperature is determined by the number of collisions during the gas expansion. For the limiting case of the continuum flow ($\Theta = 1000$), a strong temperature drop can be described in the framework of the adiabatic process. Indeed, for an ideal gas $pV^\gamma = \text{const}$, from which we obtain $T \sim n^{\gamma-1}$. For the monatomic gas the adiabatic exponent is $\gamma = (5 + j)/(3 + j) = 5/3$, and finally we get $T \sim n^{5/3} \sim t^{-2/3}$, that actually can be observed in figure 2 (c). For polyatomic gas the adiabatic exponent is smaller, and accordingly the temperature can be much higher, as it was demonstrated in the previous study for the near continuum regime [10].

Figure 2. Temporal evolution of the average plume density, velocity, and temperature under evaporation into vacuum from one-dimensional calculation ($b = \infty$) for the number of monolayers $\Theta = 0.01, 0.1, 1, 10, 100, 1000$. 
Figure 3. Temporal evolution of the average plume density (a,d), the axial velocity component (b,e), and temperature (c,f) under evaporation into vacuum for the number of monolayers $\Theta = 1$ (left) and 10 (right) for different values of the spot radius $b$. 
Figure 3 shows typical temporal evolution of the average flow characteristics from the two-dimensional calculations for the number of monolayers $\Theta = 1$ and 10 for different sizes of the evaporation spot $b$. At the initial stage, in fact, there is a plane expansion into a vacuum, under which the density falls linearly (see figure 3 (a, d)). Then, starting from a certain time $t_{3D}$ (which depends on the spot size $b$), a strong expansion of the gas in the lateral directions begins. The volume occupied by the gas increases with time as $V(t) = L_X(t) \cdot L_Y(t) \cdot L_Z(t) \sim t^3$, and the density falls, respectively, as $n \sim t^{-3}$. In view of such a sharp density drop, the flow rapidly becomes collisionless, and the directed velocity ceases to increase (see figure 3 (b, e)). During collisionless expansion into vacuum, a natural separation of particles with different velocities takes place, so that in each elementary cell of space there are particles with practically identical velocities and a very small energy of thermal motion. As a result, the temperature falls very strongly ($\sim t^{-2}$) (see figure 3, c), in spite of the fact that the directed velocity remains constant. The temperature drop can also be described on the assumption that the process is adiabatic. Since $n \sim t^{-3}$, we obtain $T \sim n^{\frac{1}{3}} \sim t^{-2}$, which actually can be observed in figure 3 (c) for large times.

The transition time $t_{3D}$ from the plane one-dimensional expansion of the gas cloud to the three-dimensional expansion (as from a spherical source) depends both on the spot size and on the number of monolayers. The obtained time $t_{3D}$ values for different parameters of the problem are shown in figure 4. The dependence of this time on the spot size has the power-law form $t_{3D}/(\tau b) \sim b^d$, where $d$ varies from zero for collisionless expansion ($\Theta = 0$) to $d = 0.41$ at $\Theta = 100$. Using these dependences, we can estimate duration of one-dimensional stage for any conditions of pulsed laser ablation.

When rotational degrees of freedom are taken into account, the "freezing" of the rotational temperature likewise occurs at a certain limiting value of $T_{\text{rot,limit}}$. Figure 5 shows a typical time evolution of the mean rotational temperature for the number of monolayers $\Theta = 1$. In this case, the "freezing" of the temperature looks like for stationary supersonic jets, with the only difference being that for jets the process of "freezing" depends on the spatial coordinate, while for the pulsed evaporation it depends on the time coordinate. The dependence of the limiting rotational temperature $T_{\text{rot,limit}}$ on the spot size $b$ for different values of the number of monolayers $\Theta$ and for the number of internal degrees of freedom $j = 3$ is shown in figure 6. It can be seen that the limiting rotational temperature depends strongly on the number of monolayers and depends weakly on the size of the evaporation spot (especially for $b > 10$). In principle, given the experimentally measured rotational temperature of the plume and the number of evaporated monolayers, the surface temperature can be estimated using these dependences.
Gas-dynamic processes during the plume expansion are determined primarily by the number of collisions between the particles. Figure 7 shows the temporal evolution of the normalized mean number of collisions per one particle $N_{col}$ for different values of the spot radius $b$ for the number of monolayers $\Theta = 1$ for the number of internal degrees of freedom $j = 3$. It is seen that as the spot radius increases, the number of collisions increases also and tends to the dependence obtained from the one-dimensional calculations ($b = \infty$). After time moment $t = 10 \div 100 \tau$ there is practically no collisions in the plume, and the number of collisions $N_{col}$ tends to a...
certain limit value $N_{\text{col,limit}}$. The dependence of this quantity on the spot radius $b$ is shown in figure 8. With decreasing the number of monolayers, the normalized number of collisions increases. This tendency well agrees with results of one-dimensional calculations [7]. The obtained data on the number of collisions can be useful for analysis of efficiency of rotational-translational and vibrational-translational energy transfer during pulsed expansion of polyatomic gas into vacuum [10].

4. Conclusion
Numerical study of dynamics of the laser-induced plume expansion into vacuum has been performed. Analysis of transition from one-dimensional to three-dimensional expansion has been performed based on the spatially-averaged characteristics of the plume. Data on the number of collisions per particle during expansion is calculated for a wide range of the problem parameters. The obtained results allow to determine the gas dynamic parameters of the plume in dependence of the problem parameters.

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