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Simulation of Polyatomic Gas Cloud Expansion under Pulsed Laser Ablation by Model Boltzmann Equation

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Polyatomic gas cloud expansion into vacuum under pulsed laser ablation is studied on the basis of one-dimensional model kinetic equation. To account for the influence of internal energy on the vapor-gas cloud parameters (density, temperature, and velocity) a model kinetic equation of the BGK-type is applied, which considers the energy exchange using a two-temperature model. In this approach, the collision integral is approximated by the sum of two terms corresponding to elastic (translational relaxation) and inelastic (rotational relaxation) collisions. Note that the vibrational energy is not taken into account in this paper. The independence of the differential part of transfer equation from the rotational energy makes it possible to reduce the equation to a system with two functions. A comparison of the gas flow macroparameters obtained by the kinetic equations and the DSMC is carried out. The influence of the number of rotational degrees of freedom on the evolution of average temperature and on the gas parameters is shown. The calculations are performed on non-uniform grids in the phase space with global dynamic velocity mesh adaptation to suppress the "ray effect".

Keywords: model kinetic equations, rotational degrees of freedom, pulsed laser ablation, non-stationary problems.

Introduction

This paper is devoted to the simulation of a widely used technology for nanomaterials synthesis due to nanosecond pulsed laser ablation (PLA). A large number of numerical, theoretical, and experimental studies is focused on the physical phenomena caused by PLA, see, for example, [1–4] and references therein. However, further research is needed because of the rapid development of technology and the large number of factors affecting the structure of the vapor-gas cloud.

Since the vapor cloud dynamics is accompanied by a transition from a continuum regime to the free-molecular one, numerical modeling of the process at large time intervals is a rather complicated computational problem. At present, the calculations are most often carried out by the direct simulation Monte-Carlo (DSMC). The kinetic approach based on integrating the exact Boltzmann equation or its model approximations by discrete ordinate method (DOM) is rarely used because of high computational cost.

It should be noted that the usage of a fixed velocity grid in the DOM in the case of discontinuous boundary or initial conditions can lead to unphysical oscillations of macroparameters ("ray effect"). Furthermore in the considered problem, there is an additional source of "ray effect", due to the narrow kernel of the velocity distribution function (VDF) in the velocity space. This is a consequence of boundary values transfer of the distribution function along the characteristics in velocity interval, that decreases with time. The non-uniform velocity grid with refinement in the neighborhood of zero velocity [5, 6] allows to obtain monotonic behavior of macroparameters for high intensity evaporation regime, and in comparison with the results obtained by the DSMC shows a close solution. However, more rarefied flow regimes require dynamic adaptation of the velocity grid. Despite the computational difficulties, the usage of kinetic equations for modeling physical processes represents an important alternative approach.

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The vapor-gas cloud after laser ablation can consist of polyatomic particles, so it seems important to study the influence of the molecular internal energy on the vapor dynamics, since the energy exchange affects the density, temperature, and flow velocity, which, in turn, affect the deposition rate and coating quality.

The molecular vapor cloud dynamics was studied using DSMC and continuum approach in [7, 8] and in other papers referenced in [8]. The goal of this paper is to determine the possibility of numerical simulation of the molecular cloud expansion by integration of model kinetic equation and comparing the obtained results with DSMC. Note that only rotational degrees of freedom are considered, since accounting for vibrational degrees of freedom based on model equations in the laser ablation problem requires additional theoretical studies.

The article is organized as follows. In Section 1, we give the formulation of the problem and a generalized form of the model kinetic equation of BGK type for a polyatomic gas. In Section 2, we introduce characteristic quantities for normalizing the kinetic equation in the problem of gas cloud expansion into vacuum during pulsed laser ablation. In Section 3, we compare the results obtained by the model equation and DSMC and show the influence of internal energy on the vapor-gas cloud parameters for different numbers of vaporized monolayers. The good agreement obtained in comparison allows us to consider the model equation as an alternative approach to reduce the computational complexity of solving these kinds of problems.

1. Formulation of the Problem and Kinetic Equations

Model equation, that takes into account the rotational degrees of freedom, describes the evolution of the distribution function $f(t, \boldsymbol{r}, \boldsymbol{\xi}, I_r)$ that depends on the coordinate vector $\boldsymbol{r} = (x, y, z)$, velocity vector $\boldsymbol{\xi}$, time t, and the continuous variable I_r corresponding to the rotational energy.

The macroparameters of the gas (particle number density n, velocity vector $\boldsymbol{u}$, and temperatures T_{tr}, T_{rot}) are determined using the intrinsic molecular velocity $\boldsymbol{C} = \boldsymbol{\xi} - \boldsymbol{u}$ and the notation

$$\langle\langle f \rangle\rangle = \int\limits_{R^3 \times R^+} f(t, \boldsymbol{r}, \boldsymbol{\xi}, I_r) d\boldsymbol{\xi} dI_r$$

as follows (the lower index tr corresponds to translational variables and rot to rotational ones):

$$n = \langle\langle f \rangle\rangle, \;\; n\boldsymbol{u} = \langle\langle \boldsymbol{\xi} f \rangle\rangle, \;\; 3nk_B T_{tr} = \langle\langle m\boldsymbol{C}^2 f \rangle\rangle, \;\; (k_{rot}/2)nk_B T_{rot} = \langle\langle I_r f \rangle\rangle,$$

where m is the molecular mass, k_B is the Boltzmann constant, and k_{rot} is the number of rotational degrees of freedom. The translational pressure p_{tr} and the equilibrium temperature T_{eqr}, which is set due to the exchange of translational and rotational energies, are determined according to the formulas

$$p_{tr} = nk_B T_{tr}, \;\; Teqr = \frac{3T_{tr} + k_{rot} Trot}{3 + k_{rot}}.$$

In this study, the calculations for a polyatomic gas are based on the generalized form of BGK equation [9], which takes into account the internal energies. This model is a special case of the Rykov equation [9] when the rotational and translational heat fluxes are equal to zero. In this approach, the collision integral is approximated by the sum of two relaxation terms which correspond to the elastic and inelastic collisions.

By averaging the VDF over internal energies and integrating over the variable I_r with weight coefficients $+1$, I_r,

$$f_0 = \int f \; dI_r, \;\; f_1 = \int I_r f dI_r,$$

we reduce the kinetic equation to the system of two model equations,

$$\frac{\partial f_j}{\partial t} + \left(\boldsymbol{\xi}, \frac{\partial f_j}{\partial \boldsymbol{r}}\right) = \nu_{tr}(n f_j^{tr} - f_j) + \nu_{rot}(n f_j^{rot} - f_j), \;\; j = 0, 1.$$

Here

$$f_0^{tr} = f_M(T_{tr}), \;\; f_0^{rot} = f_M(T_{eqr}), \;\; f_1^{tr} = 0.5 k_{rot} k_B T_{rot} f_0^{tr}, \;\; f_1^{rot} = 0.5 k_{rot} k_B T_{eqr} f_0^{rot},$$

$$f_M(T) = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} \exp\left(-\frac{m\boldsymbol{C}^2}{2k_B T}\right), \;\; \nu_{rot} = \frac{\nu}{Z_r}, \;\; \nu_{tr} = \nu(1 - \frac{1}{Z_r}),$$

where Z_r is the rotational collision number, $\nu = p_{tr}/\mu_{tr}$ is the collision frequency, and μ_{tr} is the viscosity coefficient, which depends on the translational temperature. The obtained system of model equations satisfies the conservation laws of density, momentum, and total energy.

2. Details of Calculations

The calculations use dimensionless quantities by introducing characteristic values of the evaporation spot radius R, surface temperature T_s, number density n_s, the most probable molecular velocity of the evaporating gas $v_m = \sqrt{2RT_s}$, and the time scale $t_0 = R/v_m$. The hard spheres intermolecular interactions are assumed.

The introduced characteristic quantities lead to a dimensionless form of the kinetic equation with the Knudsen number $Kn = \lambda_s/R$, where $\lambda_s = 1/(n_s \sigma_T \sqrt{2})$ is the mean free path and σ_T is the collision cross section. Assuming that the particle flux $\Psi_{VAP} = n_s u_t/4$ is constant, where $u_t = 2v_m/\sqrt{\pi}$ is the thermal molecular velocity, the Knudsen number can be related to the number of evaporated monolayers $\Theta = N/N_0$, where $N = \tau_{imp} \Psi_{VAP} \pi R^2$ is the total number of molecules evaporated from the surface, N_0 is the number of molecules in one layer, and $\tau_{imp} = \tau t_0$ is the laser pulse duration. Then $Kn = \tau\sqrt{2/\pi}/16/\Theta$ [5].

In the general case, the rotational collision number Z_r depends on the temperature, but for the considered range of the evaporation parameters as indicated in [7], the value of Z_r weakly affects the vapor cloud dynamics, so $Z_r = 4$.

3. Results

The problem of particle evaporation from a surface with expansion into vacuum is considered in one dimensional geometry. The VDF $f\,(x = 0, \xi_x > 0, t)$ at $t < \tau$ is Maxwellian with particle number density $n_1 = 1$, temperature $T_1 = 1$, and $\mathbf{u}_1 = 0$ (in dimensionless form). For $t > \tau$, $f\,(x = 0, \xi_x > 0, t) = 0$, since full absorbtion is assumed. The initial value of the VDF for the vacuum simulation $f\,(x > 0, \xi_x, t)$ is Maxwellian with parameters $n_0 = 1.e^{-12}$, $T_0 = 300K/T_s$, $\mathbf{u}_0 = 0$.

To study the effect of internal energy on the vapor-gas cloud dynamics, a series of calculations with different numbers of evaporated monolayers $\Theta = 1, 10, 100$ ($Kn = 0.04986\tau/\Theta$) and different numbers of rotational degrees of freedom are carried out. The numerical solution is

found by the discrete ordinate method with a finite volume TVD scheme. At the beginning of the calculations, the cell size near the target for $\Theta \leq 10$ is chosen of the order of the mean free path. For $\Theta = 100$ the cell size is larger than mean free path, but its reducing does not lead to noticeable changes in the solution. The boundary of the computational physical domain is defined by the estimate of the position cloud boundary at time $t = 1000\tau$.

The calculations are carried out by two software codes. The first of them is Unified Flow Solver (UFS) [10] in which the distribution functions are reduced to two-dimensional functions in the velocity space. This code is used for $\Theta = 100$, when high refine level necessary for Knudsen layer and the "ray effect" due to the intense relaxation of VDF to equillibrium is weak. The stationary non-uniform velocity grid with fine meshes near zero velocity can be used.

At the beginning of the calculations, the high level of grid refinement is implemented in the boxes closest to the $x = 0$. In other boxes, the refinement level is set to zero. At time moments $t > \tau$, the grid is changed using the adaptive mesh refinement algorithm according to predefined patterns, which take into account the cloud move and the increasing Knudsen number. In this case, the calculation can utilize about 10^8 cells in the phase space and efficient parallel implementation is essential. The parallel implementation of the UFS is single-level and uses the decomposition in the physical space with optimal balance between processors. The calculations were run in Joint Supercomputing Center of RAS using up to 1024 processors.

For $\Theta = 10$ and $\Theta = 1$, another kinetic module with the reduction to a one-dimensional distribution functions is used. This 1D code tests the algorithm of velocity dynamic adaptation to supress "ray effect". At the begining of calculations, velocity intervals (boxes) of an arbitrary size are given, and a uniform partition is introduced in each of them with the increasing refinement level in the neighborhood of zero velocity. The grid is changed by doubling the number of cells in the velocity interval at given times if $2h_v/\sqrt{T} > C$ (where C is a given constant and h_v is a velocity step in the corresponding interval). The mapping of the distribution function to a new grid is carried out with the density conservation.

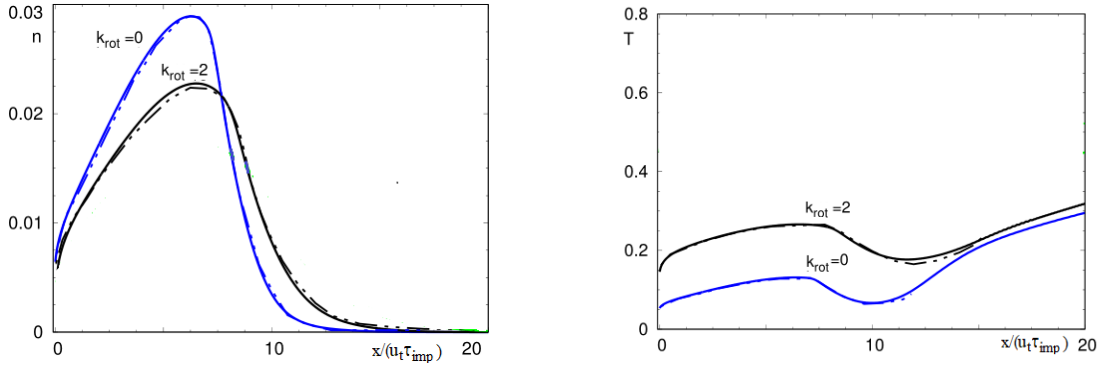
Calculations show a significant change in the behavior of macroparameters. Thus, during impulse expansion of the polyatomic gas, intermolecular collisions lead to intensive energy transfer from internal degrees of freedom to translational ones. Increasing translational temperature leads to a significant acceleration of the cloud. Figure 1 shows comparison of numerical results obtained by DSMC [7] and the kinetic equation for different number of rotational degrees of freedom at time moment $t = 5\tau$. Figure 1 shows that the profiles of macroparameters are very close.

The effect of internal energy on the cloud dynamics over a large time interval can be determined from the time dependence of the average values of gas parameters (translational temperature, velocity, or density). For this purpose, the mean value $\overline{F}$ is defined as

$$\bar{F} = \int nFdx / \int ndx.$$

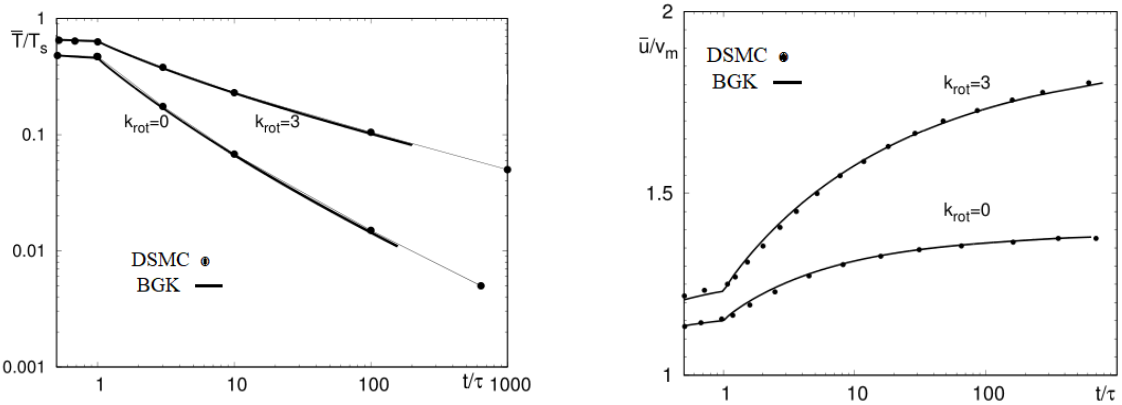
The average temperatures and velocities for monoatomic gas and for $k_{rot} = 3$ are given in Fig. 2, which shows that the results obtained by the model equations and by the DSMC practically coincide.

The effect of the number of evaporated monolayers on the vapor-gas cloud dynamics is presented in Fig. 3 for $k_{rot} = 3$ in time moments $t = 100\tau$. Figure 3 shows that as the number of monolayers decreases, the energy exchange becomes weaker and the difference between the rotational and translational temperatures increases.



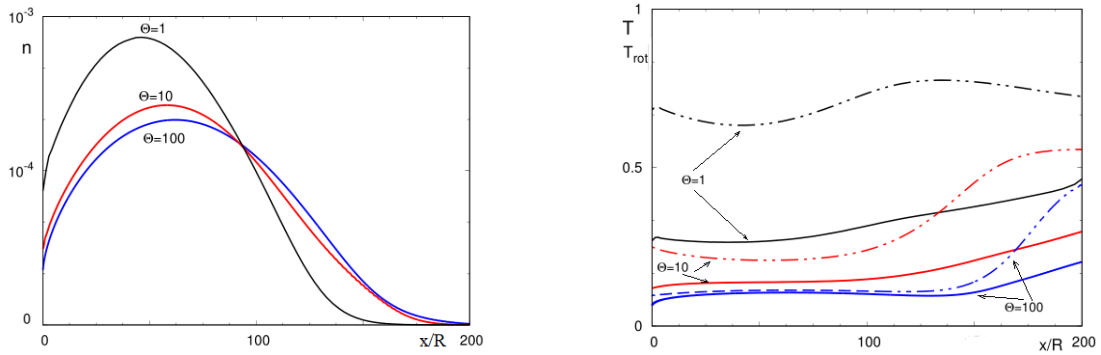
(a) Density (b) Temperaturee

Figure 1. Density and temperature at time moment $t = 5\tau$ and $\Theta = 100$, solid lines correspond to model equations, dashed lines to DSMC



(a) The average translational cloud temperature (b) The average velocity

Figure 2. Influence of the number of rotational degrees of freedom on the temporal evolution of the average temperature and velocity



(a) Density (b) Temperature

Figure 3. Density and temperature at moment time $t = 100\tau$ for different numbers of evaporated monolayers and for $k_{rot} = 3$, solid lines on Fig. 3b translation temperature, dashed lines rotational temperature

Conclusion

Calculations of evaporation of molecular gas into vacuum induced by a nanosecond laser pulse using model kinetic equations, that take into account the rotational degrees of freedom, are

carried out. These calculations describe the experiment more correctly, because they correspond to a more complete formulation of the problem.

A comparison of the molecular vapor cloud dynamics with the case of a monoatomic gas shows an increase in the forward temperature and velocity of the gas and comparison of the results obtained using the DSMC and the integration of model kinetic equations demonstrates a very close behavior of the macroparameters that makes it possible to use an alternative approach, based on model equations and to study the complex physical process of laser ablation.

Calculations were carried out on the resources of the Joint Supercomputer Center of the Russian Academy of Sciences.

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