

# Effect of Vibrational Energy on Dynamics of Pulsed Vapor Cloud Expansion

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**Abstract.** Polyatomic gas cloud expansion is studied on the basis of one-dimensional direct Monte Carlo simulation. Effect of rotational-translational (RT) and vibrational-translational (VT) energy transfer on dynamics of cloud expansion is considered. Efficiency of VT energy transfer in dependence on the amount of evaporated matter is discussed. VT energy transfer analysis is based on calculation of the number of collisions per molecule during expansion. To estimate VT energy transfer efficiency, the effective number of vibrational degrees of freedom is defined. It is shown how to predict the effective number of vibrational degrees of freedom based on the known parameters of the problem.

**Keywords:** pulsed laser ablation; vibrational energy transfer; direct simulation Monte Carlo.

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## INTRODUCTION

Laser ablation of solids with nanosecond pulses of moderate intensity is widely used in modern technologies [1]. Pulsed laser irradiation of solid targets leads to formation of a vapor cloud of the ablation products. This cloud often consists of polyatomic molecules [2-4]. Energy transfer from internal degrees of freedom to translational ones due to intermolecular collisions can considerably increase translational energy of molecules and hence appreciably change the cloud expansion dynamics. Vibrational degrees of freedom are known to demand a large number of collisions for energy relaxation. For pulsed evaporation of a small amount of matter, the number of collisions during the cloud expansion can be not enough for effective vibrational-translational (VT) energy transfer. The objective of this work is to study efficiency of rotational-translational (RT) and VT energy transfer and its impact on dynamics of polyatomic cloud expansion.

There are a lot of papers dedicated to study of pulsed evaporation or pulsed expansion of polyatomic molecules into vacuum. Different self-similar analytical solutions are considered in [5-7]. An analytical gas dynamics solution for pulsed emission without recondensation at the surface is presented in [8]. The general solution of the space- and time-dependent flow field for arbitrary adiabatic coefficient  $\gamma$  is presented in [9]. However all these theoretical studies do not take into consideration quite different energy transfer rate between different degrees of freedom, which substantially decrease possibility for their using in analysis of laser ablation experimental results.

Although large particles or clusters can present among the products of the laser ablation, our investigation is restricted by the case when the vapor cloud consists only of identical molecules. Since pulsed evaporation of a small quantity of material is accompanied by strongly non-equilibrium gas state, the most suitable method for this purpose is the direct simulation Monte Carlo (DSMC) method [10]. This method was widely used for laser ablation simulation, including polyatomic gas consideration [11, 12]. However in these works, attention was not drawn to the internal energy impact on the cloud expansion.

## FORMULATION OF THE PROBLEM

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  $T_0$ . During time interval  $\tau$ , particle flux  $\Psi_{VAP}$  is constant and equal to  $\Psi_{VAP} = n_0 u_T / 4$ , where  $n_0$  is

the density of the saturated gas corresponding to the temperature  $T_0$ ,  $u_T = \sqrt{8kT_0/(\pi m)}$ ,  $m$  is the molecular mass, and  $k$  is the Boltzmann constant. To describe particle interaction, the hard sphere model is used [10]. All backscattered particles are assumed to recondense at the surface. During calculation, the simulated zone gradually expands in such a way that no molecule can reach the boundary and consequently leave the zone. The parameter determining the amount of evaporated matter is the number of evaporated monolayers  $\Theta = \Psi_{VAP} \tau \Sigma$ , where  $\Sigma = \sigma/4$  is an area occupied by one molecule at the surface,  $\sigma$  is the collision cross-section.

To account for the internal degrees of freedom, the Larsen-Borgnakke model is used [10]. To treat the rotational and vibrational energy separately, different numbers of rotational and vibrational degrees of freedom are prescribed ( $j_R$  and  $j_V$ , respectively). Each rotational degree of freedom gives energy  $0.5 kT$  to the total molecular energy; each vibrational degree, energy  $kT$ . For real gases, the number of active internal degrees of freedom is determined by temperature. For expansion of polyatomic particles, the temperature decreases insignificantly (in comparison with monatomic gas expansion) because of collisional RT and VT energy transfer. The small change of temperature during expansion allows to consider values  $j_R$  and  $j_V$  as constant.

All collisions are classified as elastic or inelastic. If a collision is considered as inelastic, the total energy is reallocated between the translational and rotational (or vibrational) modes by sampling from the equilibrium distributions of these modes which are appropriate to the total energy of the colliding molecules. The relaxation rate is determined by the relaxation collision numbers  $Z_{R,DSMC}$  (for rotational energy) and  $Z_{V,DSMC}$  (for vibrational energy). The inverse of the number  $Z_{R,DSMC}$  (or  $Z_{V,DSMC}$ ) provides a fraction of collisions that are regarded as rotationally (or vibrationally) inelastic. Knowing values of  $Z_{R,DSMC}$  and  $Z_{V,DSMC}$ , we can define continual values of  $Z_R$  and  $Z_V$ , corresponding to relaxation rate in Jeans and Landau-Teller equations. Relation between these values was taken from work [13]

$$Z_{R,DSMC} = \frac{2j_R}{j_T + 2j_R} \frac{1}{1 - \sqrt{1 - \frac{j_R}{j_T} \frac{j_T + j_R}{j_T + 2j_R} \frac{4}{Z_R}}},$$

$$Z_{V,DSMC} = \frac{2\tilde{j}_V}{j + 2\tilde{j}_V} \frac{1}{1 - \sqrt{1 - \frac{\tilde{j}_V}{j} \frac{j + \tilde{j}_V}{j + 2\tilde{j}_V} \frac{4}{Z_V}}},$$

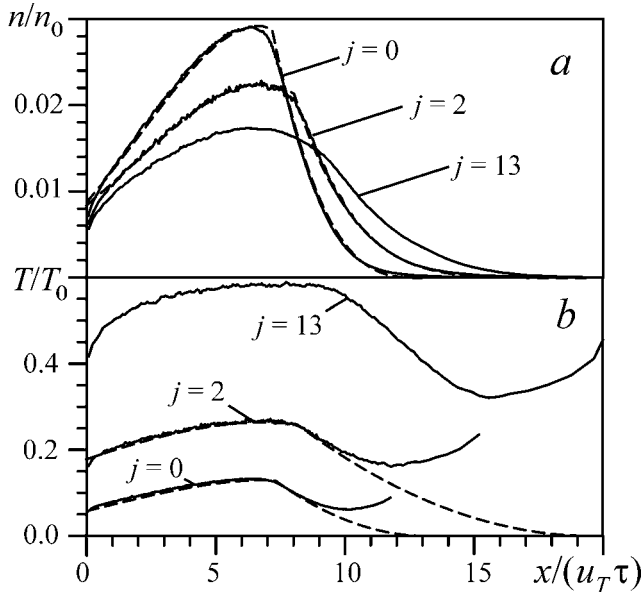
where  $j_T = 5 - 2\omega$  is the number of degrees of freedom corresponding to translational energy of colliding molecules,  $\omega$  is the temperature exponent of the viscosity coefficient,  $j = j_T + 2j_R$ ,  $\tilde{j}_V = 2j_V$  (doubling the number of vibrational degrees of freedom in the formula is caused by the fact that energy for each vibrational degree is twice as large as that for each rotational degree). For the hard sphere model (which is used in the simulation),  $\omega = 0.5$  and  $j_T = 4$ .

The internal energy relaxation is characterized by four parameters:  $j_R$ ,  $j_V$ ,  $Z_R$ , and  $Z_V$ . To avoid scanning all possible combinations of these parameters, selection of the most typical values is important. Assuming that molecules consist of three atoms at least, the number of rotational degrees of freedom was set  $j_R = 3$ . For most of polyatomic gases, the number of collisions required for de-excitation of rotational degrees of freedom does not exceed value  $Z_R = 10$  [14]. Calculations have demonstrated that  $Z_{R,DSMC}$  variation in the range from 1 to 10 slightly influences on dynamics of the cloud expansion. Therefore the value  $Z_{R,DSMC} = 1$  was taken, which correspond to  $Z_R = 2.5$ .

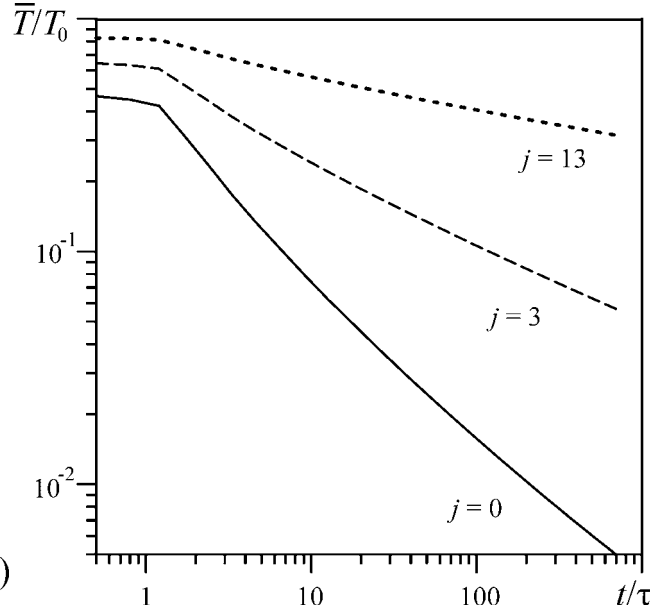
The vibrational energy consideration is much complicated. For polyatomic particles, presence of low frequency modes is a common case. Therefore for typical temperature for laser ablation of polymers (up to 1000 K), tens of vibrational degrees of freedom can be active. Thus in calculations  $j_V$  was varied in the range from 0 to 50. The vibrational energy relaxation was based on the so-called "series model" [14, 15], which assumes VT energy transfer to the lowest frequency mode only, this being coupled by some form of fast inter- or intramolecular vibrational-vibrational transfer to the other modes. Given the collision number  $Z_{10}$  necessary for the lowest frequency mode de-excitation, the number of collisions necessary for the overall vibrational energy de-excitation was estimated as

$$Z_V = Z_{10} j_V.$$

Numerous experiments show that  $Z_{10}$  strongly depends on the frequency of the lowest vibrational mode [14]. For some molecules it takes values close to unity (e.g., for  $C_2H_4Cl_2$   $\nu_{MIN} = 125 \text{ cm}^{-1}$  and  $Z_{10} = 3$ , for  $n-C_4H_{10}$   $\nu_{MIN} = 102 \text{ cm}^{-1}$  and  $Z_{10} = 1.6$  at temperature 300 K [14]), whereas for small molecules  $Z_{10}$  can takes values up to  $10^{10}$  (e.g., for  $N_2$   $\nu_{MIN} = 2143 \text{ cm}^{-1}$  and  $Z_{10} \sim 5 \cdot 10^9$ , for  $CH_4$   $\nu_{MIN} = 1306 \text{ cm}^{-1}$  and  $Z_{10} = 15160$  at 300 K) [14]. Assuming large polyatomic particles in calculations,  $Z_{10}$  was varied in the range from 1 to 100. The value  $Z_{10}$  considerably decreases with temperature increase, but dependence  $Z_{10} = Z_{10}(T)$  is unknown for most of gases. Considering our interest to molecules with small values  $Z_{10}$  first of all, effect of  $Z_{10}$  decrease at high temperature was neglected.



**FIGURE 1.** Profiles of density (a) and temperature (b) for pulsed evaporation into vacuum in time  $t = 5 \tau$  for the number of internal degrees of freedom  $j = 0, 2, 13$ . Solid lines correspond to DSMC calculation ( $\Theta = 100, Z_{DSMC} = 1$ ), dashed lines, to analytical solution [9].



**FIGURE 2.** Temporal evolution of the average cloud temperature for the number of internal degrees of freedom  $j = 0, 2, 13$  for  $\Theta = 100, Z_{DSMC} = 1$ .

## INTERNAL ENERGY CONTRIBUTION TO CLOUD EXPANSION

Fig. 1 presents typical profiles of density and temperature for pulsed evaporation into vacuum for different numbers of internal degrees of freedom  $j$ . All internal degrees of freedom are considered as rotational ones with the relaxation collision number  $Z_{DSMC} = 1$ . Also analytical solution [9] for  $j = 0$  and  $j = 2$  is shown (details of comparison of the calculated profiles with the analytical ones are presented in Appendix). At the front of the cloud, temperature profiles from the calculation and from the analytical solution are quite different, which is related with nonequilibrium gas state due to low density. With this exception, one can see excellent agreement of the numerical and analytical results. It is worth noting that analytical solution availability does not reject necessity for numerical calculation, since explicit solutions are obtainable for some particular values of  $\gamma$  only. During pulsed expansion of polyatomic gas cloud, intermolecular collisions result in permanent energy transfer from internal degrees of freedom to translational ones. As a result, cloud temperature for polyatomic gas is far above than temperature for monatomic gas (Fig. 1, b). Accordingly the temperature increase gives noticeable acceleration of the cloud (Fig. 1, a).

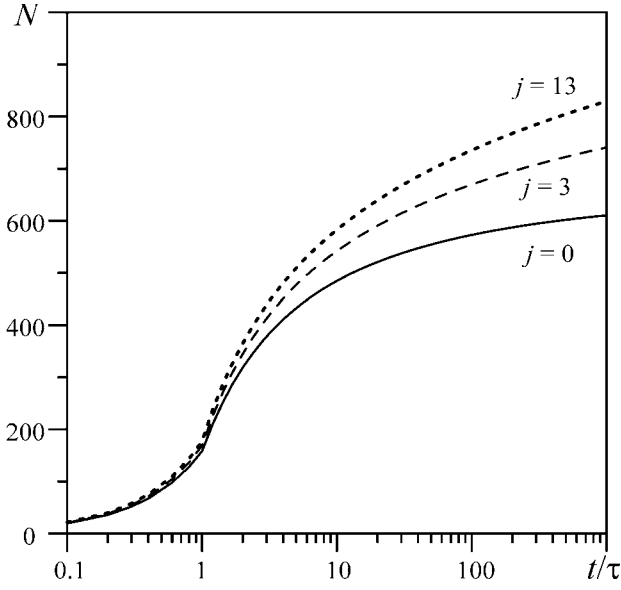
To trace for energy exchange contribution throughout expansion, it is convenient to use average cloud parameters for analysis. For that the average temperature of the cloud was determined as

$$\bar{T} = \frac{\int_0^\infty n(x)T(x)dx}{\int_0^\infty n(x)dx}.$$

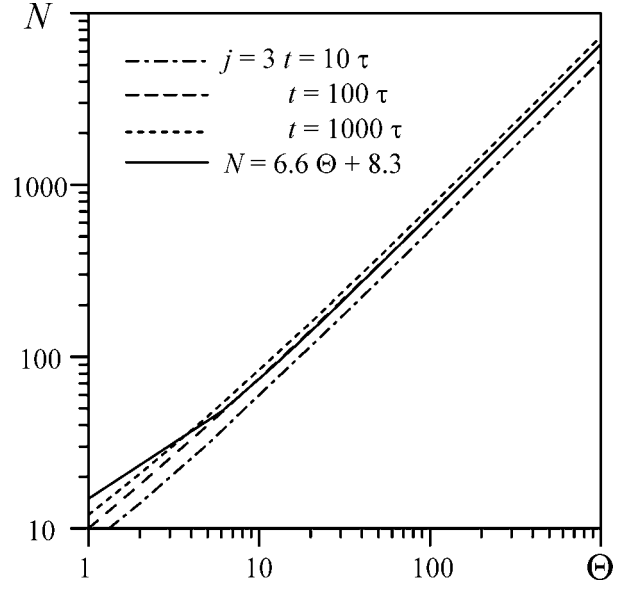
Temporal evolution of the cloud temperature  $\bar{T}$  is presented at Fig. 2. With time temperature difference becomes more pronounced and important.

It would appear reasonable that VT energy transfer efficiency is directly connected with the number of vibrationally inelastic intermolecular collisions (i.e. collisions accompanied by VT energy transfer) during the cloud expansion. Within the context of the considered model of internal energy, this number is defined as  $N/Z_V$ , where  $N$  is the total number of collisions per molecule during expansion (both elastic and inelastic). Therefore for analysis of efficiency of VT energy transfer, the number of collision per molecule  $N$  during the cloud expansion was calculated. Temporal evolution of  $N$  is shown in Fig. 3. In time with density decrease, the collision rate becomes negligible, and the collision number  $N$  tends to a limit value.

One can see that the number of collisions  $N$  weakly depends on the number of internal degrees of freedom  $j$ . Such a small rise of  $N$  was slightly surprising, since the collision rate is directly connected with temperature, and



**FIGURE 3.** Temporal evolution of the number of collisions per molecule  $N$  during expansion for the number of internal degrees of freedom  $j = 0; 3; 13$  ( $\Theta = 100$ ,  $Z_{DSMC} = 1$ ).



**FIGURE 4.** Number of collisions  $N$  per molecule during expansion as a function of the number of evaporated monolayers  $\Theta$  for the number of internal degrees of freedom  $j = 3$  (dashed lines). The solid line corresponds to fitting by formula (1).

temperature has been demonstrated to strongly depend on the number of internal degrees of freedom  $j$  (Fig. 2). This effect can be explained by considerable increase of flux of molecules back recondensed at the evaporation surface [16], which leads to appreciable density decrease and correspondingly to collision rate decrease. In fact our additional calculations with reflection of molecules from the evaporation surface have given a significantly greater number of collisions.

Dependence of the number of collisions  $N$  on the number of evaporated monolayers is presented in Fig. 4. Starting with  $\Theta > 50$ , the number of collisions is linearly proportional to  $\Theta$  and can be evaluated as

$$N = 6.6 \Theta + 8.3. \quad (1)$$

This dependence allows to simply predict the number of collisions during expansion.

## EFFECTIVE NUMBER OF VIBRATIONAL DEGREES OF FREEDOM

To analyze VT energy exchange, it is convenient to introduce the effective number of vibrational degrees of freedom  $j_E$  as the number of vibrational degrees of freedom that involved in VT energy transfer in such a way that their energy corresponds to translational temperature ( $E_{VE} = j_E k \bar{T}$ ). And vice versa, the number of fictitious degrees of freedom  $j_F = j_V - j_E$  is the number of degrees of freedom that completely does not involved in VT energy transfer (their energy is  $E_{VF} = j_F k T_0$ ). Then vibrational energy of the cloud can be presented as

$$E_V = j_V k \bar{T}_V = E_{VE} + E_{VF} = j_E k \bar{T} + (j_V - j_E) k T_0,$$

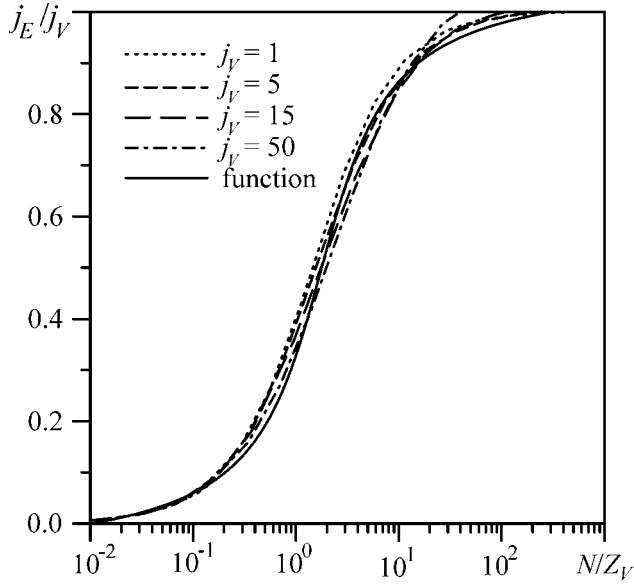
where  $\bar{T}_V$  is the average vibrational temperature of the cloud. From this it follows that

$$j_E = j_V \frac{T_0 - \bar{T}_V}{T_0 - \bar{T}}.$$

Given fixed values of  $j_V$ ,  $\Theta$ , and  $t$ , dependence of  $j_E$  on the number of vibrationally inelastic collisions  $N/Z_V$  can be presented (Fig. 5). Such a presentation allows to generalize the obtained results. Dependencies for different values of  $j_V$  practically coincide with a single curve, which can be approximated by the formula

$$j_E / j_V = 0.37 \arctg(2 \cdot \log(N / Z_V) - 0.5) + 0.5. \quad (2)$$

The same common curve was obtained also for other values of the number of evaporated monolayers  $\Theta$  and time moments  $t$ . For  $N/Z_V < 0.1$  there is  $j_E < 0.05 j_V$ , so gas can be considered as monatomic one. For  $N/Z_V > 50$   $j_E > 0.95 j_V$ , and gas can be considered as polyatomic one with close translational and internal temperatures. For intermediate



**FIGURE 5.** The effective number of vibrational degrees of freedom as a function of the number of vibrationally inelastic collisions  $N/Z_V$  for the number of vibrational degrees of freedom  $j_V = 1, 5, 15, 50$  (dashed lines) ( $\Theta = 100, t = 100 \tau$ ). The solid line corresponds to formula (2).

range  $0.1 < N/Z_V < 50$ , vibrational degrees of freedom are partially frozen, and the effective number of vibrational degrees of freedom should be found from Fig. 5.

Thus knowing the initial parameters of the problem, we can estimate the number of collisions  $N$  (based on eq. (1) and Fig. 3, 4) and then assess the effective number of vibrational degrees of freedom  $j_E$  (eq. (2) and Fig. 5).

## CONCLUSION

On the basis of the direct Monte Carlo simulation, effect of vibrational energy on dynamics of cloud expansion is studied. The number of collisions per molecule  $N$  is considered a prime characteristic determining efficiency of VT energy transfer. To estimate VT energy transfer efficiency, the effective number of vibrational degrees of freedom  $j_E$  is defined. The obtained data allows to estimate a priori both values of  $N$  and  $j_E$ . The effective number of vibrational degrees of freedom  $j_E$  can be used for estimation of the cloud parameters (temperature, velocity, etc.) during expansion.

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## APPENDIX. COMPARISON WITH THE ANALYTICAL SOLUTION

D. Sibold and H.M. Urbassek presented an analytical solution for pulsed adiabatic expansion of gas desobing into vacuum [9], with explicit results being derived for cases of monatomic gas ( $\gamma = \frac{5+j}{3+j} = 5/3$ ) and diatomic gas ( $\gamma = 1.4$ ). The position of the cloud front  $\tilde{x}_f$  and the point of the maximum cloud density  $\tilde{x}_{\max}$  (for  $t > \tau$ ) are determined by the following relations:

$$\tilde{x}_f(\tilde{t}) = \frac{\gamma+1}{\gamma-1} \tilde{t}, \quad \tilde{x}_{\max}(\tilde{t}) = \frac{\gamma+1}{\gamma-1} \left( \tilde{t} - \tilde{t}^{\frac{3-\gamma}{\gamma+1}} \right),$$

where  $\tilde{t} = t/\tau$ ,  $\tilde{x} = x/(u_K \tau)$ ,  $\tau$  is the pulse duration,  $u_K = c_K = \sqrt{\gamma k T_K / m}$  is velocity at the boundary of the Knudsen layer (where the Mach number  $M = 1$ ).

Solution for the zone  $\tilde{x}_{\max} < \tilde{x} < \tilde{x}_f$  is determined by the formulas

$$\begin{cases} \tilde{u}(\tilde{x}, \tilde{t}) = 1 + \frac{2}{\gamma+1} \frac{\tilde{x}}{\tilde{t}}, \\ \tilde{c}(\tilde{x}, \tilde{t}) = 1 - \frac{\gamma-1}{\gamma+1} \frac{\tilde{x}}{\tilde{t}}, \end{cases}$$

where  $\tilde{u} = u/u_K$ ,  $\tilde{c} = c/c_K$ ,  $u$  is velocity,  $c$  is the speed of sound.

Solution in the zone  $0 < \tilde{x} < \tilde{x}_{\max}$  should be found separately for any particular case of  $\gamma$ . For monatomic gas ( $\gamma = 5/3$ ), the solution is

$$\begin{cases} \tilde{t}(\tilde{u}, \tilde{c}) = \frac{(18\tilde{c}^2 + 3\tilde{c}\tilde{u} - 12\tilde{c} - \tilde{u}^2 + 2\tilde{u} + 8)(3\tilde{c} + \tilde{u} + 2)}{108\tilde{c}^3}, \\ \tilde{x}(\tilde{u}, \tilde{c}) = -\frac{(9\tilde{c}^2 - \tilde{u}^2 + 4\tilde{u})(3\tilde{c} + \tilde{u} + 2)(3\tilde{c} - \tilde{u} - 2)}{108\tilde{c}^3}. \end{cases}$$

For diatomic gas ( $\gamma = 1.4$ ), the solution is more complicated:

$$\begin{cases} \tilde{u}(r, s) = r - s, \\ \tilde{c}(r, s) = \frac{\gamma - 1}{2}(r + s), \\ \tilde{t}(r, s) = \frac{(r^4 + 5r^3s - 2r^3 + 10r^2s^2 - 10r^2s + 4r^2 - 20rs^2 + 65rs - 18r - 5s^2 - 90s + 216)(r + 2)}{(r + s)^5}, \\ \tilde{x}(r, s) = -\frac{6(2r^2s^2 + 4r^2s - r^2 - 4rs^2 + 4rs + 18r - s^2 - 18s)(r + 2)(s - 2)}{(r + s)^5}. \end{cases}$$

Given the flow velocity  $u$  and the speed of sound  $c$  and assuming the adiabatic law  $n = \text{const} \cdot c^{\frac{2}{\gamma-1}}$ , temperature and density can be calculated.

To compare results of the DSMC calculation with the analytical solution, it is necessary to find the parameters at the boundary of the Knudsen layer. The well-known analytical solution of Cercignani [17] for strong evaporation of polyatomic gas presents these parameters, but they have not allowed fitting computational solutions to the analytical ones. Therefore we used more accurate solutions of Sone [18] (for  $\gamma = 5/3$ ) and Skovorodko [19] (for  $\gamma = 1.4$ ), which allowed to get good coincidence of analytical and computational results (Fig. 1). Summary of the used parameters is presented in Table I.

**TABLE I.** Parameters of the Knudsen layer used for comparison of the analytical and numerical solutions.

|                 | $\gamma = 5/3$ |           | $\gamma = 1.4$ |           |
|-----------------|----------------|-----------|----------------|-----------|
|                 | $T_K/T_0$      | $n_K/n_0$ | $T_K/T_0$      | $n_K/n_0$ |
| Cercignani [17] | 0.669          | 0.308     | 0.781          | 0.301     |
| Sone [18]       | 0.643          | 0.322     | —              | —         |
| Skovorodko [19] | —              | —         | 0.758          | 0.312     |

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