Kinetic Description of the Expansion of a Supersonic Pulsed Jet to Vacuum: II. Mixtures of Monoatomic Gases

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Abstract—A model for the expansion of a pulsed jet of a mixture of monoatomic gases was advanced on the basis of the Boltzmann kinetic equation. The Grad method was used to solve the Boltzmann equation. The set of moment equations was analyzed by matching asymptotic expansions. The behavior of the velocity slip and temperature difference was analyzed as a function of the conditions in the source and the component-gas concentrations in the mixture. A functional relationship between these quantities and the form of the interaction potential has been established.

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Supersonic pulsed gas jets and molecular beams are used in many fields of physics and chemistry, such as chemical reactions, energy relaxation, cluster preparation and characterization, epitaxial growth, and others [1, 2]. In this context, the modeling of pulsed mixed gas jets is of interest for deriving correlations between the jet macroparameters, on one hand, and the conditions in the source and the atomic interaction potential, on the other.

The model of a one-component supersonic pulsed jet of a monoatomic gas expanding to vacuum was built in [3]. It is of interest to generalize this model to cover multicomponent jets, as was done for continuous jets [4, 5]. The effects caused by nonequilibrium energy and momentum exchange between dissimilar particles also appear here as the velocity slip and the temperature difference between the component gases. Theoretical consideration of these effects can provide the basis for the determination of the parameters of the interaction potential between dissimilar particles from experimentally measured component temperatures and velocities and for the description of the speeding up of the heavy component from the gas jet and the gas-dynamic separation of the components.

The asymptotic analysis of the equations for a multicomponent jet model is, in general, more complex than for a one-component jet because of the appearance of dimensionless parameters (the Knudsen number for the interaction of dissimilar particle pairs, component weight ratios, and component concentration ratios). More difficulties arise from the fact that the orders of magnitude of these quantities can depend on the situation, and in each case it is necessary to analyze the order of smallness of the quantity for which expansion is performed and to determine the range of its allowed values.

This work generalizes the kinetic model of a pulsed supersonic jet of a monoatomic gas expanding to vacuum to cover a multicomponent case. This work also considers the limiting ratios of the component weights and mole fractions.

MODEL

In the formulation of the problem, the modeling of the non-steady-state expansion of a multicomponent jet to vacuum does not differ from the modeling of a onecomponent jet. Inasmuch as the jet is considered as a perturbed equilibrium gas flow and the continuum gas dynamic methods can be used to describe the unperturbed equilibrium flow, a boundary point is chosen at which the flow is still continuous, and the jet parameters are computed. These values of the parameters will be the boundary conditions for moment equations. In this work, the boundary conditions and scale values are determined as in [3], but the expanding mixture is considered as a gas with the average molecular weight equal to

$$
\overline{m} = \sum_{\alpha} m_{\alpha} y_{\alpha},
$$

where y_α is the mole fraction of component α . It is assumed that the flow is spherically symmetrical and particles interact with the exponential potential $V_{\alpha\beta}(r)$ = $-4\varepsilon_{\alpha\beta}(\sigma_{\alpha\beta}/r)^6$. For the details of the model, see [3].

The set of Boltzmann kinetic equations for the nonsteady-state, spherically symmetrical expansion of a gas mixture to vacuum is written in a dimensionless form as

$$
\frac{\partial f_{\alpha}}{\partial t} + (\xi + u) \left(\frac{\partial f_{\alpha}}{\partial r} - \frac{\partial u}{\partial r} \frac{\partial f_{\alpha}}{\partial \xi} \right) + -\frac{\partial u}{\partial t} \frac{\partial f_{\alpha}}{\partial \xi} \n+ \frac{\varphi^2}{r} \frac{\partial f_{\alpha}}{\partial \xi} - \frac{\varphi(u + \xi)}{r} \frac{\partial f_{\alpha}}{\partial \varphi} = K n_s^{-1} \sum_{\beta} I^{\beta \alpha},
$$
\n(1)

where f_α is the velocity distribution function for α particles and *u* is the weight-average velocity of the mixture. In the physical space, a spherical coordinate system is used: $\vec{r} = (r, \Theta, \varsigma)$; in the velocity space, a cylindrical coordinate system is used: $\xi = (\xi, \varphi, \omega)$. Here, *I*^{βα} is the integral of collisions of β and α particles:

$$
I^{\beta\alpha}(\vec{\xi})
$$

\n
$$
\equiv \int [f_{\beta}(\vec{\xi}')f_{\alpha}(\vec{\xi}'') - f_{\beta}(\vec{\xi})f_{\alpha}(\vec{\xi}_1)]\sigma_{\beta\alpha}(g,\chi)gd\vec{\xi}_1d\Omega.
$$

Here, the source Knudsen number is introduced: $Kn_s =$ $(R_s n_s \overline{Q})^{-1}$ (subscript "s" denotes the conditions in the source); Q is the effective scattering cross section [4, 5], defined so that to account for the interactions of all types of particles with the weights proportional to their mole fractions in the mixture:

$$
\overline{Q} = \sum_{\alpha} \sum_{\beta} Q_{\alpha\beta}^{(2)}(\sqrt{RT_s}) y_{\alpha}^s y_{\beta}^s.
$$

For the exponential potential considered by the model, the *l*-order effective cross section is

$$
Q_{\alpha\beta}^{(l)}(g) = Q_{\alpha\beta 0}^{(l)}(C_n^{\alpha\beta}/E_{\alpha\beta})^{2/n},
$$

where $C_n^{\alpha\beta} = 4\varepsilon_{\alpha\beta}\sigma_{\alpha\beta}^6$ and $E_{\alpha\beta} = \mu_{\alpha\beta}g^2/2$.

(The proportionality factor is found in [6].)

The set of equations (1) is solved by the Grad method in the 13-moment approximation, with the distribution function $f_\alpha(\xi)$ being [7]

$$
f_{\alpha} = f_{\alpha}^{(0)} \left[1 + \gamma_{\alpha} w_{\alpha} \xi + \frac{1}{4} \pi_{\parallel \alpha} p_{\alpha}^{-1} \gamma_{\alpha} (2 \xi^2 - \varphi^2) + \frac{1}{5} \gamma_{\alpha}^2 p_{\alpha}^{-1} \left(q_{\alpha} - \frac{5}{2} p_{\alpha} w_{\alpha} \right) \xi (\xi^2 + \varphi^2 - 5 \gamma_{\alpha}^{-1}) \right].
$$

In the zeroth approximation, the Maxwellian local distribution is chosen:

$$
f_{\alpha}^{(0)} = n_{\alpha} \gamma_{\alpha}^{3/2} (2\pi)^{-3/2} \exp \left(-\frac{\xi^2 + \varphi^2}{2} \gamma_{\alpha}\right),
$$

where $\gamma_{\alpha} = m_{\alpha}/(kT_{\alpha})$, and n_{α} and T_{α} are the local number density and temperature of component α .

The macroscopic parameters of the component gases and the mixture are determined as the moments of the distribution function as follows:

number densities, as

$$
n_{\alpha} = \int f_{\alpha} d\vec{\xi}, \quad n = \sum_{\alpha} n_{\alpha}, \quad d\vec{\xi} = d\xi \varphi d\varphi d\omega;
$$

weight densities, as

$$
\rho_{\alpha} = m_{\alpha} n_{\alpha}, \quad \rho = \sum_{\alpha} \rho_{\alpha};
$$

kinetic temperatures (T_α and *T*), as

$$
3n_{\alpha}kT_{\alpha} = m_{\alpha}\int f_{\alpha}(\xi^2 + \varphi^2)d\xi, \quad nT = \sum_{\alpha}n_{\alpha}T_{\alpha};
$$

pressure, as

$$
p_{\alpha} = n_{\alpha} k T_{\alpha}, \quad p = \sum_{\alpha} p_{\alpha};
$$

diffusion rate, as

$$
w_{\alpha} = \frac{1}{n_{\alpha}} \int f_{\alpha} \xi d\xi = u_{\alpha} - u.
$$

From the definition of the weight-average velocity $(\rho u = \sum_{\alpha} \rho_{\alpha} u_{\alpha})$ and the diffusion velocity,

$$
\sum_{\alpha} \rho_{\alpha} w_{\alpha} = 0.
$$

The viscous stress tensor $\pi_{\parallel\alpha}$ and the heat flux q_α for component α , as well as π_{\parallel} and *q* for the mixture, are determined as follows:

$$
\pi_{\parallel\alpha} = m_{\alpha} \int f_{\alpha} \left(\frac{2}{3}\xi^2 - \frac{1}{3}\varphi^2\right) d\xi, \quad \pi_{\parallel} = \sum_{\alpha} \pi_{\parallel\alpha},
$$

$$
q_{\alpha} = \frac{1}{2} m_{\alpha} \int f_{\alpha}\xi(\xi^2 + \varphi^2) d\xi, \quad q = \sum_{\alpha} q_{\alpha}.
$$

The scales of the variables were chosen to be the same as in [3]. *m* means the average molecular weight of the mixture:

$$
\overline{m}_s = \sum_{\alpha} m_{\alpha} y_{\alpha}^s,
$$

where y_α^s is the weight fraction of component α in the source.

MOMENT EQUATIONS

The formal procedure for building the set of moment equations in the inner and outer expansion regions in any approximation for the Knudsen number Kn_s is fully identical to the case of a pure gas [3]. In the zeroth approximation, the mixture expands as a monoatomic gas with the average molecular weight \overline{m}_s . The velocity slip and temperature difference in the outer expansion region, respectively, appear in the first and second approximations for $Kn_s^{1/(4-2\omega)}$ ($\omega = 1/2 + 2/n$, *n* is the exponent in the interaction potential). To avoid tedious computations, we only write equations for the specified effects in significant approximations in the far region of interest. The detailed derivation of the set of moment equations can be found in [8].

In the zeroth approximation, the solutions of the set of moment equations are the following familiar continuum relations:

$$
\rho_{\alpha 0} = m_{\alpha} n_{\alpha 0} = m_{\alpha} y_{\alpha 0} n_0,
$$

$$
y_{\alpha 0} = y_{\alpha}^s, \quad n_0 = \frac{g}{i^3}, \quad u_0 = \lambda,
$$

$$
T_0 = \frac{g^{2/3}}{i^2}, \quad \Delta w_{\alpha \beta 0} = 0, \quad \Delta T_{\alpha \beta 0} = 0,
$$

where $\lambda = r/t$ and $g = 5^{-3/2}(1 - \lambda^2/5)^{1/2}$ [3].

In the first approximation, the component-gas temperatures are equal to the continuum temperature: $T_1^1 =$ $T_2^1 = T_0$. Therefore, the temperature difference is $\Delta T_{12}^1 = 0$. The set of equations for diffusion rates w_α and for $h_{\alpha} = q_{\alpha} - p_{\alpha} w_{\alpha}$ ($\alpha = 1$ or 2) in this approximation is

$$
\frac{\partial w_{\alpha 1}}{\partial t} + \frac{w_{\alpha 1}}{t} + \frac{5}{3} \left(\frac{1}{m_{\alpha}} - \frac{1}{m_0} \right) \frac{g^{-1/3} g'}{t^3} = R_{\alpha}^{10} / \rho_{\alpha 0},
$$
\n
$$
\frac{\partial h_{\alpha 1}}{\partial t} + u_0 \frac{6h_{\alpha 1}}{t} + \frac{5 y_{\alpha 0} g^{4/3} g'}{3 m_{\alpha} r^8} = R_{\alpha}^{11},
$$
\n(2)

where

$$
R_{\alpha}^{10} = \sum_{\beta} G_{\alpha\beta0}^{(1)} (w_{\alpha1} - w_{\beta1})
$$

+
$$
\sum_{\beta} \gamma_{\alpha\beta0} G_{\alpha\beta0}^{(2)} \left(\frac{h_{\alpha1}}{\gamma_{\alpha0} p_{\alpha0}} - \frac{h_{\beta1}}{\gamma_{\beta0} p_{\beta0}} \right),
$$

$$
R_{\alpha}^{11} = \gamma_{\alpha0}^{-1} \sum_{\beta} \left[G_{\alpha\beta0}^{(5)} \frac{h_{\alpha1}}{p_{\alpha0}} + G_{\alpha\beta0}^{(6)} \frac{h_{\beta1}}{p_{\beta0}} + \frac{5}{2} \frac{\gamma_{\alpha\beta0}}{\gamma_{\alpha0}} G_{\alpha\beta0}^{(2)} (w_{\alpha1} - w_{\beta1}) \right],
$$

$$
G_{\alpha\beta0}^{(1)} = -\frac{16}{3} \mu_{\alpha\beta} n_{\alpha0} n_{\beta0} \Omega_{\alpha\beta0}^{11},
$$

\n
$$
G_{\alpha\beta0}^{(2)} = -\frac{16}{3} \mu_{\alpha\beta} n_{\alpha0} n_{\beta0} \left(\frac{2}{5} \Omega_{\alpha\beta0}^{12} - \Omega_{\alpha\beta0}^{11} \right),
$$

\n
$$
G_{\alpha\beta0}^{(5)} = -\frac{64}{15} \mu_{\alpha\beta} \kappa_{\alpha\beta0} n_{\alpha0} n_{\beta0} \left[\Omega_{\alpha\beta0}^{22} \right]
$$

\n+
$$
\left(\frac{15 \gamma_{\alpha0}}{4 \gamma_{\beta0}} + \frac{25 \gamma_{\beta0}}{8 \gamma_{\alpha0}} \right) \Omega_{\alpha\beta0}^{11} - \frac{1 \gamma_{\beta0}}{2 \gamma_{\alpha0}} (5 \Omega_{\alpha\beta0}^{12} - \Omega_{\alpha\beta0}^{13}) \right],
$$

\n
$$
G_{\alpha\beta0}^{(6)} = -\frac{64}{15} \mu_{\alpha\beta} \kappa_{\alpha\beta0} n_{\alpha0} n_{\beta0} \left[\Omega_{\alpha\beta0}^{22} - \frac{55}{8} \Omega_{\alpha\beta0}^{11} + \frac{1}{2} (5 \Omega_{\alpha\beta0}^{12} - \Omega_{\alpha\beta0}^{13}) \right],
$$

$$
\Omega_{\alpha\beta}^{lr} = \left(\frac{1}{2\pi\gamma_{\alpha\beta}}\right)^{1/2} \int_0^\infty \int_0^\pi \xi^{2r+3} \exp(-\xi^2) Q_{\alpha\beta}^{(l)}(g) d\xi \text{ is the}
$$

Chapman–Enskog integral ($\xi = g \sqrt{\gamma_{\alpha\beta}}$ /2), and κ and γ are defined by

$$
\kappa_{\alpha\beta} = \frac{\gamma_{\alpha\beta}}{\gamma_{\alpha} + \gamma_{\beta}}, \quad \gamma_{\alpha\beta} = \frac{\gamma_{\alpha}\gamma_{\beta}}{\gamma_{\alpha} + \gamma_{\beta}}, \quad \gamma_{\alpha} = \frac{m_{\alpha}}{kT_{\alpha}}.
$$

VELOCITY SLIP AND TEMPERATURE **DIFFERENCE**

In the general case, the set of equations (2) can be numerically solved. However, let us start with a particular case where the light component gas dominates (δ = $y_{\beta}^{s}/y_{\alpha}^{s} \ll 1$). Assume that the component weights differ significantly ($\varepsilon = m_\alpha/m_\beta \le 1$). There are two cases with different relationships between δ and ε : (1) component β is a minor admixture ($\delta \le \epsilon \le 1$), or (2) component β

In both cases, the equation for $\Delta w_{\alpha\beta1}$ is the same:

is in trace amounts ($\delta \ll \varepsilon \ll 1$).

$$
\frac{\partial \Delta w_{\alpha\beta 1}}{\partial t} = -\Delta w_{\alpha\beta 1} \left(\frac{1}{t} + \frac{16 \overline{m}_0}{3} n_0 \Omega_{\alpha\beta 0}^{11} \right) \n- \frac{5 m_\beta - m_\alpha g^{-1/3} g'}{3 m_\alpha m_\beta t^3}
$$
\n(3)

$$
-\frac{16}{3}\mu_{\alpha\beta}\frac{\overline{m}_0}{M}T_0^{-1}\bigg(\frac{2}{5}\Omega^{12}_{\alpha\beta 0}-\Omega^{11}_{\alpha\beta 0}\bigg)\bigg(\frac{h_{\alpha 1}}{m_{\alpha}y_{\alpha 0}}-\frac{h_{\beta 1}}{m_{\beta}y_{\beta 0}}\bigg).
$$

In the first case, where the heavy gas is an admixture to the light gas, the distribution function for the light gas remains the Maxwellian distribution or, at high

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degrees of equilibrium, it is slightly perturbed. The equation for $h_{\alpha1}$ in its form coincides with the equation for a pure gas [6]:

$$
\frac{\partial h_{\alpha 1}}{\partial t} = -h_{\alpha 1} \left(\frac{6}{t} + \frac{16}{15}n_{\alpha 0}\Omega_{\alpha\alpha 0}^{22}\right) - \frac{5y_{\alpha 0}g^{4/3}g'}{3m_{\alpha}f^{8}};
$$
 (4)

this means that the behavior of $h_{\alpha1}$ is determined only by the self-collisions of light molecules. The equation for $h_{\beta1}$ in this case is

$$
\frac{\partial h_{\beta 1}}{\partial t} = -h_{\beta 1} \left(\frac{6}{t} + \frac{16}{15} n_{\beta 0} \Omega_{\beta \beta 0}^{22} \right) + 16 \frac{\mu_{\alpha \beta} \mu_{\beta}}{M} n_{\alpha 0} \Omega_{\alpha \beta 0}^{11} \left) - \frac{5 y_{\beta 0} g^{4/3} g'}{3 m_{\beta} r^8}.
$$
\n(5)

Decreasing δ , i.e., going to the second case or, physically, decreasing the role of self-collisions of heavy molecules, we obtain

$$
\frac{\partial h_{\beta 1}}{\partial t} = -h_{\beta 1} \left(\frac{6}{t} + 16 \frac{\mu_{\alpha \beta} \mu_{\beta}}{M} n_{\alpha 0} \Omega_{\alpha \beta 0}^{11} \right) - \frac{5 y_{\beta 0}}{3 m_{\beta}} n_0 T_0 \frac{g^{4/3} g'}{t^8}.
$$
\n(6)

When $y_{80} \rightarrow 0$, the evolution of the heavy gas is fully determined by cross-collisions. For the exponential potential used in this model,

$$
\Omega_{\alpha\beta 0}^{lr} = \Omega_{\alpha\beta}^{lr}(T_0) = T_0^{1-\omega} \Omega_{\alpha\beta}^{lr}(1),
$$

where

$$
\Omega_{\alpha\beta}^{lr}(1) = \frac{1}{2^{\omega+1}\sqrt{\pi}}\mu_{\alpha\beta}^{\omega-1}\frac{Q^{(l)}(\sqrt{RT_s})}{\overline{Q}(\sqrt{RT_s})}\Gamma\left(r+\frac{3}{2}-\omega\right),\newline \left(\omega = \frac{2}{n}+\frac{1}{2}\right).
$$

In this case, Eqs. (4) – (6) are integrated to easily arrive at the asymptotics

$$
h_{k1\infty}(\lambda, t) = h_{k1}^{\infty}(\lambda)/t^6
$$

with the determinate function $h_{k1}^{\infty}(\lambda)$ (for details, see [8]). It is now easy to find the asymptotic representation for the velocity slip: $\Delta w_{\alpha\beta}$ _{1∞}(λ , *t*) = $\Delta w_{\alpha\beta}^{\infty}$ _{*α*β1} (λ)/*t*. In so doing, we have to integrate Eq. (3) with account for the

expression for $h_{k1}^{\infty}(\lambda)$. In the limit $t \longrightarrow \infty$, using dimensional variables we obtain

$$
\Delta w_{\alpha\beta 1\infty}^{\text{dimens}}(\lambda, t)
$$

= $R_s \left[2\sqrt{2\pi} / \Gamma \left(\frac{7 - 2\omega}{2} \right) \right]^{1/(4 - 2\omega)} \left(\frac{kT_s}{p_s R_s Q} \right)^{1/(4 - 2\omega)}$ (7)

$$
\times \left[\frac{a}{4 - 2\omega} \left(\frac{4 - 2\omega}{b} \right)^{1/(4 - 2\omega)} \Gamma \left(\frac{1}{4 - 2\omega} \right) + \frac{c}{b} \right] \frac{1}{t},
$$

where

$$
a = -\frac{5m_{\beta} - m_{\alpha}}{3m_{\alpha}m_{\beta}}g^{-1/3}g',
$$

\n
$$
b = \frac{16\overline{m}_{0}}{3}\frac{g^{(5-2\omega)/3}\Omega_{\alpha\beta}^{11}(1)}{M}.
$$

\n
$$
c = -\frac{16\mu_{\alpha\beta}\overline{m}_{0}}{M}\left[\frac{2}{5}\Omega_{\alpha\beta}^{12}(1) - \Omega_{\alpha\beta}^{11}(1)\right]
$$

\n
$$
\times \left[\frac{h_{\alpha1}^{*}(\lambda)}{m_{\alpha}y_{\alpha0}} - \frac{h_{\beta1}^{*}(\lambda)}{m_{\beta}y_{\beta0}}\right]g^{-2\omega/3},
$$

and R_s is the initial radius of the gas packet (see [8]). Expression (7) shows that $\Delta w_{\alpha\beta}$ increases with decreasing pressure and increasing temperature in the source, which is due to a decrease in the extent of the equilibrium region in the flow. The evident relation between ∆*w*αβ and the Chapman–Enskog integral makes it possible to derive the interaction-potential parameters from the experimentally determined velocity slip of the component gases.

After deriving the asymptotic expressions for functions $h_{\alpha1}$, $h_{\beta1}$, and velocity slip, it is easy to analyze the temperature difference. In the second approximation for $Kn_s^{1/(4-2\omega)}$, the equation for the temperature difference is

$$
3\frac{\partial}{\partial t}(\Delta T_{\alpha\beta 2}) + 6\frac{\Delta T_{\alpha\beta 2}}{t} - \frac{g^{2/3}}{\lambda^2} \frac{\partial}{\partial t}(\Delta w_{\alpha\beta 1}^{\infty} \lambda^2) \frac{1}{t^3}
$$

$$
- \Delta w_{\alpha\beta 1}^{\infty} \left(1 + \frac{10m_{\alpha}m_{\beta}}{3} \right)g^{-1/3}g' \frac{1}{t^3}
$$

$$
+ 2\frac{t^2}{g\lambda^2} \left[\frac{1}{y_{\alpha 0}}\frac{\partial}{\partial \lambda}(q_{\alpha 1}^{\infty} \lambda^2)\right] - \frac{1}{y_{\beta 0}}\frac{\partial}{\partial \lambda}(q_{\beta 1}^{\infty} \lambda^2)
$$

$$
= -32\frac{1}{M}\Delta T_{\alpha\beta 2} \Omega_{\alpha\beta}^{11}(1) \frac{g^{(5-2\omega)/3}}{t^{5-2\omega}}.
$$

Fig. 1. Velocity slip versus distance in various moments of time for the 99% He + 1% Kr mixture: $t = (1)$ 5 and (2) 10.

The asymptotic solution of this equation is

$$
R\Delta T_{\alpha\beta2\infty}(\lambda, t) = R_s^2 \left[2\sqrt{2\pi}/\Gamma\left(\frac{7-2\omega}{2}\right) \right]^{1/(2-\omega)} \times \left(\frac{kT_s}{p_s R_s \overline{Q}} \right)^{1/(2-\omega)} \left[\left(\Omega_{\alpha\beta}^{11}(1) \right)^{-1/(4-2\omega)} \frac{K(\lambda)}{t^2}, \right]
$$
(8)

where $K(\lambda)$ is a rather complex function of λ , depending on m_k , y_{k0} , and the parameters of the interaction potential (through integrals $\Omega_{\alpha\beta}^{11}$, $\Omega_{\alpha\beta}^{12}$, and $\Omega_{\alpha\beta}^{22}$). The behavior of $\Delta T_{\alpha\beta}$ as a function of the conditions in the source is an analogue of the behavior of Δ*w*_{αβ}. The general tendencies in the behavior of $\Delta w_{\alpha\beta}$ and $\Delta T_{\alpha\beta}$ fully agree with the results obtained for continuous jets [4, 5].

Numerically, the set of equations (2) is solved in some cases for $He + Kr$ mixtures with various compositions. The timezero $t = 0$ corresponds to the moment at which the pulsed nozzle stops operating. The results of the calculations are demonstrated in Figs. 1–4.

Figures 1 and 2 demonstrate the behavior of the velocity slip $\Delta w_{\alpha\beta}$ in the center-of-mass system for the 99% He + 1% Kr mixture with $Kn_s = 10^{-3}$. $\Delta w_{\alpha\beta}$ is positive; i.e., the velocity of the light component is higher than the velocity of the heavy component. The velocity slip is zero in the center of the gas packet, and it rapidly increases with the distance from the center. This $\Delta w_{\alpha\beta}$ behavior agrees with our model: the gas packet is ini-

Fig. 2. Velocity slip versus time at various distances for the 99% He + 1% Kr mixture: *r* = (*1*) 2 and (*2*) 4.

tially continuous; as scattering progresses, only the core of the packet remains continuous, decreasing over time. The $\Delta w_{\alpha\beta}$ value at each fixed point of the packet rapidly drops with time. Notice that the infinitely great ∆*w*αβ values in Fig. 2 at small times are near the expansion front with $\lambda \approx 5^{1/2}$. Figure 3 displays the limiting $\Delta w_{\alpha\beta}t$ values for various compositions of the He + Kr mixtures with $Kn_s = 10^{-3}$. Clearly, the velocity slip increases with decreasing heavy-component fraction.

Figure 4 demonstrates the behavior of $\Delta T_{\alpha\beta}t^2$ as a function of λ for the 99% He + 1% Kr mixture with $Kn_s = 10^{-3}$. Evidently, the temperature of the light component is always lower than the temperature of the heavy component. This is made clear by the comparison of efficient collision frequencies. The total number of collisions for particles with different weights is roughly the same. For light particles, however, all collisions are efficient for relaxation, while for heavy particles, only self-collisions are. As a result, the relaxation rate for the heavy component decreases, and the deviation from the isentropic temperature becomes greater. Inasmuch as the component temperatures are by defini-

tion related to the average temperature of the mixture *T* through

$$
T_{\alpha} = \overline{T} + y_{\beta 0} \Delta T_{\alpha \beta 2},
$$

$$
T_{\beta} = \overline{T} - y_{\alpha 0} \Delta T_{\alpha \beta 2},
$$

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0 2 Δw _{αβ}*t* λ 10 1 *1* 2^{3} 5 *3*

Fig. 3. $\Delta w_{\alpha\beta}t$ versus λ for various compositions of He + Kr mixtures: (*1*) 80% He + 20% Kr, (*2*) 90% He + 10% Kr, and (*3*) 99% He + 1% Kr.

for small $y_{\beta0}$ ($y_{\alpha0} \approx 1$) the temperature of the light component is close to the average temperature of the mixture, and the temperature of the heavy component is higher than the temperature of the mixture by a value of ΔT _{αβ2}.

The temperature difference depends on the component concentrations more weakly than the velocity slip. A decrease in $y_{\beta0}$ induces only an insignificant rise in $\Delta T_{\alpha\beta}$: on passing from the 99% He + 1% Kr to 99.9% Hr + 0.1% Kr mixture, the increase in the temperature difference is as little as 1%. In addition, the $\Delta T_{\alpha\beta}$ value for asymptotic times ($t \approx 100$) is too small to be used for processing time-of-flight spectra.

To summarize, we have built a model for the expansion of a pulsed jet of monoatomic gases on the basis of the Boltzmann kinetic equation. The Grad method was used to solve the Boltzmann equation. The set of moment equations was analyzed by matching asymptotic expansions. Sets of equations were derived to describe the behavior of the jet parameters in the far expansion region, and asymptotic expressions (for large times) were derived for the component velocity slip and temperature difference. In some particular cases, the set of equations for these quantities was

Fig. 4. $\Delta T_{\alpha\beta}t^2$ versus λ for the 99% He + 1% Kr mixture.

numerically solved. The behavior of the velocity slip and temperature difference was analyzed as a function of the conditions in the source and the component concentrations. A functional relationship was found between these quantities and the form of the interaction potential.

REFERENCES

- 1. Smirnov, B.M., *Usp. Fiz. Nauk*, 2003, vol. 173, p. 609.
- 2. Makarov, G.M., *Usp. Fiz. Nauk*, 2003, vol. 173, p. 913.
- 3. Lazarev, A.V., Zastenker, N.N., Trubnikov, D.N., Tatarenko, K.A., and Pribytkov, A.V., *Vestn. Mosk. Univ., Ser. 2: Khim*., 2006, vol. 47, p. 377.
- 4. Lenin, L.V., Lazarev, A.V., and Trubnikov, D.N., *Vestn. Mosk. Univ., Ser. 2: Khim*., 1987, vol. 28, p. 347.
- 5. Lenin, L.V., Lazarev, A.V., and Trubnikov, D.N., *Chem. Phys. Lett.*, 1988, vol.148, p. 401.
- 6. Lazarev, A.V., Zastenker, N.N., and Trubnikov, D.N., *Vestn. Mosk. Univ., Ser. 2*.*: Khim*., 2004, vol. 45, p. 177.
- 7. Zhdanov, V.M., *Yavleniya perenosa v mnogokomponentnoi plazme* (Transport Phenomena in Multicomponent Plasma), Moscow, 1982.
- 8. Kolosova, T.Yu., *Cand. Sci. (Chem.) Dissertation*, Moscow, 1990.

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