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BOUNDARY CONDITIONS IN A MULTICOMPONENT GAS MIXTURE FLOW PAST A VOLATILE NONSPHERICAL SURFACE AT KNUDSEN NUMBERS 0.01 AND 0.3

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The paper presents the boundary conditions of a temperature- and concentration-inhomogeneous multicomponent gas flow past a slightly curved nonspherical surface in the presence of slow evaporation and condensation processes.

To correctly describe the behavior of moderately large volatile aerosol particles in temperature- and concentration-inhomogeneous multicomponent gas mixtures one should know the boundary conditions on their surface. Under real conditions aerosol particles have, as a rule, a nonspherical shape. At present, boundary conditions are known only for nonvolatile aerosol particles of an arbitrary shape [1], whereas for moderately large volatile nonspherical aerosol particles they are, probably, absent in literature.

In what follows, jumps of temperature and concentration and sliding velocity for moderately large aerosol particles in a temperature- and concentration-inhomogeneous multicomponent gas mixture are calculated by the method of semispatial momenta for the case of slow evaporation. The boundary conditions are obtained for normal components of molecule and energy fluxes. Thus, a complete system of boundary conditions is given which allows one to fully describe motion and evaporation (or condensation growth) of moderately large volatile aerosol particles of an arbitrary shape.

1. We consider a flow of an N-component gas near a phase interface the temperature of which is T_0. We assume that the minimum radius of the surface curvature $R_{\min}$ is such that the following relation holds: $0.01 < \mathrm{Kn} < 0.3$, where $\mathrm{Kn} = \lambda/R_{\min}$ is the Knudsen number; λ is the mean free path of gas molecules. Let M components, $M < N$, undergo phase transition on this surface. Gradients of the gas temperature and concentrations of components are given at a large distance from the surface. We introduce the following notation: f_i, m_i, v_i, $\mathrm{w}_i = \sqrt{m_i/2kT_0}\,\mathrm{v}_i$, c_i, n_{i0} are the distribution function, mass, velocity and reduced velocity of molecules, relative concentration and concentration of saturated vapors of the i-th component at a temperature T_0, respectively.

We select a curvilinear orthogonal system of coordinates such that one of the coordinate surfaces coincides with the particle surface. We designate the coordinate which is perpendicular to the surface as x_n (the surface itself is prescribed by the equation $x_n = x_{n0}$) and the remaining two as $x_{\tau 1}$ and $x_{\tau 2}$.

2. To describe a rarefied gas flow near a surface of an arbitrary shape one should solve the Boltzmann equation in the curvilinear coordinates [2]

$$\left(-\frac{v_n v_{\tau 1}}{H_n H_{\tau 1}}\frac{\partial H_n}{\partial x_{\tau 1}} - \frac{v_n v_{\tau 2}}{H_n H_{\tau 2}}\frac{\partial H_n}{\partial x_{\tau 2}} + \frac{v_{\tau 1}^2}{H_n H_{\tau 1}}\frac{\partial H_{\tau 1}}{\partial x_n} + \frac{v_{\tau 2}^2}{H_n H_{\tau 2}}\frac{\partial H_{\tau 2}}{\partial x_n}\right)\frac{\partial f_i}{\partial v_n} +$$

$$+\left(-\frac{v_{\tau 1} v_{\tau 2}}{H_{\tau 1} H_{\tau 2}}\frac{\partial H_{\tau 1}}{\partial x_{\tau 2}} - \frac{v_n v_{\tau 1}}{H_n H_{\tau 1}}\frac{\partial H_{\tau 1}}{\partial x_n} + \frac{v_n^2}{H_n H_{\tau 1}}\frac{\partial H_n}{\partial x_{\tau 1}} + \frac{v_{\tau 2}^2}{H_{\tau 1} H_{\tau 2}}\frac{\partial H_{\tau 2}}{\partial x_{\tau 1}}\right)\frac{\partial f_i}{\partial v_{\tau 1}} +$$

$$+\left(-\frac{v_{\tau 1} v_{\tau 2}}{H_{\tau 1} H_{\tau 2}}\frac{\partial H_{\tau 2}}{\partial x_{\tau 1}} - \frac{v_n v_{\tau 2}}{H_n H_{\tau 2}}\frac{\partial H_{\tau 2}}{\partial x_n} + \frac{v_n^2}{H_n H_{\tau 2}}\frac{\partial H_n}{\partial x_{\tau 2}} + \frac{v_{\tau 1}^2}{H_{\tau 1} H_{\tau 2}}\frac{\partial H_{\tau 1}}{\partial x_{\tau 2}}\right)\frac{\partial f_i}{\partial v_{\tau 2}} +$$

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$$+\frac{v_n}{H_n}\frac{\partial f_i}{\partial x_n}+\frac{v_{\tau 1}}{H_{\tau 1}}\frac{\partial f_i}{\partial x_{\tau 1}}+\frac{v_{\tau 2}}{H_{\tau 2}}\frac{\partial f_i}{\partial x_{\tau 2}}=J\,, \tag{1}$$

where J is the collision integral [2]; H_n, $H_{\tau 1}$, $H_{\tau 2}$ are the Lamé coefficients. We assume the gas state to be close to equilibrium, then the functions of gas distribution over velocities can be expanded near local Maxwell distribution functions f_{i0}:

$$f_i = f_{i0}\,(1+\varphi_i)\,,$$

where $f_{i0} = n_i(m_i/2\pi k T_0)^{3/2}\exp(-w_i^2)$. Functions φ_i can be presented as

$$\varphi_i = \delta n_i - S^1_{1/2}\,\delta T + 2 w_{ni} G_n + 2\sqrt{\left(\frac{m_i}{m_N}\right)}\,(w_{\tau 1i}G_{\tau 1} + w_{\tau 2i}G_{\tau 2}) + \psi_i^{\mathrm{CE}} + \psi_i^{\mathrm{B}} + \Phi_i^{\pm}\,, \tag{2}$$

where $\delta n_i = (n_i(x_n = x_{n0}) - n_{i0})/n_{i0}$ and $\delta T = (T(x_n = x_{n0}) - T_0)/T_0$ are temperature and concentration jumps; $\mathbf{G} = \sqrt{m_N/2kT_0}\,\mathbf{U}$; $\mathbf{U}$ is the mean-mass velocity of gas mixture flow; $\mathbf{G}_\tau$ is the reduced velocity of gas mixture sliding; G_n is the normal component of the reduced mean-mass velocity of the mixture $\mathbf{G}$. The value of G_n can be found from the condition of nonflow of molecules of the N-th component through the phase interface: $G_n = -1/2h^j_{N0}\nabla_n\Psi^j$. The function Ψ_i^{CE} is called the Chapman–Enskog function [3]. It can be written as

$$\psi_i^{\mathrm{CE}}(\mathbf{v}_i) = \mathbf{w}_i\, h_i^j(w_i)\,\nabla\Psi^j + \frac{B_i(w_i)}{\Sigma\, n_i}\left(w^i_\alpha\, w^i_\beta - \frac{1}{3}\, w^{i2}\right)\frac{\partial u_\alpha}{\partial x_\beta}\,,$$

where $h_i^j(w_i)$ are thermal and diffusion functions; $D_i(w_i)$ are viscous functions [4]:

$$\begin{aligned} &h_i^0(w_i) = a_i(w_i) \quad \text{for} \quad j = 0\,, \quad \nabla\Psi^0 = \mathrm{grad}\,(\ln T) \quad \text{for} \quad j = 0\,,\\ &h_i^j(w_i) = d_i^j(w_i) \quad \text{for} \quad j \neq 0\,, \quad \nabla\Psi^j = \mathrm{grad}\, c_j \qquad \text{for} \quad j \neq 0\,. \end{aligned}$$

Then in expansion of functions $h_i^j(w_i)$ in terms of Sonin polynomials we retain two terms, and in expansion of viscous function $B_i(w_i)$ we retain one term:

$$h_i^j(w_i) \approx h^j_{i0} + S^1_{3/2}\, h^j_{i1}\,, \quad B_i(w_i) \approx b_{i0}\,.$$

Function ψ_i^{B} entering Eq. (2) is the Barnett distribution function. Since the velocity of Barnett slipping has an order of Kn as compared to the velocity of thermal and diffusion slipping, then in the calculation of ψ_i^{B} the effects caused by surface curvature can be neglected. Therefore, the Barnett distribution function ψ_i^{B} can be presented as

$$\psi_i^{\mathrm{B}}(v_i) = w_{ni}\, w_{\tau 1i}\, h_i^{\mathrm{B}j}(w_i)\,\nabla_{n\tau 1}\Psi^j + w_{ni}\, w_{\tau 2i}\, h_i^{\mathrm{B}j}(w_i)\,\nabla_{n\tau 2}\Psi^j\,.$$

In accordance with the method of semispatial momenta the functions $\Phi_i^{\pm}$ describing the effect of the phase interface on the gas are expanded into a series in terms of semispatial polynomials of velocity. They can be presented in the form of the following sum

$$\Phi_i^{\pm} = \Phi_{ni}^{\pm} + \Phi_{\tau 1i}^{\pm} + \Phi_{\tau 2i}^{\pm}\,, \tag{3}$$

where

$$\Phi_{ni}^{\pm} = \sum_l P_{ni}^{(l)}\,(b_i^{l+} + b_i^{l-}\,\mathrm{sign}\, w_n^i)\,;$$

$$\Phi^{\pm}_{\tau 1i} = \sum_{l} P^{(l)}_{\tau 1i}\,(a^{l+}_{i1} + a^{l-}_{i1}\ \text{sign}\ w^{i}_{n})\ ;$$

$$\Phi^{\pm}_{\tau 2i} = \sum_{l} P^{(l)}_{\tau 2i}\,(a^{l+}_{i2} + a^{l-}_{i2}\ \text{sign}\ w^{i}_{n})\ .$$

In the expansion of functions $\Phi^{\pm}_{ni}$ we restrict ourselves to the terms responsible for the laws of conservation of mass, momentum and energy, and in the expansion of functions $\Phi^{\pm}_{\tau ki}$ to the terms describing the process of momentum transfer [1]. The following set of velocity polynomials

$$P^{(0)}_{ni} = 1\ ,\quad P^{(1)}_{ni} = w_{ni}\ ,\quad P^{(2)}_{ni} = S^{1}_{3/2}\ ,$$

$$P^{(0)}_{\tau ki} = w_{\tau ki}\ ,\quad P^{(1)}_{\tau ki} = w_{ni} w_{\tau ki}\ ,\quad k = 1,\,2\ .$$

corresponds to this choice.

3. Having substituted distributions (2) into formula (1), we obtain the following equation with respect to functions $\Phi^{\pm}_{i}$

$$f_{i0}\left(\frac{v_n}{H_n}\frac{\partial\Phi^{\pm}_{i}}{\partial x_n} + \frac{v_{\tau 1}}{H_{\tau 1}}\frac{\partial\Phi^{\pm}_{i}}{\partial x_{\tau 1}} + \frac{v_{\tau 2}}{H_{\tau 2}}\frac{\partial\Phi^{\pm}_{i}}{\partial x_{\tau 2}}\right) +$$

$$+ f_{i0}\left(-\frac{v_n v_{\tau 1}}{H_n H_{\tau 1}}\frac{\partial H_n}{\partial x_{\tau 1}} - \frac{v_n v_{\tau 2}}{H_n H_{\tau 2}}\frac{\partial H_n}{\partial x_{\tau 2}} + \frac{v^{2}_{\tau 1}}{H_n H_{\tau 1}}\frac{\partial H_{\tau 1}}{\partial x_n} + \frac{v^{2}_{\tau 2}}{H_n H_{\tau 2}}\frac{\partial H_{\tau 2}}{\partial x_n}\right)\frac{\partial\Phi^{\pm}_{i}}{\partial v_n} +$$

$$+ f_{i0}\left(-\frac{v_{\tau 1} v_{\tau 2}}{H_{\tau 1} H_{\tau 2}}\frac{\partial H_{\tau 1}}{\partial x_{\tau 2}} - \frac{v_n v_{\tau 1}}{H_n H_{\tau 1}}\frac{\partial H_{\tau 1}}{\partial x_n} + \frac{v^{2}_{n}}{H_n H_{\tau 1}}\frac{\partial H_n}{\partial x_{\tau 1}} + \frac{v^{2}_{\tau 2}}{H_{\tau 1} H_{\tau 2}}\frac{\partial H_{\tau 2}}{\partial x_{\tau 1}}\right)\frac{\partial\Phi^{\pm}_{i}}{\partial v_{\tau 1}} +$$

$$+ f_{i0}\left(-\frac{v_{\tau 1} v_{\tau 2}}{H_{\tau 1} H_{\tau 2}}\frac{\partial H_{\tau 2}}{\partial x_{\tau 1}} - \frac{v_n v_{\tau 2}}{H_n H_{\tau 2}}\frac{\partial H_{\tau 2}}{\partial x_n} + \frac{v^{2}_{n}}{H_n H_{\tau 2}}\frac{\partial H_n}{\partial x_{\tau 2}} + \frac{v^{2}_{\tau 1}}{H_{\tau 1} H_{\tau 2}}\frac{\partial H_{\tau 1}}{\partial x_{\tau 2}}\right)\frac{\partial\Phi^{\pm}_{i}}{\partial v_{\tau 2}} =$$

$$= \sum_{j} n_i\, n_j\, I_{ij}\,(\Phi^{\pm}_{i} + \Phi^{\pm}_{j})\ , \tag{4}$$

where $I_{ij}(\Phi^{\pm}_{i} + \Phi^{\pm}_{j})$ is the linearized Boltzmann integral of collisions.

Multiplying sequentially relation (4) by $(1 \pm \text{sign}\ w_{ni})$, $w_{ni}(1 \pm \text{sign}\ w_{ni})$, $S^{1}_{/2}(1 \pm \text{sign}\ w_{ni})$, $w_{\tau 1i}(1 \pm \text{sign}\ w_{ni})$, $w_{\tau 1i}w_{ni}(1 \pm \text{sign}\ w_{ni})$, $w_{\tau 2i}(1 \pm \text{sign}\ w_{ni})$, $w_{\tau 2i}w_{ni}(1 \pm \text{sign}\ w_{ni})$ and integrating over the entire range of velocities, we obtain a system of linear homogeneous differential equations for the coefficients of expansion $b^{l\pm}_{i}$, $a^{l\pm}_{ik}$ which is not given here since it is very cumbersome.

The obtained system of equations can be solved by the method of successive approximations by the Knudsen number [5, 6]. This solution, with allowance for the requirement that at large distances from the liquid surface the distribution functions of molecules become Chapman distribution functions, has the following form

$$b^{l\pm}_{i} = \sum_{j} B_j\,(x_{\tau 1},\, x_{\tau 2})\,\beta^{l\pm}_{ij}\ \exp\,(\gamma_i\, x)\ , \tag{5}$$

$$a^{l\pm}_{ik} = \sum_{j} A_{jk}\,(x_{\tau 1},\, x_{\tau 2})\,(\alpha^{l\pm}_{ikj} + \varepsilon\tilde{\alpha}^{l\pm}_{ikj}\,)\ \exp\,(-\,\delta_{m1}x - \varepsilon\delta_{m2}x) +$$

$$+\,\varepsilon \sum_{j} \frac{1}{H_{\tau k}}\frac{\partial B_j}{\partial x_{\tau k}}\,\mu^{l\pm}_{ij}\ \exp\,(-\,\gamma_j\, x)\ . \tag{6}$$

Substituting relations (5), (6) into the equations for $b_i^{l\pm}$, $a_{ik}^{l\pm}$ of the abovementioned system of differential equations, we obtain a system of linear homogeneous algebraic equations with respect to the coefficients $\alpha_{ikj}^{l\pm}$, $\beta_{ij}^{l\pm}$, and $\mu_{ij}^{l\pm}$. From the condition that the determinant of this system be equal to zero we find all γ_j; then we can calculate the quantities $\alpha_{ikj}^{l\pm}$, $\beta_{ij}^{l\pm}$, and $\mu_{ij}^{l\pm}$.

4. The coefficients $B_j(x_{\tau 1}, x_{\tau 2})$ and $A_{jk}(x_{\tau 1}, x_{\tau 2})$ and jumps are determined from the kinetic boundary conditions, which can be found by the Maxwell boundary conditions

$$f_i^+ (v_{ni}, v_{\tau 1 i}, v_{\tau 2 i}) = f_i' + f_i'' , \quad f_i' = \alpha_i^- f_{i0} , \tag{7}$$

$$f_i'' = (1 - \alpha_i^-) (q_{ti} f_{is} + (1 - q_{ti}) f_i^- (- v_{xi}, v_{yi}, v_{zi})) .$$

Here q_{ti} is the coefficient of accommodation of the tangential component of momentum, α_i^- is the coefficient of condensation,

$$f_{is} = n_{is} \left(\frac{m_i}{2\pi k T_{is}} \right)^{3/2} \exp \left(- \frac{m_i v_i^2}{2 k T_{is}} \right) ,$$

n_{is}, T_{is} are macroparameters characterizing molecules diffusely reflected from the surface. Substituting distribution functions (2) into Eq. (7), multiplying successively the obtained expressions by w_{ni}, w_{ni}^2, $S_{3/2}^1 w_{ni}$, $w_{\tau k i} w_{ni}$, $w_{\tau k}^i w_n^{i2}$ and integrating with respect to the positive halfspace of velocities, we obtain a system of momentum kinetic equations. Combining it with the conditions of nonflow of the nonreacting portion of the flow of molecules of the i-th component and the conditions of energy accommodation [7]

$$(1 - \alpha_i^-) J_i^- + J_i' = 0 , \tag{8}$$

$$\alpha_{Ti} = \frac{(1 - \alpha_i^-) Q_i^- + Q_i'}{(1 - \alpha_i^-) Q_i^- + Q_{wi}'} , \tag{9}$$

we have a system of linear algebraic equations the solution of which yields the determination of all the unknowns:

$$\delta T = \delta T^j \, \nabla_n \Psi^j , \tag{10}$$

$$G_{\tau k} = G_{\tau k}^j \, \nabla_{\tau k} \Psi^j + G_{n,\tau k} \, \Pi_{n,\tau k} + \mathrm{Kn}_k \, \widetilde{G}_{\tau k}^j \, \nabla_{n,\tau k} \Psi^j +$$

$$+ \mathrm{Kn}_k \frac{G_n^j}{H_n H_{\tau k}} \frac{\partial^2 \Psi^j}{\partial x_n \partial x_{\tau k}} + G_k^{\mathrm{B}} \, \nabla_{n,\tau k} \Psi^j \tag{11}$$

Coefficients $G_{\tau k}^0$ describe thermal, $G_{\tau k}^j$, $j \neq 0$ diffusion, $G_{n,\tau k}$ isothermal, and G_k^{B} Barnett slipping. The presence of coefficients $G_{\tau k}^j$ and G_n^j is caused by the curvature of the surface streamlined by the gas flow.

The analysis conducted shows that in general the coefficients of temperature jumps depend not only on the coefficients α_i^- and the coefficients of energy accommodation α_{Ti}, which characterize the velocity of evaporation (condensation) and normal heat fluxes, respectively, but also on the coefficients of momentum accommodation $q_{\tau i}$, characterizing the flows tangential to the particle surface. In turn, the coefficients of slipping depend not only on $q_{\tau i}$, but also on α_i^- and α_{Ti}.

We note that in the considered approximation jumps of temperature and concentration are independent of the slipping velocity. The coefficients of slipping can be calculated only when the jumps are determined, the allowance for which makes corrections of the order of the local Knudsen number Kn to these coefficients.

The results obtained at present are most general. They make it possible to estimate the effect of phase conversions on the velocity of slipping of a gas mixture. The results of [1] can be found by formula (11) in the limiting case of the absence of evaporation ($\alpha_i^- \to 0$) at $N = 2$.

5. We now find the boundary conditions for normal mass and energy fluxes. We write the law of mass conservation in a differential form. In a gas volume (including the Knudsen layer) we have

$$\operatorname{div} \mathbf{U}_i = 0\,, \tag{12}$$

where $\mathbf{U}_i$ is the total macroscopic velocity of motion of the i-th component of the gas mixture, which is the sum of the hydrodynamic velocity $\mathbf{u}_i$ and the mean-mass velocity of gas flow in the Knudsen layer $\mathbf{v}_i$, which is the correction to $\mathbf{u}_i$ caused by the difference of the distribution function in the Knudsen layer from the volumetric one

$$\mathbf{U}_i = \mathbf{u}_i + \mathbf{v}_i\,,$$

$$\mathbf{v}_i = \sum_i \frac{1}{n_i} \sqrt{\left(\frac{2kT_0}{m_i}\right)} \int f_{i0}\, \Phi_i^{\pm}\, \mathbf{w}_i\, d^3 v_i\,. \tag{13}$$

It is evident that $\mathbf{v}_i \to 0$ when $r \to \infty$.

Since $\mathbf{u}_i$ satisfies Eq. (12), then the following relation holds for $\mathbf{v}_i$

$$\operatorname{div} \mathbf{v}_i = 0\,, \tag{14}$$

Integrating this expression with respect to the volume element of the Knudsen layer, we obtain

$$H_{\tau 1} H_{\tau 2} v_{ni} \big|_{x_n = x_{n0}} = - \int \frac{\partial}{\partial x_{x_{\tau 1}}} (H_n H_{\tau 2} v_{\tau 1 i})\, dx_n - \int \frac{\partial}{\partial x_{x_{\tau 2}}} (H_n H_{\tau 1} v_{\tau 2 i})\, dx_n\,. \tag{15}$$

It follows from (13) that

$$u_{ni} \big|_{x_n = x_{n0}} = U_{ni} - v_{ni} \big|_{x_n = x_{n0}}\,,$$

when $U_n = \sqrt{2kT_o/m_N G_n}$ is the mean-mass velocity of gas flow.

Having calculated $v_{\tau ki}$ and substituted the obtained expressions into (15), we finally have for the normal component of the velocity of the i-th component of the mixture:

$$U_{ni} = -\frac{1}{2} \sqrt{\left(\frac{2kT_0}{m_i}\right)}\, h_{N0}^{j} \nabla_n \Psi^j -$$

$$- \sqrt{\left(\frac{2kT_0}{m_i}\right)} \sum_k \int \frac{\partial}{\partial x_{x_{\tau k}}} \left\{ \frac{H_n H_{\tau 1} H_{\tau 2}}{H_{\tau k}} \left(\frac{\overset{0+}{a}_{ki}}{2} + \frac{\overset{1-}{a}_{ki}}{2\sqrt{\pi}} \right) \right\} dx_n\,. \tag{16}$$

We note that due to the smallness of the Knudsen number in calculating the velocity $v_{\tau ki}$ it is sufficient to take the distribution function $\Phi_i^{\pm}$ calculated for a plane surface.

Similarly we can obtain an expression for the normal component of the heat flux

$$Q_n = \sum_i \sqrt{\left(\frac{2}{m_i}\right)} (kT_0)^{3/2} \frac{5}{4} \left(h_{i0}^{j} - \sqrt{\left(\frac{m_i}{m_N}\right)}\, h_{N0}^{j} + h_{i1}^{j} \right) \nabla_r \Psi^j -$$

$$- \sqrt{\left(\frac{2}{m_i}\right)} (kT_0)^{3/2} \sum_{ik} \int \frac{\partial}{\partial x_{x_{\tau k}}} \left\{ \frac{H_n H_{\tau 1} H_{\tau 2}}{H_{\tau k}} \left(\frac{5}{4}\, \overset{0+}{a}_{ik} + \frac{3\overset{1-}{a}_{ik}}{2\sqrt{\pi}} \right) \right\} dx_n\,. \tag{17}$$

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