Nonequilibrium thermodynamics of a weakly rarefied gas mixture

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1. INTRODUCTION

An inhomogeneous weakly rarefied gas, which corresponds to the condition $\lambda < L$ (λ is the mean free path of the particles, and L is the characteristic length of the problem), is an example of a nonequilibrium system for which the well-developed methods of solving the Boltzmann equation make it possible to establish the limits of applicability of phenomenological nonequilibrium thermodynamics. On the basis of the well-known studies of Prigogine,[1,2] it was assumed for a long time that the applicability of nonequilibrium thermodynamics is limited in this case to the results corresponding to the first approximation of Chapman–Enskog theory,[3] which gives rise to linear relationships between the fluxes and gradients of the fundamental thermodynamic variables (thermodynamic forces). However, Kagan[4] noted that in the general case one can include among the independent thermodynamic forces quantities having the necessary tensor dimension and obtained by differentiating with respect to the coordinates the corresponding fluxes. This conclusion followed, in particular, from an analysis of the contribution of viscous momentum transport to the diffusion of a mixture, which was calculated in Ref. 4 using the Grad 13-moment approximation.[5] The need to take into account the corresponding terms proportional to the second derivatives of the velocity and the temperature in the expressions for the fluxes also followed from the results of the second (Burnett) approximation in Chapman–Enskog theory.[3,6]

The compatibility of the principles of nonequilibrium thermodynamics with the higher approximations of the Chapman–Enskog method at the level of the linearized Burnett approximation was proved in Refs. 7–9. At this level, the expression for the entropy production on the right-hand side of the entropy balance equation acquires additional terms containing higher than first-order derivatives of the fundamental thermodynamic variables with respect to the cordinates. The system of phenomenological equations for the fluxes and forces is correspondingly extended. The need to take into account new terms in the analysis of flows of weakly rarefied gases and in the flow of gas past convex bodies was clearly demonstrated in the solution of a large number of problems.[4,10–17]

No less important effects due to rarefaction of the gas occur near an interface (for example, at the boundary of the gas and a wall[18,19]). It is well known that for inhomogeneous low-density gases the values of their macroscopic parameters—velocity, temperature, composition, etc.—directly at the surface of a body around which flow is occurring differ from the corresponding parameters that characterize the state of the surface. This difference is due to the nonzero mean free path of the molecules and can be described by the introduction of some effective boundary conditions that take the form of various apparent discontinuities of the macroscopic parameters at the boundaries of the condensed phase.[18]

As was shown by Waldmann,[20] a fairly general approach in the formulation of the boundary conditions can be developed using the methods of nonequilibrium thermodynamics. The approach is based on the notion of boundary entropy production, which is defined as the integral over unit section of the surface of the difference of the entropy fluxes in the gas and in the condensed phase. Unfortunately, the purely phenomenological approach to the derivation of the expression for the entropy production and also the neglect of the thickness of the Knudsen layer at the wall caused Waldmann and Vestner[11,20,21] to omit several boundary effects of the same order of magnitude as the effects taken into account in the method.[16,17] However, the idea advanced in Ref. 20 is very fruitful if instead of the phenomenological expression one uses the kinetic expression for the entropy[1)] and takes into account consistently the finite thickness of the Knudsen layer.[24–26]

In this paper, we develop a general scheme for applying nonequilibrium thermodynamics to the investigation of transport processes in an inhomogeneous multicomponent gas mixture in the presence of surfaces that confine the gas. We consider slow steady flows of weakly rarefied gas mixtures, for which the use of the methods of nonequilibrium thermodynamics is the most obvious. Systematic development of the Burnett approximation in the Chapman–Enskog method for the linearized kinetic equation and the use of the kinetic expression for the entropy in this approximation make it possible to write down a system of linear phenomenological equations for the fluxes that contain a dependence on not only the first but also the second derivatives of the velocity, temperature, and concentrations of the components of the mixture. In each subsystem of vector and tensor equations, in addition to the ordinary fluxes, "unphysical" fluxes arise, which automatically ensure that the Onsager symmetry relations hold for the crossed transport coefficients.

The methods of nonequilibrium thermodynamics are further used to analyze the state of a nonequilibrium gas mixture near an interphase surface. By means of the boundary

condition for the distribution function and the kinetic equation for the Knudsen correction to it, we establish balance equations for the mass, momentum, and energy at the interface. The missing boundary conditions are found from the kinetic expression for the boundary entropy production. This last is used to obtain some phenomenological relationships between the fluxes and forces on the interface, and these make it possible to determine the contribution of the fluxes localized in the Knudsen layer to the total mass, momentum, and energy transport in the gas mixture. In the conclusions, we consider some actual examples of the use of the relations obtained here and discuss the possibilities of using them in fairly general situations.

2. THE BURNETT APPROXIMATION FOR THE LINEARIZED KINETIC EQUATION

We consider the steady state of an inhomogeneous gas mixture described by means of the distribution functions $f_\alpha(\mathbf{v}_\alpha, \mathbf{r})$, where $\mathbf{v}_\alpha$ is the velocity of the particles of species α, and $\mathbf{r}$ is their position vector. In the case of weak deviation of the gas from equilibrium, we assume that

$$f_\alpha = f_\alpha^{(0)}(1 + \Phi_\alpha), \tag{1}$$

where $f_\alpha^{(0)}$ is the local Maxwell distribution

$$f_\alpha^{(0)} = n_\alpha(\beta_\alpha/\pi)^{3/2} \exp(-\beta_\alpha c_\alpha^2), \tag{2}$$

and Φ_α are small corrections that satisfy the system of linearized Boltzmann equations[9,15]

$$(\mathbf{v}_\alpha \nabla)\ln f_\alpha^{(0)} + (\mathbf{v}_\alpha \nabla)\Phi_\alpha = \sum_\beta L_{\alpha\beta}(\Phi),$$

$$\nabla \ln f_\alpha^{(0)} = \nabla \ln p_\alpha + (\beta_\alpha c_\alpha^2 - 5/2)\nabla \ln T + 2\beta_\alpha \mathbf{c}_\alpha(\nabla \mathbf{u}). \tag{3}$$

Here $L_{\alpha\beta}$ is the linearized collision operator, $\mathbf{c}_\alpha = \mathbf{v}_\alpha - \mathbf{u}$, $p_\alpha = n_\alpha kT$, $\beta_\alpha = m_\alpha/2kT$, where n_α is the number density of the particles of species α, m_α is their mass, T is the temperature, $\mathbf{u}$ is the mass-average velocity of the mixture, and k is Boltzmann's constant.

When the standard Chapman–Enskog method is used,[3] the solution of Eqs. (3) is sought in the form

$$\Phi_\alpha = \sum_{n=1}^\infty \Phi_\alpha^{(n)} = \Phi_\alpha^{(1)} + \Phi_\alpha^{(2)} + \dots,$$

where $\Phi_\alpha^{(n)}$ are found by successive approximations from the chain of integral equations

$$\sum_{k=0}^{n-1} D^{(k)}\Phi_\alpha^{(n-k-1)} = -(\mathbf{v}_\alpha\nabla)\Phi_\alpha^{n-1} + \sum_\beta L_{\alpha\beta}(\Phi^{(n)}). \tag{4}$$

Here the structure of the operator $D^{(k)}$ is determined by transforming the left-hand side of (3) with allowance for the level of the approximations that is used in writing down the conservation equations (Euler, Navier–Stokes, etc., equations).

The results of the first approximation $(n=1)$ of the Chapman–Enskog method are well known[3,27] and are given here making the treatment general and as a necessary stage for obtaining the corrections of the next approximation $(n=2)$. The transformation of the left-hand side of (3) by means of the Euler equations gives

$$D^{(0)}\Phi_\alpha^{(0)} \equiv (\beta_\alpha c_\alpha^2 - 5/2)(\mathbf{c}_\alpha \cdot \nabla)\ln T + 2\beta_\alpha \overline{\mathbf{c}_\alpha \mathbf{c}_\alpha}:\nabla\mathbf{u}$$

$$+ \frac{n}{n_\alpha} \mathbf{c}_\alpha \cdot \mathbf{d}_\alpha = \sum_\beta L_{\alpha\beta}(\Phi^{(1)}), \tag{5}$$

where

$$\mathbf{d}_\alpha = \nabla(n_\alpha/n) + (n_\alpha/n - \rho_\alpha/\rho)\nabla \ln p. \tag{6}$$

Here $\rho_\alpha = m_\alpha n_\alpha$, $\rho = \Sigma_\alpha \rho_\alpha$, $\overline{\mathbf{cc}}$ denotes the irreducible second-rank tensor with components $c_i c_k - (1/3)c^2\delta_{ik}$, and $\nabla\mathbf{u}$ corresponds to the tensor

$$\varepsilon_{ik} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i}\right) - \frac{1}{3}\nabla\mathbf{u}\delta_{ik}.$$

The symbol : is used to denote the scalar product of tensors. The expression for $\Phi_\alpha^{(1)}$ has the form

$$\Phi_\alpha^{(1)} = \Phi_{t\alpha}(\mathbf{c}_\alpha\nabla)\ln T + \Phi_{p\alpha}\overline{\mathbf{c}_\alpha \mathbf{c}_\alpha}:\overline{\nabla\mathbf{u}} + \mathbf{c}_\alpha\sum_\beta \Phi_{d\alpha}^\beta \mathbf{d}_\beta, \tag{7}$$

where Φ_t, Φ_p, and Φ_d are found by solving the integral equations

$$(\beta_\alpha c^2 - 5/2)\mathbf{c}_\alpha = \sum_\beta L_{\alpha\beta}(\mathbf{c}\Phi_t),$$

$$2\beta_\alpha \overline{\mathbf{c}_\alpha \mathbf{c}_\alpha} = \sum_\beta L_{\alpha\beta}(\overline{\mathbf{cc}} \; \Phi_p),$$

$$\frac{n}{n_\alpha}\left(\delta_{\alpha\gamma} - \frac{\rho_\alpha}{\rho}\right)\mathbf{c}_\alpha = \sum_\beta L_{\alpha\beta}(\mathbf{c}\Phi_d^\gamma). \tag{8}$$

One of the main problems of kinetic theory is to obtain expressions for the nondiagonal part of the stress tensor, the heat flux, and the diffusion velocities, which occur in the system of hydrodynamic equations (conservation equations). The general expressions for these quantities have the form

$$\hat{\pi} = \langle m\,\overline{\mathbf{cc}}|\Phi\rangle, \quad \mathbf{q} = \left\langle \frac{m}{2}\,c\mathbf{c}^2\Big|\Phi\right\rangle,$$

$$\mathbf{w}_\alpha = \mathbf{u}_\alpha - \mathbf{u} = \frac{1}{n_\alpha}\int \mathbf{c}_\alpha\Phi_\alpha f_\alpha^{(0)}d\mathbf{v}_\alpha. \tag{9}$$

Here and in what follows, $\langle g|h\rangle$ denotes the inner scalar product of the form

$$\langle g|h\rangle = \sum_\alpha \int g_\alpha h_\alpha f_\alpha^{(0)}d\mathbf{v}_\alpha.$$

In the first Chapman–Enskog approximation

$$\hat{\pi}^{(1)} = -2\eta\overline{\nabla\mathbf{u}},$$

$$\mathbf{q}^{(1)} = -\lambda'\nabla T - \sum_\beta D_{T\beta}p\mathbf{d}_\beta + \frac{5}{2}\sum_\alpha p_\alpha\mathbf{w}_\alpha^{(1)},$$

$$\mathbf{w}_\alpha^{(1)} = -\sum_\beta D_{\alpha\beta}\mathbf{d}_\beta - D_{T\alpha}\nabla\ln T, \qquad (10)$$

where η, λ', $D_{\alpha\beta}$, $D_{T\alpha}$ are, respectively, the coefficients of viscosity, thermal conductivity, multicomponent diffusion, and thermodiffusion.[27]

To find the corrections to the distribution function in the Burnett approximation ($n=2$), we have the equations

$$D^{(1)}\Phi_\alpha^{(0)} = -(\mathbf{v}_\alpha\nabla)\Phi_\alpha^{(1)} + \sum_\beta L_{\alpha\beta}(\Phi^{(2)}), \qquad (11)$$

where

$$D^{(1)}\Phi_\alpha^{(0)} = -\frac{m_\alpha}{\rho kT}(\mathbf{c}_\alpha\nabla)\hat{\pi}^{(1)} - \left(\frac{2}{3}\beta_\alpha c_\alpha^2 - 1\right)\frac{1}{p}\nabla\mathbf{q}^{(1)}$$

$$-\frac{1}{n_\alpha}\nabla n_\alpha\mathbf{w}_\alpha^{(1)} + \frac{1}{n}$$

$$\times(\beta_\alpha c_\alpha^2 - 3/2)\nabla\sum_\alpha n_\alpha\mathbf{w}_\alpha^{(1)}. \qquad (12)$$

For slow gas flows ($|\mathbf{u}| \ll (kT/m_\alpha)^{1/2}$), we can ignore the term $\sim(\mathbf{u}\cdot\nabla)\Phi_\alpha^{(1)}$, allowance for which goes beyond the linear approximation. Then, bearing in mind that

$$(\mathbf{c}_\alpha\cdot\nabla)\Phi_\alpha^{(1)} = \Phi_{t\alpha}\overline{\mathbf{c}_\alpha\mathbf{c}_\alpha}:\frac{\nabla\nabla T}{T} + \Phi_{p\alpha}(\mathbf{c}_\alpha\cdot\nabla)$$

$$\times(\mathbf{c}_\alpha\mathbf{c}_\alpha:\overline{\nabla\mathbf{u}}) + \sum_\beta \mathbf{c}_\alpha\mathbf{c}_\alpha\Phi_{d\alpha}^\beta\nabla\mathbf{d}_\beta, \qquad (13)$$

we find after simple manipulations

$$\left\{\Phi_{t\alpha}\mathbf{c}_\alpha\mathbf{c}_\alpha + \left[\left(\frac{2}{3}\beta_\alpha c_\alpha^2 - 1\right)\left(\frac{\lambda'T}{p} + \sum_\beta \frac{n_\beta}{n}D_{T\beta}\right)\right.\right.$$

$$\left.+ D_{T\alpha}\right]\delta^{(2)}\left\}:\frac{\nabla\nabla T}{T} + (\Phi_{p\alpha}\mathbf{c}_\alpha\overline{\mathbf{c}_\alpha\mathbf{c}_\alpha}\right.$$

$$+ \frac{2m_\alpha}{\rho kT}\eta\mathbf{c}_\alpha\delta^{(4)}):\nabla\overline{\nabla\mathbf{u}} + \sum_\beta \{\mathbf{c}_\alpha\mathbf{c}_\alpha\Phi_{d\alpha}^\beta$$

$$+ \left[\left(\frac{2}{3}\beta_\alpha c_\alpha^2 - 1\right)\left(D_{T\beta} + \sum_\gamma \frac{n_\gamma}{n}D_{\gamma\beta}\right)\right.$$

$$\left.+ D_{\alpha\beta}\right]\delta^{(2)}\}:\nabla\mathbf{d}_\beta = \sum_\zeta L_{\alpha\zeta}(\Phi^{(2)}), \qquad (14)$$

where $\delta^{(2)}$ and $\delta^{(4)}$ are the unit tensors of second and fourth rank, and

$$\delta_{ijkl}^{(4)} = \frac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \frac{1}{3}\delta_{ij}\delta_{kl}.$$

The solution for $\Phi_\alpha^{(2)}$ can be represented in the form

$$\Phi_\alpha^{(2)} = \Phi_{B\alpha}^T:\frac{\nabla\nabla T}{T} + \Phi_{B\alpha}:\overline{\nabla\nabla u} + \sum_\beta \Phi_{B\alpha}^{D\beta}\nabla\mathbf{d}_\beta. \qquad (15)$$

In the second term on the left-hand side of (14), it is convenient to separate the tensor $\overline{\mathbf{ccc}}$, which corresponds to the third-rank irreducible tensor

$$c_ic_jc_k - \frac{1}{5}c^2(\delta_{ij}c_k + \delta_{ik}c_j + \delta_{jk}c_i).$$

Then

$$\left(\Phi_{p\alpha}\mathbf{c}_\alpha\overline{\mathbf{c}_\alpha\mathbf{c}_\alpha} + \frac{2m_\alpha\eta}{\rho kT}\mathbf{c}_\alpha\delta^{(4)}\right):\nabla\overline{\nabla\mathbf{u}} = \Phi_{p\alpha}\overline{\mathbf{c}_\alpha\mathbf{c}_\alpha\mathbf{c}_\alpha}:\overline{\nabla\nabla\mathbf{u}}$$

$$+ \left(\Phi_{p\alpha}\frac{c_\alpha^2}{5} + \frac{m_\alpha\eta}{\rho kT}\right)\mathbf{c}_\alpha\nabla^2\mathbf{u}.$$

As a result, for the total correction to the distribution function in the Burnett approximation we have

$$\Phi_\alpha = \Phi_{t\alpha}(\mathbf{c}_\alpha\nabla)\ln T + \Phi_{p\alpha}\overline{\mathbf{c}_\alpha\mathbf{c}_\alpha}:\overline{\nabla u}$$

$$+ \mathbf{c}_\alpha\sum_\beta \Phi_{d\alpha}^\beta\mathbf{d}_\beta + \Phi_{B\alpha}^T:\frac{\nabla\nabla T}{T} + \Phi_{B\alpha}^u:\overline{\nabla\nabla u}$$

$$+ \Phi_{B\alpha}^v\mathbf{c}_\alpha\nabla^2\mathbf{u} + \sum_\beta \Phi_{B\alpha}^{D\beta}\nabla\mathbf{d}_\beta,$$

where the functions $\Phi_{B\alpha}^T$, $\Phi_{B\alpha}^u$, $\Phi_{B\alpha}^v$, and $\Phi_{B\alpha}^{D\beta}$ are found by solving a system of integral equations of the form

$$\Phi_{t\alpha}\mathbf{c}_\alpha\mathbf{c}_\alpha + \left[\left(\frac{2}{3}\beta_\alpha c_\alpha^2 - 1\right)\left(\frac{\lambda'T}{p} + \sum_\zeta \frac{n_\zeta}{n}D_{T\zeta}\right)\right.$$

$$\left.+ D_{T\alpha}\right]\delta^{(2)} = \sum_\beta L_{\alpha\beta}(\Phi_B^T),$$

$$\Phi_{p\alpha}\overline{\mathbf{c}_\alpha\mathbf{c}_\alpha\mathbf{c}_\alpha} = \sum_\beta L_{\alpha\beta}(\Phi_B^u),$$

$$\mathbf{c}_\alpha\left(\Phi_{p\alpha}\frac{c_\alpha^2}{5} + \frac{m_\alpha\eta}{\rho kT}\right) = \sum_\beta L_{\alpha\beta}(\mathbf{c}_\alpha\Phi_B^v),$$

$$\overline{\mathbf{c}_\alpha\mathbf{c}_\alpha}\Phi_{d\alpha}^\gamma + \left[\left(\frac{2}{3}\beta_\alpha c_\alpha^2 - 1\right)\left(D_{T\gamma} + \sum_\zeta \frac{n_\zeta}{n}D_{\zeta\gamma}\right)\right.$$

$$\left.+ D_{\alpha\gamma}\right]\delta^{(2)} = \sum_\beta L_{\alpha\beta}(\Phi_B^{D\gamma}). \qquad (17)$$

3. NONEQUILIBRIUM THERMODYNAMICS IN THE BURNETT APPROXIMATION

To establish the structure of the macroscopic fluxes that follows from the representation (16), we turn to the basic

propositions of nonequilibrium thermodynamics. As is well known, this is based on the entropy balance equation, which in the steady case can be written as

$$\nabla \cdot \mathbf{J}_s = \sigma, \tag{18}$$

where $\mathbf{J}_s$ is the density of the total entropy flux:

$$\mathbf{J}_s = -k \sum_\alpha \int \mathbf{v}_\alpha f_\alpha \ln f_\alpha d\mathbf{v}_\alpha, \tag{19}$$

and σ is the entropy production due to particle collisions:

$$\sigma = -k \sum_\alpha \sum_\beta \int f_\alpha^{(0)} \ln f_\alpha L_{\alpha\beta}(\Phi) d\mathbf{v}_\alpha. \tag{20}$$

In what follows, we shall be mainly interested in the entropy production σ. It is well known that the phenomenological expression for σ obtained in nonequilibrium thermodynamics is a bilinear combination of the corresponding fluxes and thermodynamic forces.[2] It is easy to shown that if the linearized Burnett approximation is used the bilinear structure of the expression for σ remains, but with not only the first derivatives of $\mathbf{u}$, T, and n_α but also the second derivatives of these quantities playing the role of thermodynamic forces; the number of fluxes associated by linear relation with thermodynamic forces is increased accordingly.

The expression (20) for σ corresponding to the linear approximation can be represented in the form

$$\sigma = -k\langle\Phi|L(\Phi)\rangle, \quad L(\Phi) = \sum_\beta L_{\alpha\beta}(\Phi). \tag{21}$$

With allowance for (4), we rewrite (21) as

$$\sigma = -k\sum_{n=1}^{\infty} \left\langle \Phi^{(n)} \middle| \left[\sum_{k=0}^{n-1} D^{(k)}\Phi^{(n-k-1)} + (\mathbf{c}\cdot\nabla)\Phi^{n-1} \right] \right\rangle. \tag{22}$$

Using the expression for $\Phi_\alpha^{(n)}$ and the terms in the square brackets (22) for $n=1,2$ that we obtained above, we can write the entropy production in the form

$$\sigma = -\frac{1}{T}\Bigg[(\mathbf{h}\cdot\nabla)\ln T + \hat{\pi}:\overset{\frown}{\nabla\mathbf{u}} + p\sum_{\beta=1}^{N-1}(\mathbf{w}_\beta - \mathbf{w}_N)\mathbf{d}_\beta$$

$$+ \hat{\mathbf{J}}^T:\frac{\nabla\nabla T}{T} + \hat{\mathbf{J}}^u:\overset{\frown}{\nabla\nabla u} + \mathbf{J}^v\nabla^2\mathbf{u}$$

$$+ \sum_{\beta=1}^{N-1}(\hat{\mathbf{J}}_\beta^D - \hat{\mathbf{J}}_N^D)\nabla\mathbf{d}_\beta \Bigg]. \tag{23}$$

Here $\mathbf{h}=\mathbf{q}-(5/2)\Sigma_\alpha p_\alpha \mathbf{w}_\alpha$ is the reduced heat flux in the mixture, and

$$\hat{\mathbf{J}}^T = kT\langle\Phi_t\mathbf{cc}|\Phi\rangle, \quad \hat{\mathbf{J}}^u = kT\langle\Phi_p\overset{\frown}{\mathbf{ccc}}|\Phi\rangle,$$

$$\mathbf{J}^v = kT\left\langle \left(\Phi_p\frac{c^2}{5} + \frac{m\eta}{\rho kT}\right)\mathbf{c}\middle|\Phi \right\rangle,$$

$$\hat{\mathbf{J}}_\beta^D = kT\langle\mathbf{cc}\Phi_d^\beta|\Phi\rangle. \tag{24}$$

The tensor dimensions for these fluxes are obvious. In writing down the first, third, and last term in (23), we have used the fact that $\Sigma_{\alpha=1}^N \mathbf{d}_\alpha = 0$ and that in the stationary case $\nabla^2 T = 0$ and $(\nabla \cdot \mathbf{d}_\beta) = 0$.

The system of linear phenomenological equations corresponding to the entropy production (23) decomposes into three subsystems of the form

$$\mathbf{w}_\alpha - \mathbf{w}_N = -\sum_{\beta=1}^{N-1}\Lambda_{\alpha\beta}p\mathbf{d}_\beta - \Lambda_{\alpha N}\nabla \ln T - \Lambda_{\alpha,N+1}\nabla^2\mathbf{u},$$

$$\mathbf{h} = -\sum_{\beta=1}^{N-1}\Lambda_{N\beta}p\mathbf{d}_\beta - \Lambda_{NN}\nabla \ln T - \Lambda_{N,N+1}\nabla^2\mathbf{u}, \tag{25}$$

$$\mathbf{J}^v = -\sum_{\beta=1}^{N-1}\Lambda_{N+1,\beta}p\mathbf{d}_\beta - \Lambda_{N+1,N}\nabla \ln T$$

$$- \Lambda_{N+1,N+1}\nabla^2\mathbf{u},$$

$$\hat{\mathbf{J}}_\alpha^D - \hat{\mathbf{J}}_N^D = -\sum_{\beta=1}^{N-1}\lambda_{\alpha\beta}\overset{\frown}{\nabla\nabla}\left(\frac{n_\beta}{n}\right) - \lambda_{\alpha N}\overset{\frown}{\nabla\mathbf{u}} - \lambda_{\alpha,N+1}\frac{\overset{\frown}{\nabla\nabla}T}{T},$$

$$\hat{\pi} = -\sum_{\beta=1}^{N-1}\lambda_{N\beta}\overset{\frown}{\nabla\nabla}\left(\frac{n_\beta}{n}\right) - \lambda_{NN}\overset{\frown}{\nabla\mathbf{u}} - \lambda_{N,N+1}\frac{\overset{\frown}{\nabla\nabla}T}{T},$$

$$\hat{\mathbf{J}}^T = -\sum_{\beta=1}^{N-1}\lambda_{N+1,\beta}\overset{\frown}{\nabla\nabla}\left(\frac{n_\beta}{n}\right) - \lambda_{N+1,N}\overset{\frown}{\nabla\mathbf{u}}$$

$$- \lambda_{N+1,N+1}\frac{\overset{\frown}{\nabla\nabla}T}{T}, \tag{26}$$

$$\hat{\mathbf{J}}^u = -L_{11}\overset{\frown}{\nabla\nabla\mathbf{u}}. \tag{27}$$

In writing down (26), we have ignored the terms $\sim\overset{\frown}{\nabla\nabla}p$, allowance for which goes beyond the linear approximation. In the case of a single-component gas $(N=1)$, the system (25)–(27) goes over into the results obtained in a somewhat different manner in Ref. 9.

An important difference between the system of Eqs. (25)–(27) and the well-known phenomenological equations of nonequilibrium thermodynamics is that it includes some "unphysical" fluxes: $\mathbf{J}^v$, $\hat{\mathbf{J}}^T$, $\hat{\mathbf{J}}^D$, and $\hat{\mathbf{J}}^u$. Their appearance in subsystems of one and the same tensor dimension is absolutely necessary to ensure the correct Onsager symmetry relations, which hold for the crossed coefficients in the subsystems (25) and (26). In particular, from this point of view one must regard as inconsistent the earlier attempt in Ref. 28 to establish symmetry relations between the coefficients occurring in the equations for fluxes of different tensor dimension, in contradiction with the well-known Curie principle for isotropic systems.[2]

The form of some of the transport coefficients in the expressions for the "physical" fluxes $\mathbf{w}_\alpha - \mathbf{w}_N$, $\mathbf{h}$, and $\hat{\pi}$ is readily established by comparison with the expressions (10). In particular,

$$p\Lambda_{\alpha\beta} = D_{\alpha\beta} - D_{\alpha N} - (D_{N\beta} - D_{NN}), \quad \alpha,\beta = 1,\ldots,N-1,$$

$$\Lambda_{\alpha N} = \Lambda_{N\alpha} = D_{T\alpha} - D_{TN}, \quad \Lambda_{NN} = \lambda'T, \quad \lambda_{NN} = 2\eta. \tag{28}$$

The formal structure of the remaining coefficients corresponding to the Burnett approximation is readily established if one substitutes Φ_α from (16) in the expressions (24) for the fluxes. We note that some of the Burnett coefficients, for example, $\Lambda_{\alpha,N+1}$, $\Lambda_{N,N+1}$, $\lambda_{N,\beta}$, and $\lambda_{N,N+1}$, can be deter-

mined by using the results of the calculations made in Refs. 4 and 28. When allowance is made for only the first terms of the expansion in Sonine polynomials in the solution of the corresponding integral equations, the expressions for these coefficients have the form

$$\Lambda_{\alpha,N+1} = \frac{1}{p} \sum_{\beta=1}^{N-1} \frac{(D_{\beta\alpha} - D_{\beta N})}{x_\beta} \eta_\beta,$$

$$\Lambda_{N,N+1} = -\frac{2}{5} \frac{T}{p} \sum_{\beta=1}^{N} \frac{\lambda_\beta \eta_\beta}{x_\beta},$$

$$\lambda_{N,\beta} = \frac{2nm_\beta}{\rho} \sum_{\alpha=1}^{N} \frac{\eta_\alpha D_{\alpha\beta}}{x_\beta},$$

$$\lambda_{N,N+1} = -\frac{4}{5} \frac{T}{p} \sum_{\beta=1}^{N} \frac{\eta_\beta \lambda_\beta}{x_\beta}, \tag{29}$$

where $x_\beta = n_\beta/n$, and η_β and λ_β are the partial coefficients of viscosity and thermal conductivity calculated in the first Chapman–Enskog approximation.[3,4] Note that the coefficients $\Lambda_{N,N+1}$ and $\lambda_{N,N+1}$ are identical within a factor of 2; in Ref. 28, this identity was taken as an Onsager symmetry relation. In order to actually show that the symmetry relations hold for the coefficients of Eqs. (25), we show as an example that $\Lambda_{\alpha,N+1} = \Lambda_{N+1,\alpha}$.

We consider the flux $\mathbf{J}^v$ given in (24). Taking into account the orthogonality of $m_\alpha \mathbf{c}_\alpha$ and the expansions in polynomials of the correction Φ in the Chapman–Enskog method, we have

$$\mathbf{J}^v = kT \left\langle \Phi_p \frac{c^2}{5} \mathbf{c} \middle| \Phi \right\rangle.$$

We separate in Φ the term with $\mathbf{d}_\beta$. Then

$$\mathbf{J}^v = kT \left\langle \Phi_p \frac{c^2}{5} \mathbf{c} \middle| \mathbf{c} \sum_\beta \Phi_d^\beta \mathbf{d}_\beta \right\rangle.$$

Using the well-known expansions for Φ_p and Φ_d^β in series of Sonine polynomials[27] and restricting ourselves to just the first terms of the expansion, we can readily obtain (taking into account the condition $\Sigma_{\alpha=1}^{N} \mathbf{d}_\alpha = 0$)

$$\mathbf{J}^v = -\sum_\alpha^{N-1} \sum_\beta^{N-1} \frac{D_{\beta\alpha} - D_{\beta N}}{x_\beta} \eta_\beta \mathbf{d}_\beta, \tag{30}$$

from which the required symmetry relation follows.

Note that the remaining coefficients that determine the Burnett contributions to the ''unphysical'' fluxes can be calculated only if we know the Burnett functions Φ_B^T, Φ_B^u, Φ_B^v, and $\Phi_B^{D\gamma}$ determined from the solution of the integral equations (17). Such a calculation is of no special interest, since these fluxes do not occur in the system of basic hydrodynamic equations. However, knowledge of the explicit form of the Burnett functions may be necessary when we consider the boundary conditions for the hydrodynamic equations.

4. BALANCE EQUATIONS AT AN INTERPHASE SURFACE

In the analysis of flows of rarefied gases near interphase surfaces, it is necessary to introduce a correction into the distribution function that reflects the abrupt change of the gas parameters at the boundary within the so-called Knudsen layer (at distances of the order of a few mean free paths of the molecules). Then the distribution function can be written in the form

$$f_\alpha = f_\alpha^{(0)}(1 + \Phi_\alpha + \varphi_\alpha),$$

where Φ_α is the volume Chapman–Enskog correction [for example, a solution in the form (16)], and φ_α is the Knudsen correction to the local Maxwellian distribution function $f_\alpha^{(0)}$. It must be emphasized that $f_\alpha^{(0)}$ is defined in this case for the values of the density, velocity, and temperature that correspond to the volume solution valid outside the Knudsen layer (we call these the hydrodynamic parameters). It is readily noted that when these parameters are extrapolated to the surface over which the flow takes place, their values need not be the true values or the values of the parameters in equilibrium with the wall, and this leads to the natural picture of jumps of the density, velocity, and temperature at the boundary.[18]

The correction φ_α obviously satisfies the system of homogeneous equations that follow from (3),

$$(\mathbf{v}_\alpha \cdot \nabla)\varphi_\alpha = \sum_\beta L_{\alpha\beta}(\varphi), \tag{31}$$

and boundary conditions that in the absence of chemical reactions on the surface can be written in the form[18,29]

$$|\mathbf{v}_\alpha \cdot \mathbf{n}| f_\alpha(\mathbf{v}_\alpha, \mathbf{x}_0) = \int_{\mathbf{v}_\alpha' \cdot \mathbf{n} < 0} R_\alpha(\mathbf{v}_\alpha' \to \mathbf{v}_\alpha)$$

$$\times |\mathbf{v}_\alpha' \cdot \mathbf{n}| f_\alpha(\mathbf{v}_\alpha', \mathbf{x}_0) d\mathbf{v}_\alpha,$$

$$\mathbf{v}_\alpha \cdot \mathbf{n} > 0, \quad \mathbf{x}_0 \in \delta S. \tag{32}$$

Here $R_\alpha(\mathbf{v}_\alpha' \to \mathbf{v}_\alpha)$ is the operator for scattering of gas particles by the interface, $\mathbf{n}$ is the inner normal, and $\mathbf{x}_0$ is the coordinate of a point on the surface that belongs to the element of surface δS.

Note that for slow flows and with allowance for the small magnitude of the density and temperature jumps on the boundary

$$f_\alpha(\mathbf{v}) = f_{\alpha w}^{(0)}(\mathbf{v}_\alpha) \left[1 + \frac{\delta p_\alpha(0)}{p_{\alpha 0}} + \frac{\delta T(0)}{T_0} \left(\beta_\alpha v_\alpha^2 - \frac{5}{2} \right) \right.$$

$$\left. + \frac{m_\alpha}{kT_0} \mathbf{v}_\alpha \cdot \mathbf{u}(0) + \Phi_\alpha(0) + \varphi_\alpha(0) \right], \tag{33}$$

where $f_{\alpha w}^{(0)}$ is the absolute Maxwellian distribution in equilibrium with the wall, and $\delta p_\alpha(0)$ and $\delta T(0)$ are the jumps of the hydrodynamic parameters on the boundary relative to the values $p_{\alpha 0}$ and T_0 in equilibrium with the wall.

We consider the problem of the exterior flow of a gas mixture over a weakly curved surface and introduce an orthogonal system of coordinates at the point $\mathbf{x}_0$ with x axis directed along the inner normal and y and z axes directed along the surface. The element of length in such a system is given by

$$dl^2 = dx^2 + h_y^2 dy^2 + h_z^2 dz^2,$$

where h_y and h_z are metric coefficients.

Writing the left-hand side of Eq. (31) in these coordinates, multiplying both sides of (31) by $h_y h_z$, and integrating over x from 0 to ∞, we find

$$v_{ax}\varphi_a(0) = -\frac{1}{h_y(0)h_z(0)}\int_0^\infty h_y h_z \sum_\beta L_{a\beta}(\varphi)dx$$
$$+ \text{div}_\tau \hat{\mathbf{j}}_{a\tau}^\varphi, \qquad (34)$$

where we use the definition

$$\text{div}_\tau \hat{\mathbf{j}}_\tau = \frac{1}{h_y(0)h_z(0)}\left[\frac{\partial}{\partial y}(h_z(0)j_y) + \frac{\partial}{\partial z}(h_y(0)j_z)\right]$$

of the two-dimensional divergence of the flux, and we introduce the two-dimensional flux

$$\hat{\mathbf{j}}_{a\tau}^\varphi = h_z^{-1}(0)\mathbf{e}_y\int_0^\infty h_z v_{ay}\varphi_a dx + h_y^{-1}(0)\mathbf{e}_z\int_0^\infty h_y v_{az}\varphi_a dx.$$

We use the relations (32)–(34) to obtain balance equations for the mass, momentum, and energy on the interphase surface. To this end, we integrate (32) over the velocity half-space $v_{ax} > 0$. Using (33) and the property

$$\int_{v_{ax}>0} R_a(\mathbf{v}_a' \to \mathbf{v}_a)d\mathbf{v}_a = 1$$

of the scattering operator, we readily obtain

$$\int v_{ax}f_{aw}^{(0)}\left[\frac{\delta p_a(0)}{p_{a0}} + \frac{\delta T(0)}{T_0}\left(\beta_a v_a^2 - \frac{5}{2}\right)\right.$$
$$\left. + \frac{m_a \mathbf{v}_a \cdot \mathbf{u}(0)}{kT_0} + \Phi_a(0) + \varphi_a(0)\right]d\mathbf{v}_a = 0, \qquad (35)$$

where the integration is over the complete velocity space. Bearing in mind that $\Phi_a(0)$ does not contribute to the mass-average velocity of the gas, we obtain after summation of (35) over a with weight m_a

$$\rho u_x(0) + \sum_a \int m_a v_{ax}f_{aw}^{(0)}\varphi_a(0)d\mathbf{v}_a = 0. \qquad (36)$$

Using the well-known property $\langle 1|L(\varphi)\rangle = 0$ of the collision integral, we find by means of (34)

$$\rho u_x(0) = -\text{div}_\tau \hat{\mathbf{j}}_\tau^m, \qquad (37)$$

where

$$\hat{\mathbf{j}}_\tau^m = h_z^{-1}(0)\mathbf{e}_y\sum_a\int_0^\infty h_z \rho_a u_{ay}^{Kn}dx$$
$$+ h_y^{-1}(0)\mathbf{e}_z\sum_a\int_0^\infty h_y \rho_a u_{az}^{Kn}dx,$$

$$\mathbf{u}_a^{Kn} = \frac{1}{n_a}\int \mathbf{v}_a f_{aw}^{(0)}\varphi_a d\mathbf{v}_a. \qquad (38)$$

Here $\hat{\mathbf{j}}^m$ is the density of the mass flux localized in the Knudsen layer. Formally, Eq. (37) means that the normal component $u_x(0)$ of the hydrodynamic velocity on the interface does not vanish. This also follows directly from the

relation (36), which corresponds to vanishing of the gas velocity determined on the total distribution function (impenetrability of the surface).

Repeating the above procedure but without summation over a, we can also readily obtain relations for the diffusion velocities $\mathbf{w}_a = \mathbf{u}_a - \mathbf{u}$ on the phase boundary:

$$w_{ax}(0) - w_{Nx}(0) = -\text{div}_\tau(\hat{\mathbf{j}}_a^w - \hat{\mathbf{j}}_N^w),$$

$$\hat{\mathbf{j}}_a^w = h_z^{-1}(0)\mathbf{e}_y\int_0^\infty h_z n_a w_{ay}^{Kn}dx$$

$$+ h_y^{-1}(0)\mathbf{e}_z\int_0^\infty h_y n_a w_{az}^{Kn}dx. \qquad (39)$$

The momentum and energy balance equations on the interface are obtained by multiplying (32) from the left and from the right by $m_a\mathbf{v}_a$ and $m_a v_a^2/2$ and integrating over the velocity half-space. The following operations are then similar to those used above. As a result, we obtain

$$P_{xj}(0) - P_{xj}^f = -\text{div}_\tau \hat{\mathbf{j}}_{\tau j}^{(p)},$$

$$Q_x(0) - Q_x^f = -\text{div}_\tau \hat{\mathbf{j}}_\tau^{(q)}. \qquad (40)$$

At the same time, $P_{xj} = p\,\delta_{xj} + \pi_{xj}$ and $Q_x = q_x + P_{xj}u_j$ are the hydrodynamic densities of the momentum and energy fluxes, and P_{xj}^f and Q_x^f are the same quantities determined on the total distribution function. The vectors $\hat{\mathbf{j}}_\tau^{(p)}$ and $\hat{\mathbf{j}}_\tau^{(q)}$ are the densities of the momentum and energy fluxes localized in the Knudsen layer. They are defined by analogy with (38) substituting for

$$\sum_a \rho_a\mathbf{u}_{ai}^{Kn} \quad (i = y,z)$$

in this expression the quantities

$$P_{xj}^{Kn} = \sum_a\int m_a v_{ax}v_{aj}f_{aw}^{(0)}\varphi_a d\mathbf{v}_a$$

and

$$Q_i^{Kn} = \sum_a\int \frac{m_a v_a^2}{2}v_{ai}f_{aw}^{(0)}\varphi_a d\mathbf{v}_a.$$

It follows from the relations (40) that the normal components of the momentum and energy fluxes have discontinuities on the wall. A purely phenomenological version of such a discontinuity for a simple gas was first introduced by Waldmann.[20]

5. NONEQUILIBRIUM THERMODYNAMICS OF BOUNDARY CONDITIONS

To obtain an additional group of boundary conditions, including conditions for the fluxes tangential to the wall, we again use the methods of nonequilibrium thermodynamics. As in Refs. 20 and 21, we shall here proceed from the entropy balance equation on the interface but use a more complete representation of the distribution function that makes it possible to take into account its variation over the thickness of the Knudsen layer.

Integrating the entropy balance equation (18) directly on the interface and using Gauss's theorem, we readily find that the entropy production density on an infinitesimal surface element is equal to the difference between the entropy fluxes in the gas and in the condensed phase (for simplicity, we shall suppose that the latter is a rigid wall). For the local entropy production (per unit surface of the wall), we have

$$\Delta S_\sigma = J_s - J_s^s, \tag{41}$$

where $J_s = \mathbf{J}_s \cdot \mathbf{n}$, where $\mathbf{n}$ is the outer normal to the surface.

For the entropy flux density on the boundary directed from the rigid body, we have

$$J_s^s = \frac{\mathbf{J}_q^s \cdot \mathbf{n}}{T_0},$$

where $\mathbf{J}_q^s$ is the heat flux density, and T_0 is the wall temperature. At the same time, $\mathbf{J}_q^s = \mathbf{Q}^f$. Substituting in the expression (19) for $\mathbf{J}_s$ the total distribution function $f_\alpha = f_\alpha^{(0)}(1 + \Phi_\alpha + \varphi_\alpha)$ and taking into account the form (2) of $f_\alpha^{(0)}$, we readily obtain

$$\Delta S_\sigma = \mathbf{Q}^f \cdot \mathbf{n}\left(\frac{1}{T_0} - \frac{1}{T(0)}\right) - \frac{1}{T(0)}(u_i(0)n_k)$$

$$\times(P_{ik}^f - p(0)\delta_{ik}) - \frac{k}{2}\sum_\alpha \int \mathbf{v}_\alpha \cdot \mathbf{n} f_\alpha^{(0)}(\Phi_\alpha$$

$$+ \varphi_\alpha)^2 d\mathbf{v}_\alpha. \tag{42}$$

We recall that $\mathbf{Q}^f$ and P_{ik}^f are defined on the total distribution function including the Knudsen correction, and $p(0) = n(0)kT(0)$; $n(0)$, $\mathbf{u}(0)$, and $T(0)$ are the extrapolated values of the hydrodynamic parameters on the wall.

It is convenient to decompose the second term in (42) into parts corresponding to the components of $\mathbf{u}$ and P_{ik}^f normal and tangential to the surface. In this case, it takes the form

$$\frac{1}{T_0}[(P_{nn}^f - p(0))\mathbf{u}(0) \cdot \mathbf{n} + \pi_{n\tau}^f u_\tau(0)],$$

where $u_\tau(0)$ is the tangential component of the hydrodynamic velocity of the gas, which actually corresponds to the slip velocity at the wall, and $\pi_{n\tau}^f$ is the nondiagonal part of the tensor P_{ik}^f.

To transform the final term on the right-hand side of (42), it is necessary to substitute the known solution for the volume distribution function Φ_α [for example, the expression (16)]. Note that the structure of the Knudsen function $\varphi_\alpha(0)$ can be established in each specific case from its relation to $\Phi_\alpha(0)$ through the boundary condition (32) with allowance for the representation (33). Analysis shows (see, for example, Ref. 14) that allowance for the terms $\sim \varphi_\alpha^2$ in the expression (42) leads merely to a renormalization of the transport coefficients in the corresponding phenomenological transport relations without loss of the symmetry properties for the crossed coefficients. For this reason, the terms $\sim \varphi_\alpha^2$ in (42) can be omitted, and the final expression for ΔS_σ can be represented in the form

$$\Delta S_\sigma = (\mathbf{Q}^f \cdot \mathbf{n})\left(\frac{1}{T(0)} - \frac{1}{T_0}\right) - \frac{1}{T(0)}(\mathbf{u}(0) \cdot \mathbf{n})(P_{nn}^f$$

$$- p(0)) - \frac{1}{T(0)} \pi_{n\tau}^f u_\tau(0) - \frac{k}{2}\sum_\alpha \int (\mathbf{v}_\alpha \cdot \mathbf{n}) f_\alpha^{(0)}$$

$$\times(\Phi_\alpha^2 + 2\Phi_\alpha \varphi_\alpha) d\mathbf{v}_\alpha. \tag{43}$$

We now show how we can use (43) to obtain some phenomenological relations between the fluxes and forces on the interphase boundary that serve, as it were, as a system of boundary conditions for the hydrodynamic equations and give the corresponding contribution to the total transport of mass, momentum, and energy that results from the fluxes localized in the Knudsen layer. To this end, it is helpful to analyze some characteristic special cases.

6. FLOWS TANGENTIAL TO THE SURFACE OF A FLAT BOUNDARY

We consider the flow of a gas mixture along a flat surface in the presence of tangential (directed along the z axis) temperature and concentration gradients and nonvanishing first and second derivatives $u_z' = du_z/dx$ and $u_z'' = d^2u_z/dx^2$ of the velocity with respect to the transverse coordinate x. In this case, the volume correction Φ_α (16) has the form

$$\Phi_\alpha = v_{\alpha z}\Phi_{t\alpha}\nabla_z \ln T + v_{\alpha x}v_{\alpha z}\Phi_{p\alpha}u_z' + v_{\alpha z}\sum_\beta \Phi_{d\alpha}^\beta d_{\beta z}$$

$$+ (\Phi_{Bxxz}^u + v_{\alpha z}\Phi_{B\alpha}^v)u_z''. \tag{44}$$

[For slow flows, when not only the gradients of the macroscopic variables but also the velocities $\mathbf{u}$ are assumed to be small, it is possible to replace $\mathbf{c}_\alpha = \mathbf{v}_\alpha - \mathbf{u}$ in (16) by $\mathbf{v}_\alpha$.]

The absence of flows normal to the surface, in conjunction with the conditions $u_x(0) = 0$ and $\pi_{xz}^f = \pi_{xz} = -\eta u_z'$, which follow from the constancy of the Knudsen flows along the surface, enable us to represent the entropy production on the surface in the form

$$\Delta S_\sigma = -\frac{1}{T_0} \pi_{xz}u_z(0) - \frac{k}{2}\sum_\alpha \int v_{\alpha x}f_\alpha^{(0)}[\Phi_\alpha^2(0)$$

$$+ 2\Phi_\alpha(0)\varphi_\alpha(0)]d\mathbf{v}_\alpha. \tag{45}$$

It is well known[27] that $\Phi_{t\alpha}$, $\Phi_{p\alpha}$, and $\Phi_{d\alpha}^\beta$ are even functions of the velocity $\mathbf{v}_\alpha$, while $\Phi_{B\alpha}$ are even functions with respect to $\mathbf{v}_\alpha$ and $v_{\alpha x}$ (Refs. 10 and 12), and therefore the term in (45) with $\Phi_\alpha^2(0)$ contains only a combination of the form

$$ku_z'\left[a_B\nabla_z \ln T + \sum_\gamma b_\gamma d_{\gamma z} + c_B u_z''\right],$$

where

$$a_B = -\langle v_z\Phi_t | v_x^2 v_z\Phi_p\rangle, \quad b_\gamma = -\langle v_z\Phi_d^\gamma | v_x^2 v_z\Phi_p\rangle,$$

$$c_B = -\langle v_z\Phi_B^v + \Phi_{Bxxz}^u | v_x^2 v_z\Phi_p\rangle. \tag{46}$$

We now determine the structure of the terms that contain $\varphi_\alpha(0)$. We consider the term with $\Phi_{t\alpha}$ in (44). Substituting it

in (45) and remembering that $v_{ax}\varphi_a(0)$ can be replaced by means of (34) by $-\int_0^\infty L_\alpha(\varphi)dx$, where $L_\alpha=\sum_\beta L_{\alpha\beta}(\varphi)$, we find

$$-k\nabla_z \ln T\sum_\alpha \int v_{az}\Phi_{t\alpha}v_{ax}\varphi_\alpha(0)f_\alpha^{(0)}dv_\alpha$$

$$=k\nabla_z \ln T\int_0^\infty \langle v_z\Phi_t|L(\varphi)\rangle dx.$$

We use the symmetry property $(\langle\Phi|L(\varphi)\rangle=\langle\varphi|L(\Phi)\rangle)$ of the linearized collision operator and the first relation of (8). As a result, we obtain

$$\int_0^\infty \langle v_z\Phi_t|L(\varphi)\rangle dx=\int_0^\infty \langle\varphi|L(v_z\Phi_t)\rangle dx$$

$$=\int_0^\infty \langle\varphi|v_z(\beta v^2-5/2)\rangle dx=\hat{j}_z^h/kT,$$

$$(47)$$

where $\hat{j}_z^h$ is the density of the reduced heat flux localized in the Knudsen layer. The upshot is that the corresponding term in the entropy production (45) takes the form

$$\frac{1}{T_0}\hat{j}_z^h\nabla_z \ln T. \qquad (48)$$

The contribution of the term with $\Phi_{p\alpha}$ to (45) vanishes, since

$$\sum_\alpha \int v_{ax}v_{az}\Phi_{p\alpha}v_{ax}\varphi_\alpha(0)f_\alpha^{(0)}dv_\alpha=$$

$$-\int_0^\infty \langle v_xv_z\Phi_p|L(\varphi)\rangle dx=-\int_0^\infty \langle\varphi|L(v_xv_z\Phi_p)\rangle dx$$

$$=-\frac{1}{kT}\int_0^\infty \langle mv_xv_z|\varphi\rangle dx=-\frac{1}{kT}\int_0^\infty (P_{xz}^f-P_{xz})dx$$

$$=0.$$

Manipulations with allowance for the third term in (44) give

$$-k\sum_\alpha \int v_{az}\sum_\beta \Phi_{d\alpha}^\beta d_{\beta z}v_{ax}\varphi_\alpha(0)f_\alpha^{(0)}dv_\alpha$$

$$=k\sum_\beta \int_0^\infty \langle v_z\Phi_d^\beta|L(\varphi)\rangle d_{\beta z}dx$$

$$=k\sum_\beta \int_0^\infty \langle\varphi|L(v_z\Phi_d^\beta)\rangle d_{\beta z}dx. \qquad (49)$$

Using the last relation in (8) and the condition $\sum_{\beta=1}^N d_{\beta z}=0$, we can readily obtain instead of (49) the expression

$$\frac{1}{T_0}\sum_{\beta=1}^{N-1}\left(\frac{\hat{j}_\beta^w}{n_\beta}-\frac{\hat{j}_N^w}{n_N}\right)_z pd_{\beta z},$$

where $\hat{j}_\alpha^w=\hat{j}_\alpha-(n_\alpha/\rho)\hat{j}^m$ is the diffusion flux of the particles of species α localized in the Knudsen layer. At the same time, $\hat{j}^m=\sum_\alpha m_\alpha\hat{j}_\alpha$ and

$$\hat{j}_\alpha=\int_0^\infty dx\int v_\alpha\varphi_\alpha f_\alpha^{(0)}dv_\alpha.$$

Finally, for the contribution to (45) from the last term in (44), we have

$$-ku_z''\sum_\alpha \int (v_{az}\Phi_{B\alpha}^v+\Phi_{Bxxz}^u)v_{ax}\varphi_\alpha(0)f_\alpha^{(0)}dv_\alpha$$

$$=ku_z''\int_0^\infty \langle\varphi|L(v_z\Phi_B^v+\Phi_{Bxxz}^u)\rangle dx.$$

In accordance with the relations (17) for Φ_B^v and Φ_B^u

$$\int_0^\infty \langle\varphi|L(v_z\Phi_B^v+\Phi_{Bxxz}^u)\rangle dx=\int_0^\infty \left\langle\varphi\left|v_z\left(\Phi_p v_x^2\right.\right.\right.$$

$$\left.\left.\left.+\frac{m\eta}{\rho kT}\right)\right\rangle dx.$$

It is easy to show that

$$\int_0^\infty \langle v_zv_x^2\Phi_p|\varphi\rangle dx=0.$$

Indeed, it follows from the momentum conservation law that $\langle mv_xv_z|\varphi\rangle=0$. From the second equation in (8) and the symmetry of the collision operator, we can write

$$\langle mv_xv_z|\varphi\rangle=\langle L(v_xv_z\Phi_p)|\varphi\rangle=\langle v_xv_z\Phi_p|L(\varphi)\rangle$$

$$=\left\langle v_x^2v_z\Phi_p\left|\frac{\partial\varphi}{\partial x}\right.\right\rangle=0.$$

After integration over x and allowance for the condition $\varphi(\infty)=0$, we obtain the required relation. As a result, the corresponding contribution to ΔS_σ takes the form

$$ku_z''\int_0^\infty \langle\varphi|L(v_z\Phi_B^v+\Phi_{Bxxz}^u)\rangle dx$$

$$=\frac{\eta}{\rho T_0}u_z''\int_0^\infty \langle\varphi|mv_z\rangle dx=\frac{\eta}{\rho T_0}\hat{j}_z^m u_z'',$$

where $\hat{j}_z^m=\int_0^\infty \langle\varphi|mv_z\rangle dx$ is the mass-average flow of the mixture localized in the Knudsen layer.

Collecting the terms obtained above, we arrive at the following final expression for the entropy production:

$$\Delta S_\sigma=ku_z'\left[\frac{\eta}{kT_0}u_z(0)+a_B\nabla_z \ln T+\sum_\gamma b_\gamma d_{\gamma z}+c_Bu_z''\right]$$

$$+\frac{1}{T_0}\hat{j}_z^h\nabla_z \ln T+\frac{1}{T_0}\sum_{\beta=1}^{N-1}\left(\frac{\hat{j}_\beta^w}{n_\beta}-\frac{\hat{j}_N^w}{n_N}\right)_z p_0d_{\beta z}$$

$$+\frac{\eta}{\rho T_0}\hat{j}_z^m u_z''. \qquad (50)$$

The system of phenomenological equations corresponding to the entropy production (50) can be written in the form

$$k\left[\frac{\eta}{kT_0}u_z(0)+a_B\nabla_z\ln T+\sum_\alpha b_\alpha d_{\alpha z}+c_B u_z''\right]$$

$$=l_{00}u_z'(0)+\frac{1}{T_0}\sum_{\beta=1}^{N-1}l_{0\beta}p_0 d_{\beta z}+\frac{l_{0N}}{T_0}\nabla_z\ln T$$

$$+l_{0,N+1}\frac{\eta}{T_0}u_z'',$$

$$\left(\frac{\hat{j}_\alpha^w}{n_\alpha}-\frac{\hat{j}_N^w}{n_N}\right)_z=l_{\alpha 0}u_z'(0)+\frac{1}{T_0}\sum_{\beta=1}^{N-1}l_{\alpha\beta}p_0 d_{\beta z}$$

$$+\frac{l_{\alpha N}}{T_0}\nabla_z\ln T+l_{\alpha,N+1}\frac{\eta}{T_0}u_z'',$$

$$\left(\hat{j}^q-\frac{5}{2}kT_0\sum_\alpha\hat{j}_\alpha^w\right)_z=l_{N0}u_z'(0)+\frac{1}{T_0}\sum_{\beta=1}^{N-1}l_{N\beta}p_0 d_{\beta z}$$

$$+\frac{l_{NN}}{T_0}\nabla_z\ln T+l_{N,N+1}\frac{\eta}{T_0}u_z'',$$

$$\frac{\hat{j}_z^m}{\rho}=l_{N+1,0}u_z'(0)+\frac{1}{T_0}\sum_{\beta=1}^{N-1}l_{N+1,\beta}p_0 d_{\beta z}$$

$$+l_{N+1,N}\frac{1}{T_0}\nabla_z\ln T+l_{N+1,N+1}\frac{\eta}{T_0}u_z''. \tag{51}$$

In Ref. 5 we used a different method to obtain an analogous system of equations for the special case of the flow of a gas mixture in a circular cylindrical capillary. For Poiseuille flows in a channel, $\eta u_z''=\nabla_z p$. For the comparison with Ref. 15, it must also be borne in mind that there the flows are determined by averaging over the channel section, as a result of which a factor $2/R$ appears, where R is the capillary radius.[2)]

7. FLOWS NORMAL TO A SURFACE

The expression (43) for the entropy production also makes it possible to obtain a set of phenomenological equations—the boundary conditions for normal flows. If for the moment we drop the final term in (43), which is indirectly related to the structure of Φ_α, then the expression (43) takes the form

$$\Delta S_\sigma=-\frac{Q_n^f}{T_0}\frac{T(0)-T_0}{T_0}-\frac{1}{T_0}u_n(0)(P_{nn}^f-p(0)). \tag{52}$$

where $u_n(0)$ is the projection of the gas velocity onto the outer normal.

This representation corresponds to a pair of phenomenological equations for the jumps of the temperature and normal components of the stress tensor at the boundary. They have the form

$$\frac{T(0)-T_0}{T_0}=L_{00}\frac{Q_n^f}{T_0}+L_{01}\frac{u_n(0)}{T_0},$$

$$P_{nn}^f-p(0)=L_{10}\frac{Q_n^f}{T_0}+L_{11}\frac{u_n(0)}{T_0}. \tag{53}$$

In contrast to the well-known results of Refs. 16, 17, and 19–25, it follows from (53) that the temperature jump is determined not only by the heat flux through the surface but also by the value of the new thermodynamic force $u_n(0)$, which, as was shown above, is also nonvanishing for impermeable surfaces. Hitherto, such relations have been obtained only when phase transitions occur at the surface(for example, for the case of evaporation and condensation[30]). The second equation of (53) describes the effect of the difference of the pressure in the gas and of the normal stresses acting on the surface. In the case of an evaporating surface, an analog is the jump of the vapor pressure. This effect can be interpreted as a certain excess surface tension in a nonequilibrium gas. In the case of a temperature gradient normal to the surface, it results from the temperature profile in the Knudsen layer.

Taking into consideration the terms obtained by decomposing the structure of the final term in the entropy production (43) leads to a significant extension of the system of phenomenological equations, since we obtain new thermodynamic forces of the form $du_x/dx, d_{\beta x}, dp/dx, d^2 u_x/dx^2, d^2T/dx^2$, etc. Unfortunately, in the general case the thermodynamic fluxes conjugate to these forces cannot be given a transparent physical meaning, and therefore we consider only the fairly simple situation in which the volume distribution function can be represented in the form

$$\Phi_\alpha=v_{\alpha x}\Phi_{t\alpha}\nabla_x\ln T+\left(v_{\alpha x}v_{\alpha x}-\frac{1}{3}v^2\right)\Phi_{p\alpha}u_x'(0)$$

$$+v_{\alpha x}\sum_\beta\Phi_{d\alpha}^\beta d_{\beta x} \tag{54}$$

[in the phenomenological approach, the same system of phenomenological equations (53) corresponds to this approximation].

Substituting (54) in the final term of (43), we can readily show that among the volume terms in the integral there remains only the combination

$$-ku_x'(0)\left(a_B^x\nabla_x\ln T+\sum_\gamma b_\gamma^x d_{\gamma x}\right), \tag{55}$$

where

$$a_B^x=-\left\langle v_x\Phi_t\left|\left(v_x v_x-\frac{1}{3}v^2\right)\Phi_p\right.\right\rangle,$$

$$b_\gamma^x=-\left\langle v_x\Phi_d^\gamma\left|\left(v_x v_x-\frac{1}{3}v^2\right)\Phi_p\right.\right\rangle. \tag{56}$$

We write the terms associated with the product of the volume and Knudsen distribution functions in the form

$$-k\Delta'\nabla_x\ln T-k\Delta^4 u_x'-k\sum_\beta\Delta_\beta^d d_{\beta x}, \tag{57}$$

where

$$\Delta' = \langle v_x \Phi_t | v_x \varphi(0) \rangle,$$

$$\Delta^u = \left\langle \left(v_x v_x - \frac{1}{3} v^2 \right) \Phi_p \middle| v_x \varphi(0) \right\rangle,$$

$$\Delta_\beta^d = \langle v_x \Phi_d^\beta | v_x \varphi(0) \rangle. \tag{58}$$

The resulting entropy production is equal to the sum of the expressions (52), (55), and (57). The corresponding system of phenomenological equations has the form

$$\frac{T(0) - T_0}{T_0} = \mathscr{L}_{00} \frac{Q_n^f}{T_0} + \sum_{\beta=1}^{N-1} \mathscr{L}_{0\beta} d_{\beta x} + \mathscr{L}_{0N} \frac{u_n(0)}{T_0}$$

$$+ \mathscr{L}_{0,N+1} u_x'(0) + \mathscr{L}_{0,N+2} \nabla_x \ln T,$$

$$k\Delta_\gamma^d = \mathscr{L}_{\gamma 0} \frac{Q_n^f}{T_0} + \sum_{\beta=1}^{N-1} \mathscr{L}_{\gamma\beta} d_{\beta x} + \mathscr{L}_{\gamma N} \frac{u_n(0)}{T_0}$$

$$+ \mathscr{L}_{\gamma,N+1} u_x'(0) + \mathscr{L}_{\gamma,N+2} \nabla_x \ln T,$$

$$P_{nn}^f - p(0) = \mathscr{L}_{N0} \frac{Q_n^f}{T_0} + \sum_{\beta=1}^{N-1} \mathscr{L}_{N\beta} d_{\beta x} + \mathscr{L}_{NN} \frac{u_n(0)}{T_0}$$

$$+ \mathscr{L}_{N,N+1} u_x'(0) + \mathscr{L}_{N,N+2} \nabla_x \ln T,$$

$$k\left[\Delta^u - a_B^x \nabla_x \ln T - \sum_\beta b_\beta^x d_{\beta x} \right] = \mathscr{L}_{N+1,0} \frac{Q_n^f}{T_0}$$

$$+ \sum_\beta^{N-1} \mathscr{L}_{N+1,\beta} d_{\beta x} + \mathscr{L}_{N+1,N} \frac{u_n(0)}{T_0}$$

$$+ \mathscr{L}_{N+1,N+1} u_x'(0) + \mathscr{L}_{N+1,N+2} \nabla_x \ln T,$$

$$k\Delta' = \mathscr{L}_{N+2,0} \frac{Q_n^f}{T_0} + \sum_{\beta=1}^{N-1} \mathscr{L}_{N+2,\beta} d_{\beta x} + \mathscr{L}_{N+2,N} \frac{u_n(0)}{T_0}$$

$$+ \mathscr{L}_{N+2,N+1} u_x'(0) + \mathscr{L}_{N+2,N+2} \nabla_x \ln T. \tag{59}$$

It can be seen from (59) that in this case the system of phenomenological equations contains not only the obvious physical fluxes but also three new "unphysical" fluxes: Δ', Δ^u, and Δ_γ^d. We have already encountered an analogous situation in the consideration of the Burnett fluxes. The same thing would have to occur for tangential (shear) flows too if we were to take into account a larger number of terms in the expansion of the volume function Φ. Note that in the expressions for the jumps of the temperature and of the normal stresses we obtain, in addition to the forces Q_n^f and $u_n(0)$ previously taken into account, a spectrum of new forces associated with the presence of gradients of the velocity, temperature, and concentration normal to the surface.

The appearance of new thermodynamic forces and the inclusion in the system of phenomenological equations of unphysical fluxes arises from the use of kinetic theory as the foundation for constructing phenomenological equations of nonequilibrium thermodynamics. It is clear that in a purely phenomenological approach it is not possible to justify the introduction of unphysical fluxes, although the inclusion of additional thermodynamic forces can be formally justified; at the same time, however, there arises a problem with establishing the Onsager symmetry. In contrast, when the kinetic and phenomenological theories are combined these problems are resolved automatically. Simultaneously, one can establish the physical basis for the appearance of the new thermodynamic forces in the system of phenomenological equations, as follows. When the distribution function is expanded in a series in gradients, each thermodynamic force is multiplied by an associated polynomial in the velocity, and therefore a quantity, say the temperature jump, associated with some thermodynamic force, will be determined by its own corresponding transport coefficient (it depends on the form of the polynomial in the velocity). However, in the phenomenological approach there appears only the one coefficient $\mathscr{L}_{00}$, and a dependence of the temperature jump on the various derivatives of the gas parameters enters indirectly through the dependence of the heat flux Q_n^f on these parameters.

Thus, the transport coefficients $\mathscr{L}_{0\beta}$, $\mathscr{L}_{0,N+1}$, and $\mathscr{L}_{0,N+2}$ "correct," as it were, the dependence of the temperature jump on the derivatives of the macroscopic variables of the gas relative to the dependence determined in the framework of the phenomenological approach. It is evident that it is the correcting nature of these coefficients that is responsible for the unphysical nature of the conjugate thermodynamics fluxes.

8. CONCLUSIONS

The above description of nonequilibrium processes in the volume of a gas mixture and at an interphase surface has a rather general nature. The resulting phenomenological equations were actually determined by the form of the given distribution function, and the actual nature of the flow of the gas mixture did not appear in them. It is clear that in specific problems certain of the thermodynamic forces, between which a variety of relationships is possible, may be absent, and this must be reflected in the form, for example, of the boundary conditions. The order of magnitude of the various thermodynamic forces must also depend strongly on the nature of the gas flow, and therefore it cannot be determined in advance. The change in the orders of the contributions from different effects on the transition from one problem to another was demonstrated for some specific examples in Refs. 16, 17, and 31. Therefore, we have not compared here the contributions from the different effects but have restricted ourselves to a general description of the present approach. In our view, it is not difficult to use the approach when considering specific problems associated with different flows of weakly rarefied gases.

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[1] The attempts to implement this approach made in the subsequent studies of Waldmann[22,23] did not lead to significant success, since they still did not take into account the change of the distribution function in the Knudsen layer.

[2] In Ref. 15, there are some misprints: The coefficients a_B, c_B, and b_α in (72) and (74) should have $+$ and not $-$ signs, and the coefficient n was omitted in the combination $\Sigma_\alpha n b_\alpha d_{\alpha z}$.

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