TRANSPORT COEFFICIENTS AND THE ONSAGER RELATIONS IN THE KINETIC THEORY OF DENSE GAS MIXTURES

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There has been increasing interest in the literature in the past few years in obtaining and solving the kinetic equations for dense gases and gas mixtures in the hydrodynamic approximation [1-10]. The most progress in deriving both hydrodynamics and also transport equations with explicit expressions for the kinetic coefficients has been achieved using the kinetic theory of dense gases for rigid spherical molecules, as developed originally by Enskog [11] using intuitive concepts. Enskog obtained a generalized Boltzmann equation which formally took into account only binary collisions [12]. However, if the change in the free volume per molecule and the screening of molecules by each other are taken into account, this theory actually includes triplet correlations. It was later shown that the χ factor in Enskog's equation is just the local equilibrium pair correlation function [1].

Attempts to extend the Enskog theory to more realistic interaction potentials were considered in [2-7]. In [13] the Enskog method was extended for a monatomic gas. Comparison of the coefficients of viscosity and thermal conductivity calculated in this method for hydrogen and oxygen showed rather good agreement with experiment over wide ranges of temperature and pressure up to the liquid state.

Generalization of the Enskog theory to dense gas mixtures was done by Thorne [12]. However, it was shown in [14] that the results of Thorne were not consistent with those derived from irreversible thermodynamics. In particular, the diffusion force vectors $\mathbf{d}_i$ obtained from kinetic theory did not agree with those from irreversible thermodynamics. This fact prompted a revision of the Enskog equation for dense gas mixtures. A modified Enskog equation was introduced in [15, 16]. In [16] it was applied to gas mixtures, and the kinetic coefficients were obtained from the linearized form of the equation by the projection operator method. The resulting kinetic coefficients satisfied the Onsager reciprocity relations. The modified Enskog equation was studied further in [17-19], where the Chapman—Enskog method was applied to solve the equation.

It must be pointed out that the modified equation was derived using the same assumptions as in the original Enskog equation. The modification concerns only the localization of the function χ. However, agreement between kinetic theory and irreversible thermodynamics can be obtained for dense gases using the modified Enskog approach. Obviously an analogous modification of the kinetic equations and hydrodynamics can be carried out for the theory of [2, 7].

In the present paper the Chapman—Enskog method is used to obtain expressions for the "physical" transport coefficients (diffusion, thermodiffusion, thermal conductivity), and it is shown that these coefficients satisfy the Onsager relations. It is also shown that in dense gas mixtures the vector $\mathbf{d}_i$ appearing in the Chapman—Enskog method cannot be identified with the thermodynamic diffusion force vector as in the case of a dilute gas. The equations of heat and mass transport are obtained in a form which is identical to the corresponding expressions derived in irreversible thermodynamics.

1. We consider an N-component, heat-conducting gas mixture close to thermodynamic equilibrium. Then for an isotropic mixture the reduced heat fluxes $\mathbf{q} = \mathbf{J}_0$ and mass diffusion fluxes $\mathbf{J}_i$ ($i = 1, \ldots, N$) can be written as linear functions of the thermodynamic forces $\mathbf{X}_i$ in the form [20]

$$\mathbf{J}_i = \sum_{j=0}^{N} \alpha_{ij}\mathbf{X}_j \quad (i = 0, 1, \ldots, N), \tag{1.1}$$

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where the α_{ij} are phenomenological coefficients.

If the forces and fluxes are chosen as the quantities appearing in the expression for the rate of entropy production due to diffusion and heat conduction, then the phenomenological coefficients α_{ij} in (1.1) will satisfy the Onsager reciprocity relations [20]

$$\alpha_{ij} = \alpha_{ji} \ (i,\ j = 0,\ 1, \ldots, N). \tag{1.2}$$

Use of the Gibbs' identity and the conservation laws for the mass of each component and the energy leads to the expressions [21]

$$\mathbf{J}_0 = \mathbf{q} = -\frac{\alpha_{00}}{T} \nabla T + nkT \sum_{j=1}^{N} \frac{\alpha_{0j}}{\rho_j} \mathbf{d}_j; \tag{1.3}$$

$$\mathbf{J}_i = -\frac{\alpha_{i0}}{T} \nabla T - nkT \sum_{j=1}^{N} \frac{\alpha_{ij}}{\rho_j} \mathbf{d}_j \quad (i = 1, \ldots, N), \tag{1.4}$$

where

$$\mathbf{q} = \mathbf{J}_q - \sum_{j=1}^{N} h_j \mathbf{J}_j; \tag{1.5}$$

$$\mathbf{d}_i = \frac{x_i}{kT} (\nabla \mu_i)_{p,T} + \frac{p}{nkT} (n v_i^* - y_i) \nabla \ln p + \frac{y_i}{nkT} \left(\sum_{j=1}^{N} \rho_j \mathbf{F}_j - \rho \mathbf{F}_i \right). \tag{1.6}$$

Here J_q is the total heat flux; h_j and μ_j, specific enthalpy and chemical potential per particle of the j-th component; $v^*_j = \left(\frac{\partial \mu_j}{\partial p}\right)_{T,x_i}$, partial molar volume of the j-th component; m_j, n_j, $x_j = n_j/n$, $y_j = (m_j/m)x_j$, mass, number density, molar concentration, and mass concentration, respectively, of the j-th component; $n = \sum_{k=1}^{N} n_k$, $m = \sum_{k=1}^{N} x_k m_k$, number density and mean molecular mass of the mixture; k, Boltzmann's constant; and $\mathbf{F}_j$, bulk force acting on the j-th component.

2. We now compare the results from the kinetic theory of dense gas mixtures [17-19] with those from irreversible thermodynamics [20, 21], i.e., with Eqs. (1.3) and (1.4). A similar comparison was done in [14] for the Thorne theory and it was shown that the transport equations cannot in general be written in form (1.3) and (1.4), so that the Thorne theory cannot be deduced from irreversible thermodynamics.

The modified Boltzmann–Enskog equation has the form

$$\frac{\partial f_i}{\partial t} + \mathbf{c}_i \frac{\partial f_i}{\partial \mathbf{r}} = \sum_{j=1}^{N} \sigma_{ij}^2 \int\int \{\chi_{ij}(\mathbf{r}_i, \mathbf{r}_i + \sigma_{ij}\mathbf{k}) f_i'(\mathbf{r}_i) f_i'(\mathbf{r}_i + \sigma_{ij}\mathbf{k}) - \\ - \chi_{ij}(\mathbf{r}_i, \mathbf{r}_i - \sigma_{ij}\mathbf{k}) f_i(\mathbf{r}_i) f_j(\mathbf{r}_i - \sigma_{ij}\mathbf{k})\} (\mathbf{g}_{ji} \cdot \mathbf{k})\, d\mathbf{k} d\mathbf{c}_j \quad (i = 1, \ldots, N), \tag{2.1}$$

where

$$\chi_{ij}(\mathbf{r}_i, \mathbf{r}_j) = 1 + \sum_{h=1}^{N} \int n_k(\mathbf{r}_k) f_{ik}(r_{ik}) f_{jk}(r_{jk})\, d\mathbf{r}_k.$$

Here $f_{ij}(r_{ij}) = \exp(-\varphi_{ij}(r_{ij})/kT)$ is the Mayer function with $\varphi_{ij}(r_{ij})$ the interaction potential of molecules of types i and j. If the center of one molecule is at point $\mathbf{r}_i$, then the center of the second molecule at the moment of collision can only be at points $\mathbf{r}_i - \sigma_{ij}\mathbf{k}$, where $\mathbf{k}$ is a unit vector directed from the center of the j-th molecule to the center of the i-th molecule; $\mathbf{g}_{ji}$ is the relative velocity vector of the colliding molecules. The function χ_{ij} depends on both $\mathbf{r}_i$ and $\mathbf{r}_j$ but its numerical value does not depend on the choice of points $\mathbf{r}_i$ and $\mathbf{r}_j$.

Because we are only interested in heat and mass fluxes, we will assume that bulk forces and velocity gradients do not exist in the system.

The transport coefficients obtained on the basis of (2.1) are described in [19] (see also [22]) using the Thorne theory and [23, 24]. The basis of the solution is the Chapman–Enskog method. The zero-order approximation is chosen to be a local Maxwellian distribution function

$$f_i^{(0)} = n_i\left(\frac{m_i}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_i \mathbf{C}_i^2}{2kT}\right), \quad \mathbf{C}_i = \mathbf{c}_i - \mathbf{v}, \tag{2.2}$$

where $\mathbf{c}_i$ is the velocity of a molecule of the i-th kind and $\mathbf{v}$ is the mass-averaged velocity of the mixture as a whole.

To first order we obtain a system of N linear nonhomogeneous Fredholm integral equations of the second kind for the functions $\varphi_i^{(1)} = f_i^{(1)}/f_i^{(0)}$

$$\sum_{j=1}^{N} \chi_{ij} I_{ij}(\varphi^{(1)}) = -f_i^{(0)}\left[L_i\left(\mathbf{W}_i^2 - \frac{5}{2}\right)\mathbf{C}_i\cdot\nabla \ln T + \frac{n_i}{n}\mathbf{d}_i'\cdot\mathbf{C}_i\right], \tag{2.3}$$

where

$$\begin{gathered}
L_i = 1 + \frac{12}{5}\sum_{j=1}^{N} B_{ij}\chi_{ij}\mu_{ij}\mu_{ji}n_j;\\
\mathbf{W}_i = \left(\frac{m_i}{2kT}\right)^{1/2}\mathbf{C}_i; \quad \mu_{ij} = \frac{m_i}{m_i + m_j}; \quad \chi_{ij} = 1 + \sum_{k=1}^{N} n_k a_{ij}^k;\\
a_{ij}^k = \frac{\pi}{12}\left[8(\sigma_{ik}^3 + \sigma_{jk}^3) - 6(\sigma_{ik}^2 + \sigma_{jk}^2)\sigma_{ij} - 3(\sigma_{ik}^2 - \sigma_{jk}^2)^2\sigma_{ij}^{-1} + \sigma_{ij}^3\right];\\
B_{ij} = \frac{2\pi}{3}\sigma_{ij}^3; \quad \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j);\\
I_{ij}(\varphi^{(1)}) = \int f_i^{(0)} f_j^{(0)}\left(\varphi_i^{(1)} + \varphi_j^{(1)} - \varphi_i^{(1)\prime} - \varphi_j^{(1)\prime}\right)\sigma_{ij}^2(\mathbf{g}_{ji}\cdot\mathbf{k})\,d\mathbf{k}\,d\mathbf{c}_j;\\
\mathbf{d}_i' = x_i\nabla\ln(n_i kT) - \frac{y_i}{nkT}\nabla p + x_i\sum_{j=1}^{N}\left\{\frac{B_{ij}}{n_j T}\nabla(n_j^2\chi_{ij}T)\right.\\
\left. + B_{ij}\chi_{ij}n_j\left[(\mu_{ij} - \mu_{ji})\nabla\ln T + \chi_{ij}^{-1}\nabla h_{ij}\right]\right\};\\
h_{ij} = \sum_{k=1}^{N} n_k(B_{jk}a_{jk}^i - B_{ik}a_{ik}^j)/B_{ij}.
\end{gathered} \tag{2.4}$$

Here all quantities are expressed in terms of the molecular diameters σ_i (i = 1, 2, ..., N).

Equation (2.3) differs from the corresponding result in the kinetic theory of a dilute gas only by the constant coefficients χ_{ij} and L_i. Thus, we can at once write down the general solution to (2.3):

$$\varphi_i^{(1)} = -\frac{1}{n}\left\{\sum_{j=1}^{N}\mathbf{D}_i^j\cdot\mathbf{d}_j' + \mathbf{A}_i\cdot\nabla\ln T\right\}, \tag{2.5}$$

where the undetermined coefficients $\mathbf{D}^j{}_i$ and $\mathbf{A}_i$ depend on $\mathbf{C}_i$.

We obtain an integral equation for the functions $\mathbf{D}^j{}_i$ and $\mathbf{A}_i$ by substituting (2.5) into (2.3) and equating the coefficients of the vectors $\mathbf{d}'_j$ and ∇ ln T:

$$\sum_{j=1}^{N}\chi_{ij}I_{ij}(\mathbf{D}^k) = \frac{n^2}{n_i}f_i^{(0)}(\delta_{ik} - y_i)\mathbf{C}_i; \tag{2.6}$$

$$\sum_{j=1}^{N}\chi_{ij}I_{ij}(\mathbf{A}) = nf_i^{(0)}\left(\mathbf{W}_i^2 - \frac{5}{2}\right)L_i\mathbf{C}_i. \tag{2.7}$$

The solution to (2.6) and (2.7) is written as an expansion in Sonine polynomials $S^m{}_n(x)$ [24]:

$$\mathbf{D}_i^j = \sum_{p=0}^{r-1} d_{i,p}^{j(r)} S_{3/2}^p (\mathbf{W}_i^2) \mathbf{C}_i; \tag{2.8}$$

$$\mathbf{A}_i = -\sum_{p=0}^{r} a_{i,p}^{(r)} S_{3/2}^p (\mathbf{W}_i^2) \mathbf{C}_i, \tag{2.9}$$

where r is the order of the approximation with respect to Sonine polynomials. The procedure is completely analogous to that in [24] and gives the following set of algebraic equations for the coefficients $d^{j(r)}{}_{i,p}$ and $a^{(r)}{}_{i,p}$:

$$\sum_{j=1}^{N} \sum_{q=0}^{r-1} \Lambda_{ij}^{pq} d_{j,q}^{l(r)} = \frac{8}{25k} (\delta_{il} - y_i) \delta_{p0}, \quad p = 0, \ldots, r-1; \tag{2.10}$$

$$\sum_{i=1}^{N} y_i d_{i,0}^{l(r)} = 0; \tag{2.11}$$

$$\sum_{j=1}^{N} \sum_{q=0}^{r} \Lambda_{ij}^{pq} a_{j,q}^{(r)} = \frac{4}{5k} L_i x_i \delta_{pi}, \quad p = 0, \ldots, r; \tag{2.12}$$

$$\sum_{i=1}^{N} y_i a_{i,0}^{(r)} = 0, \tag{2.13}$$

where the $\Lambda^{pq}{}_{ij}$ are the analogs of the well-known integral brackets of [24] and can be obtained from them by multiplying the collision cross section by χ_{ij}. In the case of rigid sphere molecules, the first approximation for $\Lambda^{pq}{}_{ij}$ is found in the form

$$\Lambda_{ij}^{00} = \sum_{k=1}^{N} \frac{x_i x_k}{2\lambda_{ik}} (\delta_{ij} - \delta_{kj}),$$

$$\Lambda_{ij}^{01} = \Lambda_{ij}^{10} = \sum_{k=1}^{N} \frac{x_i x_k}{4\lambda_{ik}} (\mu_{ik}\delta_{kj} - \mu_{kj}\delta_{ij}),$$

$$\Lambda_{ij}^{11} = \sum_{k=1}^{N} \frac{x_i x_k}{8\lambda_{ik}} [(30\mu_{ik}^2 + 13\mu_{ki}^2 + 16\mu_{ik}\mu_{ki}) \delta_{ij} - 27\mu_{ik}\mu_{ki}\delta_{kj}],$$

where

$$\lambda_{ij} = \frac{15k (m_i + m_j)}{8m_i m_j} \eta_{ij}; \quad \eta_{ij} = \frac{5}{16} \left[\frac{2m_i m_j kT}{\pi (m_i + m_j)} \right]^{1/2} \frac{1}{\chi_{ij}\sigma_{ij}^2}.$$

We can also write out the equation of state, which has the same form as in the Thorne theory [14, 22]:

$$p = \left(n + \sum_{i,j} n_i n_j B_{ij} \chi_{ij}\right) kT \tag{2.14}$$

The equation of state can also be written as a power series in the density:

$$p = \left(\sum_i n_i + \sum_{i,j} B_{ij} n_i n_j + \sum_{i,j,k} B_{ijk} n_i n_j n_k\right) kT, \tag{2.15}$$

where

$$B_{ijk} = \frac{1}{3} (B_{ij} a_{ij}^k + B_{ik} a_{ik}^j + B_{jk} a_{jk}^i).$$

Before obtaining equations for the energy and mass fluxes, it should be pointed out that our procedure will differ from that in [19] where an error was made in obtaining an expression for the heat flux. Also, the vector $\mathbf{d}'_i$ was taken for the diffusive force, in analogy to the kinetic theory of a dilute gas. However, for a dense gas $\mathbf{d}'_i$, as given by (2.4), differs from the thermodynamic diffusion force vector given by (1.6). Following [19], we write $\mathbf{d}'_i$ in terms of a derivative of the chemical potential.

In order to do this, we first find the chemical potential from the equation of state (2.15) with the help of the thermodynamic relations

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{T,N_j} = -\left(\frac{\partial p}{\partial N_i}\right)_{V,T,N_j\,(j\neq i)},$$

where V is the volume of the gas.

Integrating this equation, we obtain

$$\frac{\mu_i}{kT} = \ln n_i + 2\sum_j B_{ij} n_j + \frac{3}{2}\sum_{j,k} B_{ijk} n_j n_k + \mathrm{const}\,(T). \tag{2.16}$$

With the help of (2.16), we can write $\mathbf{d}'_i$ in the form

$$\mathbf{d}'_i = \frac{x_i}{kT}(\nabla\mu_i)_T - \frac{y_i}{nkT}\nabla p + x_i \sum_{j=1}^{N} (\delta_{ij} + 2\mu_{ij} B_{ij} \chi_{ij} n_j)\nabla \ln T$$

or in terms of the variables x_i, p, and T:

$$\mathbf{d}'_i = \frac{x_i}{kT}\sum_{j=1,\,j\neq i}^{N}\left(\frac{\partial \mu_i}{\partial x_j}\right)_{T,p,x_k\,(k\neq i,j)}\nabla x_j + \frac{p}{nkT}(n_i v_i^* - y_i)\nabla \ln p + x_i\left[1 - \frac{p v_i^*}{kT} + 2\sum_{j=1}^{N}\mu_{ij} B_{ij}\chi_{ij} n_j\right]\nabla \ln T.$$

Now it is easy to find the difference between the "kinetic" diffusion force vector $\mathbf{d}'_i$ and the thermodynamic diffusion force vector $\mathbf{d}_i$:

$$\mathbf{d}'_i - \mathbf{d}_i = \alpha_i \nabla \ln T, \tag{2.17}$$

where

$$\alpha_i = x_i\left[1 - \frac{p v_i^*}{kT} + 2\sum_{j=1}^{N}\mu_{ij} B_{ij}\chi_{ij} n_j\right].$$

Clearly, $\alpha_i \equiv 0$ for a dilute gas and the vectors $\mathbf{d}'_i$ and $\mathbf{d}_i$ are equal in this case. We also note that, in general, $\sum_i \mathbf{d}'_i = \sum_i \mathbf{d}_i = 0$.

Before proceeding to the derivation of the transport equations and Onsager relations, we describe the procedure as a whole. Our procedure is analogous to that used in [23] for a dilute mixture: From the solution of the kinetic equation, the mass fluxes and reduced heat flux are calculated and are expressed in terms of the corresponding thermodynamic forces (in the given case, $\nabla \ln T$ and $\mathbf{d}_i$). If the coefficients of these forces form a symmetric matrix, then the Onsager relations are proven.

Now we can obtain an expression for the diffusive mass fluxes

$$\mathbf{J}_i = \rho_i \mathbf{V}_i = m_i \int \mathbf{C}_i \varphi_i^{(1)} f_i^{(0)} d\mathbf{c}_i.$$

If we use the expansions (2.8) and (2.9) and formula (2.17), we obtain

$$\mathbf{J}_i = -\rho_i D_{T_i}\nabla \ln T - \rho_i \sum_{j=1}^{N} D_{ij}\mathbf{d}_j, \tag{2.18}$$

where the coefficients of diffusion and thermodiffusion in the r-th approximation are given by the formulas

$$[D_{ij}]_r = [D_{ji}]_r = \frac{1}{2n} d_{i,0}^{j(r)}; \tag{2.19}$$

$$[D_{T_i}]_r = -\frac{1}{2n}\left(a_{i,0}^{(r)} - \sum_{k=1}^{N} \alpha_k d_{i,0}^{k(r)}\right). \tag{2.20}$$

From (2.11) and (2.13) and expressions (2.19) and (2.20) it follows that the coefficients D_{ij} and D_{T_i} satisfy the conditions

$$\sum_{i=1}^{N} y_i D_{ij} = 0, \quad \sum_{i=1}^{N} y_i D_{T_i} = 0.$$

Thus, in an N-component gas mixture there are $^1/_2N(N-1)$ independent coefficients of multicomponent diffusion and $(N-1)$ independent coefficients of thermodiffusion.

We now calculate the heat flux. We have

$$\mathbf{J}_q = \sum_{j=1}^{N} \int \frac{1}{2} m_j \mathbf{C}_j^2 \mathbf{C}_j f_j^{(1)} d\mathbf{c}_j + \frac{1}{2} \sum_{i,j=1}^{N} \sigma_{ij}\chi_{ij} \int \frac{1}{2} m_i (\mathbf{C}_i'^2 - \mathbf{C}_i^2) \times$$
$$\times \left[f_i^{(0)} f_j^{(1)} + f_i^{(1)} f_j^{(0)} + \frac{1}{2}\sigma_{ij}\mathbf{k}\cdot\left(f_j^{(0)}\nabla f_i^{(0)} - f_i^{(0)}\nabla f_j^{(0)}\right)\right] \mathbf{k}\sigma_{ij}^2 (\mathbf{g}_{ji}\cdot\mathbf{k})\, d\mathbf{k}d\mathbf{c}_i d\mathbf{c}_j =$$
$$= \sum_{j=1}^{N} L_j \mathbf{q}_j - \sum_{i,j=1}^{N} \frac{3k\varkappa_{ij}}{m_i + m_j} \nabla T + kT \sum_{i,j=1}^{N} B_{ij}\chi_{ij} n_i n_j (2\mu_{ij} - 6\mu_{ij}\mu_{ji}) \mathbf{V}_i,$$

where

$$\mathbf{q}_j = \int \frac{1}{2} m_j \mathbf{C}_j \mathbf{C}_j^2 f_j^{(1)} d\mathbf{c}_j; \quad \varkappa_{ij} = \frac{4}{9}\left(2\pi kT \frac{m_i m_j}{m_i + m_j}\right)^{1/2} n_j n_i \chi_{ij} \sigma_{ij}^4;$$

and $\mathbf{q}_i$ are the partial heat fluxes and L_i is given by the formula written out after (2.3).

If we again use expansions (2.8) and (2.9), we obtain

$$\mathbf{J}_q = -\lambda''\nabla T - nkT \sum_{j=1}^{N} \left(D_{T_j} - \sum_{k=1}^{N} \alpha_k D_{jk}\right) \mathbf{d}_j' + \frac{5}{2} kT \sum_{j=1}^{N} L_j n_j \mathbf{V}_j + kT \sum_{i,j=1}^{N} B_{ij}\chi_{ij} n_i n_j (2\mu_{ij} - 6\mu_{ij}\mu_{ji}) \mathbf{V}_i. \tag{2.21}$$

Here the coefficient λ'' in the r-th approximation has the form

$$[\lambda'']_r = \frac{5k}{4} \sum_{j=1}^{N} x_j L_j a_{j,1}^{(r)} + \sum_{i,j=1}^{N} \frac{3k\varkappa_{ij}}{m_i + m_j}.$$

For the reduced heat flux **q** we now obtain the expression

$$\mathbf{q} = \mathbf{J}_q - \sum_{j=1}^{N} \rho_j h_j \mathbf{V}_j = \mathbf{J}_q - \sum_{j=1}^{N} n_j \left(\frac{3}{2} kT + pv_j^*\right) \mathbf{V}_j. \tag{2.22}$$

Substituting expression (2.21) for the heat flux into (2.22) and using relations (2.17) and (2.18) and the expression for L_i, we obtain

$$\mathbf{J}_0 = \mathbf{q} = -\lambda''\nabla T - nkT \sum_{j=1}^{N} \left(D_{T_j} - \sum_{i=1}^{N} \alpha_i D_{ij}\right) (\mathbf{d}_j + \alpha_j \nabla \ln T) -$$
$$- nkT \sum_{j=1}^{N} \alpha_j \left(D_{T_j} \nabla \ln T + \sum_{i=1}^{N} D_{ij}\mathbf{d}_i\right) = -\left[\lambda'' + nk \sum_{j=1}^{N} \alpha_j \left(2D_{T_j} -\right.\right.$$
$$\left.\left. - \sum_{i=1}^{N} \alpha_i D_{ij}\right)\right] \nabla T - nkT \sum_{i=1}^{N} D_{T_i}\mathbf{d}_i = -\lambda'\nabla T - nkT \sum_{i=1}^{N} D_{T_i}\mathbf{d}_i, \tag{2.23}$$

where the coefficient λ' in the r-th approximation has the form

$$[\lambda']_r = [\lambda'']_r + nk\sum_{i=1}^{N}\alpha_i\left(2\left[D_{T_i}\right]_r - \sum_{j=1}^{N}\alpha_j[D_{ij}]_r\right) = k\sum_{i=1}^{N}\left[\frac{5}{4}L_i x_i a_{i,1}^{(r)} - \alpha_i\left(a_{i,0}^{(r)} - \frac{1}{2}\sum_{j=1}^{N}\alpha_j d_{i,0}^{j(r)}\right)\right] + \sum_{i,j=1}^{N}\frac{3k\varkappa_{ij}}{m_i+m_j}. \quad (2.24)$$

We can also get an expression for the total thermal conductivity. In order to do this, (2.23) must be rewritten in terms of ∇T and V_i:

$$\mathbf{q} = -\lambda\nabla T + nkT\sum_{j=1}^{N}k_{T_j}\mathbf{V}_j.$$

Here the thermodiffusion ratios k_{T_j} are determined by

$$\sum_{j=1}^{N}D_{ij}k_{T_j} = D_{T_i}; \quad (2.25)$$

$$\sum_{i=1}^{N}k_{T_i} = 0. \quad (2.26)$$

Comparing (2.25) and (2.23), we get the following result for the thermal conductivity in the r-th approximation:

$$[\lambda]_r = [\lambda']_r - nk\sum_{i=1}^{N}\left[k_{T_i}\right]_r\left[D_{T_i}\right]_r.$$

Now we can compare (2.18), (2.23) with (1.3), (1.4) and find relations between the coefficients α_{ij} and λ', D_{T_i} and D_{ij}:

$$\alpha_{00} = \lambda' T, \quad \alpha_{i0} = \alpha_{0i} = \rho_i D_{T_i}, \quad \alpha_{ij} = \frac{\rho_i\rho_j}{nkT}D_{ij}.$$

Thus, we have proven that the Onsager relations are satisfied for the physical transport coefficients obtained from solution of the modified Enskog equation for a dense gas mixture.

It is interesting to compare the coefficients of diffusion, thermodiffusion, and thermal conductivity obtained by (2.19), (2.20), and (2.24) with the transport coefficients obtained in [16]. This comparison was done with the system of "forces" and "fluxes" used here, and there was a complete correspondence in the coefficients. Below we give the relations connecting the coefficients (2.19), (2.20), and (2.24) with the coefficients $L_{ll'}$ defined by formula (3.24) of [16]:

$$D_{ll'} = \frac{nkT}{\rho_l\rho_{l'}}L_{ll'}, \quad D_{Tl} = \frac{1}{\rho_l}\left(L_{l0} - \sum_{l'}L_{ll'}\frac{pv_{l'}^*}{m_{l'}}\right),$$

$$\lambda' = \frac{1}{T}\left[L_{00} - \sum_{l}\frac{pv_l^*}{m_l}\left(2L_{l0} - \sum_{l'}\frac{pv_{l'}^*}{m_{l'}}L_{ll'}\right)\right].$$

It should be pointed out that the modification to the Enskog equation apparently affects the transport coefficients only to second order in the density; this corresponds completely to the result of [14]. In particular, it can be shown that the thermodiffusion ratio k_T for a two-component mixture is equal to that calculated using the Thorne theory to the first approximation in the density [14].

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