THE KINETIC THEORY OF HEAT CONDUCTION IN GAS MIXTURES AT LOW TEMPERATURES

A. G. Shashkov and T. N. Abramenko UDC 536.23

The solution to the Boltzman equation is obtained by the Chapman–Enskog method for the case of low temperatures. An expression is found with the help of the quantum "diffusion" model for the thermal conductivity of a gas mixture at low temperatures.

Molecular translational degrees of freedom are "frozen in" at low temperatures, at a time when the molecular spin makes some contribution to the thermal conductivity of the mixture, i.e., the degree of freedom associated with the internal motion.

Both monatomic and polyatomic molecules at low temperatures therefore exhibit internal degrees of freedom. The translational degrees of freedom are "unfrozen" with a rise in temperature and beginning at about 200°K, we must begin to give consideration to the contribution of the translational degrees of freedom to the heat conduction of the mixture.

The conduction of heat in a gas mixture at low temperatures is brought about by quantum "diffusion" [5].

In calculating the low-temperature heat conduction of a mixture, we must bear in mind the quantum effect. Quantum theory introduces two variations into the classical kinetic theory of gases.

1. Collisions between two gas molecules must be treated from the standpoint of the quantum theory of collisions. The deflection of the relative-velocity vector as a consequence of the collisions of a pair of molecules with masses m_1 and m_2 is approximately the same as in the assumption – resorting to classical theory – that each molecule is surrounded by a "wave" field whose linear extent is on the order of the "wavelength" [1, 2]

$$\tilde{\lambda} = h/2\pi\sqrt{\mu kT}.$$

This quantity is the greater, the lighter the molecule and the lower the temperature. The quantity $\tilde{\lambda}$ is known as the de Broglie wavelength and characterizes deviation from the classical theory for the case in which it is commensurate with or greater than the molecule diameter.

2. The second variation of classical theory is associated with the change in the Maxwell–Boltzmann equilibrium distribution function for the Bose–Einstein and Fermi–Dirac laws.

At very low temperatures, the wave fields associated with the molecules become very much larger than the molecules and it is possible to have a state in which the lowest quantum levels are occupied. A gas in this state of level-occupation is referred to as degenerate.

The first variation (the diffraction effect) is significant when the de Broglie wavelength is on the order of the molecular dimensions.

The second variation (the symmetry effect) is significant when the de Broglie wavelength is on the order of the distance between the molecules in the gas.

Unlike the first quantum effect, the second effect will be smaller at ordinary temperature and becomes important only at very low temperatures (below 2°K) and at high densities.

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The state of the ν-component gas mixture is completely described by the distribution function f(**r**, **v**, t), which is a solution of the integrodifferential Boltzmann equation which, with consideration of the quantum effects of the gas mixtures whose molecules exhibit internal degrees of freedom, has the form

$$\frac{\partial f_{qi}}{\partial t}+\mathbf{v}_q\frac{\partial f_{qi}}{\partial \mathbf{r}}=\sum_{q'}\sum_{jkl}\iiint [f'_{qk}f'_{q'l}(1+\theta_q f_{qk})(1+\theta_{q'}f_{q'l})$$
$$-f_{qk}f_{q'l}(1+\theta_q f'_{qk})(1+\theta_{q'}f'_{q'l})]\,gI_{ij}^{kl}\sin\chi\,d\chi d\varphi\,d\mathbf{v}_{q'}. \quad (1)$$

Here $\theta = (h/m_q)^3(\delta/G_q)$, $\delta = -1$, 0, and 1, respectively, for the statistics of Fermi–Dirac, Maxwell–Boltzmann, and Bose–Einstein; I_{ij}^{kl} is the differential effective scattering cross section for the molecules and the subscripts i and j denote the molecular state prior to collision, with the superscripts k and l denoting the molecular state subsequent to the collisions.

The equilibrium distribution function is given by (1) in which the right-hand member is equal to zero. For quantum systems we have various equilibrium distribution functions:

for the Maxwell–Boltzmann statistic

$$f^{(0)}_{\mathrm{M-B}}=A_q\exp\left[-\left(\frac{m_qV_q^2}{2kT}+\varepsilon_{qi}\right)\right],$$

for the Bose–Einstein statistic

$$f^{(0)}_{\mathrm{B-E}}=\left\{A_q\exp\left(\frac{m_qV_q^2}{2kT}+\varepsilon_{qi}\right)-\theta_q\right\}^{-1},$$

for the Fermi–Dirac statistic

$$f^{(0)}_{\mathrm{F-D}}=\left\{A_q\exp\left(\frac{m_qV_q^2}{2kT}+\varepsilon_{qi}\right)+\theta_q\right\}^{-1}.$$

Let

$$f^{(0)}_{qi}=\left\{A_q\exp\left(\frac{m_qV_q^2}{2kT}+\varepsilon_{qi}\right)-\theta_q\right\}^{-1}, \quad (2)$$

where

$$\varepsilon_{qi}=E_{qi}/kT.$$

We will seek the approximate solution of the Boltzmann equation in the form

$$f_{qi}=f^{(0)}_{qi}(1+\varphi_{qi}), \quad (3)$$

where φ_{qi} is the function of the velocity, the temperature, and the pressure gradients.

Relationship (3) is substituted into (1) and the terms of second order are neglected [1, 3, 6]. Having introduced the substitution $\beta_{qi}=\varphi_{qi}/(1+\theta_q f^{(0)}_{qi})$ [3], we obtain

$$\frac{\partial f^{(0)}_{qi}}{\partial t}+\mathbf{v}_q\frac{\partial}{\partial \mathbf{r}}f^{(0)}_{qi}=\sum_{q'}\sum_{jkl}\iiint f^{(0)}_{qi}f^{(0)}_{q'j}(1+\theta_q f^{(0)'}_{qi})(1$$
$$+\theta_{q'}f^{(0)'}_{q'j})(\beta'_{qi}+\beta'_{q'j}-\beta_{qi}-\beta_{q'j})\,gI_{ij}^{kl}\sin\chi d\chi d\varphi d\mathbf{v}_{q'}. \quad (4)$$

The conditions for the solution of (4) have the form

$$\sum_i\int f^{(0)}_{qi}(1+\theta_q f^{(0)}_{qi})\,\beta_{qi}d\mathbf{v}_q=0,$$
$$\frac{1}{\rho}\sum_q m_q\sum_i\int f^{(0)}_{qi}(1+\theta_q f^{(0)}_{qi})\,\beta_{qi}\,\mathbf{v}_q d\mathbf{v}_q=0, \quad (5)$$
$$\frac{1}{\rho}\sum_q\sum_i\int f^{(0)}_{qi}(1+\theta_q f^{(0)}_{qi})\left[\frac{1}{2}m_q(\mathbf{v}_q-\mathbf{v}_0)^2+E_{qi}\right]\beta_{qi}\,d\mathbf{v}_q=0.$$

We know that

$$\sum_q m_q \sum_i f_{qi}^{(0)} d\mathbf{v}_q = \rho(\mathbf{r}, t),$$

$$\sum_q m_q \sum_i \int f_{qi}^{(0)} \mathbf{v}_q d\mathbf{v}_q = \sum_q m_q n_q \mathbf{v}_q = \rho \mathbf{v}_0(\mathbf{r}, t),$$

$$\sum_q \sum_i \int f_{qi}^{(0)} \left[\frac{1}{2} m_q (\mathbf{v}_q - \mathbf{v}_0)^2 + E_{qi} \right] d\mathbf{v}_q$$

$$= U_{\text{trans}}(\mathbf{r}, t) + U_{\text{in}}(\mathbf{r}, t) = U(\mathbf{r}, t). \tag{6}$$

We can calculate the derivatives of the function $f_{qi}^{(0)}(\mathbf{r}, \mathbf{v}_q, t)$, in Eq. (4). The final expression for these derivatives include the coordinate and time derivatives of the functions $n_q(\mathbf{r}, t)$, $\mathbf{v}_0(\mathbf{r}, t)$, and $T(\mathbf{r}, t)$. The time derivatives are eliminated by means of transfer equations.

As a result of these transformations, the equation for the function β_{qi} has the form

$$f_{qi}^{(0)} (1 + \theta_q f_{qi}^{(0)}) \left\{ \frac{n}{n_q} (\mathbf{V}_q \cdot \mathbf{d}_q) + \left(\mathbf{b}_q' : \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 \right) - \left[\left(\frac{5}{2} - W_q^2 \right) \right. \right.$$
$$\left. \left. + (\varepsilon_{qi} - \bar{\varepsilon}_q) \right] \left(\mathbf{V}_q \frac{\partial \ln T}{\partial \mathbf{r}} \right) + \frac{c_{v\text{in}}}{c_v} \left[\left(\frac{2}{3} W_q^2 - 1 \right) - \frac{k}{c_{\text{v in}}} (\varepsilon_{qi} - \bar{\varepsilon}_q) \right] \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 \right\} = I_{qq'}. \tag{7}$$

Here

$$\mathbf{d}_q = \frac{\partial}{\partial \mathbf{r}} \left(\frac{n_q}{n} \right) + \left(\frac{n_q}{n} - \frac{n_q m_q}{\rho} \right) \frac{\partial \ln p}{\partial \mathbf{r}},$$

$$\mathbf{b}_q' = 2 \left(\mathbf{W}_q \mathbf{W}_q - \frac{1}{3} W_q^2 \mathbf{U}' \right), \quad \mathbf{W}_q = \left(\frac{m_q}{2kT} \right)^{1/2} \mathbf{V}_q,$$

$$\bar{\varepsilon}_q = Q_q^{-1} \sum_i \varepsilon_{qi} \exp(-\varepsilon_{qi}),$$

$$I_{qq'} = \sum_{q'} \sum_{jkl} \iiint f_{qi}^{(0)} f_{q'j}^{(0)} (1 + \theta_q f_{qi}^{(0)\prime}) (1 + \theta_{q'} f_{q'j}^{(0)\prime}) (\beta_{qi}' + \beta_{q'j}' - \beta_{qi} - \beta_{q'j}) g I_{ij}^{kl} \sin \chi d\chi d\varphi d\mathbf{v}_{q'}.$$

It is convenient to transform the collision integral to the form

$$I_{qq'} = F_{1/2}(A_q) F_{1/2}(A_{q'}) J_{qq'}, \tag{8}$$

where

$$J_{qq'} = F_{1/2}^{-1}(A_q) F_{1/2}^{-1}(A_{q'}) \sum_{q'} \sum_{jkl} \iiint f_{qi}^{(0)} f_{q'j}^{(0)} (1 + \theta_q f_{qi}^{(0)\prime})$$
$$\times (1 + \theta_{q'} f_{q'j}^{(0)\prime}) (\beta_{qi}' + \beta_{q'j}' - \beta_{qi} - \beta_{q'j}) g I_{ij}^{kl} \sin \chi d\chi d\varphi d\mathbf{v}_{q'}. \tag{9}$$

Here $F_s(A_q) = \frac{1}{\Gamma(s+1)} \int_0^\infty \frac{u^s du}{A_q (\exp u) - \theta_q}$ is the Sommerfeld integral [2], in the case of s = 1/2 equal to

$$F_{1/2}(A_q) = \frac{2}{3} (\ln A_q)^{3/2} \left[1 + \frac{\pi^2}{8} (\ln A_q)^{-2} \right].$$

On the other hand,

$$F_{1/2}(A_q) = n_q \left(\frac{m_q}{2\pi kT} \right)^{3/2} \theta_q.$$

Equation (7) then assumes the form

$$f_{qi}^{(0)} (1 + \theta_q f_{qi}^{(0)}) \left\{ \frac{n}{n_q} (\mathbf{V}_q \cdot \mathbf{d}_q) + \left(\mathbf{b}_q' : \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 \right) - \left[\left(\frac{5}{2} - W_q^2 \right) \right. \right.$$
$$\left. \left. + (\varepsilon_{qi} - \bar{\varepsilon}_q) \right] \left(\mathbf{V}_q \cdot \frac{\partial \ln T}{\partial \mathbf{r}} \right) + \frac{c_{\text{v in}}}{c_v} \left[\left(\frac{2}{3} W_q^2 - 1 \right) - \frac{k}{c_{\text{v in}}} (\varepsilon_{qi} - \bar{\varepsilon}_q) \right] \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 \right\} = F_{1/2}(A_q) F_{1/2}(A_{q'}) J_{qq'}. \tag{10}$$

We can present the function β_{qi} as

$$\beta_{qi} = -(1+\theta_q f_{qi}^{(0)}) \left[\left(\tilde{\mathbf{A}}_q \cdot \frac{\partial \ln T}{\partial \mathbf{r}} \right) + \left(\mathbf{B}_q' : \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 \right) - n \sum_{q'} (\mathbf{C}_q^{q'} \cdot \mathbf{d}_{q'}) - D_q \frac{\partial}{\partial \mathbf{r}} \mathbf{v}_0 \right]. \tag{11}$$

Substituting (11) into (10) and equating the coefficients for identical gradients, we obtain the integral equations for the functions $\tilde{\mathbf{A}}_q$, $\mathbf{B}_q'$, $\mathbf{C}_q^{q'}$, and D_q. In particular, for $\tilde{\mathbf{A}}$ and $\mathbf{C}_q^{q'}$ we have:

$$F_{1/2}^{-1}(A_q) f_{qi}^{(0)} (1+\theta_q f_{qi}^{(0)}) \left[\left(W_q^2 - \frac{5}{2} \right) + (\varepsilon_{qi} - \bar{\varepsilon}_q) \right] \mathbf{V}_q$$

$$= \sum_{q'} \sum_{jkl} \iiint (\tilde{\mathbf{A}}_q' + \tilde{\mathbf{A}}_{q'}' - \tilde{\mathbf{A}}_q - \tilde{\mathbf{A}}_{q'}) g I_{ij}^{kl} f_{qi}^{(0)} f_{q'j}^{(0)} (1+\theta_q f_{qi}^{(0)'}) (1+\theta_{q'} f_{q'j}^{(0)'}) \sin\chi d\chi d\varphi d\mathbf{v}_{q'}, \tag{12}$$

$$F_{1/2}^{-1}(A_q) n_q^{-1} (1+\theta_q f_{qi}^{(0)}) (\delta_{qh} - \delta_{qk}) \mathbf{V}_q \mathbf{d}_q = \sum_{q'} \sum_{jkl} \iiint (\mathbf{C}_q^{(k)} + \mathbf{C}_{q'}^{(k)}$$

$$- \mathbf{C}_q^{(h)} - \mathbf{C}_{q'}^{(h)} + \mathbf{C}_q^{(k)'} + \mathbf{C}_{q'}^{(k)'} - \mathbf{C}_q^{(h)'} - \mathbf{C}_{q'}^{(h)'}) g I_{ij}^{kl} f_{qi}^{(0)} f_{q'j}^{(0)} (1+\theta_q f_{qi}^{(0)'}) (1+\theta_{q'} f_{q'j}^{(0)'}) \sin\chi d\chi d\varphi d\mathbf{v}_{q'}. \tag{13}$$

The additional conditions are

$$\sum_q \sqrt{m_q} \int (\mathbf{C}_q^{(q')} - \mathbf{C}_q^{(k)}) \mathbf{W}_q f_{qi}^{(0)} (1+\theta_q f_{qi}^{(0)}) d\mathbf{v}_q = 0,$$

$$\sum_q \sqrt{m_q} \int (\tilde{\mathbf{A}}_q \mathbf{W}_q) f_{qi}^{(0)} (1+\theta_q f_{qi}^{(0)}) d\mathbf{v}_q = 0.$$

The quantities $\tilde{\mathbf{A}}_q$ and $\mathbf{C}_q$ have the form

$$\tilde{\mathbf{A}}_q = \mathbf{W}_q \tilde{A}_q (W_q),$$

$$\mathbf{C}_q = \mathbf{W}_q C_q (W_q)$$

and are expressed in terms of the coefficients of the expansion in Sonin polynomials [6]

$$\tilde{\mathbf{A}}_q = \mathbf{W}_q \sum_m \sum_n a_{qmn} S_{3/2}^{(m)} (W_q^2) P^{(n)} (\varepsilon_{qi}),$$

$$\mathbf{C}_q^{q'} - \mathbf{C}_q^{q''} = \mathbf{W}_q \sum_m \sum_n c_{qmn}^{q'q''} S_{3/2}^{(m)} (W_q^2) P^{(n)} (\varepsilon_{qi}).$$

The Sonin polynomials satisfy the orthogonality conditions

$$\int_0^\infty x^n e^{-x} S_n^{(m)}(x) S_n^{(m')}(x) dx = \frac{\Gamma(n+m)}{m!} \delta_{mm'},$$

with the following relationships satisfied:

$$F_{1/2}^{-1}(A_q) \int f_{qi}^{(0)} (1+\theta_q f_{qi}^{(0)}) S_{3/2}^{(m)} (W_q^2) V_q^2 d\mathbf{V}_q = \frac{3 n_q k T}{m_q} \delta_{m0},$$

$$F_{1/2}^{-1}(A_q) \int f_{qi}^{(0)} (1+\theta_q f_{qi}^{(0)}) S_{3/2}^{m} (W_q^2) \left[\left(\frac{5}{2} - W_q^2 \right) + (\varepsilon_{qi} - \bar{\varepsilon}_q) \right] W_q^2 d\mathbf{V}_q = n_q \frac{2kT}{m_q} \left(\frac{15}{4} \delta_{m1} - \frac{3}{2} \frac{c_{\text{vin}}}{k} \delta_{m0} \right).$$

$P^{(n)}(\varepsilon_{qi})$ represent polynomials of n-th degree such that $P^{(0)} = 1$ and $P^{(1)} = \varepsilon_{qi} - \bar{\varepsilon}_q$.

Using the variational method of [1] to solve the integral equations (12) and (13), we derive an equation for the determination of the expansion coefficients a_{qmn} and $c_{qmn}^{q'q''}$. In general form

$$\sum_{q'} \sum_{m'} \sum_n \tilde{Q}_{qq'}^{mm'} t_{q'm'n}^{(h,k)} = -R_{qm}^{(h,k)}, \tag{14}$$

where

$$\tilde{Q}_{qq'}^{mm'} = Q_{qq'}^{mm'} - \frac{n_{q'}\sqrt{m_{q'}}}{n_q\sqrt{m_q}} Q_{qq}^{mm'} \delta_{m0}\delta_{m'0};$$

$$t_{q'm'n}^{(h,k)} = \begin{cases} a_{q'm'n} \\ c_{q'm'n}^{q'q''} \end{cases}.$$

Here

$$Q_{qq'}^{mm'} = F_{1/2}^{-1}(A_q) F_{1/2}^{-1}(A_{q'}) \sum_l n_q n_l \{\delta_{qq}[\mathbf{W}_q P^{(s)}(\varepsilon_{qi}) S_n^{(m)}(W_q^2);\ \mathbf{W}_q P^{(s')}(\varepsilon_{qi}) \times S_n^{(m')}(W_q^2)]_{ql} + \delta_{q'l}[\mathbf{W}_q P^{(s)}(\varepsilon_{qi}) S_{n'}^{(m)}(W_q^2); \mathbf{W}_l P^{(s')}(\varepsilon_{qi}) S_n^{(m')}(W_l^2)]_{ql}\}$$

and

$$[L;\ G]_{qq'} = 4\left(\frac{2kT}{\pi\mu_{qq'}}\right)^{1/2} (Q_q Q_{q'})^{-1}$$

$$\sum_{ijkl}\int_0^\infty d\gamma \int_0^{2\pi} d\varphi \int_0^\pi \sin\ \chi d\chi \gamma^3 I_{ij}^{kl} \exp(-\gamma^2 - \varepsilon_{qi} - \varepsilon_{qj}) L(L-G).$$

The quantity $R_{qm}^{(h,k)}$ in the case of the functions $\tilde{\mathbf{A}}_q$ and $\mathbf{C}_q^{q'}$ is equal to

$$\int f_{qi}^{(0)}(1+\theta_q f_{qi}^{(0)}) \left[\left(\frac{5}{2} - W_q^2\right) + (\varepsilon_{qi} - \bar{\varepsilon}_q)\right] \mathbf{V}_q \mathbf{W}_q S_{3/2}^{(m)} d\mathbf{V}_q,$$

$$\int n_q^{-1} f_{qi}^{(0)} (1+\theta_q f_{qi}^{(0)})(\delta_{kh} - \delta_{qk}) \mathbf{V}_q \mathbf{W}_q S_{3/2}^{(m)} d\mathbf{V}_q.$$

The expression for the heat-flux vector has the form

$$\mathbf{q} = kT\sum_q \left(\frac{5}{2} + \bar{\varepsilon}_q\right) n_q \bar{\mathbf{V}}_q - \lambda\frac{\partial T}{\partial \mathbf{r}} + \frac{kT}{n}\sum_{qq'} \frac{n_{q'} D_q^T}{m_q D_{qq'}}, \tag{15}$$

in which case

$$\lambda = \lambda' - \frac{k}{2n}\sum_{qq'} \frac{n_q n_{q'}}{D_{qq'}}\left[\frac{D_q^T}{n_q m_q} - \frac{D_{q'}^T}{n_{q'} m_{q'}}\right]^2. \tag{16}$$

We know that

$$D_q^T = F_{1/2}^{-1}(A_q) \frac{m_q}{3}\sqrt{\frac{m_q}{2kT}} \sum_{m=0}^{\xi-1} a_{qm}(\xi) \int V_q^2 S_{3/2}^{(m)} f_{qi}^{(0)} (1+\theta_q f_{qi}^{(0)}) d\mathbf{V}_q,$$

$$D_{qq'} = F_{1/2}^{-1}(A_q) \frac{\rho}{3nm_q}\sqrt{\frac{m_q}{2kT}} \sum_{m=0}^{\xi-1} c_{qm}(\xi) \int V_q^2 S_{3/2}^{(m)} f_{qi}^{(0)} (1+\theta_q f_{qi}^{(0)}) d\mathbf{V}_q,$$

$$\lambda' = -F_{1/2}^{-1}(A_q) \frac{\sqrt{2}}{3} k\sqrt{kT} \sum_{q'}\sum_{m=0}^{\xi-1} \frac{1}{\sqrt{m_q}} a_{qm}(\xi) \int W_q^2 \left(\frac{5}{2} - W_q^2\right) S_{3/2}^{(m)} f_{qi}^{(0)} (1+\theta_q f_{qi}^{(0)}) d\mathbf{V}_q$$

or by means of the orthogonality conditions for the Sonin polynomials we obtain

$$D_q^T = m_q n_q (kT/2m_q)^{1/2} a_{q0},$$

$$D_{qq'} = \rho (n_q/m_q)(kT/2m_q)^{1/2} c_{q0}^{qq'},$$

$$\lambda' = -\frac{5}{4} k \sum_q n_q (2kT/m_q)^{1/2} a_{q1}.$$

Relationship (16) is somewhat indeterminate, because of the fact that it contains approximations of various orders for λ', $D_{qq'}$, and D_q^T. To eliminate this indeterminacy, the second approximation for the diffusion coefficient must be substituted into (16).

We know that the coefficient of mutual diffusion and the coefficient of thermal diffusion are associated by the relationship

$$\overline{\mathbf{V}}_q = \frac{n^2}{n_q \rho} \sum_{q'=1} m_{q'} D_{qq'} \mathbf{d}_{q'} - (n_q m_q)^{-1} D_q^T \frac{\partial \ln T}{\partial \mathbf{r}}.$$

To find $\mathbf{d}_{q'}$ we introduce the substitution [7]

$$\vec{\alpha}_q = \frac{2}{n} \left(\frac{m_q}{2kT}\right)^{1/2} \left(\overline{\mathbf{V}}_q + \frac{D_q^T}{n_q m_q} \frac{\partial \ln T}{\partial \mathbf{r}}\right). \tag{17}$$

Then

$$\vec{\alpha}_q = \sum_{q'} c_{q0}^{q'h} \mathbf{d}_{q'}. \tag{18}$$

In this case the relationship

$$\sum_{q'} \sum_{n} \sum_{m} \tilde{Q}_{qq'}^{mm'} c_{q'm'n}^{hk} = -R_{qm}^{hk},$$

where

$$R_{qm}^{hk} = -\frac{3}{2} \left(\frac{2kT}{m_q}\right)^{1/2} \delta_{m0} (\delta_{qh} - \delta_{qk}),$$

with (16) for m = 0, m' = 0 and 1 can be written in the form

$$\sum_q \tilde{Q}_{kq}^{00} \vec{\alpha}_q = -\sum_{q'} \left[\frac{3}{2} \left(\frac{2kT}{m_q}\right)^{1/2} \delta_{m0} (\delta_{qh} - \delta_{qk}) + \sum_q c_{q0}^{q'h} \tilde{Q}_{kq}^{01}\right], \tag{19}$$

for m = 1 and m' = 0 and 1 we obtain

$$\sum_q \tilde{Q}_{kq}^{10} \vec{\alpha}_q = -\sum_q \sum_{q'} \mathbf{d}_{q'} c_{q1}^{q'h} \tilde{Q}_{kq}^{11}. \tag{20}$$

Having determined the matrix $P_{qq'}$ that is the reciprocal of $\tilde{Q}_{qq'}^{11}$ by the relationship

$$\sum_q P_{kq} \tilde{Q}_{qq'}^{11} = \delta_{kq'}, \tag{21}$$

multiplying (20) by the sum $\sum_i P_{ki} \tilde{Q}_{q'i'}^{01}$, and substituting the result into (19), we obtain

$$\mathbf{d}_k = -\frac{2}{3} \left(\frac{m_q}{2kT}\right)^{1/2} \sum_q \vec{\alpha}_q \left(\tilde{Q}_{kq}^{00} - \sum_{q'} \tilde{Q}_{qi'}^{01} \tilde{Q}_{q'q}^{10} P_{q'i'}\right). \tag{22}$$

We will evaluate the last term in (15) for the heat-flux vector, representing it in the form

$$-nkT \sum_{q'} \frac{D_{q'}^T}{n_{q'} m_{q'}} \mathbf{d}_{q'} = \mathbf{Y} - \Lambda \frac{\partial T}{\partial \mathbf{r}}. \tag{23}$$

With (17) and (22) we find

$$\mathbf{Y} = \frac{2}{3} \sum_{qk} \left(\frac{m_q}{m_k}\right)^{1/2} \frac{D_k^T}{n_k} \overline{\mathbf{V}}_q \left[\tilde{Q}_{kq}^{00} - \sum_{i'q'} \tilde{Q}^{01} P_{q'i'} \tilde{Q}_{q'i}^{10}\right], \tag{24}$$

$$\Lambda = \frac{2}{3} \sum_{qk} \frac{D_q^T D_k^T}{n_q n_k (m_q m_k)^{1/2}} \left[\sum_{i'q'} \left(\tilde{Q}_{qi'}^{01} P_{q'i'} \tilde{Q}_{qq'}^{10}\right) - \tilde{Q}_{kq}^{00}\right]. \tag{25}$$

We determine $\lambda = \lambda' + \Lambda$, and the quantity Y characterizes the contribution to the heat flow as a result of diffusion.

Using the relationship

$$\sum_{q'=1}^{\xi-1}\sum_{n}\sum_{m'}\tilde{Q}_{qq'}^{mm'}a_{q'm'n} = -R_{qm},$$

where

$$R_{qm} = -n_q(2kT/m_q)^{1/2}\left[\frac{15}{4}\delta_{m1} - \frac{3}{2}\frac{c_{v\,\mathrm{in}}}{k}\delta_{m0}\right],$$

and the relationship

$$D_q^T = m_q n_q (kT/2m_q)^{1/2} a_{q0},$$

we find that

$$\sum_{q}\frac{D_q^T}{n_q m_q^{1/2}}\tilde{Q}_{q'q}^{10} = -\left(\frac{kT}{2}\right)^{1/2}\left(R_{q'1} + \sum_{n}\sum_{q}a_{q1n}\tilde{Q}_{q'q}^{11}\right), \tag{26}$$

$$\sum_{q}\frac{D_q^T}{n_q m_q^{1/2}}\tilde{Q}_{kq}^{00} = -\left(\frac{kT}{2}\right)^{1/2}\sum_{n}\sum_{q}a_{q1n}\tilde{Q}_{kq}^{01}. \tag{27}$$

Having substituted these relationships into (25) and using the equation $\tilde{Q}_{qq'}^{01} = \tilde{Q}_{q'q}^{10}$, we obtain

$$\Lambda = \frac{k}{3}\left(\sum_{q}\sum_{q'}R_{q1}P_{qq'}R_{q'1} + \sum_{q}a_{q1}R_{q1}\right),$$

where

$$R_{q1} = \frac{15}{4}n_q\left(\frac{2kT}{m_q}\right)^{1/2}.$$

Then

$$\lambda = \frac{k}{3}\sum_{q}\sum_{q'}R_{q1}P_{qq'}R_{q'1}.$$

Assuming that $\lambda_{\mathrm{trans}} = 0$, we obtain the expression for the coefficient of thermal conductivity resulting from the internal degrees of freedom in terms of the matrix determinant $\tilde{Q}_{qq'}^{11}$,

$$\lambda_{\mathrm{in}} = 4\begin{vmatrix} L_{qq'}^{10,10}, & L_{qq'}^{10,01}, & \cdots & x_q \\ L_{qq'}^{01,10}, & L_{qq'}^{01,01}, & \cdots & x_{q'} \\ \cdots & \cdots & \cdots & \\ x_q & x_{q'} & \cdots & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} L_{qq'}^{10,10}, & L_{qq'}^{10,01} & \cdot \\ L_{qq'}^{01,10}, & L_{qq'}^{01,01} & \cdot \\ \cdots & \cdots & \cdot \end{vmatrix} \tag{28}$$

Here

$$L_{qq'}^{10,01} = L_{qq'}^{01,10} = 0,$$

$$L_{qq'}^{10,10} = \frac{2x_q x_{q'} M_q M_{q'}}{(M_q + M_{q'})^2 A_{q'}^{*}\lambda_{qq'}}\left(\frac{55}{4} - 3B_{qq'}^{*} - 4A_{qq'}^{*}\right),$$

$$L_{qq'}^{01,01} = 0 \text{ when } q \neq q',$$

$$L_{qq}^{01,01} = -\frac{64}{3}\frac{x_q m_q}{kT}\frac{1}{c_{v_q\,\mathrm{in}}}\sum_{q''}\frac{x_{q''}m_{q''}}{m_q + m_{q''}}\Omega_{qq''}^{(1,1)}. \tag{29}$$

Relationship (28) can be presented in the form

$$\lambda_{in} = 4 \sum_q x_q^2 / L_{qq}^{01,01}, \tag{30}$$

and the term $\Omega_{qq''}^{(1,1)}$ can be expressed in the form of a ratio of the diffusion coefficient so that

$$\lambda_{in} = \sum_{q=1}^{\nu} n D_{qq} c_{v_{q\text{вн}}} \left(\sum_{q'} \frac{x_{q'}}{x_q} \frac{D_{qq}}{D_{qq'}} \right)^{-1}. \tag{31}$$

Since $\lambda_q = nD_{qq}c_{v_q in}$, the expression for the coefficient of thermal conductivity for the gas mixture at low temperatures has the form

$$\lambda = \sum_{q=1}^{\nu} \frac{\lambda_q}{1 + \sum\limits_{\substack{q'=1 \\ q \neq q'}}^{\nu} \frac{x_{q'}}{x_q} \frac{D_{qq}}{D_{qq'}}}. \tag{32}$$

NOTATION

m_q	is the mass of the q-th kind of molecule;
h	is the Planck constant;
k	is the Boltzmann constant;
μ	is the reduced mass of the molecule;
v_q	is the velocity of the q-th kind of molecule;
G_q	is the statistical weight of the q-th kind of molecule;
$V_q = v_q - v_0$	is the thermal velocity of the molecule;
T	is the temperature;
n_q	is the numerical density of the q-th kind of molecule;
ρ	is the total density of the gas mixture;
W_q	is the reduced velocity of the q-th kind of molecule;
$\vec{\gamma}_{qq'} = \sqrt{(\mu_{qq'}/2kT)} g_{qq'}$	is the reduced initial relative velocity;
$g = v_q - v_{q'}$	is the relative velocity;
$S_n^{(m)}(x)$	are Sonin polynomials;
λ	is the coefficient of thermal conductivity for the mixture;
$D_{qq'}$	is the coefficient of mutual diffusion;
D_q^T	is the coefficient of thermal diffusion;
$\underline{v}_q$	is the diffusion velocity of the q-th kind of molecule;
x_q	is the molar concentration of the q-th component;
c_{vin}	is the heat capacity due to the internal degrees of freedom;
v_0	is the mean mass velocity;
λ_q	is the thermal conductivity of the q-th component;
t	is the time.

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