A KINETIC THEORY OF GAS MIXTURES WITH REGARD TO THE LAWS OF THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

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The derivation of the hydrodynamic equations for a gaseous mixture from the system of kinetic Boltzmann equations is analyzed. The form of the hydrodynamic equations is a unique consequence of necessary and sufficient conditions for the solvability of systems of linear integral equations with symmetrical kernels, which define the terms in the expansion of the distribution functions in a series with respect to a parameter of spatial nonhomogeneity (actually, the Knudsen number). The transport laws are presented in a form for which the Onsager symmetry relations hold. In deriving the Onsager relations use is made of symmetry properties of integral operators, which are a consequence of the invariance of the equations of mechanics with respect to a transformation involving changing the sign of the time and the impulses of the particles. The Onsager relations are also derived from expressions for the kinetic coefficients in terms of correlation functions.

In the thermodynamics of irreversible processes the laws of transport in multicomponent mixtures of liquids or gases are written in a symmetrical form, i.e., the Onsager relations hold for the kinetic coefficients; these relations express the equality of the kinetic coefficients, which correspond to crossed phenomena [1]. However, in handbooks on the kinetic theory of gases [2-4] the laws of transport are represented in a nonsymmetrical form. Symmetrical laws of transport for multicomponent mixtures of liquids were obtained by the author in [5].

1. The behavior of a mixture of gases of L components is describable by means of the distribution functions $f^{(k)}$ $(\mathbf{r}, \mathbf{p}, t)$ of particles of the k-th kind with respect to the coordinates $\mathbf{r}$ and momenta $\mathbf{p}$ in a six-dimensional μ-space. The hydrodynamic variables describing the macroscopic state of the system, for example, the density n_k of the number of particles of the k-th kind, the mean bulk velocity u, and temperature T, which depend on the coordinates and time $(\mathbf{r}, t)$, may with the aid of the functions $f^{(k)}$ be represented in the form

$$n_k = \int f^{(k)} d\mathbf{p}, \quad n = \sum_k n_k, \quad \rho u_\alpha = \sum_k \int f^{(k)} p_\alpha \, d\mathbf{p}, \; T = \frac{2}{3Kn} \sum_k \int f^{(k)} \frac{(\mathbf{p} - m_k \mathbf{u})^2}{2m_k} d\mathbf{p},$$
$$\rho = \sum_k m_k n_k, \quad \alpha = (x, y, z) \tag{1.1}$$

Here k is Boltzmann's constant, and the functions $f^{(k)}$ satisfy the system of Boltzmann integrodifferential equations

$$\frac{\partial f^{(k)}}{\partial t} + \frac{p_\alpha}{m_k} \frac{\partial f^{(k)}}{\partial r_\alpha} = \sum_l J(f^{(k)}, f^{(l)}) \quad (k = 1, \ldots, L) \tag{1.2}$$
$$J(f^{(k)}, f^{(l)}) = \int [f^{(k)}(\mathbf{r}, \mathbf{p}', t) f^{(l)}(\mathbf{r}, \mathbf{p}_1', t) - f^{(k)}(\mathbf{r}, \mathbf{p}, t) f^{(l)}(\mathbf{r}, \mathbf{p}_1, t)] g_{kl} b \, db \, d\varepsilon \, d\mathbf{p}_1$$
$$g_{kl} = |(\mathbf{p}_1 / m_l) - (\mathbf{p} / m_k)|$$

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where $\mathbf{p}'$, $\mathbf{p}_1'$ are momenta of molecules of the k-th and l-th kinds after a collision characterized by initial $\mathbf{p}$, $\mathbf{p}_1$, sight-line distance b, and azimuth ε; repeated Greek indices will correspond to summation from 1 to 3.

2. In obtaining the hydrodynamic equations we consider distributions with a small spatial nonhomogeneity and allow for only a slow dependence of the distribution functions on the time, which is characteristic of the hydrodynamic equations. Introducing the small parameter ε of the spatial nonhomogeneity, we put $\boldsymbol{\xi} = \varepsilon\, \mathbf{r}$ and seek the functions $f^{(k)}(\mathbf{r}, \mathbf{p}, t)$ and the hydrodynamic equations in the form of expansions [6, 7]:

$$f^{(k)}(\mathbf{r}, \mathbf{p}, t) = \sum_{q=0}^{\infty} \varepsilon^q f_q^{(k)}(\xi, \mathbf{p} \mid n_s, \mathbf{u}, T), \quad \frac{\partial n_k(\xi, t)}{\partial t} = \sum_{q=1}^{\infty} \varepsilon^q A_k^{(q)}(\xi \mid n_s, \mathbf{u}, T) \tag{2.1}$$

$$\frac{\partial u_\alpha(\xi, t)}{\partial t} = \sum_{q=1}^{\infty} \varepsilon^q B_\alpha^{(q)}(\xi \mid n_s, \mathbf{u}, T), \quad \frac{\partial T(\xi, t)}{\partial t} = \sum_{q=1}^{\infty} \varepsilon^q C^{(q)}(\xi \mid n_s, \mathbf{u}, T) \tag{2.2}$$

In addition, we require that already in the zero-th approximation the functions $f_0^{(k)}$ define completely the variables of the hydrodynamic state:

$$n_k = \int f_0^{(k)} d\mathbf{p}, \qquad \rho u_\alpha = \sum_k \int f_0^{(k)} p_\alpha \, d\mathbf{p}$$
$$T = \frac{2}{3Kn} \sum_k \int f_0^{(k)} \frac{p^{\circ 2}}{2m_k} d\mathbf{p}, \qquad p_\alpha^\circ = p_\alpha - m_k u_\alpha \tag{2.3}$$

Using Eqs. (2.1), (2.2), we write the derivative of $f^{(k)}$ with respect to the time in the form

$$\frac{\partial f^{(k)}}{\partial t} = \sum_{q=1}^{\infty} \sum_{p=0}^{\infty} \varepsilon^{p+q} \Delta^{(q)} f_p^{(k)} \tag{2.4}$$

$$\Delta^{(q)} = \sum_{k'} A_{k'}^{(q)} \frac{\delta}{\delta n_{k'}} + B_\alpha^{(q)} \frac{\delta}{\delta u_\alpha} + C^{(q)} \frac{\delta}{\delta T}$$

Substituting Eqs. (2.1), (2.4) into Eqs. (1.2) and collecting terms having the same powers of ε, we obtain the following equations for determining the functions $f_q^{(k)}$:

$$\sum_{k'} J(f_0^{(k)}, f_0^{(k')}) = 0 \tag{2.5}$$

$$\sum_{k'} [J(f_0^{(k)}, f_q^{(k')}) + J(f_q^{(k)}, f_0^{(k')})] = D_q^{(k)} - I_q^{(k)} \quad (q \geqslant 1) \tag{2.6}$$

$$D_q^{(k)} = \frac{p_\alpha}{m_k} \frac{\partial f_{q-1}^{(k)}}{\partial \xi_\alpha} + \sum_{q'=1}^{q} \Delta^{(q')} f_{q-q'}^{(k)}, \quad I_q^{(k)} = \sum_{k'} \sum_{q'=1}^{q-1} J(f_{q-q'}^{(k)}, f_{q'}^{(k')})$$

In addition, substituting Eq. (2.1) into Eq. (1.1) and taking account of the relations (2.3), we have

$$\int f_q^{(k)} d\mathbf{p} = 0, \quad \sum_k \int f_q^{(k)} p_\alpha \, d\mathbf{p} = 0, \quad \sum_k \int f_q^{(k)} \frac{p^2}{2m_k} d\mathbf{p} = 0 \quad (q \geqslant 1) \tag{2.7}$$

With regard to the conditions (2.3) and in accord with Boltzmann's H-theorem, Eqs. (2.5) have the solutions

$$f_0^{(k)} = \frac{n_k}{(2\pi m_k KT)^{3/2}} \exp \frac{-p^{\circ 2}}{2m_k KT} \tag{2.8}$$

For fixed q the Eqs. (2.6) serve to determine the functions $f_q^{(k)}$, k = 1, ..., L. On the right sides of these equations there appear the functions $f_{q'}^{(k)}$ with $q' < q$ and the functions $A_{k'}^{(q')}$, $B_\alpha^{(q')}$, $C^{(q')}$ with $q' \leq q$ (where the functionals with $q' = q$ are to be considered as unknowns), and the left sides of the equations may be represented in the form of linear integral operators with symmetric kernels [2], operating on the functions

$$\Phi_q^{(k)} = f_q^{(k)} / f_0^{(k)} \tag{2.9}$$

For solvability of the Eqs. (2.6) it is necessary and sufficient that their right sides be orthogonal to the solutions of the system of homogeneous integral equations, these solutions being, in accord with the H-theorem, the following L + 4 linearly independent vector-functions $\psi_s^{(k)}$, s = 1, ..., L + 4:

$$\psi_s^{(k)} = \delta_{ks} \quad (s = 1, \ldots, L), \quad \psi_{L+\alpha}^{(k)} = p_\alpha \quad (\alpha = 1, 2, 3), \quad \psi_{L+4}^{(k)} = \frac{p^2}{2m_k} \tag{2.10}$$

The conditions of solvability have the form

$$\sum_k \int (D_q^{(k)} - I_q^{(k)}) \psi_s^{(k)} d\mathbf{p} = 0 \tag{2.11}$$

and serve to determine the form of the unknown functions $A_k^{(q)}$ (k = 1, ..., L), $B_\alpha^{(q)}$ (α = 1, 2, 3), $C^{(q)}$. Thus the hydrodynamic equations are a unique consequence of the way in which the normal solution of the Boltzmann Eq. (1.2) is constructed. Since

$$\sum_k \int I_q^{(k)} \psi_s^{(k)} d\mathbf{p} = 0 \tag{2.12}$$

the conditions (2.11) may be written in the form

$$\sum_k \int D_q^{(k)} \psi_s^{(k)} d\mathbf{p} = \sum_k \int \left[\frac{p_\alpha}{m_k} \frac{\partial f_{q-1}^{(k)}}{\partial \xi_\alpha} + \sum_{q'=1}^{q} \Delta^{(q')} f_{q-q'}^{(k)} \right] \psi_s^{(k)} d\mathbf{p} = 0 \tag{2.13}$$

Since the function (2.10) does not depend on ξ_α the derivative with respect to ξ_α may be taken out from behind the integral sign. In addition, by virtue of the conditions (2.7), among the terms with $f_{q-q'}^{(k)}$, only the term with $q - q' = 0$ is different from zero. As a result the condition (2.13) assumes the form

$$\frac{\partial}{\partial \xi_\alpha} \sum_k \int \frac{p_\alpha}{m_k} f_{q-1}^{(k)} \psi_s^{(k)} d\mathbf{p} + \Delta^{(q)} \sum_k \int f_0^{(k)} \psi_s^{(k)} d\mathbf{p} = 0 \tag{2.14}$$

In accord with the relations (2.3) and (2.10),

$$\sum_k \int f_0^{(k)} \psi_s^{(k)} d\mathbf{p} = \begin{cases} {}_s & s = 1, \ldots, L \\ \rho u_\alpha, & s = L + \alpha,\ \alpha = 1, 2, 3 \\ {}^1/_2 \rho u^2 + {}^3/_2 nKT, & s = L + 4 \end{cases} \tag{2.15}$$

therefore the Eqs. (2.14) assume the form

$$\frac{\partial}{\partial \xi_\alpha} \int \frac{p_\alpha}{m_k} f_{q-1}^{(k)} d\mathbf{p} + A_k^{(q)} = 0 \qquad (k = 1, \ldots, L) \tag{2.16}$$

$$\frac{\partial}{\partial \xi_\alpha} \sum_k \int \frac{p_\alpha p_\beta}{m_k} f_{q-1}^{(k)} d\mathbf{p} + \sum_k m_k u_\beta A_k^{(q)} + \rho B_\beta^{(q)} = 0 \qquad (\beta = 1, 2, 3)$$

$$\frac{\partial}{\partial \xi_\alpha} \sum_k \int \frac{p_\alpha}{m_k} \frac{p^2}{2m_k} f_{q-1}^{(k)} d\mathbf{p} + \sum_k \left(\frac{1}{2} m_k u^2 + \frac{3}{2} KT \right) A_k^{(q)} + \rho u_\alpha B_\alpha^{(q)} + {}^3/_2 nKC^{(q)} = 0$$

From this we obtain for q = 1

$$A_k^{(1)} = -\frac{\partial}{\partial \xi_\alpha} n_k u_\alpha, \qquad B_\alpha^{(1)} = -u_\beta \frac{\partial u_\alpha}{\partial \xi_\beta} - \frac{1}{\rho} \frac{\partial}{\partial \xi_\alpha} nKT$$

$$C^{(1)} = -u_\alpha \frac{\partial T}{\partial \xi_\alpha} - \frac{2}{3} T \frac{\partial u_\alpha}{\partial \xi_\alpha} \tag{2.17}$$

For q > 1 it follows from Eqs. (2.16) that

$$A_k^{(q)} = -\frac{\partial J_{k\alpha}^{(q-1)}}{\partial \xi_\alpha}, \qquad B_\beta^{(q)} = -\frac{1}{\rho} \frac{\partial P_{\alpha\beta}^{(q-1)}}{\partial \xi_\alpha} \tag{2.18}$$

$$C^{(q)} = -\frac{2}{3Kn} \frac{\partial Q_\alpha^{(q-1)}}{\partial \xi_\alpha} + \frac{T}{n} \sum_k \frac{\partial J_{k\alpha}^{(q-1)}}{\partial \xi_\alpha} + \frac{2}{3Kn} u_\beta \frac{\partial P_{\alpha\beta}^{(q-1)}}{\partial \xi_\alpha}$$

where

$$J_{k\alpha}^{(q)} = \int \frac{p_\alpha^\circ}{m_k} f_q^{(k)} d\mathbf{p}^\circ, \qquad P_{\alpha\beta}^{(q)} = \sum_k \int \frac{p_\alpha^\circ p_\beta^\circ}{m_k} f_q^{(k)} d\mathbf{p}^\circ$$

$$Q_\alpha^{(q)} = \sum_k \int \frac{p_\alpha^\circ}{m_k} \frac{p^{\circ 2}}{2m_k} f_q^{(k)} d\mathbf{p}^\circ \tag{2.19}$$

The logical scheme of constructing the hydrodynamic equations is now completed. At the same time the hydrodynamic equations of the first approximation have been constructed [relations (2.17)].

3. We proceed now to a derivation of the laws of transport in the second approximation. However, here, instead of the complete set of hydrodynamic variables n_k, u_α, T we consider another complete set:

$$\nu_k, \; u_\alpha, \; \beta \qquad (\beta = (KT)^{-1}, \; \nu_k = \beta\mu_k)$$

Here μ_k is the chemical potential of the k-th component of the mixture. In the case of a gaseous mixture

$$\nu_k = \ln [n_k (\beta/2\pi m_k)^{3/2}]$$

This choice of parameters of the hydrodynamic state simplifies the derivation of the following relations since the factor preceding the exponential in Eq. (2.8) is now included in the exponent, and in addition, the laws of transport, the expressions in terms of the derivatives of these parameters, satisfy the Onsager relations.

The equations for the variables ν_k, u_α in the first approximation have the form

$$\frac{\partial \nu_k}{\partial t} = -u_\alpha \frac{\partial \nu_k}{\partial r_\alpha}, \quad \frac{\partial u_\alpha}{\partial t} = -u_\beta \frac{\partial u_\alpha}{\partial r_\beta} - \frac{1}{\beta\rho} \sum_k n_k \frac{\partial \nu_k}{\partial r_\alpha} + \frac{h}{\beta\rho} \frac{\partial \beta}{\partial r_\alpha} \tag{3.2}$$

$$\frac{\partial \beta}{\partial t} = -u_\alpha \frac{\partial \beta}{\partial r_\alpha} + \frac{2}{3} \beta \frac{\partial u_\alpha}{\partial r_\alpha} \qquad (h = {}^5/_2\, nKT)$$

Here h is the enthalpy density.

Using these equations we transform the functional $D_1^{(k)}$ to the form (the expression for $\Delta^{(q)}$ may be written in terms of the functional derivatives with respect to the variables ν_k, u_α, β, using the corresponding terms of the expansion of their derivatives in powers of the parameter ε)

$$D_1^{(k)} = f_0^{(k)} \left[\frac{p_\alpha^\circ}{m_k} \left(\frac{\partial \nu_k}{\partial \xi_\alpha} \sum_{k'} \frac{m_k n_{k'}}{\rho} \frac{\partial \nu_{k'}}{\partial \xi_\alpha} \right) - \frac{p_\alpha^\circ}{m_k} \left(\frac{p^{\circ 2}}{2m_k} - \frac{m_k h}{\rho} \right) \frac{\partial \beta}{\partial \xi_\alpha} + \frac{\beta}{2m_k} \times \left(p_\alpha^\circ p_\beta^\circ - \frac{1}{3} p^{\circ 2} \delta_{\alpha\beta} \right) D_{\alpha\beta} \right] \tag{3.3}$$

where $D_{\alpha\beta}$ is the deformation-velocity tensor

$$D_{\alpha\beta} = \frac{\partial u_\alpha}{\partial \xi_\beta} + \frac{\partial u_\beta}{\partial \xi_\alpha} - \frac{2}{3} \delta_{\alpha\beta} \frac{\partial u_\gamma}{\partial \xi_\gamma}$$

For the functions $\Phi^{(k)}_1$ defined in Eq. (2.9), we obtain a system of integral equations:

$$\sum_l I_{kl}(\Phi_1) = D_1^{(k)} \tag{3.4}$$

$$I_{kl}(\Phi_1) = \int f_0^{(k)} f_0^{(l)} [\Phi_1^{(k)}(\mathbf{r}, \mathbf{p}', t) + \Phi_1^{(l)}(\mathbf{r}, \mathbf{p}_1', t) - \Phi_1^{(k)}(\mathbf{r}, \mathbf{p}, t) - \Phi_1^{(l)} \times (\mathbf{r}, \mathbf{p}_1, t)]\, g_{kl} b\, db\, d\varepsilon\, d\mathbf{p}_1 \tag{3.5}$$

In accord with Eq. (3.3), the solution of Eqs. (3.4) can be written in the form

$$\Phi_1^{(k)} = A_\alpha^{(k)} \frac{\partial \beta}{\partial \xi_\alpha} - \frac{1}{2} B_{\alpha\beta}^{(k)} D_{\alpha\beta} - \sum_{k'} C_{k'\alpha}^{(k)} \frac{\partial \nu_{k'}}{\partial \xi_\alpha} \tag{3.6}$$

The functions $A_\alpha^{(k)}$, $B_{\alpha\beta}^{(k)}$, $C_{k'\alpha}^{(k)}$ satisfy the equations

$$-f_0^{(k)} \frac{p_\alpha^\circ}{m_k} \left(\frac{p^{\circ 2}}{2m_k} - \frac{m_k h}{\rho} \right) = \sum_l I_{kl}(A_\alpha)$$

$$-f_0^{(k)} \frac{\beta}{m_k} \left((p_\alpha^\circ p_\beta^\circ - \frac{1}{3} p^{\circ 2} \delta_{\alpha\beta} \right) = \sum_l I_{kl}(B_{\alpha\beta}) \tag{3.7}$$

$$-f_0^{(k)} \frac{p_\alpha^0}{m_k} \left(\delta_{kk'} - \frac{m_k n_{k'}}{\rho} \right) = \sum_p I_{kl}(C_{k'\alpha})$$

Since the molecular interaction potential is assumed to be spherically symmetric, the matrix of the integral operators in Eqs. (3.7) is invariant under rotations of a three-dimensional space, and therefore the functions $A_\alpha^{(k)}$, $B_{\alpha\beta}^{(k)}$, $C_{k'\alpha}^{(k)}$ must have the following tensorial structure:

$$A_\alpha^{(k)}(\mathbf{p}^\circ) = p_\alpha^\circ A^{(k)}(p^\circ), \qquad C_{k'\alpha}^{(k)}(\mathbf{p}^\circ) = p_\alpha^\circ C_{k'}^k(p^\circ) \tag{3.8}$$

$$B_{\alpha\beta}^{(k)}(\mathbf{p}^\circ) = (p_\alpha^\circ p_\beta^\circ - {}^1/_3 p^{\circ 2} \delta_{\alpha\beta}) B^{(k)}(p^\circ)$$

The conditions (2.7) with q = 1 serve to determine the solutions of Eqs. (3.7) uniquely; these conditions may be reduced to the conditions

$$\sum_k \int f_0^{(k)} p_\alpha{}^\circ A_\alpha^{(k)} d\mathbf{p}^\circ = 0, \qquad \sum_k \int f_0^{(k)} p_\alpha{}^\circ C_{k'\alpha}^{(k)} d\mathbf{p}^\circ = 0 \tag{3.9}$$

by substituting the expressions (3.6) into them and taking note of Eqs. (3.8).

Substituting Eq. (3.6) into Eqs. (2.19) with $q=1$ and using the relations (3.8), we obtain the laws of transport in the form

$$J_{k\alpha}^{(1)} = -D_k{}' \left(-\frac{\partial\beta}{\partial\xi_\alpha}\right) - D_{kk'}\frac{\partial \nu_{k'}}{\partial \xi_\alpha} \qquad (k=1,\ldots,L)$$

$$P_{\alpha\beta}^{(1)} = -\eta D_{\alpha\beta}, \qquad Q_\alpha^{(1)} = \lambda K T^2 \frac{\partial\beta}{\partial\xi_\alpha} - \sum_k D_k \frac{\partial \nu_k}{\partial \xi_\alpha}$$

where the kinetic coefficients are defined by the formulas

$$D_k{}' = \frac{1}{3}\int f_0^{(k)} \frac{p_\alpha{}^\circ}{m_k} A_\alpha^{(k)} d\mathbf{p}^\circ, \qquad D_k = \frac{1}{3}\sum_{k'}\int f_0^{(k')} \frac{p_\alpha{}^\circ}{m_{k'}} \frac{p^{\circ 2}}{2m_{k'}} C_{k\alpha}^{(k')} d\mathbf{p}^\circ$$

$$D_{kk'} = \frac{1}{3}\int f_0^{(k)} \frac{p_\alpha{}^\circ}{m_k} C_{k'\alpha}^{(k)} d\mathbf{p}^\circ, \qquad \eta = \frac{1}{10}\sum_k \int f_0^{(k)} \frac{p_\alpha{}^\circ p_\beta{}^\circ}{m_k} B_{\alpha\beta}^{(k)} d\mathbf{p}^\circ$$

$$\lambda = \frac{1}{3KT^2}\sum_k \int f_0^{(k)} \frac{p_\alpha{}^\circ}{m_k} \frac{p^{\circ 2}}{2m_k} A_\alpha^{(k)} d\mathbf{p}^\circ \tag{3.10}$$

4. We show now that the Onsager relations are satisfied for the coefficients of diffusion and thermal diffusion:

$$D_k{}' = D_k, \qquad D_{kk'} = D_{k'k} \tag{4.1}$$

In fact, if we use the second of the supplementary conditions (3.9), we can put the expression for D_k into the form

$$D_k = \frac{1}{3}\sum_{k'}\int f_0^{(k')} \frac{p_\alpha{}^\circ}{m_{k'}} \left(\frac{p^{\circ 2}}{2m_{k'}} - \frac{h m_{k'}}{\rho}\right) C_{k\alpha}^{(k')} d\mathbf{p}^\circ = -\frac{1}{3}\sum_{k',l}\int I_{k'l}(A_\alpha) C_{k\alpha}^{(k')} d\mathbf{p}^\circ$$

Here we have also used the first of Eqs. (3.7). Since the matrix of integral operators is symmetric [3],

$$\sum_l \int I_{kl}(A) B^{(k)} d\mathbf{p}^\circ = \sum_l \int A^{(k)} I_{kl}(B)\, d\mathbf{p}^\circ \tag{4.2}$$

and if we then use the third of Eqs. (3.7), we obtain

$$D_k = -\frac{1}{3}\sum_{k',l}\int A_\alpha^{(k')} I_{k'l}(C_{k\alpha})\, d\mathbf{p}^\circ = \frac{1}{3}\sum_{k'}\int A_\alpha^{(k')} f_0^{(k')} \frac{p_\alpha{}^\circ}{m_{k'}} \left(\delta_{kk'} - \frac{m_{k'} n_k}{\rho}\right) d\mathbf{p}^\circ = \frac{1}{3}\int f_0^{(k)} \frac{p_\alpha{}^\circ}{m_k} A_\alpha^{(k)} d\mathbf{p}^\circ = D_k{}'$$

Here we have also used the first of the conditions (3.9). We have thus established the equality of the coefficients D_k and $D_k{}'$.

Consider now the coefficients of diffusion. Upon repeating similar calculations, we find as a result that

$$D_{kk'} = \frac{1}{3}\sum_l \int f_0^{(l)} \frac{p_\alpha{}^\circ}{m_l}\left(\delta_{k'l} - \frac{n_{k'} m_l}{\rho}\right) C_{k\alpha}^{(l)} d\mathbf{p}^\circ = -\frac{1}{3}\sum_{l,m}\int I_{lm}(C_{k'\alpha}) C_{k\alpha}^{(l)} d\mathbf{p}^\circ$$

The last form, in accord with Eq. (4.2), is symmetric in the indices k and k'. In proving the Onsager relations we have used the relation (4.2), which is a consequence of the invariance of the equations of mechanics with respect to the transformations $t \to -t$, $\mathbf{p} \to -\mathbf{p}$.

5. For completeness we also give the derivation of the Onsager relations for the kinetic coefficients, expressed in terms of correlation functions [5]:

$$D_k{}' = \frac{1}{3}\int_0^\infty dt \lim_{V\to\infty} \frac{1}{V}\langle J_{k\hat\alpha} S_{\hat\alpha}(t)\rangle$$

$$D_{kk'} = \frac{1}{3}\int_0^\infty dt \lim_{V\to\infty} \frac{1}{V}\langle J_{k\hat\alpha} I_{k'\hat\alpha}(t)\rangle \tag{5.1}$$

$$D_k = \frac{1}{3}\int_0^\infty dt \lim_{V\to\infty} \frac{1}{V}\langle Q_{\hat\alpha} I_{k\hat\alpha}(t)\rangle$$

$$I_{k\hat\alpha} = I_{k\hat\alpha} - \frac{n_k}{\rho}P_{\hat\alpha}, \quad S_{\hat\alpha} = Q_{\hat\alpha} - \frac{h}{\rho}P_{\hat\alpha}, \quad \hat a(t) = \exp\{-tH\}\hat a$$

Here exp $\{-tH\}$ is an operator of evolution for a system of N particles.

The dynamic variables, distinguished by the carat symbol, are defined by the relations

$$J_{k\hat{\alpha}} = \sum_{i \in (k)} \frac{p_{i\alpha}}{m_k}, \qquad P_{\hat{\alpha}} = \sum_{i=1}^{N} p_{i\alpha}, \qquad Q_{\hat{\alpha}} = \sum_{i=1}^{N} \frac{p_{i\alpha}}{m_i} \frac{p_i^2}{2m_i}$$

(in the case of a liquid, there enter also into the expression for $Q_{\hat{\alpha}}$ terms containing a two-particle interaction potential: these terms, in the limit of a gas, are of higher order in the density when compared with those written down); the symbol $i \in (k)$ denotes that the summation is taken only over particles of the k-th kind. The angular parentheses denote an average taken over an equilibrium (or a local equilibrium, a matter of no consequence in later calculations) canonical ensemble.

By virtue of the microscopic reversibility (i.e., the invariance of the equations of mechanics with respect to the transformations $t \to -t$, $p_{i\alpha} \to -p_{i\alpha}$), the autocorrelation portions of the expressions for D_k and $D_{k'}$, $D_{kk'}$ and $D_{k'k}$ are equal. To prove the Onsager relations it remains to show that

$$\lim_{V\to\infty} \frac{1}{V} \left\langle J_{k\hat{\alpha}} \frac{h}{\rho} P_{\hat{\alpha}}(t) \right\rangle = \lim_{V\to\infty} \frac{1}{V} \left\langle Q_{\hat{\alpha}} \frac{n_k}{\rho} P_{\hat{\alpha}}(t) \right\rangle \tag{5.2}$$

$$\lim_{V\to\infty} \frac{1}{V} \left\langle J_{k\hat{\alpha}} \frac{n_{k'}}{\rho} P_{\hat{\alpha}}(t) \right\rangle = \lim_{V\to\infty} \frac{1}{V} \left\langle J_{k'\hat{\alpha}} \frac{n_k}{\rho} P_{\hat{\alpha}}(t) \right\rangle \tag{5.3}$$

We remark that $P_{\hat{\alpha}}$ is the total momentum of the system, which is an integral of the motion of the system and does not depend on the time, $P_{\hat{\alpha}}(t) = P_{\hat{\alpha}}(0)$. Therefore, the correlators in Eqs. (5.2), (5.3) are independent of the time and readily calculable. Our calculations show that both sides in the relation (5.2) are equal to $^{15}/_{2} n_k \rho^{-1} (KT)^2$, and in the relation (5.3) are equal to $3\rho^{-1} n_k n_{k'} KT$. We have thus established the Onsager relations (4.1).

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