KINETIC EQUATIONS FOR MIXTURES OF MODERATELY DENSE GASES

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Abstract

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KINETIC EQUATIONS FOR MIXTURES OF MODERATELY DENSE GASES

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The derivation of kinetic equations and of hydrodynamic equations from the equations of mechanics has attracted much attention ([1–5]). In addition to deriving the Boltzmann equation, which describes the evolution of a rarefied gas, a theory of moderately dense gases is also being developed ([5,6]), in which triple collisions between molecules, i.e., terms of second order in the density, are taken into account. In the present work, by N. N. Bogolyubov' s method ([1]), the chain of equations of the kinetic theory of multicomponent mixtures is solved to second order in the density. A system of kinetic equations is obtained; moreover, the terms taking account of triple collisions can be simplified by carrying out the integration over time. This system of kinetic equations serves as the basis for deriving the equations of hydrodynamics and expressions for the transport coefficients in mixtures of moderately dense gases.

Consider a system of N interacting molecules of L different species in a volume V. Let N_k be the number, and $c_k = N_k/N$ the concentration, of molecules of the k-th species. The Hamiltonian of the system has the form

$$H_N = \sum_{k=1}^{L} \sum_{i=1}^{N_k} \left[\frac{p_i^{(k)2}}{2m_k} + \frac{1}{2} \sum_{s=1}^{L} \sum_{j=1}^{N_s} \Phi_{ij}^{(ks)} \right], \tag{1}$$

where $\Phi_{ij}^{(ks)} = \Phi^{(ks)}(|q_i^{(k)} - q_j^{(s)}|)$ is the spherically symmetric potential of the pair interaction of a molecule of species k, located at the point $q_i^{(k)}$, with a molecule of species s, located at the point $q_j^{(s)}$. Introduce the distribution function $D_N(x_1^{(1)}, \dots, x_{N_1}^{(1)}, x_1^{(2)}, \dots, x_{N_L}^{(L)}; t)$. Here $x_i^{(k)} = (q_i^{(k)}, p_i^{(k)})$ are the coordinates and momenta of the i-th molecule of species k.

As is known, the distribution function is normalized to unity and satisfies the Liouville equation

$$\partial D_N / \partial t = [H_N, D_N] \equiv -\mathscr{H}_N D_N, \tag{2}$$

where $[\cdots]$ are Poisson brackets; $\mathcal{H}_N$ is the N-particle Hamiltonian operator. Introduce s-particle distribution functions by the formulas

$$\overline{x_1^{(i_1)} = x_1, \quad x_{1+\delta_{i_1 i_2}}^{(i_2)} = x_2, \dots, x_{1+\delta_{i_1 i_2}+\dots+\delta_{i_s - i_s}}^{(i_s)} = x_s}$$
$$c_{i_1} \cdots c_{i_s} F_s^{(i_1 \dots i_s)}(x_1, \dots, x_s; t) = V^s \, \overline{D_N(x_1^{(1)}, \dots, x_{N_L}^{(L)}; t)}. \tag{3}$$

Here the bar and the symbols above the function D_N indicate integration over the coordinates and momenta of all molecules, except for the specified s molecules, whose coordinates and momenta are set equal to $x_1, \dots, x_s$, respectively. Using definition (3), from the Liouville equation it is easy to obtain a chain of equations for the s-particle distribution functions which, after passage to the limit $V \to \infty$, $N_k \to \infty$, $k = 1, 2, \dots, L$, with fixed values of the quantities $n_k = N_k/V$, takes the form

$$\frac{\partial F_s^{(i_1 \dots i_s)}}{\partial t} + \mathcal{H}_s^{(i_1 \dots i_s)} F_s^{(i_1 \dots i_s)} = \frac{1}{v} \sum_{i_{s+1}=1}^{L} \int dx_{s+1} \sum_{k=1}^{s} \theta_{k,s+1}^{(i_k i_{s+1})} F_{s+1}^{(i_1 \dots i_{s+1})},$$

$$\theta_{ij}^{(pq)} f = \left[\Phi^{(pq)}(|q_i - q_j|), f \right]. \tag{4}$$

The system of equations (4) is an infinite chain of integro-differential equations. Following N. N. Bogoliubov, we shall seek special solutions of equations (4) in which all F_s with $s \geqslant 2$ depend functionally on time through the time dependence of the functions $F_1^{(i)}$:

$$F_s^{(i_1 \dots i_s)}(x_1, \dots, x_s; t) = F_s^{(i_1 \dots i_s)}(x_1, \dots, x_s \mid F_1^{(1)}, \dots, F_1^{(L)}) \tag{5}$$

and, moreover, are subject to asymptotic conditions of weakening of correlations of the form

$$\lim_{\tau \to \infty} \exp\left(-\tau \mathcal{H}_s^{0(i_1 \dots i_s)}\right) \left[F_s^{(i_1 \dots i_s)} \left(\dots \mid \exp(\tau \mathcal{H}_1^0) F_1 \right) - \prod_{k=1}^{s} \exp\left(\tau \mathcal{H}_1^{0(k)}\right) F_1^{(i_k)}(x_k; t) \right] = 0. \tag{6}$$

To solve the problem posed we use the fact that on the right-hand sides of equations (4) there is the parameter $1/v$, which is small for moderately dense gases. We shall seek the solution of equations (4) in the form of an expansion in powers of the small parameter $1/v$

$$F_s^{(i_1 \dots i_s)}(x_1, \dots, x_s \mid F_1) = F_{s0}^{(i_1 \dots i_s)}(x_1, \dots, x_s \mid F_1) + (1/v) F_{s1}^{(i_1 \dots i_s)}(x_1, \dots, x_s \mid F_1) + \dots \tag{7}$$

Then the system of kinetic equations will have the form

$$\partial F_1^{(i)}(x_1;t)/\partial t = A_i(x_1 \mid F_1) = \sum_{q=0}^{\infty} \frac{1}{v^q} A_{iq}(x_1 \mid F_1), \tag{8}$$

$$A_{i0}(x_1 \mid F_1) = -\frac{\mathbf{p}_1}{m_i}\frac{\partial F_1^{(i)}}{\partial \mathbf{q}_1}, \tag{9}$$

$$A_{i,q+1}(x_1 \mid F_1) = \sum_{k=1}^{i} \int \theta_{12}^{(ik)} F_{2q}^{(ik)}(x_1, x_2 \mid F_1)\, dx_2, \qquad q \geqslant 0.$$

Since the functionals F_s depend on time only through the functional arguments $F_1^{(k)}$, the derivative of F_s with respect to t can be represented in the form

$$\frac{\partial F_s^{(i_1 \ldots i_s)}(\ldots \mid F_1)}{\partial t} = \sum_{k=1}^{L} \sum_{p,q=0}^{\infty} \frac{1}{v^{p+q}} \frac{\delta F_{sp}^{(i_1 \ldots i_s)}(\ldots \mid F_1)}{\delta F_1^{(k)}} A_{kq}(\ldots \mid F_1). \tag{10}$$

For brevity of notation we omit the arguments of the functions F_s and F_1 and replace the set of functional arguments $F_1^{(1)}, \ldots, F_1^{(L)}$ by one symbol F_1, since, if necessary, these arguments are not difficult to write out. Substituting expression (10) into equation (4) and equating the terms at identical powers of $1/v$, we obtain

$$\sum_{k=1}^{L} \frac{\delta F_{sp}^{(i_1 \ldots i_s)}}{\delta F_1^{(k)}} A_{k0} + \mathcal{H}_s^{0(i_1 \ldots i_s)} F_{sp}^{(i_1 \ldots i_s)} = \psi_{sp}, \tag{11}$$

where

$$\psi_{sp}(\ldots \mid F_1) = 0, \qquad p = 0,$$

$$\psi_{sp}(\ldots \mid F_1) = -\sum_{q=1}^{p} \frac{\delta F_{s,p-q}^{(i_1 \ldots i_s)}}{\delta F_1^{(k)}} A_{kq} + \sum_{i_{s+1}=1}^{L} \int dx_{s+1} \sum_{k=1}^{s} \theta_{k,s+1}^{(i_k i_{s+1})} F_{s+1,p-1}^{(i_1 \ldots i_{s+1})}, \qquad p \geqslant 1. \tag{12}$$

For the system of equations (11), the asymptotic conditions are obtained from (6) by means of the expansion (7)

$$\lim_{\tau\to\infty} \exp(-\tau \mathcal{H}_s^{0(i_1 \ldots i_s)}) \left[F_{s0}^{(i_1 \ldots i_s)}(\ldots \mid \exp(\tau \mathcal{H}_1) F_1) - \prod_{k=1}^{s} \exp(\tau \mathcal{H}_1^{0(i_k)}) F_1^{(i_k)}(x_k;t) \right] = 0, \tag{13}$$

$$\lim_{\tau\to\infty} \exp(-\tau\mathcal{H}_s^{0(i_1\dots i_s)}) F_{sp}^{(i_1\dots i_s)}(\dots \mid \exp(\tau\mathcal{H}_1)F_1) = 0, \qquad p \geqslant 1.$$

It is easy to see that the system of equations (11), supplemented by the definitions (9), (12) and the conditions (13), is recurrent, i.e. it is soluble term by term. Let us consider the first approximation:

$$\sum_{k=1}^{L} \frac{\delta F_{s0}^{(i_1\dots i_s)}(\dots \mid F_1)}{\delta F_1^{(k)}} A_{k0}(\dots \mid F_1) + \mathcal{H}_{s\Delta}^{0(i_1\dots i_s)} F_{s0}^{(i_1\dots i_s)}(\dots \mid F_1) = 0. \tag{14}$$

Replacing the arbitrary functional arguments $F_1^{(k)}$ by $\exp(\tau\mathcal{H}_1^{0(k)})F_1^{(k)}$, we obtain the differential equation

$$-\partial F_{s0}^{(i_1\dots i_s)}(\dots \mid \exp(\tau\mathcal{H}_1)F_1)/\partial\tau + \mathcal{H}_s^{0(i_1\dots i_s)} F_{s0}^{(i_1\dots i_s)}(\dots \mid \exp(\tau\mathcal{H}_1)F_1) = 0, \tag{15}$$

whose solution satisfying the conditions (13) is

$$F_{s0}^{(i_1\dots i_s)}(x_1, \dots, x_s \mid F_1) = J_s^{(i_1\dots i_s)}(x_1, \dots, x_s) \prod_{k=1}^{s} F_1^{(i_k)}(x_k; t), \tag{16}$$

$$J_s^{(i_1\dots i_s)}(x_1, \dots, x_s) = \lim_{\tau\to\infty} \exp(-\tau\mathcal{H}_s^{0(i_1\dots i_s)})(x_1, \dots, x_s) \prod_{k=1}^{s} \exp(\tau\mathcal{H}_{1s}^{0(i_k)}(x_k)). \tag{17}$$

As a result, for the right-hand sides of the kinetic equations we obtain

$$A_{i1}(x_1 \mid F_1) = \sum_{k=1}^{L} \int \theta_{12}^{(ik)} J_2^{(ik)}(x_1, x_2) F_1^{(i)}(x_1; t) F_1^{(k)}(x_2; t). \tag{18}$$

The equations of the next approximation have the form

$$\sum_{k=1}^{L} \frac{\delta F_{s1}^{(i_1\dots i_s)}(\dots \mid F_1)}{\delta F_1^{(k)}} A_{k0}(\dots \mid F_1) + \mathcal{H}_s^{0(i_1\dots i_s)} F_{s1}^{(i_1\dots i_s)}(\dots \mid F_1) = \psi_{s1}^{(i_1\dots i_s)}(\dots \mid F_1). \tag{19}$$

This equation, by means of the same replacement of the functional argument, is again reduced to a differential equation, whose solution under the condition (13) is

$$F_{s1}^{(i_1\dots i_s)}(\dots \mid F_1) = \int_0^\infty \exp(-\tau \mathcal{H}_s^{0(i_1\dots i_s)})\psi_{s1}^{(i_1\dots i_s)}(\dots \mid \exp(\tau \mathcal{H}_1)F_1)\, d\tau. \quad (20)$$

Let us show that in formula (20) the integration with respect to τ can be performed. Using the definition (12) and formulas (16) and (18), we have

$$F_{s1}^{(i_1\dots i_s)}(\dots \mid F_1) = \int_0^\infty d\tau\, \exp(-\tau \mathcal{H}_s^{0(i_1\dots i_s)}) \int dx_{s+1} \sum_{i_{s+1}=1}^{L} \Bigg[\sum_{k=1}^{s} \theta_{k,s+1}^{(i_k i_{s+1})} J_{s+1}^{(i_1\dots i_{s+1})} - J_s^{(i_1\dots i_s)} \sum_{k=1}^{s} \theta_{k,s+1}^{(i_k i_{s+1})} J_2^{(i_k i_{s+1})} \Bigg] \prod_{l=1}^{s+1} \exp(\tau \mathcal{H}_1^{0(i_l)}) F_1^{(i_l)}(x_l; t). \quad (21)$$

Using the identities

$$\sum_{k=1}^{s} \theta_{k,s+1}^{(i_k i_{s+1})} = -\mathcal{H}_{s+1}^{(i_1\dots i_{s+1})} + \mathcal{H}_s^{(i_1\dots i_s)} + \frac{\mathbf{p}_{s+1}}{m_{i_{s+1}}} \frac{\partial}{\partial \mathbf{q}_{s+1}},$$

$$\theta_{k,s+1}^{(i_k i_{s+1})} = \sum_{k=1}^{s} \frac{\mathbf{p}_k}{m_{i_k}} \frac{\partial}{\partial \mathbf{q}_k} - \mathcal{H}_2^{(i_k i_{s+1})} - \sum_{\substack{l=1 \\ l\neq k}}^{s} \frac{\mathbf{p}_l}{m_{i_l}} \frac{\partial}{\partial \mathbf{q}_l} + \frac{\mathbf{p}_{s+1}}{m_{i_{s+1}}} \frac{\partial}{\partial \mathbf{q}_{s+1}}$$

and the fact that, as a consequence of equations (15) and (16),

$$J_s^{(i_1\dots i_s)} \sum_{k=1}^{s} \frac{\mathbf{p}_k}{m_{i_k}} \frac{\partial}{\partial \mathbf{q}_k} \prod_{l=1}^{s} \exp(\tau \mathcal{H}_1^{(i_l)}) F_1^{(i_l)}(x_l; t) = \mathcal{H}_s^{(i_1\dots i_s)} J_s^{(i_1\dots i_s)} \times \prod_{l=1}^{s} \exp(\tau \mathcal{H}_1^{(i_l)}) F_1^{(i_l)}(x_l; t) = \frac{\partial}{\partial \tau} J_s^{(i_1\dots i_s)} \prod_{l=1}^{s} \exp(\tau \mathcal{H}_1^{(i_l)}) F_1^{(i_l)}(x_l; t),$$

formula (21) can be rewritten in the form

$$F_{s1}^{(i_1\dots i_s)}(\dots \mid F_1) = \int_1^\infty d\tau\, \exp(-\tau \mathcal{H}_s^{(i_1\dots i_s)}) \int dx_{s+1} \sum_{i_{s+1}=1}^{L} \Big[\mathcal{H}_s^{(i_1\dots i_s)} (J_{s+1}^{(i_1\dots i_{s+1})} - J_s^{(i_1\dots i_s)} \sum_{k=1}^{s} J_2^{(i_k i_{s+1})} + (s-1) J_s^{(i_1\dots i_s)}) - \frac{\partial}{\partial \tau} (J_{s+1}^{(i_1\dots i_{s+1})} - J_s^{(i_1\dots i_s)} \sum_{k=1}^{s} J_2^{(i_k i_{s+1})} + (s-1) J_s^{(i_1\dots i_s)}) \Big] \prod_{l=1}^{s+1} \exp(\tau \mathcal{H}_1^{(i_l)}) F_1^{(i_l)}(x_l; t). \quad (22)$$

Here we have added and subtracted the term

$$(s-1)\mathcal{H}_s^{(i_1\ldots i_s)} J_s^{(i_1\ldots i_s)} \prod_{k=1}^{s+1} \exp(\tau \mathcal{H}_1^{(i_k)}) F_1^{(i_k)}(x_k; t)$$

and integrated the term with the derivative with respect to q_{s+1}, which vanishes. Using the equality

$$\exp(-\tau \mathcal{H}_s^{(i_1\ldots i_s)}) \mathcal{H}_s^{(i_1\ldots i_s)} = -\frac{\partial}{\partial \tau} \exp(-\tau \mathcal{H}_s^{(i_1\ldots i_s)})$$

and introducing the operator

$$\mathcal{P}_{s+1}^{(i_1\ldots i_{s+1})} = J_{s+1}^{(i_1\ldots i_{s+1})} - J_s^{(i_1\ldots i_s)} \sum_{k=1}^{s} J_2^{(i_k i_{s+1})} + (s-1) J_s^{(i_1\ldots i_s)}, \tag{23}$$

from (22) we obtain

$$F_{s1}^{(i_1\ldots i_s)}(x_1, \ldots, x_s \mid F_1) = \int dx_{s+1} \sum_{i_{s+1}=1}^{L} \mathcal{P}_{s+1}^{(i_1\ldots i_{s+1})} \prod_{k=1}^{s+1} F_1^{(i_k)}(x_k; t). \tag{24}$$

Thus, the functionals A_{i2} have the form

$$A_{i2}(x_1 \mid F_1) = \sum_{j,k=1}^{L} \int \theta_{12}^{(ij)} \, dx_2 \int \mathcal{P}_3^{(ijk)} F_1^{(i)}(x_1; t) F_1^{(j)}(x_2; t) F_1^{(k)}(x_3; t) \, dx_3. \tag{25}$$

In the case of a slow variation of the one-particle distribution functions in configuration space, the functionals A_{i1} are easily transformed into Boltzmann collision integrals.

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Note: Figure translations are in progress. See original paper for figures.