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# On the Nonequilibrium Statistical Mechanics of a Binary Mixture. I. The Distribution Functions

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In this paper, we obtain the generalization of the BBGKY hierarchy for a binary mixture of chemically neutral particles. Using modified boundary conditions different from the ones proposed by Bogoliubov, we solve the hierarchy, and obtain explicitly the set of two-particle distribution functions for the several species of the mixture, up to first order in the density.

**KEY WORDS:** Binary mixture; convergent kinetic theory; hydrodynamic equations for a binary mixture; two-body distribution function for a binary mixture; Hilbert-Enskog method; BBGKY hierarchy for a binary mixture.

## 1. INTRODUCTION

In earlier papers,[1-3] the kinetic theory of a dense one-component gas was developed using a method which differs essentially from the one advanced by Bogoliubov in that the boundary conditions are not the same. In fact, the new boundary conditions take into account explicitly the effects of the medium composed by the remaining particles of the gas, and in this way using this new approach, one obtains divergenceless expressions for the transport coefficients to all orders in the density.

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In this paper, we generalize the work presented in Ref. 2 to the case of a binary mixture. This has been done for several reasons. First of all, to obtain expressions for the transport coefficients of such systems without any reference to a density expansion. Results of this nature are, to our knowledge, not available in the literature. Second, to give a basis from first principles to the work which has been done recently for the specific case of a binary mixture of hard spheres.[4] The third reason is of practical importance, namely the fact that very accurate experimental results reported for the binary diffusion of a dense gas at high pressures are in open contradiction with the theoretical predictions of Thorne's theory.[5] Although it is now known that in the particular case of the diffusion coefficients Thorne's theory is incomplete,[6] the diffusion force being corrected by an additional term arising from the point between the two spheres where the correlation functions are to be evaluated,[7] we hope that our calculation will yield a systematic method which will clearly exhibit many of the obscure points which are present in the available methods dealing with this subject. Also, we expect to account for the difference between theory and experiment in the case of the hard-sphere system.

In Section 2, we sketch a derivation of the BBGKY hierarchy for a binary mixture. In Section 3, we obtain a solution of this hierarchy making a density expansion of the relevant quantities and using the new boundary conditions. We explicitly write down the two-body distribution functions up to first order in the density. Finally, Section 4 is devoted to a brief discussion of the results.

## 2. THE BBGKY HIERARCHY FOR A BINARY MIXTURE

Let us consider a two-component gas consisting of particles of mass $m_a$ and $m_b$ which do not react chemically. We assume that there are $N_a$ and $N_b$ particles of each species, and that they are enclosed in a volume $V$. The Hamiltonian of the system will be taken in the form

$$H = \sum_{\gamma=1}^{2} \sum_{i=1}^{N_\gamma} \frac{p_{\gamma i}^2}{2m_\gamma} + \frac{1}{2} \sum_{\beta=1}^{2} \sum_{\alpha=1}^{2} \sum_{\substack{k=1 \\ (\alpha i \neq \beta k)}}^{N_\beta} \sum_{i=1}^{N_\alpha} \varphi_{\alpha\beta}(|\mathbf{q}_{\alpha i} - \mathbf{q}_{\beta k}|) \tag{1}$$

Here, $\gamma = 1$ corresponds to the species labeled by $a$ and $\gamma = 2$ to the species labeled by $b$; $\mathbf{p}_{\gamma i}$ and $\mathbf{q}_{\gamma i}$ denote the momentum and position of the $i$th particle of species $\gamma$. We will label the particles with two indices: the first one, with a greek letter, will denote the species, and the second one, with a latin letter, will denote the number of the particle of the corresponding species.

The potential energy is assumed to be pairwise additive, with the potential between the particles $\alpha i$ and $\beta k$ given by $\varphi_{\alpha\beta}(|\mathbf{q}_{\alpha i} - \mathbf{q}_{\beta k}|)$. The potentials that we will consider are strongly repulsive ones.

The Liouville equation of our system is

$$(\partial F/\partial t) - [H, F] = 0 \tag{2}$$

with the Poisson bracket given by

$$[H, \ ] = \sum_{\alpha=1}^{2} \sum_{i=1}^{N_\alpha} \left( \frac{\partial H}{\partial \mathbf{q}_{\alpha i}} \cdot \frac{\partial}{\partial \mathbf{p}_{\alpha i}} - \frac{\partial H}{\partial \mathbf{p}_{\alpha i}} \cdot \frac{\partial}{\partial \mathbf{q}_{\alpha i}} \right) \tag{3}$$

Here, $F$ is the distribution function in the phase space of our system. Substituting Eq. (1) into (2) one finds that

$$\frac{\partial F}{\partial t} + \left\{ - \sum_{\alpha=1}^{2} \sum_{i=1}^{N_\alpha} \left[ \sum_{\gamma=1}^{2} \sum_{k=1}^{N_\gamma} \frac{\partial \varphi_{\alpha\gamma}(|\mathbf{q}_{\alpha i} - \mathbf{q}_{\gamma k}|)}{\partial \mathbf{q}_{\alpha i}} \cdot \frac{\partial}{\partial \mathbf{p}_{\alpha i}} + \frac{\mathbf{p}_{\alpha i}}{m_\alpha} \cdot \frac{\partial}{\partial \mathbf{q}_{\alpha i}} \right] \right\} F = 0 \tag{4}$$

We now define the reduced distribution functions of the sets of $s_a$ and $s_b$ particles

$$F_{\{s_a\}\{s_b\}} = (1/V^{s_a+s_b}) \int F \, d\{N_a - s_a\} \, d\{N_b - s_b\} \tag{5}$$

Here the integrations are performed over the phases $x$ of the remaining particles, $N_a - s_a$ and $N_b - s_b$. Applying the operator

$$V^{-\{s_a+s_b\}} \int d\{N_a - s_a\} \, d\{N_b - s_b\}$$

on both sides of Eq. (4) and using the definition (5), one finds that

$$\frac{\partial F_{\{s_a\}\{s_b\}}}{\partial t} + \sum_{\alpha=1}^{2} \sum_{i=1}^{s_\alpha} \frac{\mathbf{p}_{\alpha i}}{m_\alpha} \cdot \frac{\partial}{\partial \mathbf{q}_{\alpha i}} F_{\{s_a\}\{s_b\}}$$

$$- \left\{ \sum_{i=1}^{s_a} \sum_{k=1}^{s_b} \frac{\partial \varphi_{aa}(|\mathbf{q}_{ai} - \mathbf{q}_{ak}|)}{\partial \mathbf{q}_{ai}} \cdot \frac{\partial}{\partial \mathbf{p}_{ai}} + \sum_{i=1}^{s_b} \sum_{k=1}^{s_a} \frac{\partial \varphi_{bb}(|\mathbf{q}_{bi} - \mathbf{q}_{bk}|)}{\partial \mathbf{q}_{bi}} \cdot \frac{\partial}{\partial \mathbf{p}_{bi}} \right.$$

$$+ \sum_{i=1}^{s_b} \sum_{k=1}^{s_a} \frac{\partial \varphi_{ba}(|\mathbf{q}_{bi} - \mathbf{q}_{ak}|)}{\partial \mathbf{q}_{bi}} \cdot \frac{\partial}{\partial \mathbf{p}_{bi}}$$

$$\left. + \sum_{i=1}^{s_a} \sum_{k=1}^{s_b} \frac{\partial \varphi_{ab}(|\mathbf{q}_{ai} - \mathbf{q}_{bk}|)}{\partial \mathbf{q}_{ai}} \cdot \frac{\partial}{\partial \mathbf{p}_{ai}} \right\} F_{\{s_a\}\{s_b\}}$$

$$- \frac{N_a - s_a}{V} \sum_{i=1}^{s_a} \int dx_{a,s_a+1} \frac{\partial \varphi_{aa}(|\mathbf{q}_{ai} - \mathbf{q}_{a,s_a+1}|)}{\partial \mathbf{q}_{ai}} \cdot \frac{\partial}{\partial \mathbf{p}_{ai}} F_{\{s_a+1\}\{s_b\}}$$

$$- \frac{N_b - s_b}{V} \sum_{i=1}^{s_b} \int dx_{b,s_b+1} \frac{\partial \varphi_{bb}(|\mathbf{q}_{bi} - \mathbf{q}_{b,s_b+1}|)}{\partial \mathbf{q}_{bi}} \cdot \frac{\partial}{\partial \mathbf{p}_{bi}} F_{\{s_a\}\{s_b+1\}}$$

$$- \frac{N_a - s_a}{V} \sum_{i=1}^{s_b} \int dx_{a,s_a+1} \frac{\partial \varphi_{ba}(|\mathbf{q}_{bi} - \mathbf{q}_{a,s_a+1}|)}{\partial \mathbf{q}_{bi}} \cdot \frac{\partial}{\partial \mathbf{p}_{bi}} F_{\{s_a+1\}\{s_b\}}$$

$$- \frac{N_b - s_b}{V} \sum_{i=1}^{s_a} \int dx_{b,s_b+1} \frac{\partial \varphi_{ab}(|\mathbf{q}_{ai} - \mathbf{q}_{b,s_b+1}|)}{\partial \mathbf{q}_{ai}} \cdot \frac{\partial}{\partial \mathbf{p}_{ai}} F_{\{s_a\}\{s_b+1\}} = 0 \tag{6}$$

Taking the so-called thermodynamic limit $N_\alpha \to \infty$, $V \to \infty$, $N_\alpha / V = n_\alpha$, $(\alpha = 1, 2)$, one can write Eq. (6) in the form

$$\frac{\partial F_{\{s_a\}\{s_b\}}}{\partial t} + \mathscr{H}_{\{s_a\}\{s_b\}} F_{\{s_a\}\{s_b\}} = \sum_{\beta=1}^{2} n_\beta \sum_{\alpha=1}^{2} \sum_{i=1}^{s_\alpha} \int dx_{\beta, s_\beta+1}$$
$$\times\ \theta_{\alpha\beta}(x_{\alpha i}, x_{\beta, s_\beta+1}) F_{\{s_a-\beta+2\}\{s_b+\beta-1\}} \tag{7}$$

where

$$\mathscr{H}_{\{s_a\}\{s_b\}} = \sum_{\alpha=1}^{2} \sum_{i=1}^{s_\alpha} \frac{\mathbf{p}_{\alpha i}}{m_\alpha} \cdot \frac{\partial}{\partial \mathbf{q}_{\alpha i}}$$
$$- \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} \sum_{i=1}^{s_\beta} \sum_{k=1}^{s_{3-\beta}} \theta_{\alpha\beta}(x_{\alpha i}, x_{\beta k}) \tag{8}$$

and

$$\theta_{\alpha\beta}(x_{\alpha i}, x_{\beta j}) \equiv \frac{\partial \varphi_{\alpha\beta}(|\mathbf{q}_{\alpha i} - \mathbf{q}_{\beta j}|)}{\partial \mathbf{q}_{\alpha i}} \cdot \frac{\partial}{\partial \mathbf{p}_{\alpha i}} + \frac{\partial \varphi_{\alpha\beta}(|\mathbf{q}_{\alpha i} - \mathbf{q}_{\beta j}|)}{\partial \mathbf{q}_{\beta j}} \cdot \frac{\partial}{\partial \mathbf{p}_{\beta j}} \tag{9}$$

Equation (7) is the generalization of the BBGKY hierarchy for binary mixtures.

## 3. FORMAL SOLUTION OF THE BBGKY HIERARCHY

In this section, we will proceed to solve the BBGKY hierarchy for the binary mixture.

The hierarchy equations corresponding to the one-body distribution functions are given by [see Eq. (7)]

$$\frac{\partial F_{\{1\}\{0\}}(x_{a1})}{\partial t} + \frac{\mathbf{p}_{a1}}{m_a} \cdot \frac{\partial F_{\{1\}\{0\}}(x_{a1})}{\partial \mathbf{q}_{a1}} = n_a \int dx_{a2}\, \theta_{11}(x_{a1}, x_{a2}) F_{\{2\}\{0\}}(x_{a1}, x_{a2})$$
$$+ n_b \int dx_{b1}\, \theta_{12}(x_{a1}, x_{b1}) F_{\{1\}\{1\}}(x_{a1}, x_{b1}) \tag{10}$$

$$\frac{\partial F_{\{0\}\{1\}}(x_{b1})}{\partial t} + \frac{\mathbf{p}_{b1}}{m_b} \cdot \frac{\partial F_{\{0\}\{1\}}(x_{b1})}{\partial \mathbf{q}_{b1}} = n_a \int dx_{a1} \theta_{21}(x_{b1}, x_{a1}) F_{\{1\}\{1\}}(x_{b1}, x_{a1}) + n_b \int dx_{b2} \theta_{22}(x_{b1}, x_{b2}) F_{\{0\}\{2\}}(x_{b1}, x_{b2}) \tag{11}$$

These two equations can be written compactly as

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}_{\gamma 1}}{m_\gamma} \cdot \frac{\partial}{\partial \mathbf{q}_{\gamma 1}}\right) F_{\{2-\gamma\}\{\gamma-1\}}(x_{\gamma 1}) = \sum_{\alpha=1}^{2} n_\alpha \int dx_{\alpha,\xi(\alpha,\gamma)}\, \theta_{\gamma\alpha}(x_{\gamma 1}, x_{\alpha,\xi(\alpha,\gamma)})\, F_{\{4-\gamma-\alpha\}\{\gamma+\alpha-2\}}(x_{\gamma 1}, x_{\alpha,\xi(\alpha,\gamma)}), \qquad \gamma = 1, 2 \tag{12}$$

where the index $\xi(\alpha, \gamma)$ is given by

$$\xi(\alpha, \gamma) = (\alpha - 2)(2\gamma - 3) + \gamma, \qquad \alpha, \gamma = 1, 2 \tag{13}$$

We will assume, as usual, that the distribution functions of more than one particle are time-independent functionals of single-particle distribution functions, namely, of $F_{\{1\}\{0\}}$ and $F_{\{0\}\{1\}}$. Thus, we may write that

$$F_{\{s_a\}\{s_b\}}(\cdots ; t) \to F_{\{s_a\}\{s_b\}}(\cdots \mid F_{\{1\}\{0\}}, F_{\{0\}\{1\}}) \tag{14}$$

where the usual notation is used. Substituting Eq. (14) into Eq. (12), we find that the kinetic equations have the form

$$\frac{\partial F_{\{2-\gamma\}\{\gamma-1\}}(x_{\gamma 1})}{\partial t} = A_{\{2-\gamma\}\{\gamma-1\}}(x_{\gamma 1} \mid F_{\{1\}\{0\}}, F_{\{0\}\{1\}}), \qquad \gamma = 1, 2 \tag{15}$$

Let us now expand both functionals $A_{\{2-\gamma\}\{\gamma-1\}}$ and $F_{\{s_a\}\{s_b\}}$ in powers of the density:

$$A_{\{2-\gamma\}\{\gamma-1\}} = A^{(0)}_{\{2-\gamma\}\{\gamma-1\}} + \sum_{\alpha=1}^{2} n_\alpha A^{(1)}_{\{2-\gamma\},\{\gamma-1\},\alpha} + \tfrac{1}{2} \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} n_\alpha n_\beta A^{(2)}_{\{2-\gamma\}\{\gamma-1\},\alpha\beta} + \cdots \tag{16}$$

$$F_{\{s_a\}\{s_b\}} = F^{(0)}_{\{s_a\}\{s_b\}} + \sum_{\alpha=1}^{2} n_\alpha F^{(1)}_{\{s_a\}\{s_b\},\alpha} + \tfrac{1}{2} \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} n_\alpha n_\beta F^{(2)}_{\{s_a\}\{s_b\},\alpha\beta} + \cdots \tag{17}$$

Following the usual procedure, we find that

$$A^{(0)}_{\{2-\gamma\}\{\gamma-1\}}(x_{\gamma 1} \mid \cdots) = -\frac{\mathbf{p}_{\gamma 1}}{m_\gamma} \cdot \frac{\partial}{\partial \mathbf{q}_{\gamma 1}} F_{\{2-\gamma\}\{\gamma-1\}}(x_{\gamma 1}) \tag{18}$$

$$\begin{aligned} A^{(1)}_{\{2-\gamma\}\{\gamma-1\},\alpha}(x_{\gamma 1} \mid \cdots) &= \int dx_{\alpha,\xi(\alpha,\gamma)}\, \theta_{\gamma\alpha}(x_{\gamma 1}, x_{\alpha,\xi(\gamma,\gamma)}) \\ &\quad \times F^{(0)}_{\{4-\gamma-\alpha\}\{\gamma+\alpha-2\}}(x_{\gamma 1}, x_{\alpha,\xi(\alpha,\gamma)}) \end{aligned} \tag{19}$$

$$\vdots$$

$$\begin{aligned} A^{(l)}_{\{2-\gamma\}\{\gamma-1\},\underbrace{\alpha\beta\cdots}_{l\ \text{indices}}} &= l \int dx_{\alpha,\xi(\alpha,\gamma)}\, \theta_{\gamma\alpha}(x_{\gamma 1}, x_{\alpha,\xi(\alpha,\gamma)}) \\ &\quad \times F^{(l-1)}_{\{4-\gamma-\alpha\}\{\gamma+\alpha-2\}}(x_{\gamma 1}, x_{\alpha,\xi(\alpha,\gamma)}) \end{aligned} \tag{20}$$

Writing

$$\begin{aligned} \frac{\partial F_{\{s_a\}\{s_b\}}(\cdots \mid F_{\{1\}\{0\}}, F_{\{0\}\{1\}})}{\partial t} &= \sum_{\gamma=1}^{2} \frac{\delta F_{\{s_a\}\{s_b\}}}{\delta F_{\{2-\gamma\}\{\gamma-1\}}} \frac{\partial F_{\{2-\gamma\}\{\gamma-1\}}}{\partial t} \\ &= \sum_{\gamma=1}^{2} \frac{\delta F_{\{s_a\}\{s_b\}}}{\delta F_{\{2-\gamma\}\{\gamma-1\}}} A_{\{2-\gamma\}\{\gamma-1\}} \\ &= \sum_{\gamma=1}^{2} \left\{ \frac{\delta F^{(0)}_{\{s_a\}\{s_b\}}}{\delta F_{\{2-\gamma\}\{\gamma-1\}}} A^{(0)}_{\{2-\gamma\}\{\gamma-1\}} \right. \\ &\quad + \sum_{\alpha=1}^{2} n_\alpha \left[ \frac{\delta F^{(0)}_{\{s_a\}\{s_b\}}}{\delta F_{\{2-\gamma\}\{\gamma-1\}}} A^{(1)}_{\{2-\gamma\}\{\gamma-1\},\alpha} \right. \\ &\quad \left.\left. + \frac{\delta F^{(1)}_{\{s_a\}\{s_b\}}}{\delta F_{\{2-\gamma\}\{\gamma-1\}}} A^{(0)}_{\{2-\gamma\}\{\gamma-1\}} \right] + \cdots \right\} \end{aligned} \tag{21}$$

and defining the operators $D^{(l)}$ as

$$D^{(l)}_{\{2-\gamma\}\{\gamma-1\},\underbrace{\alpha\beta\cdots}_{l\ \text{indices}}} \psi = \frac{\delta\psi}{\delta F_{\{2-\gamma\}\{\gamma-1\}}} A^{(l)}_{\{2-\gamma\}\{\gamma-1\},\underbrace{\alpha\beta\cdots}_{l\ \text{indices}}} \tag{22}$$

one finds the following differential equations:

(a) To zeroth order in the density

$$\sum_{\gamma=1}^{2} D^{(0)}_{\{2-\gamma\}\{\gamma-1\}} F^{(0)}_{\{s_a\}\{s_b\}} + \mathscr{H}_{\{s_a\}\{s_b\}} F^{(0)}_{\{s_a\}\{s_b\}} = 0 \tag{23}$$

(b) To first order in the density

$$\sum_{\gamma=1}^{2} D^{(0)}_{\{2-\gamma\}\{\gamma-1\}} F^{(1)}_{\{s_a\}\{s_b\},\alpha} + \mathscr{H}_{\{s_a\}\{s_b\}} F^{(1)}_{\{s_a\}\{s_b\},\alpha}$$

$$= -\sum_{\gamma=1}^{2} D^{(1)}_{\{2-\gamma\}\{\gamma-1\},\alpha} F^{(0)}_{\{s_a\}\{s_b\}}$$

$$+ \sum_{\beta=1}^{2} \sum_{i=1}^{s_\beta} \int dx_{\alpha,s_\alpha+1}\, \theta_{\beta\alpha}(x_{\beta i}, x_{\alpha,s_\alpha+1})\, F^{(0)}_{\{s_a-\alpha+2\}\{s_b+\alpha-1\}}$$

$$\equiv \psi^{(1)}_{\{s_a\}\{s_b\},\alpha} \tag{24}$$

For the other orders in the density, one can find analogous equations.

The formal solution to Eq. (13) is obtained in the same way as was done for a one-component gas.[2] The result is given by

$$F^{(0)}_{\{s_a\}\{s_b\}}(\cdots \mid F_{\{1\}\{0\}}, F_{\{0\}\{1\}})$$

$$= S^{-\tau}_{\{s_a\}\{s_b\}} F^{(0)}_{\{s_a\}\{s_b\}}(\cdots \mid S^{\tau}_{\{1\}\{0\}} F_{\{1\}\{0\}}, S^{\tau}_{\{0\}\{1\}} F_{\{0\}\{1\}}) \tag{25}$$

The solution to Eq. (24) is

$$F^{(1)}_{\{s_a\}\{s_b\},\alpha}(\cdots \mid F_{\{1\}\{0\}}, F_{\{0\}\{1\}})$$

$$= S^{-\tau}_{\{s_a\}\{s_b\}} F^{(1)}_{\{s_a\}\{s_b\},\alpha}(\cdots \mid S^{\tau}_{\{1\}\{0\}} F_{\{1\}\{0\}}, S^{\tau}_{\{0\}\{1\}} F_{\{0\}\{1\}})$$

$$+ \int_0^{\tau} d\tau'\, S^{-\tau'}_{\{s_a\}\{s_b\}} \psi^{(1)}_{\{s_a\}\{s_b\},\alpha} \tag{26}$$

Here we have introduced the streaming operator

$$S^{\tau}_{\{s_a\}\{s_b\}} \equiv \exp\{\tau \mathscr{H}_{\{s_a\}\{s_b\}}\}.$$

As was done in Refs. 1 and 2 we shall introduce the following boundary conditions:

$$\lim_{\tau\to\infty} S^{-\tau}_{\{s_a\}\{s_b\}} F^{(0)}_{\{s_a\}\{s_b\}}(\cdots \mid S^{\tau}_{\{1\}\{0\}} F_{\{1\}\{0\}}, S^{\tau}_{\{0\}\{1\}} F_{\{0\}\{1\}})$$

$$= (1 - g^{(0)}_{\{s_a\}\{s_b\}}) \lim_{\tau\to\infty} S^{-\tau}_{\{s_a\}\{s_b\}} \prod_{i=1}^{s_a} \prod_{k=1}^{s_b} S^{\tau}_{\{1\}\{0\}}(x_{ai})\, F_{\{1\}\{0\}}(x_{ai})$$

$$\times S^{\tau}_{\{0\}\{1\}}(x_{bk})\, F_{\{0\}\{1\}}(x_{bk}) \tag{27a}$$

$$\lim_{\tau\to\infty} S^{-\tau}_{\{s_a\}\{s_b\}} F^{(l)}_{\{s_a\}\{s_b\},\underbrace{\alpha\beta\cdots}_{l\text{ indices}}}(\cdots \mid S^{\tau}_{\{1\}\{0\}} F_{\{1\}\{0\}}, S^{\tau}_{\{0\}\{1\}} F_{\{0\}\{1\}})$$

$$= g^{(l)}_{\{s_a\}\{s_b\},\underbrace{\alpha\beta\cdots}_{l\text{ indices}}} \lim_{\tau\to\infty} S^{-\tau}_{\{s_a\}\{s_b\}} \prod_{i=1}^{s_a} \prod_{k=1}^{s_b}$$

$$\times S^{\tau}_{\{1\}\{0\}}(x_{ai}) F_{\{1\}\{0\}}(x_{ai}) S^{\tau}_{\{0\}\{1\}}(x_{bk}) F_{\{0\}\{1\}}(x_{bk}) \qquad (27b)$$

Here $g_{\{s_a\}\{s_b\}}$ is the equilibrium $(s_a + s_b)$-body correlation function, which is expressed as the following density expansion:

$$g_{\{s_a\}\{s_b\}} = g^{(0)}_{\{s_a\}\{s_b\}} + \sum_{\alpha=1}^{2} n_\alpha g^{(1)}_{\{s_a\}\{s_b\},\alpha}$$

$$+ \tfrac{1}{2} \sum_{\alpha=1}^{2} \sum_{\beta=1}^{2} n_\alpha n_\beta g^{(2)}_{\{s_a\}\{s_b\},\alpha\beta} + \cdots \qquad (28)$$

The boundary conditions given by Eqs. (27a) and (27b) are a generalization to binary mixtures of the boundary conditions discussed in Refs. 1 and 2 for a one-component gas. It should be mentioned that our boundary conditions take into account the statistical effects of the medium.

Substitution of Eqs. (27a) and (27b) into Eqs. (25) and (26) and a straightforward calculation leads to the result that

$$F^{(0)}_{\{s_a\}\{s_b\}}(\cdots \mid F_{\{1\}\{0\}}, F_{\{0\}\{1\}})$$

$$= \Gamma_{\{s_a\}\{s_b\}} \mathscr{S}_{\{s_a\}\{s_b\}} \prod_{i=1}^{s_a} \prod_{k=1}^{s_b} F_{\{1\}\{0\}}(x_{ai}) F_{\{0\}\{1\}}(x_{bk}) \qquad (29)$$

$$F^{(1)}_{\{4-2\gamma\}\{2\gamma-2\},\alpha}(x_{\gamma 1}, x_{\gamma 2} \mid F_{\{1\}\{0\}}, F_{\{0\}\{1\}})$$

$$= g^{(1)}_{\{4-2\gamma\}\{2\gamma-2\},\alpha}(x_{\gamma 1}, x_{\gamma 2}) \mathscr{S}_{\{4-2\gamma\}\{2\gamma-2\}}(x_{\gamma 1}, x_{\gamma 2}) \prod_{i=1}^{2} F_{\{2-\gamma\}\{\gamma-1\}}(x_{\gamma i})$$

$$+ \int_0^\infty d\tau\, S^{-\tau}_{\{4-2\gamma\}\{2\gamma-2\}}(x_{\gamma 1}, x_{\gamma 2}) \int dx_{\alpha,k(\alpha,\gamma)+1} \{-\Gamma_{\{4-2\gamma\}\{2\gamma-2\}}(x_{\gamma 1}, x_{\gamma 2})$$

$$\times \mathscr{S}_{\{4-2\gamma\}\{2\gamma-2\}}(x_{\gamma 1}, x_{\gamma 2})[\theta_{\gamma\alpha}(x_{\gamma 2}, x_{\alpha,k(\alpha,\gamma)+1}) \Gamma_{\{4-\alpha-\gamma\}\{\alpha+\gamma-2\}}(x_{\gamma 2}, x_{\alpha,k+1})$$

$$\times \mathscr{S}_{\{4-\alpha-\gamma\}\{\alpha+\gamma-2\}}(x_{\gamma 2}, x_{\alpha,k(\alpha,\gamma)+1})$$

$$+ \theta_{\gamma\alpha}(x_{\gamma 1}, x_{\alpha,k(\alpha,\gamma)+1}) \Gamma_{\{4-\alpha-\gamma\}\{\alpha+\gamma-2\}}(x_{\gamma 1}, x_{\alpha,k(\alpha,\gamma)+1})$$

$$\times \mathscr{S}_{\{4-\alpha-\gamma\}\{\alpha+\gamma-2\}}(x_{\gamma 1}, x_{\alpha,k(\alpha,\gamma)+1})]$$

$$+ [\theta_{\gamma\alpha}(x_{\gamma 1}, x_{\alpha,k(\alpha,\gamma)+1}) + \theta_{\gamma\alpha}(x_{\gamma 2}, x_{\alpha,k(\alpha,\gamma)+1})]$$

$$\times \Gamma_{\{6-\alpha-2\gamma\}\{\alpha+2\gamma-3\}}(x_{\gamma 1}, x_{\gamma 2}, x_{\alpha,k+1})$$

$$\times \mathscr{S}_{\{6-\alpha-2\gamma\}\{\alpha+2\gamma-3\}}(x_{\gamma 1}, x_{\gamma 2}, x_{\alpha,k+1})\}$$

$$\times F_{\{2-\gamma\}\{\gamma-1\}}(x_{\gamma 1}) F_{\{2-\gamma\}\{\gamma-1\}}(x_{\gamma 2}) F_{\{2-\alpha\}\{\alpha-1\}}(x_{\alpha,k+1}) \qquad (30)$$

$$
\begin{aligned}
F^{(1)}_{\{1\}\{1\},\alpha}&(x_{a1}, x_{b1} \mid F_{\{1\}\{0\}}, F_{\{0\}\{1\}}) \\
&= g^{(1)}_{\{1\}\{1\},\alpha}(x_{a1}, x_{b1}) \mathscr{S}_{\{1\}\{1\}}(x_{a1}, x_{b1}) F_{\{1\}\{0\}}(x_{a1}) F_{\{0\}\{1\}}(x_{b1}) \\
&\quad + \int_0^\infty d\tau\, S^{-\tau}_{\{1\}\{1\}}(x_{a1}, x_{b1}) \int dx_{\alpha 2} \{-\Gamma_{\{1\}\{1\}}(x_{a1}, x_{b1}) \\
&\quad \times \mathscr{S}_{\{1\}\{1\}}(x_{a1}, x_{b2})[\theta_{a\alpha}(x_{a1}, x_{\alpha 2}) \Gamma_{\{3-\alpha\}\{\alpha-1\}}(x_{a1}, x_{\alpha 2}) \\
&\quad \times \mathscr{S}_{\{3-\alpha\}\{\alpha-1\}}(x_{a1}, x_{\alpha 2}) + \theta_{b\alpha}(x_{b1}, x_{\alpha 2}) \\
&\quad \times \Gamma_{\{2-\alpha\}\{\alpha\}}(x_{b1}, x_{\alpha 2}) \mathscr{S}_{\{2-\alpha\}\{\alpha\}}(x_{b1}, x_{\alpha 2})] \\
&\quad + [\theta_{a\alpha}(x_{a1}, x_{\alpha 2}) + \theta_{b\alpha}(x_{b1}, x_{\alpha 2})] \\
&\quad \times \Gamma_{\{3-\alpha\}\{\alpha\}}(x_{a1}, x_{b1}, x_{\alpha 2}) \mathscr{S}_{\{3-\alpha\}\{\alpha\}}(x_{a1}, x_{b1}, x_{\alpha 2})\} \\
&\quad \times F_{\{1\}\{0\}}(x_{a1}) F_{\{0\}\{1\}}(x_{b1}) F_{\{2-\alpha\}\{\alpha-1\}}(x_{\alpha 2})
\end{aligned} \tag{31}
$$

In these expressions we have used:

$$
\Gamma_{\{s_a\}\{s_b\}} \equiv 1 - g^{(0)}_{\{s_a\}\{s_b\}}, \tag{32}
$$

$$
\mathscr{S}_{\{s_a\}\{s_b\}} \equiv \lim_{\tau\to\infty} S^{-\tau}_{\{s_a\}\{s_b\}} \prod_{i=1}^{s_a} S^{\tau}_{\{1\}\{0\}}(x_{ai}) \prod_{k=1}^{s_b} S^{\tau}_{\{0\}\{1\}}(x_{bk}) \tag{32}
$$

$$
k(\alpha, \gamma) = 4\alpha\gamma - 6\gamma - 6\alpha + 10 \tag{34}
$$

If we now substitute Eqs. (29)–(31) into Eqs. (11a) and (11b), we can obtain the explicit kinetic equations for the binary mixture up to first order in the density.

## 4. CONCLUSIONS

In this paper, we have obtained the kinetic equations for a binary mixture using the new boundary conditions expressed by Eqs. (27a) and (27b). In these boundary conditions, we take into account explicitly the effect of the medium. We will use this innovation in order to compute transport coefficients, which will be reported in a subsequent paper.

When our kinetic equations are applied to a binary mixture of hard spheres, neglecting the effect of triple collisions, one obtains a set of equations which are identical to the first order in the density terms of the equations recently derived by Robles–Dominguez and Piña.[8] These equations are the generalization to binary mixtures of Enskog's kinetic equation.

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