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A Convergent Nonequilibrium Statistical Mechanical Theory for Dense Gases. III. Transport Coefficients to Second Order in the Density

E. Braun,[1,2] A. Flores,[1] and G. Coutiño[1]

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The purpose of this paper is to obtain general expressions for the second-order terms of the transport coefficients of a dense gas. These expressions are obtained using the convergent kinetic theory proposed recently by Braun and Flores.

KEY WORDS: Convergent kinetic theory for dense gases; transport coefficients to second order in the density.

[1] Reactor, Centro Nuclear, Instituto Nacional de Energía Nuclear, México, D.F., México.
[2] Facultad de Ciencias, Universidad Nacional Autónoma de México, México, D.F., México.

1. INTRODUCTION

The problem of evaluating transport coefficients for a dense gas from the theory proposed by Bogolyubov[1] has come to a stalemate. This is due to the fact that when obtaining the second order in the density of the transport coefficients of a system of hard spheres it was found that they diverged.[2] Moreover, it was also found that higher-order terms in the transport coefficients also diverged. This means that integrals over configuration space diverge.

Several attempts to remedy this situation have been made. We mention, for example, the resummation technique,[3] which gives rise to a nonanalytical density dependence of the transport coefficients. In fact, this technique gives rise to transport coefficients which contain logarithms in the density.

Kestin and collaborators[4] have performed a series of very accurate experiments in which they measure the transport coefficients in a very wide range of pressures. They found that, within their accuracy, the experimental data do not support the conclusion of a logarithmic dependence in the transport coefficients, as predicted by the theory mentioned above. Further, the experimental results establish that the best fit for the transport coefficients is a power series in the density. This means that there is experimental support for a convergent virial expansion of the transport coefficients.

On the other hand, an analysis of the hypotheses made by Bogolyubov was done by Braun and Flores.[5] It was found that one of the assumptions, namely the boundary conditions used in solving the BBGKY hierarchy, does not reflect the physical properties of the system, and that this is the reason for the appearance of the divergences.

The difficulty with the boundary conditions proposed by Bogolyubov is that they do not take into account the medium when expressing properties of clusters of few particles. This difficulty was overcome by proposing a new set of boundary conditions which do take into account the medium.[5] As a consequence, when calculating transport coefficients this new theory gives a convergent virial expansion of the transport coefficients. To zeroth order in the density the Boltzmann results were recovered,[6] and to first order in the density results were obtained which are different from the results obtained by Choh and Uhlenbeck.[7]

It is the purpose of this paper to obtain general expressions for the second-order terms of the transport coefficients using the new theory mentioned above.

In Section 2 we write down several basic expressions which will be used in the rest of the paper. In Section 3 we solve the BBGKY hierarchy to obtain the two-body distribution function to second order in the density, using the new boundary conditions. In Section 4 we obtain the general expressions for the second order in the density terms of the transport coefficients. Finally, in Section 5 we discuss our results and show that they converge.

2. BASIC EXPRESSIONS

The kinetic equation is obtained from the first equation of the BBGKY hierarchy, using the functional assumption

$$\frac{\partial F_1}{\partial t} + \frac{\mathbf{p}}{m}\cdot\frac{\partial F_1}{\partial \mathbf{q}} = \Phi(x|F_1) \tag{1}$$

where

$$\Phi(x|F_1) = n \int dx_2\, \theta_{12} F_2(x, x_2|F_1) \tag{2}$$

Here n is the particle density, $x \equiv (\mathbf{p}, \mathbf{q})$, and F_2 is the two-body distribution function in phase space as a time-independent functional of F_1.

Linearizing this kinetic equation, one finds[8]

$$\frac{\partial F_1}{\partial t} + \frac{\mathbf{p}}{m}\cdot\frac{\partial F_1}{\partial \mathbf{q}} = \Phi(x|F_1(\mathbf{q})) + \int dx'\, \Phi'(x, x'|F_1(\mathbf{q}))(\mathbf{q}' - \mathbf{q})\cdot\left(\frac{\partial F_1}{\partial \mathbf{q}'}\right)_{\mathbf{q}'=\mathbf{q}} \tag{3}$$

where $\Phi(x|F_1(\mathbf{q}))$ is evaluated at the local distribution function $F_1(\mathbf{q})$ and $\Phi'(x, x'|F_1(\mathbf{q}))$ denotes the functional derivative of Φ with respect to F_1 taken at the point x' and evaluated for the local distribution function $F_1(\mathbf{q})$.

Using the Chapman–Enskog method to solve Eq. (3) with the introduction of the perturbation function by means of

$$F_1 = F_1^{\text{eq}}(1 + \phi) \tag{4}$$

where ϕ represents the linear nonuniformities in the macroscopic variable, and F_1^{eq} the local equilibrium single distribution function, we obtain a unique solution in the form

$$\phi = \mathscr{G}(\mathscr{P}^2)\mathscr{P}\cdot\frac{\partial \ln \theta}{\partial \mathbf{q}} + \mathscr{A}(\mathscr{P}^2)\mathscr{P}^0\mathscr{P} : \frac{\partial \mathbf{u}}{\partial \mathbf{q}} + \mathscr{B}(\mathscr{P}^2)\,\frac{\partial}{\partial \mathbf{q}}\cdot\mathbf{u} \tag{5}$$

The notation used is explained in Ref. 6. The functions $\mathscr{G}$, $\mathscr{A}$, and $\mathscr{B}$ satisfy certain integral equations[6] whose kernels contain the function F_2. Having determined the functions $\mathscr{G}$, $\mathscr{A}$, and $\mathscr{B}$, one can then obtain the transport coefficients.

If we now make a density expansion of F_2

$$F_2(\cdots|F_1) = \sum_{l=0}^{\infty} n^l F_2^{(l)}(\cdots|F_1) \tag{6}$$

where $F_2^{(0)}$ and $F_2^{(1)}$ were explicitly obtained in Ref. 5, one obtains density expansions for Φ and the functions $\mathscr{G}$, $\mathscr{A}$, and $\mathscr{B}$ as follows:

$$\Phi = \sum_{l=1}^{\infty} n^{l+2}\Phi^{(l)} \tag{7}$$

$$\mathscr{G} = (1/n)\mathscr{G}_B + \mathscr{G}_0 + n\mathscr{G}_1 + \cdots \tag{8}$$

$$\mathscr{A} = (1/n)\mathscr{A}_B + \mathscr{A}_0 + n\mathscr{A}_1 + \cdots \tag{9}$$

and

$$\mathscr{B} = (1/n)\mathscr{B}_B + \mathscr{B}_0 + n\mathscr{B}_1 + \cdots \tag{10}$$

The integral equations satisfied by the quantities labeled with B and 0 were discussed in Ref. 6. We will now proceed to obtain the integral equations to second order in the density, i.e., for the quantities $\mathscr{A}_1$, $\mathscr{G}_1$, and $\mathscr{B}_1$.

Since in the general integral equations for $\mathscr{A}$, $\mathscr{G}$, and $\mathscr{B}$ given in Ref. 8 the quantities $(\beta/n\kappa)$ and L appear, we expand them in power series in the density, with the result

$$\frac{\beta}{n\kappa} = \frac{1}{n}\left(\frac{\partial\pi}{\partial\theta}\right)_n = k\left\{1 - \frac{n}{2}\frac{d(\theta\beta_1)}{d\theta} - \frac{2}{3}n^2\frac{d(\theta\beta_2)}{d\theta} + \cdots\right\} \tag{11}$$

and

$$L = \left(1 - \frac{\mathscr{P}^2}{3m\theta}\right)\left(1 - \frac{3}{2}\frac{\beta}{n\kappa C_v}\right) = \left(1 - \frac{\mathscr{P}^2}{3m\theta}\right)(n\zeta + n^2\xi + \cdots) \tag{12}$$

with

$$\zeta = -\{\tfrac{1}{2}\beta_1 + \tfrac{7}{6}\beta_1' + \tfrac{1}{3}\theta^2\beta_1''\} \tag{13a}$$

$$\begin{aligned}\xi = -\{&\tfrac{2}{3}\beta_2 + \tfrac{10}{9}\theta\beta_2' + \tfrac{2}{9}\theta^2\beta_2'' - \tfrac{7}{9}\theta^2\beta_1'^2 - \tfrac{1}{3}\theta\beta_1\beta_1' - \tfrac{1}{6}\theta^2\beta_1\beta_1'' \\ &- \tfrac{1}{9}\theta^4\beta_1''^2 - \tfrac{1}{6}\theta^2\beta_1'\beta_1'' - \tfrac{4}{9}\theta^3\beta_1'\beta_1''\}\end{aligned} \tag{13b}$$

In these equations π is the local equilibrium pressure, $\beta_1(\theta)$ and $\beta_2(\theta)$ are the second and third virial coefficients, respectively; the primes on β_i denote derivatives with respect to θ. The rest of the symbols are defined in Ref. 8.

Substituting Eqs. (7)–(13) into Eqs. (4.10) of Ref. 8, we find, to second order in the density, the following integral equations:

$$\begin{aligned}&\frac{2}{3}k\chi(\mathbf{p})\frac{d(\theta\beta_2)}{d\theta}\frac{\mathscr{P}}{m} - \int \Phi'^{(1)}(\cdots x'|\chi)(\mathbf{q}' - \mathbf{q})\left(\frac{\mathscr{P}'^2}{2m\theta} - \frac{3}{2}\right)\chi(\mathbf{p}')\,dx' \\ &\quad = \int \Phi'^{(2)}(\cdots \mathbf{p}'|\chi)\chi(\mathbf{p}')\mathscr{P}'\mathscr{G}_B\,d\mathbf{p}' + \int \Phi'^{(1)}(\cdots \mathbf{p}'|\chi)\chi(\mathbf{p}')\mathscr{P}'\mathscr{G}_0\,d\mathbf{p}' \\ &\qquad + \int \Phi'^{(0)}(\cdots \mathbf{p}'|\chi)\chi(\mathbf{p}')\mathscr{P}'\mathscr{G}_1\,d\mathbf{p}'\end{aligned} \tag{14a}$$

$$-(1/\theta)\int \Phi'^{(1)}(\cdots x'|\chi)\chi(\mathbf{p}')S^0S\,dx'$$
$$= \int \Phi'^{(2)}(\cdots \mathbf{p}'|\chi)\chi(\mathbf{p}')\mathscr{P}'^0\mathscr{P}'\mathscr{A}_B\,d\mathbf{p}'$$
$$+ \int \Phi'^{(1)}(\cdots \mathbf{p}'|\chi)\chi(\mathbf{p}')\mathscr{P}'^0\mathscr{P}'\mathscr{A}_1\,d\mathbf{p}'$$
$$+ \int \Phi'^{(0)}(\cdots \mathbf{p}'|\chi)\chi(\mathbf{p}')\mathscr{P}'^0\mathscr{P}'\mathscr{A}_0\,d\mathbf{p}' \tag{14b}$$

$$[1-(\mathscr{P}^2/3m\theta)]\xi\chi(\mathbf{p}) - (1/3\theta)\int \Phi'^{(1)}(\cdots x'|\chi)\chi(\mathbf{p}')\,\mathscr{P}'\cdot(\mathbf{q}'-\mathbf{q})\,dx'$$
$$= \int \Phi'^{(0)}(\cdots \mathbf{p}'|\chi)\chi(\mathbf{p}')\mathscr{B}_1\,d\mathbf{p}' \tag{14c}$$

In order to evaluate the kernels of the integrals given above, we need the explicit expressions for $F_2^{(l)}$ $(l = 0, 1, 2)$. For $l = 0, 1$ we have already calculated these expressions.[5] Therefore we only need $F_2^{(2)}$. This quantity will be obtained in the next section.

3. THE TWO-BODY DISTRIBUTION FUNCTION TO SECOND ORDER IN THE DENSITY

From the formal solution of the BBGKY hierarchy, given by Eq. (16) of Ref. 5, and using the boundary conditions introduced there and expressed by Eqs. (20a) and (20b) of Ref. 5, we find that to second order in the density the two-body distribution function is

$$F_2^{(2)}(x_1x_2|F_1) = g_2^{(2)}(\mathbf{q}_1,\mathbf{q}_2)\mathscr{S}_2(x_1x_2)\prod_{i=1}^{2}F_1(x_i) - \int_0^\infty d\tau\, S_2^{-\tau}(x_1x_2)\psi_2^{(2)}(x_1x_2|F_1) \tag{15}$$

where

$$\psi_2^{(2)}(x_1,x_2|F_1) = -D_1F_2^{(1)} - D_2F_2^{(0)} + \int dx_3\,(\theta_{13}+\theta_{23})F_3^{(1)}(x_1,x_2,x_3|F_1) \tag{16}$$

Using the expressions for the lower orders in the density of the distribution functions obtained earlier,[5] one finds after a lengthy calculation that the two-body distribution function to second order in the density has the following form:

$$F_2^{(2)}(x_1x_2|F_1) = g_2^{(2)}(\mathbf{q}_1,\mathbf{q}_2)\mathscr{S}_2(x_1,x_2)\prod_{i=1}^{2}F_1(x_i;t) + \int dx_3\,M_3(x_1,x_2,x_3)\prod_{i=1}^{3}F_1(x_i;t) + \int dx_3\int dx_4\,N_4(x_1,x_2,x_3,x_4)\prod_{i=1}^{4}F_1(x_i;t) \tag{17}$$

Here the operators $M_3(x_1, x_2, x_3)$ and $N_4(x_1, x_2, x_3, x_4)$ are given by

$$
\begin{aligned}
&M_3(x_1, x_2, x_3) \\
&\quad = \int_0^\infty d\tau\, S_{-\tau}^{(2)}(x_1, x_2)\{g_2^{(1)}(\mathbf{q}_1, \mathbf{q}_2)\mathscr{S}_2(x_1, x_2)[\theta_{13}\Gamma_2(\mathbf{q}_1, \mathbf{q}_3)\mathscr{S}_2(x_1, x_3) \\
&\qquad + \theta_{23}\Gamma_2(\mathbf{q}_2, \mathbf{q}_3)\mathscr{S}_2(x_2, x_3)] + \Gamma_2(\mathbf{q}_1, \mathbf{q}_2)\mathscr{S}_2(x_1, x_2) \\
&\qquad \times [\theta_{13} g_2^{(1)}(\mathbf{q}_1, \mathbf{q}_3)\mathscr{S}_2(x_1, x_3) + \theta_{23} g_2^{(1)}(\mathbf{q}_2, \mathbf{q}_3)\mathscr{S}_2(x_2, x_3)] \\
&\qquad - (\theta_{13} + \theta_{23}) g_3^{(1)}(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)\mathscr{S}_3(x_1, x_2, x_3)\}
\end{aligned}
\tag{18}
$$

$$
\begin{aligned}
&N_4(x_1, x_2, x_3, x_4) \\
&= \int_0^\infty d\tau\, S_{-\tau}^{(2)}(x_1, x_2)\Bigg[\int_0^\infty d\tau\, S_{-\tau}^{(2)}(x_1, x_2)\{(\theta_{13}+\theta_{23})\Gamma_3(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3)\mathscr{S}_3(x_1, x_2, x_3) \\
&\quad - \Gamma_2(\mathbf{q}_1, \mathbf{q}_2)\mathscr{S}_2(x_1, x_2)[\theta_{13}\Gamma_2(\mathbf{q}_1, \mathbf{q}_3)\mathscr{S}_2(x_1, x_3) \\
&\quad + \theta_{23}\Gamma_2(\mathbf{q}_2, \mathbf{q}_3)\mathscr{S}_2(x_2, x_3)]\}[\theta_{14}\Gamma_2(\mathbf{q}_1, \mathbf{q}_4)\mathscr{S}_2(x_1, x_4) \\
&\quad + \theta_{24}\Gamma_2(\mathbf{q}_2, \mathbf{q}_4)\mathscr{S}_2(x_2, x_4) + \theta_{34}\Gamma_2(\mathbf{q}_3, \mathbf{q}_4)\mathscr{S}_2(x_3, x_4)] \\
&\quad + \Gamma_2(\mathbf{q}_1, \mathbf{q}_2)\mathscr{S}_2(x_1, x_2)\Bigg\{\theta_{13}\int_0^\infty d\tau\, S_{-\tau}^{(2)}(x_1, x_3)\{(\theta_{14} + \theta_{34})\Gamma_3(\mathbf{q}_1, \mathbf{q}_3, \mathbf{q}_4) \\
&\quad \times \mathscr{S}_3(x_1, x_3, x_4) - \Gamma_2(\mathbf{q}_1, \mathbf{q}_3)\mathscr{S}_2(x_1, x_3)[\theta_{14}\Gamma_2(\mathbf{q}_1, \mathbf{q}_4)\mathscr{S}_2(x_1, x_4) \\
&\quad + \theta_{34}\Gamma_2(\mathbf{q}_3, \mathbf{q}_4)\mathscr{S}_2(x_3, x_4)]\} + \theta_{23}\int_0^\infty d\tau\, S_{-\tau}^{(2)}(x_2, x_3) \\
&\quad \times \{(\theta_{24} + \theta_{34})\Gamma_3(\mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4)\mathscr{S}_3(x_2, x_3, x_4) - \Gamma_2(\mathbf{q}_2, \mathbf{q}_3)\mathscr{S}_2(x_2, x_3) \\
&\quad \times [\theta_{24}\Gamma_2(\mathbf{q}_2, \mathbf{q}_4)\mathscr{S}_2(x_2, x_4) + \theta_{34}\Gamma_2(\mathbf{q}_3, \mathbf{q}_4)\mathscr{S}_2(x_3, x_4)]\}\Bigg\} \\
&\quad - (\theta_{13} + \theta_{23})\int_0^\infty d\tau\, S_{-\tau}^{(2)}(x_1, x_2, x_3)\{(\theta_{14} + \theta_{24} + \theta_{34}) \\
&\quad \times \Gamma_4(\mathbf{q}_1, \mathbf{q}_2, \mathbf{q}_3, \mathbf{q}_4)\mathscr{S}_4(x_1, x_2, x_3, x_4)[\theta_{14}\Gamma_2(\mathbf{q}_1, \mathbf{q}_4)\mathscr{S}_2(x_1, x_4) \\
&\quad + \theta_{24}\Gamma_2(\mathbf{q}_2, \mathbf{q}_4)\mathscr{S}_2(x_2, x_4) + \theta_{34}\Gamma_2(\mathbf{q}_3, \mathbf{q}_4)\mathscr{S}_2(x_3, x_4)]\}\Bigg]
\end{aligned}
\tag{19}
$$

4. TRANSPORT COEFFICIENTS

In order to calculate the explicit form of the integral equations $\mathscr{G}_1$, $\mathscr{A}_1$, and $\mathscr{B}_1$, we use the explicit expressions for $F_2^{(l)}$ $(l = 0, 1, 2)$ obtained in an earlier paper[5] and in the preceding section, in the integral equations given by Eqs. (14a)–(14c). We obtain the following results:

For $\mathscr{G}_1$

$$\tfrac{2}{3}k\chi(\mathbf{p})(\mathscr{P}/m)[d(\theta\beta_2)/d\theta] - \int dx_2\ \theta_{12}\Big\{ g_2^{(1)}(q_1q_2)\mathscr{S}_2(x_1x_2)\chi(p_1)\chi(p_2)$$
$$\times \sum_{i=1}^{2} (\mathbf{q}_i - \mathbf{q})[(\mathscr{P}_i^2/2m\theta) - \tfrac{3}{2}] + \int dx_3\ \mathscr{O}_3(x_1x_2x_3)\chi(p_1)\chi(p_2)\chi(p_3)$$
$$\times \sum_{i=1}^{3} (\mathbf{q}_i - \mathbf{q})[(\mathscr{P}_i^2/2m\theta) - \tfrac{3}{2}]\Big\} - \int dx_2\ \theta_{12}\Big[g_2^{(2)}(q_1q_2)\mathscr{S}_2(x_1x_2)\chi(p_1)\chi(p_2)$$
$$\times \sum_{i=1}^{2} \mathscr{P}_i\mathscr{G}_{\mathrm{B}}(p_i) + \int dx_3\ M_3(x_1x_2x_3)\chi(p_1)\chi(p_2)\chi(p_3)$$
$$\times \sum_{i=1}^{3} \mathscr{P}_i\mathscr{G}_{\mathrm{B}}(p_i) + \int dx_3 \int dx_4\ N_4(x_1x_2x_3x_4)\chi(p_1)\chi(p_2)\chi(p_3)\chi(p_4)$$
$$\times \sum_{i=1}^{4} \mathscr{P}_i\mathscr{G}_{\mathrm{B}}(p_i)\Big] - \int dx_2\ \theta_{12}\Big[g_2^{(1)}(q_1q_2)\mathscr{S}_2(x_1x_2)\chi(p_1)\chi(p_2)$$
$$\times \sum_{i=1}^{2} \mathscr{P}_i\mathscr{G}_0(p_i) + \int dx_3\ \theta_3(x_1x_2x_3)\chi(p_1)\chi(p_2)\chi(p_3)$$
$$\times \sum_{i=1}^{3} \mathscr{P}_i\mathscr{G}_0(p_i)\Big] = \mathscr{C}_{\mathrm{B}}(\mathscr{P}\mathscr{G}_1) \tag{20}$$

For $\mathscr{A}_1$

$$-(1/\theta) \int dx_2\ \theta_{12}\Big\{ g_2^{(1)}(q_1, q_2)\mathscr{S}_2(x_1, x_2)\chi(p_1)\chi(p_2)$$
$$\times \sum_{i=1}^{2} (S^0S)_i + \int dx_3\ \mathscr{O}_3(x_1, x_2, x_3)\chi(p_1)\chi(p_2)\chi(p_3)$$
$$\times \sum_{i=1}^{3} (S^0S)_i\Big\} - \int dx_2\ \theta_{12}\Big[g_2^{(2)}(q_1, q_2)\mathscr{S}_2(x_1, x_2)\chi(p_1)\chi(p_2)$$
$$\times \sum_{i=1}^{2} (\mathscr{P}^0\mathscr{P})_i\mathscr{A}_{\mathrm{B}}(p_i) + \int dx_3\ M_3(x_1x_2x_3)\chi(p_1)\chi(p_2)\chi(p_3)$$
$$\times \sum_{i=1}^{3} (\mathscr{P}^0\mathscr{P})_i\mathscr{A}_{\mathrm{B}}(p_i) + \int dx_3 \int dx_4\ N_4(x_1, x_2, x_3, x_4)\chi(p_1)\chi(p_2)\chi(p_3)\chi(p_4)$$
$$\times \sum_{i=1}^{4} (\mathscr{P}^0\mathscr{P})_i\mathscr{A}_{\mathrm{B}}(p_i)\Big] - \int dx_2\ \theta_{12}\Big[g_2^{(1)}(q_1, q_2)\mathscr{S}_2(x_1x_2)\chi(p_1)\chi(p_2)$$
$$\times \sum_{i=1}^{2} (\mathscr{P}^0\mathscr{P})_i\mathscr{A}_0(p_i) + \int dx_3\ \mathscr{O}_3(x_1x_2x_3)\chi(p_1)\chi(p_2)\chi(p_3)$$
$$\times \sum_{i=1}^{3} (\mathscr{P}^0\mathscr{P})_i\mathscr{A}_0(p_i)\Big] = \mathscr{C}_{\mathrm{B}}(\mathscr{P}^0\mathscr{P}\mathscr{A}_1) \tag{21}$$

For $\mathscr{B}_1$

$$\chi(\mathbf{p})[1 - (\mathscr{P}^2/3m\theta)]\xi - (1/3\theta) \int dx_2\, \theta_{12}\Big[g_2^{(1)}(q_1, q_2)\mathscr{S}_2(x_1, x_2)\chi(p_1)\chi(p_2) \times \sum_{i=1}^{2} \mathscr{P}_i\cdot(\mathbf{q}_i - \mathbf{q}) + \int dx_3\, \mathscr{O}_3(x_1, x_2, x_3)\chi(p_1)\chi(p_2)\chi(p_3) \times \sum_{i=1}^{3} \mathscr{P}_i\cdot(\mathbf{q}_i - \mathbf{q})\Big] = \mathscr{C}_{\mathrm{B}}(\mathscr{B}_1) \tag{22}$$

Furthermore, the quantities $\mathscr{G}_1$ and $\mathscr{B}_1$ must satisfy the subsidiary conditions given by Eqs. (4.8) of Ref. 8. To second order in the density these are

$$\int \chi(\mathbf{p})\mathscr{P}^2\mathscr{G}_1(p)\, d\mathbf{p} = 0 \tag{23}$$

$$\int \chi(\mathbf{p})\mathscr{B}_1(\mathscr{P}^2)\, d\mathbf{p} = 0 \tag{24}$$

$$\int d\mathbf{p}'\, \chi(\mathbf{p}')\mathscr{B}_1(p')(\mathscr{P}'^2/2m) + \tfrac{1}{2} \int d\mathbf{p}\;\; \chi(\mathbf{p}')\mathscr{B}_0(p') \int d\mathbf{p}\, dx_2\, \phi(r)F_2^{(0)\prime}(x_1, x_2, \mathbf{p}'|F_1^{(0)}) = -(1/6\theta)\int d\mathbf{p} \int dx_2\, dx'\, \phi(r)F_2^{(0)\prime}(x_1, x_2, x'\,|F_1^{(0)})\mathscr{P}'\cdot(\mathbf{q}' - \mathbf{q})\chi(\mathbf{p}') \tag{25}$$

There is no further condition on $\mathscr{A}_1$. Having solved the integral equations (20)–(22) for $\mathscr{G}_1$, $\mathscr{A}_1$, and $\mathscr{B}_1$, one can write formal expressions for the transport coefficients to second order in the density. From Eqs. (5.8), (5.9), (5.14), and (5.16) of Ref. 8, we obtain the following results, to second order in the density.

Heat conductivity

$$(\lambda)_2 = (\lambda^\kappa)_2 + (\lambda_1^{\phi_1})_2 + (\lambda_2^{\phi_1})_2 + (\lambda_1^{\phi_2})_2 + (\lambda_2^{\phi_2})_2 \tag{26}$$

with

$$(\lambda^\kappa)_2 = (1/6m^2\theta) \int d\mathbf{p}\, \mathscr{P}^4\mathscr{G}_1(p)\chi(p) \tag{27}$$

$$(\lambda_1^{\phi_1})_2 = (1/12m\theta) \iint dx_2\, d\mathbf{p}\, \mathbf{r}\cdot(\mathscr{P} + \mathscr{P}_2)[\phi'(r)/r]\mathbf{r}\cdot\int d\mathbf{p}'\, \mathscr{P}' \times [F_2^{(1)\prime}(x_1x_2, \mathbf{p}'|\chi)\mathscr{G}_{\mathrm{B}}(p') + F_2^{(0)\prime}(x_1x_2, \mathbf{p}'|\chi)\mathscr{G}_0(p')]\chi(p') \tag{28}$$

$$(\lambda_2^{\phi_1})_2 = (1/24m^2\theta^2) \iint dx_2\, d\mathbf{p}\, \mathbf{r}\cdot(\mathscr{P} + \mathscr{P}_2)[\phi'(r)/r]\mathbf{r}\cdot\int dx'\, \mathscr{P}'^2(\mathbf{q}' - \mathbf{q})\chi(p') \times F_2^{(0)\prime}(x_1x_2x'|\chi) \tag{29}$$

$$(\lambda_1{}^{\phi_2})_2 = (1/6m\theta) \int d\mathbf{p}\, dx_2\, \phi(r)\mathscr{P}\cdot\int d\mathbf{p}'\, \mathscr{P}'$$
$$\times [F_2{}^{(0)\prime}(x_1x_2, \mathbf{p}'|\chi)\mathscr{G}_0(p') + F_2{}^{(1)\prime}(x_1x_2, \mathbf{p}'|\chi)\mathscr{G}_B(p')] \tag{30}$$

$$(\lambda_2{}^{\phi_2})_2 = (1/12m^2\theta^2) \iint dx_2\, d\mathbf{p}\, \phi(r)\mathbf{p}\cdot\int dx'\mathscr{P}'^2(\mathbf{q}' - \mathbf{q})\chi(\mathbf{p}')$$
$$\times F_2{}^{(0)\prime}(x_1x_2x'|\chi) \tag{31}$$

Shear viscosity

$$(\eta)_2 = (\eta^\kappa)_2 + (\eta_1{}^\phi)_2 + (\eta_2{}^\phi)_2 \tag{32}$$

with

$$(\eta^\kappa)_2 = (1/15m) \int d\mathbf{p}\, \mathscr{P}^4\chi(p)\mathscr{A}_1(\mathscr{P}^2) \tag{33}$$

$$(\eta_1{}^\phi)_2 = \tfrac{1}{20} \iiint dx_2\, d\mathbf{p}\, d\mathbf{p}'[\phi'(r)/r][(\mathbf{r}\cdot\mathscr{P}')^2 - \tfrac{1}{3}r^2\mathscr{P}'^2]$$
$$\times \chi(p')F_2{}^{(1)\prime}(x_1x_2, \mathbf{p}'|\chi)\mathscr{A}_B(p') + F_2{}^{(0)\prime}(x_1x_2, \mathbf{p}'|\chi)\mathscr{A}_0(p') \tag{34}$$

$$(\eta_2{}^\phi)_2 = (1/20\theta) \iiint dx_2\, d\mathbf{p}\, dx'\, [\phi'(r)/r][\mathbf{r}\cdot(\mathbf{q}' - \mathbf{q})\mathbf{r}\cdot\mathscr{P} - (r^2/3)\mathscr{P}'\cdot(\mathbf{q}' - \mathbf{q})]$$
$$\times \chi(p')F_2{}^{(0)\prime}(x_1x_2x'|\chi) \tag{35}$$

Bulk viscosity

$$(\xi)_2 = (\xi^\kappa)_2 + (\xi^{\phi_1})_2 + (\xi^{\phi_2})_2 \tag{36}$$

with

$$(\xi^\kappa)_2 = -(1/3m) \int d\mathbf{p}\, \mathscr{P}^2\chi(p)\mathscr{B}_1(\mathscr{P}^2) \tag{37}$$

$$(\xi^{\phi_1})_2 = \tfrac{1}{6} \iiint dx_2\, d\mathbf{p}\, d\mathbf{p}'\, r\phi'(r)F_2{}^{(0)\prime}(x_1x_2, \mathbf{p}'|\chi)\mathscr{B}_0(p')\chi(p') \tag{38}$$

$$(\xi^{\phi_2})_2 = (1/18\theta) \iiint dx_2\, d\mathbf{p}\, dx'\, r\phi'(r)\mathscr{P}'\cdot(\mathbf{q}' - \mathbf{q})\chi(p')F_2{}^{(0)\prime}(x_1x_2x'|\chi) \tag{39}$$

5. CONCLUSIONS

In the last section we obtained the explicit general expressions for the heat conductivity and shear and bulk viscosities to second order in the density. From inspection of these expressions (and of the integral equations that the function $\mathscr{G}_1$, $\mathscr{A}_1$, and $\mathscr{B}_1$ satisfy) we see that the integrals over configuration space appearing in these equations are finite. This is due to the fact that the factors Γ_s and $g_s^{(l)}$ act as convergence factors. It should be recalled that these are precisely the factors introduced in the boundary conditions that reflect the physical situation in a dense medium. As a matter of fact, it is through these factors that the medium is introduced in the statistical dynamics of a cluster of s particles.

Therefore we can conclude that insofar as the existence of a convergent virial expansion of the transport coefficients is concerned, our theory is consistent with experimental results. Of course, we still have to compare the numerical results obtained from this theory with experimental data. This implies the use of explicit intermolecular models. This will be the subject of forthcoming communications.

REFERENCES

1. N. N. Bogolyubov, *Problems of a Dynamical Theory in Statistical Mechanics*, Vol. 1 of *Studies in Statistical Mechanics*, J. de Boer and G. E. Uhlenbeck, eds., North-Holland, Amsterdam (1962).
2. J. Weinstock, *Phys. Rev.* **140A** (1965); E. A. Frieman and R. Goldman, *Bull. Am. Phys. Soc.* **10**:531 (1965); K. Kawasaki and I. Oppenheim, *Phys. Letters* **11**:124 (1964); K. Kawasaki and I. Oppenheim, *Phys. Rev.* **139A**:1763 (1965); J. R. Dorfman and E. G. D. Cohen, *Phys. Letters* **16**:124 (1965), *J. Math. Phys.* **8**:282 (1967); M. H. Ernst, L. K. Haines, and J. R. Dorfman, *Revs. Mod. Phys.* **41**:296 (1969).
3. J. R. Dorfman, in *Lectures in Theoretical Physics*, Vol. 9C, W. E. Brittin, ed., Gordon and Breach, New York (1967).
4. J. Kestin, E. Paykoc, and J. V. Sengers, *Physica* **54**:1 (1971).
5. E. Braun and A. Flores, *J. Stat. Phys.* **8**(2):155 (1973).
6. A. Flores and E. Braun, *J. Stat. Phys.* **8**(2):167 (1973).
7. S. T. Choh, "The kinetic theory of phenomena in dense gases," Doctoral Dissertation, University of Michigan, 1958.
8. L. S. García-Colín, M. S. Green, and F. Chaos, *Physica* **32**:450 (1966).