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Correlation-Function Method for the Transport Coefficients of Dense Gases. I. First Density Correction to the Shear Viscosity*

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The first density correction to the shear viscosity of the classical gas is calculated using the autocorrelation function expression. The technique employed is that due to Zwanzig suitably generalized to include dynamical fluxes containing particle coordinates. If we restrict ourselves to repulsive forces, our result is in complete agreement with that of Choh and Uhlenbeck obtained with the use of Bogolyubov's theory.

I. INTRODUCTION

THE statistical-mechanical treatment of irreversible processes can be carried out either in terms of time-dependent distribution functions which are the solutions of transport equations, or in terms of frequency and wave vector-dependent correlation functions which involve averages over the equilibrium distribution functions. These two approaches must yield the same results. In order to obtain expressions for the phenomenological transport coefficients (diffusion constant, viscosity coefficient, thermal conductivity, etc.), however, a number of physical correspondences and approximations must be introduced. Since these steps differ depending on which approach is used, there has been some question as to whether the expressions for the transport coefficients obtained from the transport equation are identical to the expressions obtained from the correlation functions.

The first step in the transport equation approach is to develop an equation for the time-dependent singlet distribution, the generalized Boltzmann equation, which involves an expansion in powers of the density.[1,2] This step involves assumptions concerning the initial correlations in the system. The next step is to introduce a Chapman-Enskog expansion[2] for the distribution function and to associate the coefficients in this expansion with the transport coefficients. In this step, it is assumed that the system is close to equilibrium. Thus, one arrives at density expansions for the transport coefficients.

In the correlation function approach these steps are inverted. The transport coefficients are associated with low-frequency and long-wavelength limits of the correlation functions.[3] These expressions are valid for any density but involve the dynamics of the N-body system in an intractable fashion. In order to arrive at tractable expressions, density expansions are introduced and again one arrives at density expansions for the transport coefficients.

So far it has been established that, in the lowest order in the density, the transport coefficients obtained from the Boltzmann equation and from the correlation function expressions are the same[3,4]; not much has been done to generalize these results to higher order in the density.[5,6] It is the aim of this paper to develop a method which enables one to obtain density expansions of the correlation function expressions for the transport coefficients. We present an explicit expression for the first density correction to the shear viscosity and demonstrate that it is identical to that obtained by Choh and Uhlenbeck[2] from the transport equation.

We calculate the first density correction to the shear viscosity of a classical gas from the correlation function expression, employing and generalizing the technique discovered recently by Zwanzig.[6] Introduction of a convergence factor $e^{-\epsilon t}(\epsilon>0)$ into the correlation function expression leads to an expression for the viscosity in terms of the resolvent operator of the N-particle system. A binary collision expansion of the resolvent operator gives a density series for the correlation function expression, which involves singularities at $\epsilon=$zero. However, inversion of this expansion gives a unique well defined density expansion for the viscosity; the lowest order term of this expansion agrees with the result of Chapman and Enskog.[7] For systems with repulsive intermolecular forces of finite range, the first density correction to the viscosity is compared with the

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[1] N. N. Bogolyubov, *Studies in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, p. 5; M. S. Green, Physica **24**, 393 (1958), E. G. D. Cohen, *ibid.* **28**; 1025 and 1045 (1962); M. S. Green and R. A. Piccirelli, Phys. Rev. **132**, 1388 (1963).

[2] S. T. Choh and G. E. Uhlenbeck, The Kinetic Theory of Phenomena in Dense Gases, University of Michigan, 1958 (unpublished).

[3] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 898 (1954); R. Kubo, *Some Aspects of Statistical-Mechanical Theory of Irreversible Processes, Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959), Vol. I; H. Mori, I. Oppenheim, and J. Ross, *Studies in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962), Vol. I, p. 217; H. Mori, Progr. Theoret. Phys. (Kyoto) **28**, 763 (1962); L. P. Kadanoff and P. C. Martin. Ann. Phys. (N. Y.) **24**, 419 (1963).

[4] J. A. McLennan and R. J. Swenson, J. Math. Phys. **4**, 1527 (1963) and references cited therein.

[5] (a) E. W. Montroll and J. C. Ward, Physica **25**, 423 (1959); (b) E. G. D. Cohen and M. H. J. J. Ernst, Phys. Letters **5**, 192 (1963); (c) E. G. D. Cohen, International Seminar on the Transport Theory of Gases at Brown University, 1964 (to be published), and private communication; (d) I. Prigogine and G. Severne, Phys. Letters **6**, 177 (1963); I. Prigogine, P. Résibois, and G. Severne (private communication).

[6] R. Zwanzig, Phys. Rev. **129**, 486 (1963).

[7] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

result of Choh and Uhlenbeck[2] obtained from Bogolyubov's generalized Boltzmann equation,[1] and complete agreement is obtained.[8]

In the next section the correlation function expression for the shear viscosity is re-expressed in terms of the resolvent operator and the Fourier transform of the configurational distribution functions of the equilibrium ensemble. Some useful formulas related to the binary collision expansion of the resolvent operator are established. In Secs. III, IV, and V detailed calculations of the viscosity coefficient are presented. Zwanzig's method is generalized to include dynamical fluxes which contain coordinates. The result for the first density correction to the shear viscosity is given in Sec. VI and comparison with the theory of Choh and Uhlenbeck is carried out in Sec. VII.

II. CORRELATION FUNCTION EXPRESSION FOR VISCOSITY

In this section, as a preliminary to the calculation, following Zwanzig,[6] we shall rewrite the correlation function expression for the viscosity in terms of the resolvent operator and the Fourier transform of the equilibrium configurational distribution function.

We consider a classical fluid at temperature T consisting of N identical molecules of mass m contained in the volume V. The well-known correlation function expression[3] for the shear viscosity in the low-frequency and long-wavelength limit is written as

$$\eta = \lim_{\epsilon \to 0+} \lim_{\substack{N,V\to\infty \\ ((N/V)=\text{constant})}} \eta(\epsilon), \tag{2.1}$$

where

$$\eta(\epsilon) \equiv \frac{1}{VKT}\int_0^\infty dt e^{-\epsilon t}\langle II(t)\rangle. \tag{2.2}$$

K is the Boltzmann constant and the angular bracket means an average over the equilibrium ensemble. Here I denotes the dynamical flux for the shear viscosity defined as

$$I = I_K + I_U, \tag{2.3}$$

with

$$I_K \equiv \sum_{i=1}^{N} \chi(\mathbf{p}_i), \tag{2.4}$$

$$\chi(\mathbf{p}) \equiv p^x p^y/m, \tag{2.5}$$

$$I_U = \sum_{i<j} \psi(\mathbf{r}_{ij}), \tag{2.6}$$

$$\psi(\mathbf{r}) = -r^x[\partial u(\mathbf{r})/\partial r^y], \tag{2.7}$$

where p_i^x is the x component of the momentum of the ith molecule, $\mathbf{r}_{ij}$ is the relative position vector between the ith and jth particles, given by $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, and $u(\mathbf{r})$ is the two-body potential of interaction which is assumed to be spherically symmetric. We have assumed that the potential of the N-body system can be written as a sum of pair potentials.

In order to describe the temporal development of the system, we introduce the self-adjoint Liouville operator L by

$$L = L_0 + L', \tag{2.8}$$

where L_0 describes the free motion of the particles and is given by

$$L_0 = -i(1/m)\mathbf{p}^N \cdot (\partial/\partial \mathbf{r}^N) \tag{2.9}$$

and L' contains the effect of interaction and is given by

$$L' = i\sum_{i<j}\theta_{ij}, \tag{2.10}$$

$$\theta_{ij} \equiv \frac{\partial u(\mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j}\right). \tag{2.11}$$

In (2.9) we have used the $3N$-dimensional vector notation. The quantity $I(t)$ can be expressed in terms of the Liouville operator in the form $I(t) = e^{iLt}I$.

For later convenience we rewrite (2.2) by making use of the time reversal invariance of the autocorrelation function as

$$\begin{aligned}\eta(\epsilon) &= \frac{1}{VKT}\int_0^\infty dt e^{-\epsilon t}\langle II(-t)\rangle \\ &= \frac{1}{VKT}\int_0^\infty dt e^{-\epsilon t}\langle I e^{-itL} I\rangle \\ &= (VKT)^{-1}\langle I G(\epsilon) I\rangle,\end{aligned} \tag{2.12}$$

where

$$G(\epsilon) = (\epsilon + iL)^{-1} \tag{2.13}$$

is the resolvent operator.[9] Explicitly, (2.12) is given by

$$\eta(\epsilon) = (VKT)^{-1}\int\int d\mathbf{r}^N d\mathbf{p}^N I G(\epsilon) I \rho(\mathbf{r}^N) \prod_{j=1}^{N} \varphi(p_j), \tag{2.14}$$

where $\varphi(p)$ is the normalized Maxwell distribution $\varphi(p) = (2\pi mKT)^{-3/2}\exp(-p^2/2mKT)$ and $\rho(\mathbf{r}^N)$ is the normalized configurational distribution function defined by

$$\rho(\mathbf{r}^N) = \exp[-U(\mathbf{r}^N)/KT] \Big/ \int d\mathbf{r}^N \exp[-U(\mathbf{r}^N)/KT], \tag{2.15}$$

where $U(\mathbf{r}^N)$ is the total potential energy. We have placed the equilibrium distribution function to the right of the resolvent operator since it is more convenient

[8] The same conclusion has been obtained by Cohen apparently by a different method. See Ref. 5(c). Since details of his work are not yet available, we shall not discuss his theory in this paper.

[9] The resolvent operator defined in (2.13) is different from that of Zwanzig (Ref. 6) since we are considering $\langle II(-t)\rangle$. This facilitates comparison with the results obtained from the generalized Boltzmann equation.

when comparison is made with the generalized Boltzmann equation treatment. This is permissible since

$$L[\rho(\mathbf{r}^N)\prod_{j=1}^{N}\varphi(p_j)]=0.$$

The Fourier transform of $\rho(\mathbf{r}^N)$, $P(\mathbf{k}^N)$, is defined by

$$P(\mathbf{k}^N)=\int d\mathbf{r}^N e^{i\mathbf{k}^N\cdot\mathbf{r}^N}\rho(\mathbf{r}^N). \tag{2.16}$$

Inversion of (2.16) gives

$$\rho(\mathbf{r}^N)=\frac{1}{V^N}\sum_{\mathbf{k}^N} e^{-i\mathbf{k}^N\cdot\mathbf{r}^N}P(\mathbf{k}^N). \tag{2.16a}$$

Substitution of (2.16a) into (2.14) yields

$$\eta(\epsilon)=(VKT)^{-1}V^{-N}\sum_{\mathbf{k}^N}P^*(\mathbf{k}^N)$$
$$\times\int\int d\mathbf{p}^N d\mathbf{r}^N IG(\epsilon)Ie^{i\mathbf{k}^N\cdot\mathbf{r}^N}\prod_{j=1}^{N}\varphi(p_j), \tag{2.17}$$

where we have used the fact that $\rho(\mathbf{r}^N)$ is real. When (2.3) is substituted into (2.12), $\eta(\epsilon)$ splits into four terms,

$$\eta(\epsilon)=\eta_{KK}(\epsilon)+\eta_{KU}(\epsilon)+\eta_{UK}(\epsilon)+\eta_{UU}(\epsilon), \tag{2.18}$$

where

$$\eta_{LM}(\epsilon)=(VKT)^{-1}\langle I_L G(\epsilon)I_M\rangle,\quad L, M=K \text{ or } U. \tag{2.19}$$

In the following sections, we shall consider these four terms separately.

We now present some properties of the resolvent operator which will be used frequently. The binary collision expansion formula for the resolvent operator is[6,10,11]

$$G=G_0-\sum_{\alpha}G_0T_\alpha G_0+\sum_{\alpha,\beta}{}' G_0T_\alpha G_0T_\beta G_0-\cdots, \tag{2.20}$$

where G_0 is the resolvent operator for noninteracting particles defined by

$$G_0=(\epsilon+iL_0)^{-1}; \tag{2.21}$$

T_α is the binary collision operator of the pair α (Greek indices α, β, $\cdots$ denote particle pairs), defined as the solution of the equation

$$T_\alpha=-\theta_\alpha+\theta_\alpha G_0 T_\alpha \tag{2.22}$$
$$=-\theta_\alpha+T_\alpha G_0\theta_\alpha; \tag{2.22$'$}$$

and the summations in (2.20) are over all possible pairs with the restriction that consecutive T's do not refer to the same pair. We now define the resolvent operator for a system in which interaction exists only between the particles of pair α by

$$G_2(\alpha)=(\epsilon+iL_2(\alpha))^{-1}, \tag{2.23}$$

where

$$L_2(\alpha)=L_0+i\theta_\alpha. \tag{2.24}$$

The binary collision expansion of $G_2(\alpha)$ then yields

$$G_2(\alpha)=G_0-G_0T_\alpha G_0. \tag{2.25}$$

Substitution of (2.25) in (2.22) and (2.22′) gives

$$T_\alpha=-\theta_\alpha G_2(\alpha)G_0^{-1} \tag{2.26}$$

and

$$T_\alpha=-G_0^{-1}G_2(\alpha)\theta_\alpha, \tag{2.26$'$}$$

respectively.

Before leaving this section, it is useful for what follows to mention some properties of the binary collision operator T_α. Zwanzig[6] has already noted the following properties: (1) T_α is proportional to $1/V$ as $V\rightarrow\infty$; (2) $T_\alpha(0|0)$ is simply related to the Boltzmann collision operator.[12]

In order to investigate another relevant property of T_α, we first note from (2.24) that

$$G_0^{-1}=G_2^{-1}(\alpha)+\theta_\alpha. \tag{2.27}$$

If we substitute (2.27) into (2.26), we obtain for $\alpha=(1,2)$

$$T_{12}=-\theta_{12}[1+G_2(12)\theta_{12}]$$
$$=-\theta_{12}\left[1+\int_0^\infty dte^{-\epsilon t}e^{-itL_2(12)}\theta_{12}\right]. \tag{2.28}$$

For a repulsive intermolecular force of a finite range, the integrand in (2.28) is seen to vanish for times greater than the duration of collisions, and the integral converges. Thus T_{12} is finite as $\epsilon\rightarrow 0$ for this case.

III. CALCULATION OF η_{KK}

The quantity $\eta_{KK}(\epsilon)$ has been considered by Zwanzig,[13] but we shall treat it here in a somewhat different manner by using the particle exchange operator. Since I_K does not contain $\mathbf{r}^N$, Eq. (2.17) for $\eta_{KK}(\epsilon)$ becomes

$$\eta_{KK}(\epsilon)=(VKT)^{-1}\sum_{\mathbf{k}^N}P^*(\mathbf{k}^N)$$
$$\times\int d\mathbf{p}^N I_K G(0|\mathbf{k}^N)I_K\prod_{i=1}^{N}\varphi(p_i), \tag{3.1}$$

where we define the Fourier transform of any operator O by

$$O(\mathbf{k}^N|\mathbf{k}'^N)=V^{-N}\int d\mathbf{r}^N e^{-i\mathbf{k}^N\cdot\mathbf{r}^N}Oe^{i\mathbf{k}'^N\cdot\mathbf{r}^N}. \tag{3.2}$$

[10] A. J. F. Siegert and E. Teramoto, Phys. Rev. **110**, 1232 (1958).

[11] We frequently write G instead of $G(\epsilon)$ for the resolvent operator. The operator T_α also depends on ϵ.

[12] For the notation, see Eq. (3.2). In this connection see also Eq. (3.25).

[13] R. Zwanzig (private communication).

The operator $O(\mathbf{k}^N|\mathbf{k}'^N)$ operates on the momenta only. Since the particles are identical, we can write (3.1) as

$$\eta_{KK}(\epsilon)=(KT)^{-1}\rho\sum_{\mathbf{k}^N}P^*(\mathbf{k}^N)\int d\mathbf{p}^N\chi(\mathbf{p}_1)G(0|\mathbf{k}^N)\times[1+(N-1)\mathcal{P}_{12}]\chi(\mathbf{p}_1)\prod_{i=1}^N\varphi(p_i),\quad(3.3)$$

where we have introduced the particle exchange operator $\mathcal{P}_{12}$ which is defined by

$$\mathcal{P}_{12}\mathbf{p}_1=\mathbf{p}_2,\quad \mathcal{P}_{12}\mathbf{p}_2=\mathbf{p}_1,\quad \mathcal{P}_{12}\mathbf{p}_j=\mathbf{p}_j,\quad j=3,4,\cdots,N\quad(3.4)$$

and $\rho=N/V$ denotes the number density. In (3.3), and in the following, we stipulate that *the particle exchange operators do not act on the momenta in the Maxwell distribution.*

The next step is to utilize the binary collision expansion (2.20) for $G(0|\mathbf{k}^N)$. Thus we have

$$G(0|\mathbf{k}^N)=\epsilon^{-1}\{\Delta(\mathbf{k}^N)-\sum_\alpha T_\alpha(0|\mathbf{k}^N)g(\mathbf{k}^N)+\sum_{\alpha,\beta}{}'\sum_{\mathbf{k}'^N}T_\alpha(0|\mathbf{k}'^N)g(\mathbf{k}'^N)\times T_\beta(\mathbf{k}'^N|\mathbf{k}^N)g(\mathbf{k}^N)+\epsilon G^r(0|\mathbf{k}^N)\},\quad(3.5)$$

where $\Delta(\mathbf{k}^N)$ is the $3N$-dimensional Kronecker delta defined by

$$\Delta(\mathbf{k}^N)=\begin{cases}1 & \mathbf{k}^N=0\\ 0 & \text{otherwise}\end{cases}\quad(3.6)$$

and we have used the fact that

$$G_0(\mathbf{k}^N|\mathbf{k}'^N)=g(\mathbf{k}^N)\Delta(\mathbf{k}^N-\mathbf{k}'^N),\quad(3.7)$$

with

$$g(\mathbf{k}^N)\equiv(\epsilon+i\mathbf{p}^N\cdot\mathbf{k}^N/m)^{-1}.\quad(3.8)$$

The symbol $G^r(0|\mathbf{k}^N)$ is defined by Eq. (3.5). It contains the terms in the binary collision expansion of $G(0|\mathbf{k}^N)$ which have not been written explicitly in (3.5).

Corresponding to the four different terms of (3.5), we split $\eta_{KK}(\epsilon)$ into four parts

$$\eta_{KK}(\epsilon)=\eta_{KK}{}^0(\epsilon)+\eta_{KK}{}^1(\epsilon)+\eta_{KK}{}^2(\epsilon)+\eta_{KK}{}^r(\epsilon).\quad(3.9)$$

We then immediately find, noting that $P(0)=1$, that

$$\eta_{KK}{}^0(\epsilon)=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)^2\varphi(p_1)\epsilon^{-1}.\quad(3.10)$$

By considering the identity of particles, we easily find that

$$\eta_{KK}{}^1(\epsilon)=\rho(KT)^{-1}\sum_{\mathbf{k}^N}P^*(\mathbf{k}^N)\int d\mathbf{p}^N\chi(\mathbf{p}_1)\epsilon^{-1}\times\{-(N-1)T_{12}(0|\mathbf{k}^N)g(\mathbf{k}^N)(1+\mathcal{P}_{12})-Q_1-Q_2-Q_3-Q_4\}\chi(\mathbf{p}_1)\prod_{i=1}^N\varphi(p_i),\quad(3.11)$$

where

$$\left.\begin{aligned}Q_1&\equiv2^{-1}(N-1)(N-2)T_{23}(0|\mathbf{k}^N)g(\mathbf{k}^N)\\ Q_2&\equiv(N-1)(N-2)T_{13}(0|\mathbf{k}^N)g(\mathbf{k}^N)\mathcal{P}_{12},\end{aligned}\right\},\quad(3.12)$$

$$Q_3\equiv(N-1)(N-2)T_{23}(0|\mathbf{k}^N)g(\mathbf{k}^N)\mathcal{P}_{12},\quad(3.13)$$

$$Q_4\equiv2^{-1}(N-1)(N-2)(N-3)T_{34}(0|\mathbf{k}^N)g(\mathbf{k}^N)\mathcal{P}_{12}.\quad(3.14)$$

We now show that Q_1, Q_2, Q_3 and Q_4 give no contribution to $\eta_{KK}{}^1(\epsilon)$. The Q_1 term involves an integral of the form

$$\int\int d\mathbf{p}_2d\mathbf{p}_3T_{23}(0|\mathbf{k}^N)\cdots\quad(3.15)$$

or

$$\int\int\int d\mathbf{p}_2d\mathbf{p}_3d\mathbf{r}_3\theta_{23}\cdots.\quad(3.16)$$

This vanishes because of the form of θ_α given by (2.11) and the fact that the Maxwell distributions vanish strongly as the momenta tend to $\pm\infty$. The Q_3 and Q_4 terms vanish for the same reason. The only dependence on $\mathbf{p}_2$ of the Q_2 term involves $\chi(\mathbf{p}_2)\varphi(p_2)$. The integral

$$\int\chi(\mathbf{p}_2)\varphi(p_2)d\mathbf{p}_2\quad(3.17)$$

vanishes because of symmetry. Thus we are left with the first term of (3.11), which becomes, after integrating over $\mathbf{p}_3,\cdots\mathbf{p}_N$,

$$\eta_{KK}{}^1(\epsilon)=\rho(KT)^{-1}\sum_{\mathbf{k}}P^*(\mathbf{k},-\mathbf{k})\int\int d\mathbf{p}_1d\mathbf{p}_2\chi(\mathbf{p}_1)\times\{-\epsilon^{-1}(N-1)T_{12}(0|\mathbf{k},-\mathbf{k})\times g(\mathbf{k},-\mathbf{k})(1+\mathcal{P}_{12})\chi(\mathbf{p}_1)\}\varphi(p_1)\varphi(p_2).\quad(3.18)$$

The quantity $P^*(\mathbf{k},-\mathbf{k})$ can be expressed in terms of the pair correlation function $F(\mathbf{r}_{12})$ as

$$P^*(\mathbf{k},-\mathbf{k})=\Delta(\mathbf{k})+V^{-1}f^{(2)*}(\mathbf{k}),\quad(3.19)$$

where

$$f^{(2)}(\mathbf{k})=\int d\mathbf{r}_{12}e^{i\mathbf{k}\cdot\mathbf{r}_{12}}F(\mathbf{r}_{12})$$

and

$$F(\mathbf{r}_{12})=V^2\int\rho(\mathbf{r}^N)d\mathbf{r}^{N-2}-1.\quad(3.20)$$

In the low-density limit, $F(\mathbf{r}_{12})$ reduces to the Ursell-Mayer function $F_0(\mathbf{r}_{12})$ defined by

$$F_0(\mathbf{r}_{12})=\exp[-u(\mathbf{r}_{12})/KT]-1.\quad(3.21)$$

To the order in density that we are considering, it is sufficient to use $F_0(\mathbf{r})$ instead of $F(\mathbf{r})$.

Thus we finally obtain for $\eta_{KK}{}^1(\epsilon)$

$$\eta_{KK}{}^1(\epsilon)=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)[-\rho\epsilon^{-2}\mathfrak{L}(\mathbf{p}_1)-\rho\epsilon^{-1}t_1(\mathbf{p}_1)]\chi(\mathbf{p}_1)\varphi(p_1),\quad(3.22)$$

where

$$\mathcal{L}(\mathbf{p}_1)\equiv\int d\mathbf{p}_2 V T_{12}(0|0)(1+\mathcal{P}_{12})\varphi(p_2) \quad (3.23)$$

and[14]

$$t_1(\mathbf{p}_1)\equiv\int d\mathbf{p}_2(0|VT_{12}G_0F_0(\mathbf{r}_{12})|0)(1+\mathcal{P}_{12})\varphi(p_2). \quad (3.24)$$

The operators $\mathcal{L}(\mathbf{p}_1)$ and $t_1(\mathbf{p}_1)$ can be shown to have a well defined limit as N, $V\to\infty$ with N/V fixed.[6]

One can show, in the same manner as Zwanzig,[6] that $\mathcal{L}(\mathbf{p}_1)$ is identical to the linearized Boltzmann collision operator in the limit as $\epsilon\to 0+$. That is, for any function $J(\mathbf{p}_1)$, using the impact parameter b and the cylindrical angle ψ, we have

$$-\lim_{\epsilon\to 0+}\mathcal{L}(\mathbf{p}_1)J(\mathbf{p}_1)\varphi(p_1)$$

$$=\int d\mathbf{p}_2\int_0^{2\pi}d\psi\int_0^{\infty}bdb\frac{|\mathbf{p}_1-\mathbf{p}_2|}{m}[J(\mathbf{p}_1^*)+J(\mathbf{p}_2^*)-J(\mathbf{p}_1)-J(\mathbf{p}_2)]\varphi(p_1)\varphi(p_2), \quad (3.25)$$

where the $\mathbf{p}_i^*$ are the momenta before the collision and the $\mathbf{p}_i$ are the momenta after the collision. The operator $t_1(\mathbf{p}_1)$ can be thought of as a correction to $\mathcal{L}(\mathbf{p}_1)$ due to particle correlations in the equilibrium ensemble.

In obtaining this result for $\eta_{KK}{}^1(\epsilon)$, as well as in the following, we have suppressed the terms of higher order in ρ or ϵ^{-1} which do not contribute to the first density correction to the viscosity.

By a similar analysis we obtain for $\eta_{KK}{}^2(\epsilon)$,

$$\eta_{KK}{}^2(\epsilon)=\rho(KT)^{-1}\int d\mathbf{p}_1\chi(\mathbf{p}_1)\times[\rho^2\epsilon^{-3}t_{21}(\mathbf{p}_1)+\rho^2\epsilon^{-2}t_{22}(\mathbf{p}_1)]\chi(\mathbf{p}_1)\varphi(p_1), \quad (3.26)$$

where

$$t_{21}\equiv\int\int d\mathbf{p}_2 d\mathbf{p}_3 VT_{12}(0|0)[VT_{13}(0|0)+VT_{23}(0|0)]\times(1+\mathcal{P}_{13}+\mathcal{P}_{23})\varphi(p_2)\varphi(p_3), \quad (3.27)$$

$$t_{22}\equiv\int\int d\mathbf{p}_2 d\mathbf{p}_3 VT_{12}(0|0)\times(0|[VT_{13}G_0F_0(r_{13})+VT_{23}G_0F_0(r_{23})]|0)\times(1+\mathcal{P}_{13}+\mathcal{P}_{23})\varphi(p_2)\varphi(p_3). \quad (3.28)$$

Here, t_{21} and t_{22} are well defined as N, $V\to\infty$, N/V fixed. Again t_{22} is the correction to t_{21} due to spatial correlation in the equilibrium ensemble.

Next we consider $\eta_{KK}{}^r(\epsilon)$. We group the terms contributing to $\eta_{KK}{}^r(\epsilon)$ into a part which involves three particles and a part involving more than three particles. The latter part has a factor ρ^4 as N, $V\to\infty$. Higher order terms in ϵ^{-1} also occur in this part but we shall assume that these terms produce no difficulty. Under these circumstances the part involving more than three particles will give no contribution to the first density correction to the viscosity and will be neglected. Restricting our considerations to the terms involving three particles, we obtain

$$\eta_{KK}{}^r(\epsilon)=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)\times[-\rho^2\epsilon^{-2}t^r(\mathbf{p}_1)]\chi(\mathbf{p}_1)\varphi(p_1), \quad (3.29)$$

where

$$t^r(\mathbf{p}_1)=\frac{1}{2}\int\int d\mathbf{p}_2 d\mathbf{p}_3 V^2(0|\tau(123)|0)\times(1+\mathcal{P}_{12}+\mathcal{P}_{13})\varphi(p_2)\varphi(p_3) \quad (3.30)$$

and

$$\tau(123)\equiv\sum_{\alpha,\beta,\gamma}{}'\,T_\alpha G_0 T_\beta G_0 T_\gamma-\sum_{\alpha,\beta,\gamma,\delta}{}'\,T_\alpha G_0 T_\beta G_0 T_\gamma G_0 T_\delta+\cdots, \quad (3.31)$$

where the summations are over all possible pairs of particles 1, 2, and 3. A correction to $t^r(\mathbf{p}_1)$ due to spatial correlation in the equilibrium ensemble gives a contribution of order $\rho^3\epsilon^0$ to $\eta_{KK}{}^r(\epsilon)$. This correction is omitted here because it does not contribute to the first density correction to the viscosity.

Collecting together (3.10), (3.22), (3.26), and (3.29) we finally obtain as N, $V\to\infty$,

$$\eta_{KK}(\epsilon)=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)\mathcal{G}(\epsilon)\chi(\mathbf{p}_1)\varphi(p_1)+O(\rho^2), \quad (3.32)$$

where

$$\mathcal{G}(\epsilon)=\epsilon^{-1}-\rho[\epsilon^{-2}\mathcal{L}+\epsilon^{-1}t_1]+\rho^2(\epsilon^{-3}t_{21}+\epsilon^{-2}t_{22}-\epsilon^{-2}t^r). \quad (3.33)$$

In this form, we cannot take the limit $\epsilon\to 0+$. However, as in the case of the self-diffusion coefficient,[6] if we make a density expansion of $\mathcal{G}^{-1}(\epsilon)$ for finite ϵ, the resulting series has a well-defined limit as $\epsilon\to 0+$.

Expansion of $\mathcal{G}^{-1}(\epsilon)$ in a power series in ρ for a fixed finite ϵ yields

$$\mathcal{G}^{-1}(\epsilon)=\epsilon+\rho\mathcal{L}+\rho^2[-t_{22}+(\mathcal{L}t_1+t_1\mathcal{L})+t^r+\epsilon^{-1}(\mathcal{L}^2-t_{21})]+\epsilon(\rho t_1+\rho^2 t_1^2)+\cdots. \quad (3.34)$$

In the limit as $\epsilon\to 0+$,[15]

$$\mathcal{G}_+^{-1}\equiv\lim_{\epsilon\to 0+}\mathcal{G}^{-1}(\epsilon)=\lim_{\epsilon\to 0+}\rho[\mathcal{L}+\rho(t_1\mathcal{L}+t^r+R_1+R_2)], \quad (3.35)$$

[14] We sometimes write $(\mathbf{k}^N|O|\mathbf{k}'^N)$ instead of $O(\mathbf{k}^N|\mathbf{k}'^N)$.

[15] We attach the subscript $+$ to the symbols of those operators for which the limit $\epsilon\to 0+$ is already taken.

where

$$R_1 \equiv \epsilon^{-1}(\mathcal{L}^2 - t_{21}) \qquad (3.36)$$

and

$$R_2 \equiv \mathcal{L} t_1 - t_{22}. \qquad (3.37)$$

With this result and (3.32), we have

$$\eta_{KK} \equiv \lim_{\epsilon \to 0+} \eta_{KK}(\epsilon)$$
$$= \frac{1}{KT} \int d\mathbf{p}_1 \chi(\mathbf{p}_1)^2 W_{KK}(p_1) \varphi(p_1), \qquad (3.38)$$

where the function $W_{KK}(p_1)$ satisfies the equation

$$\rho^{-1} \mathcal{G}_+^{-1} [W_{KK}(p_1) \chi(\mathbf{p}_1) \varphi(p_1)] = \chi(\mathbf{p}_1) \varphi(p_1). \qquad (3.39)$$

Substitution of the expansion

$$W_{KK}(p_1) = W^{(0)}(p_1) + \rho W_{KK}^{(1)}(p_1) + \cdots \qquad (3.40)$$

into Eq. (3.39), use of (3.35) and collecting coefficients of powers of ρ yields the equations

$$\mathcal{L}_+ W^{(0)}(p_1) \chi(\mathbf{p}_1) \varphi(p_1) = \chi(\mathbf{p}_1) \varphi(p_1), \qquad (3.41)$$

$$\mathcal{L}_+ W_{KK}^{(1)}(p_1) \chi(\mathbf{p}_1) \varphi(p_1)$$
$$= -t_{1+} \chi(\mathbf{p}_1) \varphi(p_1)$$
$$- (t^r + R_1 + R_2)_+ W^{(0)}(p_1) \chi(\mathbf{p}_1) \varphi(p_1), \qquad (3.42)$$

where we have used (3.41) in obtaining the first term in (3.42). Equation (3.41) determines $W^{(0)}(p_1)$, and Eq. (3.42) determines $W_{KK}^{(1)}(p_1)$. We demonstrate in Appendix I that

$$(R_1 + R_2) W^{(0)}(p_1) \chi(\mathbf{p}_1) \varphi(p_1) = 0 \qquad (3.43)$$

and thus (3.42) becomes

$$\mathcal{L}_+ W_{KK}^{(1)}(p_1) \chi(\mathbf{p}_1) \varphi(p_1)$$
$$= -t_{1+} \chi(\mathbf{p}_1) \varphi(p_1) - t_+^r W^{(0)}(p_1) \chi(\mathbf{p}_1) \varphi(p_1). \qquad (3.44)$$

The equations determining $W^{(0)}$ and $W_{KK}^{(1)}$ are thus well defined in the limit as $\epsilon \to 0+$.

Using these results, we obtain the following density expansion for η_{KK}

$$\eta_{KK} = \eta^{(0)} + \rho \eta_{KK}^{(1)}, \qquad (3.45)$$

where

$$\eta^{(0)} = \frac{1}{KT} \int d\mathbf{p}_1 \chi(\mathbf{p}_1)^2 W^{(0)}(p_1) \varphi(p_1) \qquad (3.46)$$

and

$$\eta_{KK}^{(1)} = \frac{1}{KT} \int d\mathbf{p}_1 \chi(\mathbf{p}_1)^2 W_{KK}^{(1)}(p_1) \varphi(p_1). \qquad (3.47)$$

Equation (3.46) is the Enskog-Chapman result. Equation (3.47) represents the first density correction to the Enskog-Chapman result due to the kinetic parts of the dynamical fluxes.

IV. CALCULATION OF η_{KU}

Using the Fourier transform of $\psi(\mathbf{r})$, (2.7),

$$\psi(\mathbf{k}) = \int \psi(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}. \qquad (4.1)$$

$\eta_{KU}(\epsilon)$ can be expressed from (2.17) and (2.19) as

$$\eta_{KU}(\epsilon) = (VKT)^{-1} V^{-N} \sum_{\mathbf{k}^N} P^*(\mathbf{k}^N) V^{-1} \sum_{\mathbf{q}} \psi(\mathbf{q}) \int\int d\mathbf{p}^N d\mathbf{r}^N \sum_i \sum_{j<l} \chi(\mathbf{p}_i) G(\epsilon) e^{-i\mathbf{q}\cdot\mathbf{r}_{jl}} e^{i\mathbf{k}^N\cdot\mathbf{r}^N} \prod_{m=1}^{N} \varphi(p_m). \qquad (4.2)$$

By making use of the identity of particles, we can express (4.2) as

$$\eta_{KU}(\epsilon) = \rho (KT)^{-1} \sum_{\mathbf{k}^N} P^*(\mathbf{k}^N) \frac{N-1}{V} \sum_{\mathbf{q}} \psi(\mathbf{q}) \int d\mathbf{p}^N \chi(\mathbf{p}_1) [G(0|\mathbf{k}_1 - \mathbf{q}, \mathbf{k}_2 + \mathbf{q}, \mathbf{k}^{N-2})$$
$$+ \tfrac{1}{2}(N-2) G(0|\mathbf{k}_1, \mathbf{k}_2 - \mathbf{q}, \mathbf{k}_3 + \mathbf{q}, \mathbf{k}^{N-3})] \prod_{m=1}^{N} \varphi(p_m), \qquad (4.3)$$

where we have used (3.2). The binary collision expansion of G, (2.20) and (3.5) yields a series for $\eta_{KU}(\epsilon)$ similar to (3.9) for $\eta_{KK}(\epsilon)$, in the form

$$\eta_{KU}(\epsilon) = \eta_{KU}^0(\epsilon) + \eta_{KU}^1(\epsilon) + \eta_{KU}^2(\epsilon) + \cdots. \qquad (4.4)$$

The first term is given by

$$\eta_{KU}^0(\epsilon) = \epsilon^{-1} \rho^2 (KT)^{-1} \sum_{\mathbf{q}} P^*(\mathbf{q}, -\mathbf{q}) \psi(\mathbf{q}) \frac{N}{2} \int d\mathbf{p}_1 \chi(\mathbf{p}_1) \varphi(p_1) = 0. \qquad (4.5)$$

Equation (4.5) vanishes since the integration over $\mathbf{p}_1$ vanishes. In the following, we shall omit terms of relative order N^{-1}.

In obtaining an expression for $\eta_{KU}^1(\epsilon)$, we note that T_α must involve particle 1, since otherwise the term involves

$\int \chi(\mathbf{p}_1)\varphi(p_1)d\mathbf{p}_1$ which vanishes. Thus,

$$\eta_{KU}{}^1(\epsilon)=-\epsilon^{-1}\rho^2(KT)^{-1}\sum_{\mathbf{q}}{}'\psi(\mathbf{q})\sum_{\mathbf{k}_1}\int d\mathbf{p}^N\chi(\mathbf{p}_1)\{P^*(\mathbf{k}_1,-\mathbf{k}_1)T_{12}(0|\mathbf{k}_1-\mathbf{q},\mathbf{q}-\mathbf{k}_1,0)$$
$$\times g(\mathbf{k}_1-\mathbf{q},\mathbf{q}-\mathbf{k}_1,0)+(N-2)P^*(\mathbf{k}_1,-\mathbf{q},\mathbf{q}-\mathbf{k}_1)T_{13}(0|\mathbf{k}_1-\mathbf{q},0,\mathbf{q}-\mathbf{k}_1)g(\mathbf{k}_1-\mathbf{q},0,\mathbf{q}-\mathbf{k}_1)$$
$$+2^{-1}(N-2)P^*(\mathbf{k}_1,\mathbf{q}-\mathbf{k}_1,-\mathbf{q})T_{12}(0|\mathbf{k}_1,-\mathbf{k}_1,0)g(\mathbf{k}_1,-\mathbf{k}_1,0)$$
$$+2^{-1}(N-2)P^*(\mathbf{k}_1,\mathbf{q},-\mathbf{q}-\mathbf{k}_1)T_{13}(0|\mathbf{k}_1,0,-\mathbf{k}_1)g(\mathbf{k}_1,0,-\mathbf{k}_1)\}\prod_{i=1}^{N}\varphi(p_i),\quad(4.6)$$

where the summation over $\mathbf{q}$ excludes $\mathbf{q}=0$ because $\int\psi(\mathbf{r})d\mathbf{r}=0$ by symmetry. In (4.6) we have dropped the terms which involve four particles since these terms have a factor $N(N-1)(N-2)(N-3)$ and are of the order of ρ^4; later we shall find that we need at most terms of order ρ^3 for the first density correction to the viscosity. More detailed investigation shows that the only nonvanishing term involving four particles has a factor $\epsilon^{-1}\rho^4$.

If we use (3.19) and the formula,[6]

$$P(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)=\Delta(\mathbf{k}_1)\Delta(\mathbf{k}_2)\Delta(\mathbf{k}_3)+V^{-1}[\Delta(\mathbf{k}_1+\mathbf{k}_2)\Delta(\mathbf{k}_3)f^{(2)}(\mathbf{k}_2)+\Delta(\mathbf{k}_2+\mathbf{k}_3)\Delta(\mathbf{k}_1)f^{(2)}(\mathbf{k}_3)$$
$$+\Delta(\mathbf{k}_3+\mathbf{k}_1)\Delta(\mathbf{k}_2)f^{(2)}(\mathbf{k}_1)]+V^{-2}\Delta(\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3)f^{(3)}(\mathbf{k}_2,\mathbf{k}_3),\quad(4.7)$$

where

$$f^{(2)}(\mathbf{k}_2,\mathbf{k}_3)\equiv\int\int d\mathbf{r}_2d\mathbf{r}_3e^{i\mathbf{k}_2\cdot\mathbf{r}_{12}+i\mathbf{k}_3\cdot\mathbf{r}_{13}}F(\mathbf{r}_{12},\mathbf{r}_{13})\quad(4.8)$$

with $F(\mathbf{r}_{12},\mathbf{r}_{13})$ the cluster function of three particles which is defined by

$$F(\mathbf{r}_{12},\mathbf{r}_{13})\equiv V^3\int\cdots\int d\mathbf{r}_4\cdots d\mathbf{r}_N\rho(\mathbf{r}^N)-F(\mathbf{r}_{12})-F(\mathbf{r}_{23})-F(\mathbf{r}_{31})-1.$$

Equation (4.6) reduces to

$$\eta_{KU}{}^1(\epsilon)=-\epsilon^{-1}\rho^2(KT)^{-1}\sum_{\mathbf{q}}\psi(\mathbf{q})\int\int d\mathbf{p}_1d\mathbf{p}_2\chi(\mathbf{p}_1)\{T_{12}(0|-\mathbf{q},\mathbf{q})g(-\mathbf{q},\mathbf{q})$$
$$+V^{-1}\sum_{\mathbf{k}}f^{(2)*}(\mathbf{k})T_{12}(0|\mathbf{k}-\mathbf{q},\mathbf{q}-\mathbf{k})g(\mathbf{k}-\mathbf{q},\mathbf{q}-\mathbf{k})\}\varphi(p_1)\varphi(p_2)-\epsilon^{-2}\rho^3(KT)^{-1}\sum_{\mathbf{q}}\psi(\mathbf{q})f^{(2)*}(\mathbf{q})$$
$$\times\int\int\int d\mathbf{p}_1d\mathbf{p}_2d\mathbf{p}_3\chi(\mathbf{p}_1)\{T_{13}(0|0)+2^{-1}T_{12}(0|0)+2^{-1}T_{13}(0|0)\}\prod_{i=1}^{3}\varphi(p_i)+O(\epsilon^{-1}\rho^3).\quad(4.9)$$

The term of order $\epsilon^{-2}\rho^3$ vanishes since $\sum_{\mathbf{q}}\psi(\mathbf{q})f^{(2)*}(\mathbf{q})=0$ by symmetry. The result can be written in a more concise manner in the low-density limit where we replace $F(\mathbf{r}_{12})$ by an Ursell-Mayer function, (3.21). In this case (4.9) becomes

$$\eta_{KU}{}^1(\epsilon)=-\epsilon^{-1}\frac{\rho^2}{KT}\int\int d\mathbf{p}_1d\mathbf{p}_2\chi(\mathbf{p}_1)(0|VT_{12}G_0\exp\{-u(\mathbf{r}_{12})/KT\}\psi(\mathbf{r}_{12})|0)\varphi(p_1)\varphi(p_2).\quad(4.10)$$

A similar but more lengthy analysis yields for $\eta_{KU}{}^2(\epsilon)$ (see Appendix II),

$$\eta_{KU}{}^2=\epsilon^{-2}\rho^3\frac{1}{KT}\int\int\int\chi(\mathbf{p}_1)VT_{13}(0|0)(1+\mathcal{P}_{13})(0|VT_{12}G_0\exp\{-u(\mathbf{r}_{12})/KT\}\psi(\mathbf{r}_{12})|0)\prod_{i=1}^{3}\varphi(p_i)d\mathbf{p}_i.\quad(4.11)$$

If we now extend the meaning of the operator $\mathcal{L}$ defined in (3.23) in such a way that for any operator $J(\mathbf{p}_1)$ acting on a function of $\mathbf{p}_1$ we define

$$\mathcal{L}(\mathbf{p}_1)J(\mathbf{p}_1)\varphi(p_1)=\int d\mathbf{p}_2VT_{12}(0|0)[J(\mathbf{p}_1)+J(\mathbf{p}_2)]\varphi(p_1)\varphi(p_2),\quad(4.12)$$

then we may rewrite (4.11) as

$$\eta_{KU}{}^2(\epsilon)=\epsilon^{-2}\frac{\rho^3}{KT}\int\int\chi(\mathbf{p}_1)\mathcal{L}(\mathbf{p}_1)(0|VT_{12}G_0\exp\{-u(\mathbf{r}_{12})/KT\}\psi(\mathbf{r}_{12})|0)\varphi(p_1)\varphi(p_2)d\mathbf{p}_1d\mathbf{p}_2.\quad(4.13)$$

Thus, adding together (4.5), (4.10), and (4.13), we find

$$\eta_{KU}(\epsilon)=-\frac{\rho^2}{KT}\int\int d\mathbf{p}_1 d\mathbf{p}_2 \chi(\mathbf{p}_1)\{\epsilon^{-1}-\epsilon^{-2}\rho\mathcal{L}(\mathbf{p}_1)\}(0|VT_{12}G_0\exp\{-u(\mathbf{r}_{12})/KT\}\psi(\mathbf{r}_{12})|0)\varphi(p_1)\varphi(p_2). \quad (4.14)$$

As in Sec. III, the operator in the curly bracket in (4.14) is singular at $\epsilon\to 0+$, but its inverse has a well-defined limit as $\epsilon\to 0+$; that is,

$$\{\epsilon^{-1}-\epsilon^{-2}\rho\mathcal{L}\}^{-1}=\epsilon+\rho\mathcal{L}+\cdots\to\rho\mathcal{L}_+ \quad \text{as} \quad \epsilon\to 0+. \quad (4.15)$$

Therefore, we finally obtain,

$$\eta_{KU}=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)^2 W_{KU}(p_1)\varphi(p_1), \quad (4.16)$$

where the function $W_{KU}(p_1)$ satisfied the equation,

$$\mathcal{L}_+(\mathbf{p}_1)W_{KU}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)=-\int d\mathbf{p}_2(0|VT_{12}G_0\exp\{-u(\mathbf{r}_{12})/KT\}\psi(\mathbf{r}_{12})|0)_+\varphi(p_1)\varphi(p_2). \quad (4.17)$$

V. CALCULATION OF η_{UK} AND η_{UU}

The simplest way of obtaining η_{UK} is to utilize the fact that for classical systems η_{UK} is equal to η_{KU}, which can be proved by making use of the properties of the dynamical flux and the Hamiltonian under time-reversal. However, to obtain an expression for η_{UK} which is more convenient in comparing with the result of the generalized Boltzmann equation, we shall calculate η_{UK} directly from its definition (2.19).

More explicitly, we can express $\eta_{UK}(\epsilon)$ as

$$\eta_{UK}(\epsilon)=\rho^2(KT)^{-1}\sum_{\mathbf{q}}\sum_{\mathbf{k}^N}P^*(\mathbf{k}^N)\psi(\mathbf{q})\int d\mathbf{p}^N G(\mathbf{q},-\mathbf{q}|\mathbf{k}^N)\left(1+\frac{N-2}{2}\mathcal{P}_{13}\right)\chi(\mathbf{p}_1)\prod_{i=1}^{N}\varphi(p_i), \quad (5.1)$$

where we have used (4.1) and (3.2). As in the preceding sections, use of the binary collision expansion formula for G, (2.20), yields a series expansion for $\eta_{UK}(\epsilon)$ in the form

$$\eta_{UK}(\epsilon)=\eta_{UK}{}^0(\epsilon)+\eta_{UK}{}^1(\epsilon)+\eta_{UK}{}^2(\epsilon)+\cdots. \quad (5.2)$$

The first term is given by

$$\eta_{UK}{}^0(\epsilon)=\rho^2(KT)^{-1}\sum_{\mathbf{q}}{}' P^*(\mathbf{q},-\mathbf{q})\psi(\mathbf{q})\int\int d\mathbf{p}_1 d\mathbf{p}_2 g(\mathbf{q},-\mathbf{q})\chi(\mathbf{p}_1)\varphi(p_1)\varphi(p_2). \quad (5.3)$$

This is finite at $\epsilon=0+$, and is omitted here since it is of order ρ^2. The second term is

$$\eta_{UK}{}^1(\epsilon)=-\rho^2(KT)^{-1}\sum_{\mathbf{q}}{}'\sum_{\mathbf{k}^N}P^*(\mathbf{k}^N)\psi(\mathbf{q})\int d\mathbf{p}^N g(\mathbf{q},-\mathbf{q})(\mathbf{q},-\mathbf{q}|\{T_{12}(1+\tfrac{1}{2}(N-2)\mathcal{P}_{13})$$
$$+(N-2)(T_{13}+T_{23})(1+2^{-1}\mathcal{P}_{13})\}|\mathbf{k}^N)g(\mathbf{k}^N)\chi(\mathbf{p}_1)\prod_{i=1}^{N}\varphi(p_i). \quad (5.4)$$

The only terms in (5.4) which contribute to the first density correction are those with a factor ϵ^{-1} for which we must have $\mathbf{k}^N=0$. Therefore, only the term involving T_{12} contributes and we obtain, noting that $\int d\mathbf{p}\chi(\mathbf{p})\varphi(p)=0$,

$$\eta_{UK}{}^1(\epsilon)=-\epsilon^{-1}\rho^2(KT)^{-1}\sum_{\mathbf{q}}{}'\psi(\mathbf{q})\int g(\mathbf{q},-\mathbf{q})T_{12}(\mathbf{q},-\mathbf{q}|0)\chi(\mathbf{p}_1)\varphi(p_1)\varphi(p_2)d\mathbf{p}_1 d\mathbf{p}_2+O(\epsilon^0\rho^2). \quad (5.5)$$

A similar but more involved analysis gives for $\eta_{UK}{}^2(\epsilon)$ (see Appendix III),

$$\eta_{UK}{}^2(\epsilon)=\epsilon^{-2}\rho^3(KT)^{-1}\sum_{\mathbf{q}}{}'\psi(\mathbf{q})\int g(\mathbf{q},-\mathbf{q})T_{12}(\mathbf{q},-\mathbf{q}|0)\mathcal{L}(\mathbf{p}_1)\chi(\mathbf{p}_1)\varphi(p_1)\varphi(p_2)+O(\epsilon^{-1}\rho^3), \quad (5.6)$$

where we have used (3.23).

Adding (5.3), (5.5), and (5.6) together, we find

$$\eta_{UK}(\epsilon)=-\rho^2(KT)^{-1}\sum_{\mathbf{q}}{}'\psi(\mathbf{q})\int g(\mathbf{q},-\mathbf{q})T_{12}(\mathbf{q},-\mathbf{q}|0)\{\epsilon^{-1}-\epsilon^{-2}\rho\mathcal{L}(\mathbf{p}_1)\}\chi(\mathbf{p}_1)\varphi(p_1)\varphi(p_2)d\mathbf{p}_1d\mathbf{p}_2. \tag{5.7}$$

The operator in the curly bracket is the same as that in (4.14). We again take its inverse, consider the limit as $\epsilon\rightarrow 0+$ and make use of (3.41) to obtain in the limit $\epsilon\rightarrow 0+$

$$\eta_{UK}=-\rho(KT)^{-1}\sum_{\mathbf{q}}{}'\psi(\mathbf{q})\int g(\mathbf{q},-\mathbf{q})T_{12+}(\mathbf{q},-\mathbf{q}|0)W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)\varphi(p_2)d\mathbf{p}_1d\mathbf{p}_2. \tag{5.8}$$

We now turn to η_{UU}, which can be written as

$$\eta_{UU}(\epsilon)=2^{-1}\rho^2(KT)^{-1}V\langle\psi(\mathbf{r}_{12})G\sum_{j<l}\psi(\mathbf{r}_{jl})\rangle. \tag{5.9}$$

If we use (2.17), (3.2), and the Fourier transform of $\psi(\mathbf{r}_{12})$, (4.1), this becomes

$$\eta_{UU}(\epsilon)=2^{-1}\rho^2(VKT)^{-1}\sum_{\mathbf{k}^N}P^*(\mathbf{k}^N)\sum_{\mathbf{q}}{}'\sum_{\mathbf{q}'}{}'\sum_{j<l}\psi(\mathbf{q})\psi^*(\mathbf{q}')\int d\mathbf{p}^N(\mathbf{q},-\mathbf{q}|G|\mathbf{k}_j+\mathbf{q}',\mathbf{k}_l-\mathbf{q}',\mathbf{k}^{N-2})\prod_{i=1}^{N}\varphi(p_i). \tag{5.10}$$

As before, corresponding to the binary collision expansion of G, (2.20), we obtain a series for $\eta_{UU}(\epsilon)$:

$$\eta_{UU}(\epsilon)=\eta_{UU}^0(\epsilon)+\eta_{UU}^1(\epsilon)+\eta_{UU}^2(\epsilon)+\cdots. \tag{5.11}$$

Because $\mathbf{q},\mathbf{q}'\neq 0$, $\eta_{UU}^0(\epsilon)$ has no singularity at $\epsilon=0+$. The term having a factor ϵ^{-1} in $\eta_{UU}^1(\epsilon)$ vanishes because it involves $\sum_{\mathbf{q}'}P(-\mathbf{q}',\mathbf{q}')\psi^*(\mathbf{q}')$. Thus the terms singular in ϵ appear only at higher powers in ρ, and we cannot expect η_{UU} to contribute to the first density correction to viscosity. Therefore we shall neglect this term.

VI. FIRST DENSITY CORRECTION TO THE VISCOSITY

Collecting together the results of the preceding sections, (3.45), (3.46), (3.47), (4.16), (4.17), and (5.8), we obtain the following results for the shear viscosity:

$$\eta=\eta^{(0)}+\rho\eta^{(1)}, \tag{6.1}$$

where $\eta^{(0)}$ is the Chapman-Enskog result given by (3.46) and $\rho\eta^{(1)}$ is the first density correction, which is expressed as follows:

$$\eta^{(1)}=\frac{1}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)^2W^{(1)}(p_1)\varphi(p_1)+\eta_{ct}, \tag{6.2}$$

where ct stands for collision transfer and η_{ct} is given by (5.8), or

$$\eta_{ct}=-\frac{\rho}{KT}\int\int d\mathbf{p}_1d\mathbf{p}_2(0|\psi(\mathbf{r}_{12})G_0VT_{12}|0)_+ \times W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)\varphi(p_2) \tag{6.3}$$

and the function $W^{(1)}(p_1)=W_{KK}^{(1)}(p_1)+W_{KU}(p_1)$ satisfies the equation,

$$\mathcal{L}_+(\mathbf{p}_1)W^{(1)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1) =-t_+^r(\mathbf{p}_1)W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)-\mathfrak{M}(\mathbf{p}_1), \tag{6.4}$$

where

$$\mathfrak{M}(\mathbf{p}_1)\equiv t_{1+}(\mathbf{p}_1)\chi(\mathbf{p}_1)\varphi(p_1)+\int d\mathbf{p}_2(0|VT_{12}G_0 \times\exp\{-u(\mathbf{r}_{12})/KT\}\psi(\mathbf{r}_{12})|0)_+ \times\varphi(p_1)\varphi(p_2). \tag{6.5}$$

In the following, we shall compare our results with those of Choh and Uhlenbeck. For this purpose it is convenient to express our results in terms of resolvent operators.

First, as we show in Appendix IV by straightforward algebra, $t^r(\mathbf{p}_1)$ can be transformed into

$$t_+^r(\mathbf{p}_1)=-\int\int d\mathbf{x}_2d\mathbf{x}_3\theta_{12}\{G_3(123)G_0^{-1} -G_2(12)G_0^{-1}G_2(13)G_0^{-1}-G_2(12)G_0^{-1}G_2(23)G_0^{-1} +G_2(12)G_0^{-1}\}_+(1+\mathcal{P}_{12}+\mathcal{P}_{13})\varphi(p_2)\varphi(p_3), \tag{6.6}$$

where $d\mathbf{x}_i=d\mathbf{p}_id\mathbf{r}_i$ and $G_3(123)$ is the resolvent operator for the system in which only particles 1, 2, and 3 interact with each other, namely,

$$G_3(123)=[\epsilon+iL_3(123)]^{-1} \tag{6.7}$$

with

$$L_3(123)=L_0+i(\theta_{12}+\theta_{23}+\theta_{31}). \tag{6.8}$$

Next, we consider (6.3). Use of (2.25) and the fact that

$$\int\psi(\mathbf{r}_{12})d\mathbf{r}_{12}=0$$

transforms (6.3) into

$$\eta_{ct}=\frac{\rho}{KT}\int d\mathbf{r}_{12}\psi(\mathbf{r}_{12})Z_{xy}(\mathbf{r}_{12}), \qquad (6.9)$$

where $Z_{xy}(\mathbf{r}_{12})$ is the xy component of the traceless symmetric tensor function of the 2nd rank $Z_{\kappa\sigma}(\mathbf{r}_{12})$ defined by

$$Z_{\kappa\sigma}(\mathbf{r}_{12})\equiv\int\int d\mathbf{p}_1d\mathbf{p}_2G_2(12)G_0^{-1}W^{(0)}(p_1)\times\chi_{\kappa\sigma}(\mathbf{p}_1)\varphi(p_1)\varphi(p_2), \quad (\kappa,\sigma=x,y,z) \qquad (6.10)$$

with

$$\chi_{\kappa\sigma}(\mathbf{p})\equiv(p^\kappa p^\sigma-3^{-1}\delta_{\kappa\sigma}p^2)/m. \qquad (6.11)$$

Because of the tensor property of $Z_{\kappa\sigma}(\mathbf{r}_{12})$, it has the form

$$Z_{\kappa\sigma}(\mathbf{r})=(r^\kappa r^\sigma-3^{-1}\delta_{\kappa\sigma}r^2)z(r), \qquad (6.12)$$

where $z(r)$ is a function of $r=|\mathbf{r}|$. From the definition of $\psi(\mathbf{r})$, (2.7), we get

$$\psi(\mathbf{r})=-r^xr^yu'(r)/r, \qquad (6.13)$$

where $u'(r)$ is the derivative of $u(r)$ with respect to r. Thus, if we note that

$$\int(r^xr^y)^2d\Omega=\frac{1}{10}\int\sum_{\kappa,\sigma}^{x,y,z}r^\kappa r^\sigma(r^\kappa r^\sigma-3^{-1}\delta_{\kappa\sigma}r^2)d\Omega, \qquad (6.14)$$

where the integral is over the directions of $\mathbf{r}$, (6.9) becomes

$$\eta_{ct}=-\frac{1}{10}\frac{\rho}{KT}\sum_{\kappa,\sigma}^{x,y,z}\int d\mathbf{r}_{12}r_{12}^\sigma\frac{\partial u(\mathbf{r}_{12})}{\partial r_{12}^\kappa}Z_{\kappa\sigma}(\mathbf{r}_{12})$$

$$=-\frac{1}{10}\frac{\rho}{KT}\sum_{\kappa,\sigma}^{x,y,z}\int d\mathbf{r}_{12}\int\int d\mathbf{p}_1d\mathbf{p}_2\frac{\partial u(\mathbf{r}_{12})}{\partial r_{12}^\kappa}\frac{r_{12}^\sigma}{2}[G_2(12)G_0^{-1}]_+\sum_{i=1}^{2}W^{(0)}(p_i)\chi_{\kappa\sigma}(\mathbf{p}_i)\varphi(p_1)\varphi(p_2). \qquad (6.15)$$

Now we turn to (6.5). Using (3.24) for $t_1(\mathbf{p}_1)$ and replacing $T_{12}G_0$ by $-\theta_{12}G_2(12)$ according to (2.26), we get

$$\mathfrak{M}(\mathbf{p}_1)=-\int\theta_{12}G_{2+}[\{\chi(\mathbf{p}_1)+\chi(\mathbf{p}_2)\}F_0(\mathbf{r}_{12})+\psi(\mathbf{r}_{12})\exp\{-u(\mathbf{r}_{12})/KT\}]\times\varphi(p_1)\varphi(p_2)d\mathbf{x}_2. \qquad (6.16)$$

By adding the expression

$$\int d\mathbf{x}_2\theta_{12}(p_1^xr_1^y+p_2^xr_2^y)\times\exp\{-u(\mathbf{r}_{12})/KT\}\varphi(p_1)\varphi(p_2), \qquad (6.17)$$

which is easily seen to vanish to (6.16), and noting that

$$iL_2(12)(p_1^xr_1^y+p_2^xr_2^y)=\chi(\mathbf{p}_1)+\chi(\mathbf{p}_2)+\psi(\mathbf{r}_{12}), \qquad (6.18)$$

(6.16) becomes after some rearrangement,

$$\mathfrak{M}(\mathbf{p}_1)=-\int\theta_{12}[(G_2iL_2-1)(p_1^xr_1^y+p_2^xr_2^y)\times\exp\{-u(\mathbf{r}_{12})/KT\}-G_2\{\chi(\mathbf{p}_1)+\chi(\mathbf{p}_2)\}]_+\varphi(p_1)\varphi(p_2)d\mathbf{x}_2. \qquad (6.19)$$

Substitution of (2.23) in the form

$$G_2iL_2-1=-\epsilon G_2 \qquad (6.20)$$

into (6.19) results in

$$\mathfrak{M}(\mathbf{p}_1)=\int\theta_{12}[\lim_{\epsilon\to0+}\epsilon G_2(p_1^xr_1^y+p_2^xr_2^y)\times\exp\{-u(\mathbf{r}_{12})/KT\}+G_{2+}\{\chi(\mathbf{p}_1)+\chi(\mathbf{p}_2)\}]\varphi(p_1)\varphi(p_2)d\mathbf{x}_2. \qquad (6.21)$$

Finally, by using

$$iL_0(p_1^xr_1^y+p_2^xr_2^y)=\chi(\mathbf{p}_1)+\chi(\mathbf{p}_2) \qquad (6.22)$$

and (2.21) and by rearranging the terms, we transform (6.21) to

$$\mathfrak{M}(\mathbf{p}_1)=\int\theta_{12}[G_2G_0^{-1}(p_1^xr_1^y+p_2^xr_2^y)+\epsilon G_2(p_1^xr_1^y+p_2^xr_2^y)F_0(\mathbf{r}_{12})]_+\times\varphi(p_1)\varphi(p_2)d\mathbf{x}_2. \qquad (6.23)$$

Thus, the first density correction to the viscosity is obtained from (6.2), (6.4), (6.6), (6.15), and (6.23).

VII. COMPARISON WITH RESULTS OF CHOH AND UHLENBECK

The first density correction to the viscosity has previously been calculated by Choh and Uhlenbeck from the generalized Boltzmann equation of Bogolyubov.[2] Their results for the first density correction to the viscosity $\tilde{\eta}^{(1)}$ which corresponds to $\eta^{(1)}$ of (6.1) can be written

$$\tilde{\eta}^{(1)}=\frac{1}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)^2\tilde{W}^{(1)}(p_1)\varphi(p_1)+\tilde{\eta}_{ct}, \qquad (7.1)$$

where

$$\tilde{\eta}_{ct}=-\frac{\rho}{KT}\int d\mathbf{r}_{12}\int\int d\mathbf{p}_1 d\mathbf{p}_2 \sum_{\kappa,\sigma}^{x,y,z}\frac{\partial u(\mathbf{r}_{12})}{\partial r_{12}{}^{\kappa}}\frac{r_{12}{}^{\sigma}}{2}\mathcal{S}(12)$$

$$\times\sum_{i=1}^{2}W^{(0)}(p_i)\frac{\chi_{\kappa\sigma}(\mathbf{p}_i)}{KT}\varphi(p_1)\varphi(p_2) \quad (7.2)$$

and $\tilde{W}^{(1)}(p_1)$ satisfies the equation

$$\mathcal{L}_+(\mathbf{p}_1)\tilde{W}^{(1)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)$$

$$=-2^{-1}\beta_1\chi(\mathbf{p}_1)\varphi(p_1)-\int\int d\mathbf{r}_2 d\mathbf{p}_2\theta_{12}\mathcal{S}(12)$$

$$\times\frac{r_{12}{}^{x}}{2}(p_1{}^{y}-p_2{}^{y})\varphi(p_1)\varphi(p_2)$$

$$-\tilde{t}^r(\mathbf{p}_1)W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1), \quad (7.3)$$

where

$$\mathcal{S}(12)\equiv\lim_{t\to\infty}S_{-t}{}^{(2)}(12)S_t{}^{(0)} \quad (7.4)$$

with $S_{-t}{}^{(2)}(12)$ and $S_t{}^{(0)}$ the streaming operators defined by

$$S_{-t}{}^{(2)}(12)\equiv e^{-itL_2(12)}, \quad S_t{}^{(0)}\equiv e^{itL_0} \quad (7.5)$$

and

$$\beta_1\equiv\int F_0(\mathbf{r}_{12})d\mathbf{r}_{12}. \quad (7.6)$$

Here $\tilde{t}^r(\mathbf{p}_1)$ is Bogolyubov's triple collision operator defined by

$$\tilde{t}^r(\mathbf{p}_1)=-\int\int d\mathbf{x}_2 d\mathbf{x}_3\theta_{12}\int_0^\infty dt S_{-t}{}^{(2)}(12)\{(\theta_{13}+\theta_{23})\mathcal{S}(123)$$

$$-\mathcal{S}(12)[\theta_{13}\mathcal{S}(13)+\theta_{23}\mathcal{S}(23)]\}$$

$$\times(1+\mathcal{P}_{12}+\mathcal{P}_{13})\varphi(p_2)\varphi(p_3), \quad (7.7)$$

where $\mathcal{S}(123)$ is the analog of $\mathcal{S}(12)$ for the three particles 1, 2, and 3.

In order to compare these results with ours, it is necessary to clarify the relation between the resolvent operators and the streaming operators.

First we consider an operator of the following type, where G is the resolvent operator of the system with an arbitrary interaction

$$\epsilon G=\epsilon\int_0^\infty dt e^{-\epsilon t}S_{-t}, \quad S_{-t}\equiv e^{-itL}, \quad (7.8)$$

where L is the Liouville operator associated with G. When this operator acts on an arbitrary function the contribution to the time integral from a finite time vanishes in the limit $\epsilon\to 0+$, and a contribution arises only from the infinite past. This can be seen formally as follows:

$$\epsilon G=1-iLG=1-\int_0^\infty dt e^{-\epsilon t}iLS_{-t},$$

$$=1+\int_0^\infty dt e^{-\epsilon t}\frac{d}{dt}S_{-t}.$$

Therefore,

$$\lim_{\epsilon\to 0+}\epsilon G=1+\int_0^\infty dt\frac{d}{dt}S_{-t}=S_{-\infty}. \quad (7.9)$$

The equality in (7.9) is meant only in the weak sense; that is, when the operators $\lim_{\epsilon\to 0+}\epsilon G$ and $S_{-\infty}$ act on a suitable function the results are the same. Next we consider an operator of the type

$$GG_0{}^{-1}, \quad (7.10)$$

where G_0 is given by (2.21). When this operator operates on a function of momenta only, (7.10) reduces to ϵG. In general, at first one might argue that since (7.10) can be written as $\epsilon G\cdot(\epsilon G_0)^{-1}$, then

$$\lim_{\epsilon\to 0+}GG_0{}^{-1}=\mathcal{S}\equiv\lim_{t\to\infty}S_{-t}\cdot S_t{}^{(0)}. \quad (7.11)$$

However, a closer investigation shows that this is not always correct. As an example, we consider the operator $G_2G_0{}^{-1}$ that occurs in (6.23). Deferring the details to Appendix V, the result is that, for a repulsive interaction with a finite range,

$$\lim_{\epsilon\to 0+}G_2G_0{}^{-1}(p_1{}^{x}r_1{}^{y}+p_2{}^{x}r_2{}^{y})\varphi(p_1)\varphi(p_2)$$

$$=\mathcal{S}(12)(p_1{}^{x}r_1{}^{y}+p_2{}^{x}r_2{}^{y})\varphi(p_1)\varphi(p_2)$$

$$+\int_0^\infty dt(S_{-t}{}^{(2)}-S_{-\infty}{}^{(2)})$$

$$\times\{\chi(\mathbf{p}_1)+\chi(\mathbf{p}_2)\}\varphi(p_1)\varphi(p_2). \quad (7.12)$$

Thus, for repulsive interactions with a finite range, taking into account the fact that the second term of (6.23) vanishes, since $|\mathbf{r}_{12}|$ in $F_0(\mathbf{r}_{12})$ goes to infinity due to (7.9), we obtain

$$\mathfrak{M}(\mathbf{p}_1)=\tilde{\mathfrak{M}}(\mathbf{p}_1)+\Delta\mathfrak{M}(\mathbf{p}_1), \quad (7.13)$$

where

$$\tilde{\mathfrak{M}}(\mathbf{p}_1)\equiv\int\theta_{12}\mathcal{S}(12)(p_1{}^{x}r_1{}^{y}+p_2{}^{x}r_2{}^{y})\varphi(p_1)\varphi(p_2)d\mathbf{x}_2 \quad (7.14)$$

and

$$\Delta\mathfrak{M}(\mathbf{p}_1)\equiv\int d\mathbf{x}_2\theta_{12}\int_0^\infty dt(S_{-t}{}^{(2)}-S_{-\infty}{}^{(2)})$$

$$\times\{\chi(\mathbf{p}_1)+\chi(\mathbf{p}_2)\}\varphi(p_1)\varphi(p_2). \quad (7.15)$$

Equation (7.14) appears also in the theory of Choh and Uhlenbeck and can be transformed in the same manner as they do. If we rewrite (7.14) as

$$\tilde{\mathfrak{M}}(\mathbf{p}_1)=\int \theta_{12}\mathcal{S}(12)\frac{(p_1{}^x+p_2{}^x)(r_1{}^y+r_2{}^y)}{2}\times\varphi(p_1)\varphi(p_2)d\mathbf{x}_2+\int\theta_{12}\mathcal{S}(12)\times\frac{(p_1{}^x-p_2{}^x)r_{12}{}^y}{2}\varphi(p_1)\varphi(p_2)d\mathbf{x}_2; \quad (7.16)$$

the first term can be simplified by utilizing the fact that $\mathcal{S}(12)$ does not affect the center-of-mass motion, and becomes

$$\int\theta_{12}\frac{(p_1{}^x+p_2{}^x)(r_1{}^y+r_2{}^y)}{2}S_{-\infty}{}^{(2)}(12)\varphi(p_1)\varphi(p_2)d\mathbf{x}_2 \quad (7.17)$$

since $\mathcal{S}(12)$ reduces to $S_{-\infty}{}^{(2)}(12)$ when applied to a function of momenta only. Equation (7.17) can be reduced further by noting that the only contribution to the integral comes from configurations in which the particles are close together; thus $S_{-\infty}{}^{(2)}(12)$ brings the two particles far apart from each other in the infinite past and the kinetic energy in the infinite past must be equal to the total energy at the time zero. In other words,

$$S_{-\infty}{}^{(2)}\varphi(p_1)\varphi(p_2)=\exp\{-u(\mathbf{r}_{12})/KT\}\varphi(p_1)\varphi(p_2). \quad (7.18)$$

Thus, (7.17) becomes

$$\int\int\theta_{12}\exp\{-u(\mathbf{r}_{12})/KT\}\times\frac{(p_1{}^x+p_2{}^x)(r_1{}^y+r_2{}^y)}{2}\varphi(p_1)\varphi(p_2)d\mathbf{x}_2 \quad (7.19)$$

which reduces after integration by parts to[16]

$$2^{-1}\beta_1\chi(\mathbf{p}_1)\varphi(p_1), \quad (7.20)$$

where β_1 is given by (7.6). Therefore, $\tilde{\mathfrak{M}}(\mathbf{p}_1)$ becomes

$$\tilde{\mathfrak{M}}(\mathbf{p}_1)=2^{-1}\beta_1\chi(\mathbf{p}_1)\varphi(p_1)+\int\int\theta_{12}\mathcal{S}(12)(p_1{}^x-p_2{}^x)\times\frac{r_{12}{}^y}{2}\varphi(p_1)\varphi(p_2)d\mathbf{x}_2. \quad (7.21)$$

We are now in a position to make a detailed comparison between our result and that of Choh and Uhlenbeck. First, we note that $G_2G_0{}^{-1}$ in (6.15) and $\mathcal{S}(12)$ in (7.2) operate on a function of momenta only and also that there is a short-range factor $\partial u(\mathbf{r}_{12})/\partial r_{12}$ in the integrand. Thus $\mathcal{S}(12)$ reduces to $S_{-\infty}{}^{(2)}$ as does $\lim_{\epsilon\to 0+}G_2G_0{}^{-1}$. Therefore, the collision transfer terms η_{ct} and $\tilde{\eta}_{ct}$ become identical.

Next, turning to the equations (6.4) and (7.3) satisfied by $W^{(1)}(p_1)$ and $\tilde{W}^{(1)}(p_1)$, Eqs. (7.3), (7.13), (7.15), and (7.21) tell us that apart from the forms of the triple collision operators $t_+{}^r$ and $\tilde{t}^r$, the two theories differ by the operator represented by $\Delta\mathfrak{M}(\mathbf{p}_1)$, (7.15).

Finally, the forms of the triple collision operators $t_+{}^r$(6.6), and $\tilde{t}^r$, (7.7), have been investigated by using the relation between the resolvent operators and the streaming operators discussed before. Particular care has been taken in the limiting process $\epsilon\to 0+$, and a finite difference between the two forms has been found. Referring the details of the calculation to another publication,[17] we simply quote the result

$$\Delta t^r(\mathbf{p}_1)\equiv t_+{}^r(\mathbf{p}_1)-\tilde{t}^r(\mathbf{p}_1)=-\int\int d\mathbf{x}_2d\mathbf{x}_3\theta_{12}\int_0^\infty[S_{-t}{}^{(2)}(12)-S_{-\infty}{}^{(2)}(12)]dt\times(T_{13}+T_{23})_+(1+\mathcal{P}_{12}+\mathcal{P}_{13})\varphi(p_2)\varphi(p_3). \quad (7.22)$$

We now consider the effect of this operator on $W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)$. We note that because of the Boltzmann property of the operator $T_{ij}(0|0)$ [see e.g., (3.25)],

$$VT_{ij}(0|0)\varphi(p_i)\varphi(p_j)\to 0 \quad \text{as} \quad \epsilon\to 0+. \quad (7.23)$$

Then we obtain, after a slight rearrangement of terms,

$$\Delta t^r(\mathbf{p}_1)W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)=-\int d\mathbf{x}_2\theta_{12}\int_0^\infty dt[S_{-t}{}^{(2)}(12)-S_{-\infty}{}^{(2)}(12)]\times(1+\mathcal{P}_{12})\mathcal{L}_+(\mathbf{p}_1)W^{(0)}(p_1)\chi(\mathbf{p}_1)\prod_{i=1}^{3}\varphi(p_i). \quad (7.24)$$

Use of (3.41) finally yields

$$\Delta t^r(\mathbf{p}_1)W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)=-\int d\mathbf{x}_2\theta_{12}\int_0^\infty dt[S_{-t}{}^{(2)}(12)-S_{-\infty}{}^{(2)}(12)]\times[\chi(\mathbf{p}_1)+\chi(\mathbf{p}_1)]\varphi(p_1)\varphi(p_2). \quad (7.25)$$

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[16] $$(7.19)=-KT\int\int\frac{\partial F_0(\mathbf{r}_{12})}{\partial\mathbf{r}_{12}}\cdot\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_2}\right)\times\frac{(p_1{}^x+p_2{}^x)(r_1{}^y+r_2{}^y)}{2}\varphi(p_1)\varphi(p_2)d\mathbf{x}_2$$
$$=-KT\int\int F_0(\mathbf{r}_{12})\left(\frac{\partial}{\partial p_1{}^y}-\frac{\partial}{\partial p_2{}^y}\right)\times\frac{p_1{}^x+p_2{}^x}{2}\varphi(p_1)\varphi(p_2)d\mathbf{x}_2$$
$$=\frac{\beta_1}{m}\int\frac{p_1{}^x+p_2{}^x}{2}(p_1{}^y-p_2{}^y)\varphi(p_1)\varphi(p_2)d\mathbf{p}_2=\frac{\beta_1}{2}\chi(\mathbf{p}_1)\varphi(p_1).$$

[17] P. Résibois, Phys. Letters **9**, 139 (1964); K. Kawasaki and I. Oppenheim, Phys. Letters **11**, 124 (1964).

Comparing this result with the other difference between our theory and that of Choh and Uhlenbeck, $\Delta\mathfrak{M}(\mathbf{p}_1)$ given by (7.15), we find that

$$\Delta\mathfrak{M}(\mathbf{p}_1)+\Delta t^r(\mathbf{p}_1)W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)=0. \quad (7.26)$$

From (6.4) we conclude that $W^{(1)}(p_1)=\tilde{W}^{(1)}(p_1)$. Therefore, our result for the first density correction to the viscosity completely agrees with that of Choh and Uhlenbeck for repulsive forces, namely,

$$\tilde{\eta}^{(1)}=\eta^{(1)}. \quad (7.27)$$

VIII. CONCLUDING REMARKS

The correlation function expression for shear viscosity for dense gases has been treated by making use of binary collision expansion techniques and the first density correction to the viscosity has been obtained. Results are contained in (6.1), (6.2), (6.4), (6.6), (6.15), and (6.23). These results may be valid for attractive intermolecular forces in the absence of bound states as well as for repulsive forces.

For repulsive interactions with a finite range, (6.23) reduces to (7.13), (7.14), and (7.15). In this particular case, our result has been compared with that obtained from the generalized Boltzmann equation by Choh and Uhlenbeck (7.1), (7.2), and (7.3). Differences have been found in the form of the triple collision operator and in the term arising from spatial inhomogeneity in the Boltzmann binary collision operator. These differences are given by (7.22) and (7.15), respectively. However, these differences exactly cancel in the equation determining $W^{(1)}(p_1)$. Thus for repulsive interactions of finite range, the correlation function expression for the first density correction to the shear viscosity is identical to that of Choh and Uhlenbeck which is based on Bogolyubov's kinetic equation.

In the analysis of the present paper, we have restricted ourselves to the case of repulsive intermolecular forces of finite range. However, the correlation function method itself does not suffer from such a restriction. Thus, we intend to extend our analysis to systems with attractive intermolecular forces.

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APPENDIX I

Here, we shall show that the R_1 and R_2 terms in (3.42) cancel each other. Substitution of (3.23), (3.24), and (3.28) into (3.37) results in

$$R_2=-\int\int d\mathbf{p}_2 d\mathbf{p}_3 VT_{12}(0|0)(0|[VT_{13}G_0F_0(\mathbf{r}_{13})\mathcal{P}_{12} + VT_{23}G_0F_0(\mathbf{r}_{23})]|0)\varphi(p_2)\varphi(p_3). \quad (\mathrm{I1})$$

On the other hand, using (3.8), (3.23), (3.27), and (3.36), we obtain

$$R_1=-\int\int d\mathbf{p}_2 d\mathbf{p}_3 VT_{12}(0|0) \times(0|[VT_{13}\mathcal{P}_{12}+VT_{23}]G_0|0)\varphi(p_2)\varphi(p_3). \quad (\mathrm{I2})$$

Addition of (I1) and (I2) yields

$$R_1+R_2=-\int\int d\mathbf{p}_2 d\mathbf{p}_3 VT_{12}(0|0)(0|[VT_{13}G_0 \times\exp\{-u(\mathbf{r}_{13})/KT\}\mathcal{P}_{12}+VT_{23}G_0 \times\exp\{-u(\mathbf{r}_{23})/KT\}]|0)\varphi(p_2)\varphi(p_3). \quad (\mathrm{I3})$$

Thus, $(R_1+R_2)W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)$ involves expressions of the form,

$$(0|VT_{13}G_0\exp\{-u(\mathbf{r}_{13})/KT\}|0)\varphi(p_1)\varphi(p_3) \quad (\mathrm{I4})$$

and

$$(0|VT_{23}G_0\exp\{-u(\mathbf{r}_{23})/KT\}|0)\varphi(p_2)\varphi(p_3). \quad (\mathrm{I5})$$

Since these expressions have the same structure, we consider only the first one of them in detail. (I4) can be expressed as

$$-\int d\mathbf{r}_{13}\theta_{13}G_2(13)\exp\{-u(\mathbf{r}_{13})/KT\}\varphi(p_1)\varphi(p_3), \quad (\mathrm{I6})$$

where we have used (2.26). Because $L_2(13)$ applied to $(p_1^2+p_3^2)/2m+u(\mathbf{r}_{13})$ vanishes, (I6) reduces to

$$-\epsilon^{-1}\int d\mathbf{r}_{13}\theta_{13}\exp\{-u(\mathbf{r}_{13})/KT\}\varphi(p_1)\varphi(p_3). \quad (\mathrm{I7})$$

Using the definition of θ_α, (2.11), (I7) is further reduced to

$$\epsilon^{-1}KT\int d\mathbf{r}_{13}\frac{\partial F_0(\mathbf{r}_{13})}{\partial \mathbf{r}_{13}}\cdot\left(\frac{\partial}{\partial \mathbf{p}_1}-\frac{\partial}{\partial \mathbf{p}_3}\right)\varphi(p_1)\varphi(p_3). \quad (\mathrm{I8})$$

Equation (I8) vanishes. Thus (I4) and, by a similar argument, (I5) vanishes and

$$(R_1+R_2)W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1)=0 \quad (\mathrm{I9})$$

for finite ϵ as well as in the limit as $\epsilon\to 0+$.

APPENDIX II. DERIVATION OF (4.11)

Here we shall derive the expression given in (4.11) for $\eta_{KU}^2(\epsilon)$. Use of the binary collision expansion formula (2.20) for G in (4.3) yields

$$\eta_{KU}^2(\epsilon)=\epsilon^{-1}\rho^2(KT)^{-1}\sum_{\mathbf{k}^N}\sum P^*(\mathbf{k}^N)\psi(\mathbf{q})\int\chi(\mathbf{p}_1)\{(0|\sum_{\alpha,\beta}{}' T_\alpha G_0 T_\beta G_0|\mathbf{k}_1-\mathbf{q},\mathbf{k}_2+\mathbf{q},\mathbf{k}^{N-2})$$
$$+\tfrac{1}{2}(N-2)(0|\sum_{\alpha,\beta}{}' T_\alpha G_0 T_\beta G_0|\mathbf{k}_1,\mathbf{k}_2-\mathbf{q},\mathbf{k}_3+\mathbf{q},\mathbf{k}^{N-3})\}\prod_{i=1}^{N}\varphi(p_i)d\mathbf{p}_i. \quad \text{(II1)}$$

We shall restrict the summations over α and β to such pairs which are composed only of particles 1, 2, or 3, because those terms involving more than three particles contribute to higher powers in ρ (at least ρ^4). Furthermore, the pair α must involve particle 1. Thus, (II1) becomes

$$\eta_{KU}^2(\epsilon)=\epsilon^{-1}\rho^2(KT)^{-1}\sum_{\mathbf{k}_1\mathbf{k}_2\mathbf{k}_3}P^*(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3)\sum_{\mathbf{q}}\psi(\mathbf{q})\int\chi(\mathbf{p}_1)(N-2)$$
$$\times\{(0|[T_{12}G_0(T_{13}+T_{23})G_0+T_{13}G_0(T_{12}+T_{23})G_0]|\mathbf{k}_1-\mathbf{q},\mathbf{k}_2+\mathbf{q},\mathbf{k}_3)$$
$$+2^{-1}(0|[T_{12}G_0(T_{13}+T_{23})G_0+T_{13}G_0(T_{12}+T_{23})G_0]|\mathbf{k}_1,\mathbf{k}_2-\mathbf{q},\mathbf{k}_3+\mathbf{q})\}\prod_{i=1}^{3}\varphi(p_i)d\mathbf{p}_i. \quad \text{(II2)}$$

For our purpose it is only necessary to extract terms having a factor of at least ϵ^{-2} from (II2) [see (4.14) and (4.15)]. The terms having a factor ϵ^{-3} must have either $\mathbf{k}_1=\mathbf{q}$, $\mathbf{k}_2=-\mathbf{q}$ and $\mathbf{k}_3=0$ or $\mathbf{k}_1=0$, $\mathbf{k}_2=\mathbf{q}$ and $\mathbf{k}_3=-\mathbf{q}$. Both of these involve a factor $\sum_{\mathbf{q}}P^*(\mathbf{q},-\mathbf{q})\psi(\mathbf{q})$ and vanish by symmetry. For the same reason, the only non-vanishing terms having a factor of ϵ^{-2} are those for which the G_0 between the T operators yields a power of ϵ^{-1}. Thus we obtain

$$\eta_{KU}^2(\epsilon)=\epsilon^{-2}\rho^2(KT)^{-1}\sum_{\mathbf{k}}\sum_{\mathbf{q}}{}'\psi(\mathbf{q})(N-2)\int\chi(\mathbf{p}_1)\{P^*(\mathbf{k},-\mathbf{q},\mathbf{q}-\mathbf{k})T_{12}(0|0)T_{13}(0|\mathbf{k}-\mathbf{q},0,\mathbf{q}-\mathbf{k})$$
$$\times g(\mathbf{k}-\mathbf{q},0,\mathbf{q}-\mathbf{k})+P^*(\mathbf{q},-\mathbf{k},-\mathbf{q}+\mathbf{k})T_{12}(0|0)T_{23}(0|0,-\mathbf{k}+\mathbf{q},+\mathbf{k}-\mathbf{q})g(0,-\mathbf{k}+\mathbf{q},+\mathbf{k}-\mathbf{q})$$
$$+P^*(\mathbf{k},-\mathbf{k})T_{13}(0|0)T_{12}(0|\mathbf{k}-\mathbf{q},\mathbf{q}-\mathbf{k})g(\mathbf{k}-\mathbf{q},\mathbf{q}-\mathbf{k},0)+P^*(\mathbf{q},-\mathbf{k},-\mathbf{q}+\mathbf{k})T_{13}(0|0)$$
$$\times T_{23}(0|-\mathbf{k}+\mathbf{q},+\mathbf{k}-\mathbf{q})g(0,-\mathbf{k}+\mathbf{q},+\mathbf{k}-\mathbf{q})+2^{-1}P^*(-\mathbf{k},\mathbf{q},+\mathbf{k}-\mathbf{q})T_{12}(0|0)$$
$$\times T_{13}(0|-\mathbf{k},+\mathbf{k})g(-\mathbf{k},0,+\mathbf{k})+2^{-1}P^*(\mathbf{k},-\mathbf{k})T_{12}(0|0)T_{23}(0|\mathbf{k}-\mathbf{q},\mathbf{q}-\mathbf{k})g(0,\mathbf{k}-\mathbf{q},\mathbf{q}-\mathbf{k})$$
$$+2^{-1}P^*(\mathbf{k},\mathbf{q}-\mathbf{k},-\mathbf{q})T_{13}(0|0)T_{12}(0|\mathbf{k},-\mathbf{k})g(\mathbf{k},-\mathbf{k},0)$$
$$+2^{-1}P^*(\mathbf{k},-\mathbf{k})T_{13}(0|0)T_{23}(0|\mathbf{k}-\mathbf{q},\mathbf{q}-\mathbf{k})g(0,\mathbf{k}-\mathbf{q},\mathbf{q}-\mathbf{k})\}\prod_{i=1}^{3}\varphi(p_i)d\mathbf{p}_i. \quad \text{(II3)}$$

If we use (3.19) and (4.7), and note that the terms for which $g=\epsilon^{-1}$ vanish, we see that only the third, sixth, and eighth terms give finite contributions, other terms being of the order of $1/N$. Thus if we interchange the particle indices 2 and 3 in the sixth term and use the symmetry properties of the functions $\psi(\mathbf{q})$ and $f^{(2)}(\mathbf{k})$, (II3) reduces to (4.11) of the text.

APPENDIX III. DERIVATION OF (5.6)

$\eta_{UK}^2(\epsilon)$ can be written explicitly from (5.1) as

$$\eta_{UK}^2(\epsilon)=\rho^2(KT)^{-1}\sum_{\mathbf{q}}{}'\sum_{\mathbf{k}^N}P^*(\mathbf{k}^N)\psi(\mathbf{q})\int d\mathbf{p}^N g(\mathbf{q},-\mathbf{q})(\mathbf{q},-\mathbf{q}|\sum_{\alpha,\beta}{}' T_\alpha G_0 T_\beta|\mathbf{k}^N)g(\mathbf{k}^N)$$
$$\times[1+2^{-1}(N-2)\mathcal{P}_{13}]\chi(\mathbf{p}_1)\prod_{i=1}^{N}\varphi(p_i)d\mathbf{p}_i. \quad \text{(III1)}$$

We again restrict the summations over particle pairs to those pairs involving only particles 1, 2, and 3. To obtain the terms with a factor ϵ^{-2}, it is necessary that $\mathbf{k}^N=0$ and G_0 between T_α and T_β must be equal to ϵ^{-1}. This situation limits α to be the 1, 2 pair because $\mathbf{q}\neq 0$. Thus, taking into account the identity of particles, (III1) becomes

$$\eta_{UK}^2(\epsilon)=\epsilon^{-2}\rho^2(KT)^{-1}\sum_{\mathbf{q}}{}'\,\psi(\mathbf{q})\int g(\mathbf{q},-\mathbf{q})T_{12}(\mathbf{q},-\mathbf{q}|0)V[T_{13}(0|0)+T_{23}(0|0)](1+2^{-1}\mathcal{P}_{13})\chi(\mathbf{p}_1)\prod_{i=1}^{3}\varphi(p_i)d\mathbf{p}_i. \quad \text{(III2)}$$

If we note that in the term involving $\mathcal{P}_{13}$, particles 1 and 2 are equivalent, and use the property[6]

$$\int VT_{23}(0|0)\varphi(p_2)\varphi(p_3)d\mathbf{p}_2d\mathbf{p}_3=0 \quad \text{as} \quad \epsilon\to 0$$

[see also (3.23) and (3.25)], (III2) reduces, for $\epsilon\to 0$ to

$$\eta_{UK}^2(\epsilon)=\epsilon^{-2}\rho^2(KT)^{-1}\sum_{\mathbf{q}}{}'\,\psi(\mathbf{q})\int g(\mathbf{q},-\mathbf{q})T_{12}(\mathbf{q},-\mathbf{q}|0)VT_{13}(0|0)(1+\mathcal{P}_{13})\chi(\mathbf{p}_1)\prod_{i=1}^{3}\varphi(p_i)d\mathbf{p}_i \qquad \text{(III3)}$$

which is identical to (5.6) of the text.

APPENDIX IV. DERIVATION OF (6.6)

Consider the operator

$$C_3(1)\equiv\frac{1}{2}\int\int d\mathbf{r}_2d\mathbf{r}_3\tau(123), \qquad \text{(IV1)}$$

where $\tau(123)$ is given by (3.31). If we note that an expression of the form (3.15) gives no contribution to $C_3(1)$ we need consider only those terms in which T_α, at the extreme left of each term in $\tau(123)$, involves particle 1. Further, noting that particles 2 and 3 are equivalent in (IV1), we may write

$$C_3(1)=\int\int d\mathbf{r}_2d\mathbf{r}_3T_{12}G_0\{\sum_{\alpha\neq 12,\beta}{}'\,T_\alpha G_0T_\beta-\cdots\} \qquad \text{(IV2)}$$

$$=\int\int d\mathbf{r}_2d\mathbf{r}_3\{T_{12}[1-G_0\sum_{\alpha\neq 12}T_\alpha+G_0\sum_{\alpha\neq 12}\sum_{\beta}{}'\,T_\alpha G_0T_\beta-\cdots]-T_{12}[1-G_0T_{13}-G_0T_{23}]\}. \qquad \text{(IV3)}$$

Here and in the following, summations are over pairs composed of particles 1, 2, and 3.

Use of the binary collision expansion formula for G_3 yields

$$G_3(123)G_0^{-1}=1-\sum_\alpha G_0T_\alpha+\sum_{\alpha,\beta}{}'\,G_0T_\alpha G_0T_\beta-\cdots. \qquad \text{(IV4)}$$

Here we divide the terms into those for which $\alpha=12$ and those for which $\alpha\neq 12$. Namely,

$$G_3(123)G_0^{-1}=1-G_0\sum_{\alpha\neq 12}T_\alpha+G_0\sum_{\alpha\neq 12}\sum_{\beta}{}'\,T_\alpha G_0T_\beta-\cdots-G_0T_{12}[1-\sum_{\alpha\neq 12}G_0T_\alpha+\cdots]$$

$$=[1-G_0T_{12}][1-G_0\sum_{\alpha\neq 12}T_\alpha+G_0\sum_{\alpha\neq 12}\sum_{\beta}{}'\,T_\alpha G_0T_\beta-\cdots]. \qquad \text{(IV5)}$$

If we use (2.22), we obtain from (IV5)

$$\theta_{12}G_3(123)G_0^{-1}=-T_{12}[1-G_0\sum_{\alpha\neq 12}T_\alpha+G_0\sum_{\alpha\neq 12}\sum_{\beta}{}'\,T_\alpha G_0T_\beta-\cdots], \qquad \text{(IV6)}$$

which is identical to the first term in the curly bracket of (IV3). The second term in the same curly bracket can be easily transformed by using (2.26) for T_{12} and (2.25) for T_{13} and T_{23}. Then we find that

$$C_3(1)=-\int\int d\mathbf{r}_2d\mathbf{r}_3\theta_{12}\{G_3G_0^{-1}-G_2(12)G_0^{-1}G_2(13)G_0^{-1}-G_2(12)G_0^{-1}G_2(23)G_0^{-1}+G_2(12)G_0^{-1}\} \qquad \text{(IV7)}$$

from which we immediately obtain (6.6) in the limit as $\epsilon\to 0+$.

APPENDIX V. DERIVATION OF (7.12)

Using

$$iL_0(p_1{}^x r_1{}^y + p_2{}^x r_2{}^y) = \chi(\mathbf{p}_1) + \chi(\mathbf{p}_2)\,, \tag{V1}$$

the function

$$D \equiv G_2(12) G_0{}^{-1}(p_1{}^x r_1{}^y + p_2{}^x r_2{}^y)\varphi(p_1)\varphi(p_2) \tag{V2}$$

becomes

$$D = \int_0^\infty dt e^{-\epsilon t} S_{-t}{}^{(2)}(12)\{\epsilon(p_1{}^x r_1{}^y + p_2{}^x r_2{}^y) + \chi(\mathbf{p}_1) + \chi(\mathbf{p}_2)\}\varphi(p_1)\varphi(p_2)\,, \tag{V3}$$

where we have used (2.21) and (7.8).

The expression D occurs in (6.23) and is multiplied on the left by θ_{12}. Therefore, contributions to the integral in (6.23) arise only when the particles are interacting at time 0. Thus we may confine our considerations to those configurations in which the particles are interacting at time 0.

For a repulsive interaction with a finite range, for any initial momenta and for an initial configuration in which the particles are interacting, there exists a finite time τ_0 such that for $t \geqslant \tau_0$ there is no interaction. Thus, if we divide the range of integration in (V3) into $0 \leqslant t \leqslant \tau_0$ and $\infty > t > \tau_0$, we obtain

$$D = \int_0^{\tau_0} dt e^{-\epsilon t} S_{-t}{}^{(2)}(12)\{\epsilon(p_1{}^x r_1{}^y + p_2{}^x r_2{}^y) + \chi(\mathbf{p}_1) + \chi(\mathbf{p}_2)\}\varphi(p_1)\varphi(p_2)$$
$$+ \int_{\tau_0}^\infty dt e^{-\epsilon t} S_{-\tau_0}{}^{(2)}(12)[\epsilon\{p_1{}^x r_1{}^y + p_2{}^x r_2{}^y - (t-\tau_0)[\chi(\mathbf{p}_1) + \chi(\mathbf{p}_2)]\} + \chi(\mathbf{p}_1) + \chi(\mathbf{p}_2)]\varphi(p_1)\varphi(p_2) \tag{V4}$$

since for $t \geqslant \tau_0$ the particles follow free motion.

We now change the range of the second integral to $0 \leqslant t < \infty$ and subtract the difference from the first integral. Then, throwing away the terms which vanish at $\epsilon = 0+$ for a finite τ_0, we find

$$D = \int_0^{\tau_0} dt e^{-\epsilon t}(S_{-t}{}^{(2)} - S_{-\tau_0}{}^{(2)})\{\chi(\mathbf{p}_1) + \chi(\mathbf{p}_2)\}\varphi(p_1)\varphi(p_2)$$
$$+ \int_0^\infty dt e^{-\epsilon t} S_{-\tau_0}{}^{(2)}\{\epsilon(p_1{}^x r_1{}^y + p_2{}^x r_2{}^y) + (\epsilon\tau_0 + 1 - \epsilon t)[\chi(\mathbf{p}_1) + \chi(\mathbf{p}_2)]\}\varphi(p_1)\varphi(p_2)\,. \tag{V5}$$

After integrating the second term over t, we take the limit $\epsilon \to 0+$, and obtain

$$D = \int_0^{\tau_0} dt (S_{-t}{}^{(2)} - S_{-\tau_0}{}^{(2)})\{\chi(\mathbf{p}_1) + \chi(\mathbf{p}_2)\}\varphi(p_1)\varphi(p_2)$$
$$+ S_{-\tau_0}{}^{(2)}\{p_1{}^x(r_1{}^y + \tau_0 m^{-1} p_1{}^y) + p_2{}^x(r_2{}^y + \tau_0 m^{-1} p_2{}^y)\}\varphi(p_1)\varphi(p_2)\,. \tag{V6}$$

The second term in (V6) can also be expressed as

$$S_{-\tau_0}{}^{(2)} S_{\tau_0}{}^{(0)}(p_1{}^x r_1{}^y + p_2{}^x r_2{}^y)\varphi(p_1)\varphi(p_2)\,. \tag{V7}$$

Since, for $t \geqslant \tau_0$, there is no interaction, we can replace $S_{-\tau_0}{}^{(2)} S_{\tau_0}{}^{(0)}$ in (V7) by $\mathcal{S}(12)$ defined by (7.4).

Furthermore, the range of the first integral can be extended to ∞ and we can replace $S_{-\tau_0}{}^{(2)}$ by $S_{-\infty}{}^{(2)}$, since for $t \geqslant \tau_0$, $S_{-t}{}^{(2)} = S_{-\tau_0}{}^{(2)} = S_{-\infty}{}^{(2)}$ when operating on functions of momenta only. Thus, finally, we find that

$$D = \int_0^\infty dt (S_{-t}{}^{(2)} - S_{-\infty}{}^{(2)})\{\chi(\mathbf{p}_1) + \chi(\mathbf{p}_2)\}\varphi(p_1)\varphi(p_2) + \mathcal{S}(12)(p_1{}^x r_1{}^y + p_2{}^x r_2{}^y)\varphi(p_1)\varphi(p_2)\,. \tag{V8}$$