Correlation Function Method for the Transport Coefficients of Dense Gases. II. First Density Correction to the Shear Viscosity for Systems with Attractive Forces*

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Extending the technique presented in our earlier work, the correlation-function expression for the shear viscosity is evaluated up to the first-density correction for a classical system of particles interacting with pair and three-body forces of short range which may have attractive parts and may allow for bound states. The results contain new terms as a result of the existence of bound states, in addition to those obtained for the first-density correction to the shear viscosity for the case of purely repulsive forces. In particular, η_{KU}, η_{UK}, and η_{UU} involve genuine three-body dynamics and give rise to finite contributions to the first-density correction. Diagrams are provided which help to visualize the various processes contributing to the shear viscosity. Finally, higher order density corrections and unstable clusters are briefly discussed.

1. INTRODUCTION

IN our previous work on the transport coefficients of dense gases,[1] we presented a method of obtaining a density expansion for the shear viscosity of classical simple gases starting from the autocorrelation function expression. The method which is a generalization of Zwanzig's work[2] employs the resolvent operator expression of the original correlation-function formula and the binary-collision expansion for the N-body resolvent operator. Inverting the resulting expansion series in a way that will avoid singularities arising from infinite time integrals, we are able to obtain a density-expansion series for the shear viscosity.

One advantage of this method is that we can avoid any assumption of a statistical nature such as Bogolyubov's[3] or some other kind of molecular chaos assumption which has been used in other theories.[4] Thus, although in I we have restricted ourselves to the case of repulsive intermolecular forces, our method is not limited to this case, and in this paper we present an extension of our work to systems with attractive forces and bound molecular clusters.

The reasons for choosing this particular problem are the following: (1) It is impossible to deal with this problem by the transport-equation approaches so far proposed because these theories are based on the fact that the multiplet-distribution functions asymptotically become products of singlet-distribution functions. This seems to have been justified for systems with repulsive short-range forces only.[5,6] Since the correlation-function approach is free from this sort of statistical assumption, it has many advantages. (2) Bound molecular clusters are supposed to play an important role in the transport coefficients (especially the thermal conductivity) of dense gases at low temperatures (say, below the Boyle point),[7,8] as well as in the understanding of the temperature dependence of the first density correction to the shear viscosity even at higher temperatures.[9] The existing theories [7–9] are all based on intuitive models and it is rather difficult to assess their validity. Thus it is highly desirable to take a more fundamental approach to this problem. We might also mention that the anomalies in the transport coefficients observed near the critical region are also attributed to molecular clusters,[10] although we are still far away from understanding such interesting phenomena.

In this paper, we shall consider a system of particles obeying classical mechanics and interacting with each other through pair and three-body potentials with a finite range. We have included the three-body potential because such many-body forces are expected to be important when we have bound molecular clusters.

In the next section we shall present a correlation-function expression for the shear viscosity which includes the three-body forces and we shall introduce an

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[6] D. K. Hoffman has improved this by adopting a more general factorization condition for the multiplet distribution functions (Ref. 5). However, the theory has not been worked out to such an extent as to allow for the bound states in the transport coefficients.

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expansion of the N-body resolvent operator which generalizes the binary-collision expansion. We shall also show that the binary-collision operator has a certain singularity for $\epsilon \to 0+$ arising from the bound states. In Secs. 3, 4, and 5 we shall present a detailed calculation of the first-density correction to the shear viscosity. Because of the singularity in the binary-collision operator mentioned, the $\mathbf{k}$ representation used in our earlier work is not always convenient, and η_{KK}, η_{UK}, η_{KU} as well as η_{UU} contribute to the first density correction.[11] In Sec. 6 we give a new expression for the shear viscosity up to the first density correction and present a diagrammatic representation of the processes contributing to the viscosity. The density dependence of contributions from various processes becomes immediately apparent. In the final section, we shall discuss briefly higher density corrections and unstable molecular clusters.

2. PRELIMINARIES

We first present the correlation-function expression for the shear viscosity which is valid in the presence of short-range three-body intermolecular potentials in addition to short-range pair potentials and obtain an expansion for the resolvent operator G_N which is a generalization of the binary-collision expansion in I.

The system we consider consists of N classical monatomic particles contained in the volume V which interact with each other through the three-body intermolecular potentials[12] $u(ijk)$ as well as the pair potentials $u(ij)$. Here i, j, k, $\cdots$ denote particles as well as their coordinates. Then the correlation-function expression for the shear viscosity[13] [I(2.1)—I(2.13)] is

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

where

$$\eta(\epsilon) \equiv (VKT)^{-1} \langle I G_N(\epsilon) I \rangle. \tag{2.2}$$

G_N denotes the resolvent operator for N interacting particles, and $\langle \cdots \rangle$ denotes the average over the equilibrium ensemble. The dynamical flux I is given by

$$I = \sum_{i=1}^{N} \chi(\mathbf{p}_i) + \sum_{i<j}^{N} \psi(ij) + \sum_{i<j<k}^{N} \psi(ijk), \tag{2.3}$$

where

$$\chi(\mathbf{p}_i) \equiv p_i^x p_i^y / m, \tag{2.4}$$

$$\psi(ij) \equiv -r_{ij}^x \partial u(ij)/\partial r_{ij}^y,$$

$$\psi(ijk) \equiv -r_{ij}^x \partial u(ijk)/\partial r_{ij}^y - r_{jk}^x \partial u(ijk)/\partial r_{jk}^y - r_{ki}^x \partial u(ijk)/\partial r_{ki}^y, \tag{2.5}$$

where the last term in (2.3) is due to the three-body forces.

Since we have three-body interactions, the binary-collision expansion for G_N used in I is not applicable, and it is necessary to generalize it. This can be done most easily by separating the various processes contributing to G_N into those involving no interactions, those involving single-binary collisions, those involving two successive binary collisions, those involving triple collisions and so on.[14] The processes not explicitly mentioned above involve more than three particles. More explicitly, we can write

$$G_N = G_0 - \sum_{\alpha} G_0 T_\alpha G_0 + \sum_{\alpha} \sum_{\beta}{}' G_0 T_\alpha G_0 T_\beta G_0 - \sum_{i<j<k}^{N} G_0 \tau(ijk) G_0 + (\text{terms describing processes involving more than three particles}), \tag{2.6}$$

where T_α is the binary-collision operator defined in I, and $\tau(ijk)$ represents the triple collision of the particles i, j, and k. The explicit expression for $\tau(123)$ can be obtained by considering (2.6) for a fictitious system in which interactions exist only among the particles 1, 2, and 3. Thus, we have

$$\tau(123) = -G_0^{-1} G_3(123) G_0^{-1} + G_0^{-1} - \sum_{\alpha} T_\alpha + \sum_{\alpha} \sum_{\beta}{}' T_\alpha G_0 T_\beta, \tag{2.7}$$

where the summations are over the pairs chosen from the particles 1, 2, and 3, and exclude consecutive appearances of the same pair.

For repulsive short-range interactions, we have shown in I that the quantities $VT_\alpha(\mathbf{k}^N | \mathbf{k}'^N)$ are nonsingular as $\epsilon \to 0+$ due to the fact that two particles initially within the range of intermolecular forces will later be far away from each other. This property has been used in the analysis in I. For attractive forces where there is a possibility of the formation of bound molecular clusters, this property need not apply. We define bound molecular clusters in the following sense: a bound molecular cluster consisting of the particles 1, 2, 3, $\cdots$, s at the time zero is meant to designate a state of motion at the time zero in which every one of these particles *always* stays within the force range of the other particles of the set when the motion of these isolated s particles is followed from the time zero into the infinite future. (An equally satisfactory definition is obtained by following the motion into the infinite past. Our choice here is due to the fact that we are choosing the direction of time such that all the interesting events occur in the past. In general, these two definitions are equivalent.)

[11] We use mostly the same notation as in I.

[12] Although the three-body potential $u(ijk)$ is a function of two independent vectors $\mathbf{r}_{ij}$ and $\mathbf{r}_{jk}$, we have, for symmetry, expressed it as a function of three vectors $\mathbf{r}_{ij}$, $\mathbf{r}_{jk}$, $\mathbf{r}_{ki}$.

[13] We refer to the equations in I in this manner.

[14] The term "collision" is used here in a broader sense including the processes that involve bound states.

Here we have defined bound states in a rather strict sense: All the bound states have infinite lifetimes if they are left alone. Recently, however, the importance of metastable or quasibound states with finite lifetimes has been pointed out.[9] We shall discuss this question in the final section.

Returning now to the binary-collision operator, the detailed investigation of the properties of T_{12} as $\epsilon \to 0+$ given in Appendix A has shown that:

(1) $VT_{12}(\mathbf{k}^N|\mathbf{k}'^N)$ is nonsingular if

$$l \equiv (\mathbf{k}_1+\mathbf{k}_2)\cdot(\mathbf{p}_1+\mathbf{p}_2)/2+\sum_{i=3}^{N}\mathbf{k}_i\cdot\mathbf{p}_i = (\mathbf{k}_1'+\mathbf{k}_2')\cdot(\mathbf{p}_1+\mathbf{p}_2)/2+\sum_{i=3}^{N}\mathbf{k}_i'\cdot\mathbf{p}_i \neq 0.$$

This enables us to restrict our considerations to the case $l=0$ when $VT_{12}(\mathbf{k}^N|\mathbf{k}'^N)$ can be written as $VT_{12}(\mathbf{k}|\mathbf{k}')$, where $\mathbf{k}\equiv(\mathbf{k}_1-\mathbf{k}_2)/2$ and $\mathbf{k}'\equiv(\mathbf{k}_1'-\mathbf{k}_2')/2$.

(2) $VT_{12}(0|0)$ has a vanishing contribution from bound states of motion of particles 1 and 2.

(3) $VT_{12}(0|\mathbf{k})$ and $VT_{12}(\mathbf{k}|0)$ where $\mathbf{k}\neq 0$ have in general finite contributions from bound states of motion.

(4) $VT_{12}(\mathbf{k}|\mathbf{k}')$ where $\mathbf{k},\mathbf{k}'\neq 0$ in general has a singular contribution of the form ϵ^{-1} from bound states of motion as $\epsilon \to 0+$.

As we shall see in Appendix A, the last result is obtained by averaging contributions oscillating in time which describe the internal degrees of freedom of the bound pair. Because of the property (4), terms additional to those derived in I appear in the formal expression for the first density correction to the shear viscosity.

Before embarking on the actual calculation we shall review the method we have employed in I and are going to use in this paper, and make some general remarks. Use of the expansion (2.6) in (2.2) yields $\eta(\epsilon)$ as a sum of expressions of the following type:

$$\rho^r \int J_1 \mathcal{E}(\epsilon) J_2 \frac{dx^r}{V} \quad (r=1,2,3), \tag{2.8}$$

where J_1 and J_2 are appropriate functions of $x_1, x_2, \cdots x_r$, where $x_i=\mathbf{r}_i$, $\mathbf{p}_i$, and where $\mathcal{E}(\epsilon)$ is an operator expressed in a formal density series as

$$\mathcal{E}(\epsilon)=\epsilon^{-1}\{1+\rho(\epsilon^{-1}h_{10}+h_{11}) +\rho^2(\epsilon^{-2}h_{20}+\epsilon^{-1}h_{21}+h_{22})+\cdots\}, \tag{2.9}$$

where the h's are finite as $\epsilon \to 0+$. Since this series contains powers of ϵ^{-1}, we cannot take the limit $\epsilon \to 0+$ at this stage. Instead, we invert the series. That is, writing (2.8) as

$$\rho^r \int J_1[\mathcal{E}^{-1}(\epsilon)]^{-1} J_2 \frac{dx^r}{V}, \tag{2.10}$$

we expand $\mathcal{E}^{-1}(\epsilon)$ in ρ, and ascertain that the resulting series

$$\mathcal{E}^{-1}(\epsilon)=\epsilon-\rho(h_{10}+\epsilon h_{11})+\rho^2[h_{10}h_{11}+h_{11}h_{10}-h_{21} +\epsilon^{-1}(h_{10}^2-h_{20})+\epsilon(h_{11}^2-h_{22})]+\cdots \tag{2.11}$$

has a well-defined limit as $\epsilon \to 0+$. Namely, as $\epsilon \to 0+$,

$$\mathcal{E}^{-1}(0+)=-\rho(h_{10})_+ +\rho^2(h_1)_+ +\cdots, \tag{2.12}$$

where

$$h_1 \equiv h_{10}h_{11}+h_{11}h_{10}-h_{21}+\epsilon^{-1}(h_{10}^2-h_{20}) \tag{2.13}$$

is nonsingular as $\epsilon \to 0+$. (See I, Ref. 15, for the notation.) However, the procedure, for instance, of terminating the series in (2.12) at the first term is justifiable only if all the terms of order of $\epsilon^{-1}(\rho/\epsilon)^n$ $(n=0,1,2,3\cdots)$ in (2.9) are correctly represented by $[\epsilon-\rho h_{10}]^{-1}$. This has been proved in certain cases.[15] Here we shall assume that this procedure, from which we obtain a well-defined density expansion for the transport coefficients, is valid. In Sec. 6, we shall make this more convincing by a diagrammatic representation of the contributing processes.

From the foregoing it is now clear that, in the formal-density expansion resulting from substituting (2.9) into (2.8), we have to retain the terms of order $(\rho/\epsilon)^n$ with $n=0,1,2, \cdots$ to get the shear viscosity in the low-density limit, and must retain the terms of order $\rho(\rho/\epsilon)^n$ with $n=0,1,2, \cdots$ for its first density correction.[16] This is in accordance with the fact that ϵ^{-1} is eventually "renormalized" to become proportional to ρ^{-1} (see Sec. 6).

3. CALCULATION OF η_{KK}

Since many of the calculations can be carried over from I, we shall be rather brief in presenting the calculations except for the differences arising from the bound states of motion. The general expression for the kinetic part of the shear viscosity is given by I (3.3) and is

$$\eta_{KK}(\epsilon)=\frac{\rho}{KT}\sum_{\mathbf{k}_N} P^*(\mathbf{k}^N)\int d\mathbf{p}^N \chi(\mathbf{p}_1) G_N(0|\mathbf{k}^N) \times[1+(N-1)\mathcal{P}_{12}]\chi(\mathbf{p}_1)\Phi(\mathbf{p}^N), \tag{3.1}$$

where

$$\Phi(\mathbf{p}^n)\equiv\prod_{j=1}^{n}\varphi(p_j).$$

Corresponding to the expansion (2.6), we can write (3.1) as

$$\eta_{KK}(\epsilon)=\eta_{KK}{}^0(\epsilon)+\eta_{KK}{}^1(\epsilon)+\eta_{KK}{}^2(\epsilon) +\eta_{KK}{}^r(\epsilon)+\cdots. \tag{3.2}$$

[15] J. A. McLennan and R. J. Swenson, J. Math. Phys. 4, 1527 (1963); S. Ono and T. Shizume, J. Phys. Soc. Japan 18, 29 (1963).

[16] In view of this, the statement in the paragraph preceding (3.29) in I that the part involving more than three particles does not contribute is wrong. In actual calculations there, we *did not* neglect such contributions. A similar remark applies to I(4.14) and I(5.7). This by no means affects the validity of our calculations. We also note that the T_α in I in the paragraph preceding I(2.27) should read $T_\alpha(\mathbf{k}^N|\mathbf{k}'^N)$.

The terms not explicitly written in (3.2) describe processes involving more than three particles.

In I [(3.10) and (3.22)] we have shown that

$$\eta_{KK}{}^{0}(\epsilon)=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)^2\epsilon^{-1}\varphi(p_1), \tag{3.3}$$

$$\eta_{KK}{}^{1}(\epsilon)=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)[-\rho\epsilon^{-2}\mathfrak{L}(\mathbf{p}_1)-\rho\epsilon^{-1}t_1(\mathbf{p}_1)]\times\chi(\mathbf{p}_1)\varphi(p_1), \tag{3.4}$$

where

$$\mathfrak{L}(\mathbf{p}_1)\equiv\int d\mathbf{p}_2 VT_{12}(0|0)(1+\mathcal{P}_{12})\varphi(p_2) \tag{3.5}$$

and

$$t_1(\mathbf{p}_1)\equiv\int d\mathbf{p}_2(0|\,VT_{12}G_0F_0(r_{12})|\,0)(1+\mathcal{P}_{12})\varphi(p_2). \tag{3.6}$$

$\mathfrak{L}(\mathbf{p}_1)$ is the linearized Boltzmann collision operator and $\mathfrak{L}(\mathbf{p}_1)$ and $t_1(\mathbf{p}_1)$ are nonsingular as $\epsilon\to 0+$ because of the properties (1)–(4) of Sec. 2.

Use of these properties also yield for $\eta_{KK}{}^{2}(\epsilon)$ the expression which is formally the same as that obtained in I, (3.26), and is given by

$$\eta_{KK}{}^{2}(\epsilon)=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)\{\rho^2\epsilon^{-3}t_{21}(\mathbf{p}_1)+\rho^2\epsilon^{-2}t_{22}(\mathbf{p}_1)\}\times\chi(\mathbf{p}_1)\varphi(p_1), \tag{3.7}$$

where $t_{21}(\mathbf{p}_1)$ and $t_{22}(\mathbf{p}_1)$ are nonsingular operators as $\epsilon\to 0+$ and are given by I (3.27) and I (3.28), namely,

$$t_{21}(\mathbf{p}_1)\equiv\int\int d\mathbf{p}_2 d\mathbf{p}_3 VT_{12}(0|0)\times[VT_{13}(0|0)+VT_{23}(0|0)]\times(1+\mathcal{P}_{13}+\mathcal{P}_{23})\varphi(p_2)\varphi(p_3), \tag{3.8}$$

$$t_{22}(\mathbf{p}_1)\equiv\int\int d\mathbf{p}_2 d\mathbf{p}_3 VT_{12}(0|0)\times(0|[VT_{13}G_0F_0(r_{13})+VT_{23}G_0F_0(r_{23})]|0)\times(1+\mathcal{P}_{13}+\mathcal{P}_{23})\varphi(p_2)\varphi(p_3). \tag{3.9}$$

Finally, the term involving the triple collision is written as

$$\eta_{KK}{}^{r}(\epsilon)=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)\left[-\frac{\rho^2}{\epsilon^2}\hat{t}^r(\mathbf{p}_1)\right]\chi(\mathbf{p}_1)\varphi(p_1), \tag{3.10}$$

where

$$\hat{t}^r(\mathbf{p}_1)\equiv\frac{1}{2}\int\int dx_2dx_3\epsilon\tau(123)G_0(1+\mathcal{P}_{12}+\mathcal{P}_{13})\times\exp\{-\beta U(123)\}\varphi(p_2)\varphi(p_3), \tag{3.11}$$

with

$$U(123)\equiv u(12)+u(23)+u(31)+u(123)$$

and

$$\beta\equiv(KT)^{-1}.$$

The factor $\exp\{-\beta U(123)\}$ is retained here because of the possibility of bound states of motion. We shall show later in this section that $\hat{t}^r(\mathbf{p}_1)$ is nonsingular as $\epsilon\to 0+$ whether or not bound states are present.

Thus, using (3.3), (3.4), (3.7), and (3.10), $\eta_{KK}(\epsilon)$ is written as in I(3.32) and I(3.33) except that t^r is replaced by $\hat{t}^r$. That is

$$\eta_{KK}(\epsilon)=\frac{\rho}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)\mathcal{G}(\epsilon)\chi(\mathbf{p}_1)\varphi(p_1)+O(\rho^2), \tag{3.12}$$

where

$$\mathcal{G}(\epsilon)\equiv\epsilon^{-1}-\rho(\epsilon^{-2}\mathfrak{L}+\epsilon^{-1}t_1)+\rho^2(\epsilon^{-3}t_{21}+\epsilon^{-2}t_{22}-\epsilon^{-2}\hat{t}^r). \tag{3.13}$$

Since the equality which was proved in I [see I(3.43)], namely,

$$[\epsilon^{-1}(\mathfrak{L}^2-t_{21})+\mathfrak{L}t_1-t_{22}]\mathfrak{L}^{-1}\chi(\mathbf{p}_1)\varphi(p_1)=0 \tag{3.14}$$

is still valid here, the same manipulations of $\mathcal{G}(\epsilon)$ as in I which are discussed in Sec. 2 yield for

$$\eta_{KK}=\lim_{\epsilon\to 0+}\eta_{KK}(\epsilon) \tag{3.15}$$

the following result up to the first-density correction:

$$\eta_{KK}=\eta_{KK}{}^{(0)}+\rho\eta_{KK}{}^{(1)}, \tag{3.16}$$

where $\eta_{KK}{}^{(0)}$ is the Chapman-Enskog result given by I(3.41) and I(3.46), and $\eta_{KK}{}^{(1)}$ is the coefficient of the first-density correction given by

$$\eta_{KK}{}^{(1)}=\frac{1}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)^2W_{KK}{}^{(1)}(p_1)\varphi(p_1), \tag{3.17}$$

with

$$\mathfrak{L}_+(\mathbf{p}_1)W_{KK}{}^{(1)}(p_1)\varphi(p_1)=-t_{1+}(\mathbf{p}_1)\chi(\mathbf{p}_1)\varphi(p_1)-\hat{t}_+{}^r(\mathbf{p}_1)W^{(0)}(p_1)\chi(\mathbf{p}_1)\varphi(p_1). \tag{3.18}$$

Thus the only way this η_{KK} differs from that for the case of repulsive forces is that here we have the modified triple-collision operator $\hat{t}_+{}^r$ instead of $t_+{}^r$. We now study $\hat{t}^r$ in more detail and shall show that it is nonsingular as $\epsilon\to 0+$. Use of (2.7) in (3.11) gives

$$\hat{t}^r(\mathbf{p}_1)=-\frac{1}{2}\int\int dx_2dx_3\epsilon^2\times[G_3-G_0+\sum_\alpha G_0T_\alpha G_0-\sum_\alpha\sum_\beta{}' G_0T_\alpha G_0T_\beta G_0]\times(1+\mathcal{P}_{12}+\mathcal{P}_{13})\exp\{-\beta U(123)\}\varphi(p_2)\varphi(p_3). \tag{3.19}$$

The operator in the square bracket represents the motion of the three particles 1, 2, and 3 from which the resolvent operators corresponding to the free motion

of these particles, the motions which involve single binary collisions and those involving two successive binary collisions, have been subtracted. Thus, we have to consider only (a) the triple collisions where no bound states are involved, (b) the triple collisions involving one bound pair of particles where creation or destruction of the pair, or the destruction of one pair and creation of another, may occur, (c) the three-particle bound states. Some typical triple collision processes are shown schematically in Fig. 1. (For simplicity, in this and other diagrams we have not included processes involving the so-called "hypothetical collisions.")

We now study the contribution of these three types of motion to $\hat{t}^r(\mathbf{p}_1)$ which we rewrite as

$$\hat{t}^r(\mathbf{p}_1)=-\frac{1}{2}\int\int d\mathbf{p}_2 d\mathbf{p}_3\epsilon^2\int_0^\infty dt e^{-\epsilon t}B(\mathbf{p}^3;t) \times(1+\mathcal{P}_{12}+\mathcal{P}_{13})\varphi(p_2)\varphi(p_3), \quad (3.20)$$

where

$$B(\mathbf{p}^3;t)\equiv\int\int d\mathbf{r}_2 d\mathbf{r}_3 S_{-t}{}^r(123)\exp\{-\beta U(123)\} \quad (3.21)$$

and $S_{-t}{}^r(123)$ is the contribution to the three-particle streaming operator coming from the three types of motions (a), (b) [further subdivided into $(b_1)-(b_4)$], and (c) occurring during the time interval $(-t, 0)$; $S_{-t}{}^r(123)$ is defined explicitly by Eq. (B4). For the process represented by Fig. 1(a) the region of the coordinate space $\mathbf{r}_2$ which contributes to $B(\mathbf{p}^3;t)$ consists of a cylinder of the length $t|\mathbf{p}_1-\mathbf{p}_2|/m$ with cross section of the order of the square of the force range plus two end sections which do not increase indefinitely as t increases or, loosely speaking, which are finite for large t. For fixed $\mathbf{r}_2$, the contributing region of $\mathbf{r}_3$ stays finite for large t. Thus $B(\mathbf{p}^3;t)$ contains a term which grows linearly in t for large t. This term produces a finite contribution to $\hat{t}^r(\mathbf{p}_1)$ for $\epsilon\to 0+$ due to the equality

$$\epsilon^2\int_0^\infty e^{-\epsilon t}t dt=1. \quad (3.22)$$

Evidently in this limit the remaining term in $B(\mathbf{p}^3;t)$ which stays finite for large t gives only a vanishing contribution to $\hat{t}^r(\mathbf{p}_1)$. A similar analysis can be applied to the processes of Fig. 1(b_1), (b_2), and (b_3). The contributing region of $\mathbf{r}_2$ space is a small sphere around $\mathbf{r}_1$ of diameter about equal to the attractive force range, whereas that of $\mathbf{r}_3$ space contains a cylinder whose length grows linearly in t, and thus gives rise to a finite contribution to $\hat{t}^r(\mathbf{p}_1)$ as $\epsilon\to 0+$. For the process of Fig. 1(b_4), when $\mathbf{r}_3$ is arbitrary, the region of $\mathbf{r}_2$ that contributes is a cylinder with one end at $\mathbf{r}_1$ which increases its length as t. If we fix $\mathbf{r}_2$ somewhere in this cylinder then the contributing region of $\mathbf{r}_3$ is fixed within the distance of intermolecular force range.

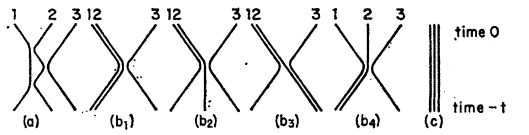

FIG. 1. The processes contributing to the triple collision $\hat{t}^r$. Here and in Figs. 3, 4, and 7, the time runs from bottom $(-t)$ to top (0).

Therefore, this process also produces a finite contribution to $\hat{t}^r(\mathbf{p}_1)$. Finally, for the process Fig. 1(c), the contribution comes entirely from the finite region around $\mathbf{r}_1$, and contains no term in $B(\mathbf{p}^3;t)$ which grows linearly in t for large t. Therefore, this process should not contribute to $\hat{t}^r(\mathbf{p}_1)$ as $\epsilon\to 0+$. Thus we have been able to verify that $\hat{t}^r(\mathbf{p}_1)$ defined by (3.19) is a nonsingular operator as $\epsilon\to 0+$. For repulsive pair potentials of short range, the finiteness of $t^r(\mathbf{p}_1)$ follows immediately from the finiteness of T_α and from I (3.30) and I (3.31) by noting that the terms for which at least one of the G_0 in I (3.31) equals ϵ^{-1} give contributions of order N^{-1} for $\epsilon\neq 0$ and vanish as $N\to\infty$.

In Appendix B we obtain explicit expressions for $\hat{t}_+{}^r(\mathbf{p}_1)$ in the form of five-dimensional surface integrals as has been obtained by Green[17] recently for the case of repulsive intermolecular forces.

4. CALCULATION OF η_{KU} AND η_{UK}

Since η_{UK} equals η_{KU} for classical systems,[1] we shall consider only one of them, namely, η_{KU}. For the moment we do not consider the part of the dynamical flux I which involves the three-body forces [the third term of (2.3)]. Then, considering the identity of particles, η_{KU} can be written as

$$\eta_{KU}(\epsilon)=\frac{N}{VKT}\int dx^N\chi(\mathbf{p}_1)G_N \times\left[(N-1)\psi(12)+\frac{(N-1)(N-2)}{2}\psi(23)\right] \times\rho(\mathbf{r}^N)\Phi(\mathbf{p}^N). \quad (4.1)$$

Use of the expansion (2.6) yields the following expansion for $\eta_{KU}(\epsilon)$:

$$\eta_{KU}(\epsilon)=\eta_{KU}{}^0(\epsilon)+\eta_{KU}{}^1(\epsilon)+\eta_{KU}{}^r(\epsilon)+\cdots, \quad (4.2)$$

where by I (4.5) and I (4.10) we find

$$\eta_{KU}{}^0(\epsilon)=0, \quad (4.3)$$

$$\eta_{KU}{}^1(\epsilon)=-\frac{\rho^2}{\epsilon KT}\int\int dx_1 dx_2\chi(\mathbf{p}_1)T_{12}G_0\psi(12) \times\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2)+O(\epsilon^{-1}\rho^3), \quad (4.4)$$

[17] M. S. Green, Phys. Rev. **136**, A905 (1964).

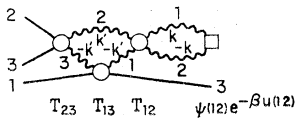

FIG. 2. A new process contributing to η_{KU} from bound states.

and further

$$\eta_{KU}{}^{r}(\epsilon)=-\frac{\rho^3}{2\epsilon^2 KT}\int\frac{dx^3}{V}\chi(\mathbf{p}_1)\epsilon^2 G_3{}^{r'}(123)\times[\psi(23)+\psi(31)+\psi(12)]\times\exp\{-\beta U(123)\}\Phi(\mathbf{p}^3)\,, \quad (4.5)$$

with

$$G_3{}^{r'}(123)\equiv G_3(123)-G_0+G_0\sum_{\alpha}T_\alpha G_0\,,\qquad(\alpha=23,31,12)\,. \quad (4.6)$$

The difference here from the case of the repulsive forces is that $\eta_{KU}{}^{r}(\epsilon)$ involves real three-body dynamics. This arises from the bound particle pair scattering the third particle. The process contributing to (4.4) or to (4.19) below is represented by Fig. 3(d).

The necessity of including the processes which involve more than successive binary collisions of the kind contained in I(4.16) and I(4.17) becomes apparent by noting the properties of the T_α's discussed in Sec. 2. As an illustration, consider the process represented by $-G_0T_{23}G_0T_{31}G_0T_{12}G_0$. We replace $G_3{}^{r'}(123)$ by this operator in (4.5) and consider the $\psi(12)$ term. This term contains a process in which first the spatial correlation between the particles 1 and 2 is created by $\psi(12)\exp(-\beta U(123))$ (namely $\mathbf{k}_1=-\mathbf{k}_2=\mathbf{k}\neq 0$), followed by a collision between the pair 12. Then the particle 1 collides with the particle 3 followed by a collision between the pair 23. This is represented schematically in Fig. 2 where wavy lines represent spatially correlated freely moving particles, the straight lines the spatially uncorrelated ones, and the circles the binary-collision processes. For bound states of the particles 1 and 2, T_{12} has a singularity of the form ϵ^{-1} as $\epsilon\to 0+$ because of the property (4) of Sec. 2, and thus this term cannot be thrown away as in I.

By the same kind of arguments as we have used in studying $\hat{t}^r(\mathbf{p}_1)$ in Sec. 2, one can verify that the coefficient of ρ^3/ϵ^2 in (4.5) is nonsingular as $\epsilon\to 0+$. As an illustration, take the term with $\psi(12)$ and consider the expression

$$\int\int d\mathbf{r}_2 d\mathbf{r}_3\epsilon^2 G_3{}^{r'}(123)\psi(12)\exp\{-\beta U(123)\}=\epsilon^2\int_0^\infty dt\exp(-\epsilon t)B'(\mathbf{p}^3;t)\,, \quad (4.7)$$

where

$$B'(\mathbf{p}^3;t)\equiv\int\int d\mathbf{r}_2 d\mathbf{r}_3 S_{-t}{}^{r'}(123)\psi(12)\times\exp\{-\beta U(123)\} \quad (4.8)$$

and $S_{-t}{}^{r'}(123)$ is the streaming operator for the three-particle motion which excludes those processes in which no collisions or single binary collisions occur during the time interval $(0,-t)$, which means that the particle 3 must be involved in collision at least once. Because of $\psi(12)$, the particles 1 and 2 must be close to each other at the time $-t$. The contributing processes can be classified as (a) those which involve no bound states, (b) those involving only one bound pair of particles, and (c) those involving three-particle bound states. Typical examples of these are shown in Fig. 3(a), (b), and (c), respectively. By an analysis of the same sort as that given for $\hat{t}^r(\mathbf{p}_1)$ in Sec. 3, we can demonstrate that the volumes of the regions in $\mathbf{r}_2$ and $\mathbf{r}_3$ space which contribute to $B'(\mathbf{p}^3,t)$, (4.8), grow linearly in time for the processes (a) and (b), but stays finite for the process (c) for sufficiently large t. Thus because of (3.22), only the processes (a) and (b) give finite contributions to (4.7) or to the coefficient of ϵ^{-2} of $\eta_{KU}{}^{r}(\epsilon)$, (4.5).

We now rewrite (4.5) as

$$\eta_{KU}{}^{r}(\epsilon)=\frac{\rho^3}{2\epsilon^2 KT}\int\frac{dx^3}{V}\chi(\mathbf{p}_1)\epsilon^2(1+\mathcal{P}_{23}+\mathcal{P}_{13})\times[G_3(123)-G_2(12)]\psi(12)\exp\{-\beta u(12)\}\times\Phi(\mathbf{p}^3)+O(\epsilon^{-1}\rho^3)\,. \quad (4.9)$$

In obtaining (4.9) the following considerations have been used: (1) The region of coordinate space in which the three particles are close together at the time $-t$ in (4.7) does not contribute to the first term in (4.9) for the same reason that the three particle bound states are neglected in $\hat{t}^r(\mathbf{p}_1)$. Therefore $\psi(ij)\exp(-\beta U(123))$ in (4.5) can be replaced by $\psi(ij)\exp(-\beta u(ij))$. (2) We note that (4.6) can be written as

$$G_3{}^{r'}(123)=G_3(123)-G_2(ij)+G_0(T_{ik}+T_{kj})G_0 \quad (4.10)$$

and consider the expression

$$\int\frac{d\mathbf{r}^3}{V}G_0T_{ik}G_0\psi(ij)\exp\{-\beta u(ij)\}\,, \quad (4.11)$$

where i,j,k is a permutation of 1, 2, 3. The expression (4.11) (in which we first integrate over $\mathbf{r}_k$) vanishes because

$$\int\psi(ij)\exp\{-\beta u(ij)\}d\mathbf{r}_{ij}=\beta^{-1}\int r_{ij}{}^{x}\frac{\partial}{\partial r_{ij}{}^{y}}F_0(r_{ij})d\mathbf{r}_{ij}=0\,. \quad (4.12)$$

Therefore, it is legitimate to replace $G_3{}^{r'}(123)$ in front of $\psi(ij)$ in (4.5) by

$$G_3(123)-G_2(ij)\,.$$

We now introduce a generalized collision operator $T(12;3)$ by

$$G_3(123)=G_2(12)-G_2(12)T(12;3)G_2(12). \quad (4.13)$$

$T(12;3)$ has a simple interpretation if the particles 1 and 2 form a bound cluster. In this case, $T(12;3)$ is a binary-collision operator for a collision between the bound pair of the particles 12 and the remaining particle 3. When there are no three-body forces, we can rearrange the series for the binary-collision expansion of $G_3(123)$ in a manner similar to that used to obtain I (IV.5), and get the following explicit expressions for $T(12;3)$:

$$G_2(12)T(12;3)=G_0\sum_{\alpha}^{\alpha\neq 12}T_\alpha-G_0\sum_{\alpha}^{\alpha\neq 12}\sum_{\beta}{}'T_\beta G_0T_\alpha$$
$$+G_0\sum_{\alpha}^{\alpha\neq 12}\sum_{\beta}{}'\sum_{\gamma}{}'T_\gamma G_0T_\beta G_0T_\alpha-\cdots \quad (4.14)$$

or

$$T(12;3)=\sum_{\alpha}^{\alpha\neq 12}T_\alpha-\sum_{\alpha}^{\alpha\neq 12}\sum_{\beta}^{\beta\neq 12}{}'T_\alpha G_0T_\beta$$
$$+\sum_{\alpha}^{\alpha\neq 12}\sum_{\beta}{}'\sum_{\gamma}^{\gamma\neq 12}{}'T_\alpha G_0T_\beta G_0T_\gamma-\cdots, \quad (4.15)$$

where the summations are over the pairs of particles (12), (23), and (31) with the restrictions indicated and consecutive appearances of the same pair excluded. The last expression can be further re-expressed as

$$T(12;3)=\sum_{\alpha}{}''T_\alpha-\sum_{\alpha}{}''\sum_{\beta}{}''T_\alpha G_2(12)T_\beta$$
$$+\sum_{\alpha}{}''\sum_{\beta}{}''\sum_{\gamma}{}''T_\alpha G_2(12)T_\beta G_2(12)T_\gamma-\cdots, \quad (4.16)$$

where the $\sum''$ are summations over the particle pairs (13) and (23) excluding the appearance of consecutive T's referring to the same pair. Equation (4.16) has a particularly revealing form in the light of the meaning given to $T(12;3)$ earlier.

With (4.13) in (4.19), we obtain

$$\eta_{KU}{}^r(\epsilon)=-\frac{\rho^3}{\epsilon^2KT}\int\int d\mathbf{p}^2d\mathbf{r}_2\chi(\mathbf{p}_1)\Gamma(12)$$
$$\times\epsilon G_2(12)\psi(12)\exp\{-\beta u(12)\}$$
$$\times\Phi(\mathbf{p}^2)+O(\rho^3/\epsilon), \quad (4.17)$$

where

$$\Gamma(12)\equiv\frac{1}{2}\int dx_3\epsilon(1+\mathcal{P}_{23}+\mathcal{P}_{13})$$
$$\times G_2(12)T(12;3)\varphi(p_3). \quad (4.18)$$

Since the coefficient of ϵ^{-2} of $\eta_{KU}{}^r(\epsilon)$ and $\epsilon G_2(12)\psi(12)\times\exp(-\beta u(12))$ are nonsingular as $\epsilon\to 0+$, $\Gamma(12)$ is also expected to be nonsingular in this limit. In Appendix C we show that $\Gamma(12)$ can be in fact regarded as a nonsingular operator for our purpose.

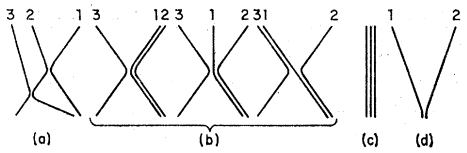

FIG. 3. (a), (b), and (c) describe the processes contributing to $\eta_{KU}{}^r(\epsilon)$ and (d) describes that contributing to $\eta_{KU}{}^1(\epsilon)$.

Combining this result with (4.4) which can be rewritten as

$$\eta_{KU}{}^1(\epsilon)=\frac{\rho^2}{\epsilon^2KT}\int\int d\mathbf{p}_1dx_2\chi(\mathbf{p}_1)\epsilon G_2(12)\psi(12)$$
$$\times\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2)+O(\rho^2,\rho^3/\epsilon), \quad (4.19)$$

we obtain

$$\eta_{KU}(\epsilon)=\eta_{KU}{}^1(\epsilon)+\eta_{KU}{}^r(\epsilon)$$
$$=\frac{\rho^2}{\epsilon KT}\int\int d\mathbf{p}_1dx_2\chi(\mathbf{p}_1)\left[1-\frac{\rho}{\epsilon}\Gamma(12)\right]$$
$$\times\epsilon G_2(12)\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2), \quad (4.20)$$

where we have omitted the terms with higher powers of ρ. We can now replace $1-\epsilon^{-1}\rho\Gamma(12)$ by

$$[1+\epsilon^{-1}\rho\Gamma(12)]^{-1}$$

in (4.20) and take the limit $\epsilon\to 0+$, and obtain

$$\eta_{KU}=\frac{\rho}{KT}\int\int d\mathbf{p}_1dx_2\chi(\mathbf{p}_1)\{\Gamma^{-1}(12)\epsilon G_2(12)\}_+\psi(12)$$
$$\times\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2). \quad (4.21)$$

In another form, this becomes

$$\eta_{KU}=\frac{\rho}{KT}\int\int d\mathbf{p}_1dx_2\chi(\mathbf{p}_1)X_+(12)\Phi(\mathbf{p}^2), \quad (4.22)$$

where X is a function of x_1 and x_2 which has the same tensor property as $\chi(\mathbf{p}_1)$, and satisfies the following equation:

$$\Gamma(12)X(12)\Phi(\mathbf{p}^2)=\epsilon G_2(12)\psi(12)$$
$$\times\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2). \quad (4.23)$$

The result (4.22) and (4.23) is a generalization of I(4.16) and I(4.17). In fact, for repulsive forces, the former reduces to the latter as we demonstrate in Appendix C. There we also present an argument which enables us to write $X(12)$ in the form

$$X(12)=\epsilon G_2(12)X_b(12)+X_u(12), \quad (4.24)$$

where $X_b(12)$ is nonvanishing only for bound states of the pair 12 for which $X_u(12)$ vanishes.

We now turn to the contribution from the part of the dynamical fluxes containing three-body forces, which by (2.2) and (2.3) we can write as

$$\Delta\eta_{KU}(\epsilon)=\frac{\rho}{KT}\int dx^N\chi(\mathbf{p}_1)G_N \times\left\{\frac{(N-1)(N-2)}{2}\psi(123) +\frac{(N-1)(N-2)(N-3)}{6}\psi(234)\right\} \times\rho(\mathbf{r}^N)\Phi(\mathbf{p}^N). \quad (4.25)$$

Corresponding to the expansion of G_N, (2.6), we split up $\Delta\eta_{KU}(\epsilon)$ as

$$\Delta\eta_{KU}(\epsilon)=\Delta\eta_{KU}{}^0(\epsilon)+\Delta\eta_{KU}{}^1(\epsilon)+\Delta\eta_{KU}{}^r(\epsilon) +(\text{terms involving more than three particles}). \quad (4.26)$$

$\Delta\eta_{KU}{}^0(\epsilon)$ involves an integral of the form

$$\int d\mathbf{p}_1\chi(\mathbf{p}_1)\varphi(p_1)$$

which obviously vanishes, and so does $\Delta\eta_{KU}{}^0(\epsilon)$. The next two terms in (4.26) become

$$\Delta\eta_{KU}{}^1(\epsilon)=-\frac{\rho^3}{\epsilon KT}\int d\mathbf{p}^3 \times\int\int d\mathbf{r}_2d\mathbf{r}_3\chi(\mathbf{p}_1)T_{12}G_0\psi(123) \times\exp\{-\beta U(123)\}\Phi(\mathbf{p}^3) \quad (4.27)$$

and

$$\Delta\eta_{KU}{}^r(\epsilon)=\frac{\rho^3}{2\epsilon^2KT}\int d\mathbf{p}^3 \times\int\int d\mathbf{r}_2d\mathbf{r}_3\chi(\mathbf{p}_1)\epsilon^2G_3{}^{r'}(123)\psi(123) \times\exp\{-\beta U(123)\}\Phi(\mathbf{p}^3), \quad (4.28)$$

where we have left out the terms of higher order in ρ coming from the configurational distribution function. In (4.27), G_0 is, in general, not equal to ϵ^{-1}, except for one term which gives a contribution of $O(N^{-1})$, and T_{12} is nonsingular as $\epsilon\to 0+$. Therefore $\Delta\eta_{KU}{}^1(\epsilon)$ is of the order of $\epsilon^{-1}\rho^3$. By an analysis similar to that given for $\Delta\eta_{KU}{}^r(\epsilon)$, (4.5), we easily see that the coefficient of ϵ^{-2} in (4.28) goes to zero as $\epsilon\to 0+$ simply because the particles 1, 2, and 3 must be close to each other at the time $-t$ because of the presence of $\psi(123)$. Thus $\Delta\eta_{KU}{}^r(\epsilon)$ is at most of the order of $\epsilon^{-1}\rho^3$. Therefore, we conclude that the part of the dynamical fluxes containing the three-body potentials does not give a first density correction to η_{KU}. This and the similar result for η_{UU} obtained below is what we would expect from the general remarks made in Sec. 2.

5. CALCULATION OF η_{UU}

If for the moment we restrict our considerations to that part of the dynamical flux which contains only pair potentials, the expression for $\eta_{UU}(\epsilon)$ given by I (5.9) becomes, by making use of the identity of the particles,

$$\eta_{UU}(\epsilon)=\frac{\rho^2V}{2KT}\int dx^N\psi(12)G_N\{\psi(12)+(N-2) \times[\psi(13)+\psi(23)]+\tfrac{1}{2}[(N-2)(N-3)]\psi(34)\} \times\rho(\mathbf{r}^N)\Phi(\mathbf{p}^N). \quad (5.1)$$

We split up (5.1) as

$$\eta_{UU}(\epsilon)=\eta_{UU}{}^0(\epsilon)+\eta_{UU}{}^1(\epsilon)+\eta_{UU}{}^r(\epsilon)+(\text{terms containing more than three particles}), \quad (5.2)$$

which corresponds to the expansion (2.6). $\eta_{UU}{}^0(\epsilon)$ is obtained by replacing G_N by G_0. It is of the order of $\epsilon^0\rho^2$ and does not contribute to the first density correction. $\eta_{UU}{}^1(\epsilon)$ involves single binary collisions and can be written as

$$\eta_{UU}{}^1(\epsilon)=\frac{\rho^2}{2\epsilon KT}\int\int d\mathbf{p}^2d\mathbf{r}_2\psi(12)\epsilon G_2(12)\psi(12) \times\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2)+O(\epsilon^0\rho^2). \quad (5.3)$$

The coefficient of ϵ^{-1} above is

$$\frac{\rho^2}{2KT}\int\int d\mathbf{p}^2d\mathbf{r}_2\epsilon \times\int_0^\infty dt\exp(-\epsilon t)\psi(12)S_{-t}{}^{(2)}(12)\psi(12) \times\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2) \quad (5.4)$$

and the contributions in the time integral come from very large values of t of order ϵ^{-1}. Thus only the bound states of the pair 12 give finite contributions to (5.4) as $\epsilon\to 0+$. $\eta_{UU}{}^r(\epsilon)$ is the remainder which involves three particles 1, 2, and 3, and can be written as

$$\eta_{UU}{}^r(\epsilon)=-\frac{\rho^3}{2\epsilon^2KT}\int\int\int d\mathbf{p}^3d\mathbf{r}_2d\mathbf{r}_3\psi(12)G_3{}^{r'}(123) \times\{\psi(12)+\psi(23)+\psi(31)\} \times\exp\{-\beta U(123)\}\Phi(\mathbf{p}^3), \quad (5.5)$$

where $G_3{}^{r'}(123)$ is defined by (4.6). Making use of the same kind of transformations which lead us from (4.5)

to (4.17), (5.5) becomes

$$\eta_{UU^r}(\epsilon)=-\frac{\rho^3}{2\epsilon^2 KT}\int\int d\mathbf{p}^2 d\mathbf{r}_2\psi(12)2\Gamma(12)$$
$$\times\epsilon G_2(12)\psi(12)\exp\{-\beta u(12)\}$$
$$\times\Phi(\mathbf{p}^2)+O(\rho^3/\epsilon), \quad (5.6)$$

where $\Gamma(12)$ is defined by (4.18) and is regarded as a nonsingular operator for $\epsilon\to 0+$.

From (5.2), (5.3), and (5.6) we obtain

$$\eta_{UU}(\epsilon)=\frac{\rho^2}{2\epsilon KT}\int\int d\mathbf{p}^2 d\mathbf{r}_2\psi(12)\left[1-\frac{2\rho}{\epsilon}\Gamma(12)\right]$$
$$\times\epsilon G_2(12)\psi(12)\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2)$$
$$+(\text{terms involving more than three particles}). \quad (5.7)$$

Here we have left out the terms of the order of $\epsilon^0\rho^2$ and $\epsilon^{-1}\rho^3$ which do not contribute to the first density correction. Again replacing $1-2\epsilon^{-1}\rho\Gamma(12)$ by

$$[1+2\epsilon^{-1}\rho\Gamma(12)]^{-1}$$

and taking the limit $\epsilon\to 0+$, we arrive at the following contribution to the first density correction to the shear viscosity:

$$\eta_{UU}=\frac{\rho}{4KT}\int\int d\mathbf{p}^2 d\mathbf{r}_2\psi(12)[\Gamma^{-1}(12)\epsilon G_2(12)]_+$$
$$\times\psi(12)\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2). \quad (5.8)$$

The same sort of arguments given for $\Delta\eta_{KU}(\epsilon)$ in Sec. 4 can be applied to the contribution of the part of dynamical fluxes containing the three-body forces to η_{UU}. We find that these terms do not contribute to the first-density correction to the shear viscosity. We have represented the processes contributing to $\eta_{UU}{}^1(\epsilon)$ and $\eta_{UU}{}^r(\epsilon)$ by Figs. 4(a) and 4(b), respectively.

6. THE RESULT AND ITS DIAGRAMMATIC REPRESENTATION

Summarizing the results of the preceding sections, (3.16), (3.17), (3.18), (4.22), (4.23), and (5.9), we obtain the following expression for the shear viscosity up to the first density correction:

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

where

$$\eta^{(0)}\equiv\frac{1}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)\mathfrak{L}_+^{-1}(\mathbf{p}_1)\chi(\mathbf{p}_1)\varphi(p_1) \quad (6.2)$$

and

$$\eta^{(1)}=\eta_{KK1}{}^{(1)}+\eta_{KKr}{}^{(1)}+\eta_{KU}{}^{(1)}+\eta_{UK}{}^{(1)}+\eta_{UU}{}^{(1)} \quad (6.3)$$

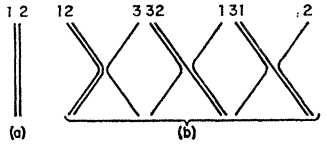

FIG. 4. (a) describes the process contributing to $\eta_{UU}{}^1(\epsilon)$ and (b) describes those contributing to $\eta_{UU}{}^r(\epsilon)$.

with

$$\eta_{KK1}{}^{(1)}\equiv-\frac{1}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)\mathfrak{L}_+^{-1}(\mathbf{p}_1)t_{1+}(\mathbf{p}_1)$$
$$\times\chi(\mathbf{p}_1)\varphi(p_1), \quad (6.4)$$

$$\eta_{KKr}{}^{(1)}\equiv-\frac{1}{KT}\int d\mathbf{p}_1\chi(\mathbf{p}_1)\mathfrak{L}_+^{-1}(\mathbf{p}_1)\hat{t}_+{}^r(\mathbf{p}_1)$$
$$\times\mathfrak{L}_+^{-1}(\mathbf{p}_1)\chi(\mathbf{p}_1)\varphi(p_1), \quad (6.5)$$

$$\eta_{KU}{}^{(1)}=\eta_{UK}{}^{(1)}\equiv\frac{1}{KT}\int\int d\mathbf{p}_1 dx_2\chi(\mathbf{p}_1)$$
$$\times[\Gamma^{-1}(12)\epsilon G_2(12)]_+\psi(12)$$
$$\times\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2), \quad (6.6)$$

$$\eta_{UU}{}^{(1)}\equiv\frac{1}{4KT}\int\int d\mathbf{p}_1 dx_2\psi(12)$$
$$\times[\Gamma^{-1}(12)\epsilon G_2(12)]_+\psi(12)$$
$$\times\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2). \quad (6.7)$$

We now present a rather intuitive interpretation of the various contributions with the help of diagrams which describe various collision processes contributing to the shear viscosity. To begin with, we consider the Chapman-Enskog result (6.2). As we have discussed in Sec. 2, the operator $\mathfrak{L}_+^{-1}(\mathbf{p}_1)$ appears when $\epsilon^{-1}-\epsilon^{-2}\rho\times\mathfrak{L}(\mathbf{p}_1)$ is replaced by $\epsilon^{-1}[1+\epsilon^{-1}\rho\mathfrak{L}(\mathbf{p}_1)]^{-1}$ and the limit $\epsilon\to 0+$ is taken. Implicit in this procedure is the fact that the term of order $\epsilon^{-1}(\rho/\epsilon)^n$ is simply $\epsilon^{-1}[-\rho\mathfrak{L}(\mathbf{p}_1)/\epsilon]^n$. Since $\mathfrak{L}(\mathbf{p}_1)$ describes a binary collision of the particle 1 with another particle, this term represents n successive binary collisions of the particle 1 with n other particles. This situation is represented in Fig. 5(a) for $n=3$, where a straight line represents the free particle propagator $1/\epsilon$, a circle represents a binary collision, and a cross means that we integrate over the phase space of the particle represented by the line with the cross. One can see now that these are the only processes that give rise to contributions of order $(\rho/\epsilon)^n$ to $\eta(\epsilon)$. These processes are then summed over all n to yield the modified one-particle propagator $\rho^{-1}\mathfrak{L}^{-1}(\mathbf{p}_1)$ as $\epsilon\to 0+$. This is described in Fig. 5(b) where the thick line represents the modified one-particle propagator which is temporarily denoted by $A_1(\mathbf{p}_1)$. The whole process contributing to $\eta^{(0)}$ is represented in Fig. 5(c) where another factor ρ comes from the N possible choices of the particle 1. The fact that

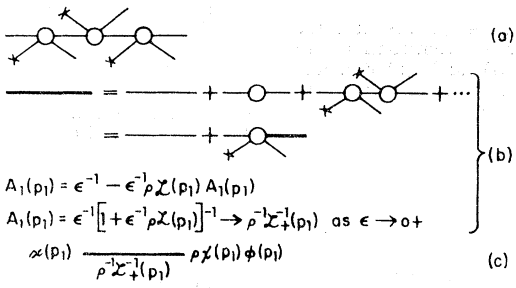

FIG. 5. The processes contributing to the zeroth order term in density of the shear viscosity.

$\eta^{(0)}$ is independent of ρ becomes apparent when the factors appearing in Fig. 5(c) are multiplied.

Before turning to the first-density correction we discuss the meaning of the modified propagator. The unmodified propagator $\epsilon^{-1}=G_0(0|0)$ describes the motion of the noninteracting particle 1 in a homogeneous, spatially uncorrelated situation, and ϵ^{-1} can be looked upon as the lifetime of such a state of motion in the absence of interactions among particles; thus it can become infinite as $\epsilon \to 0+$. The modification of the propagator introduces the collisions, and thus makes this lifetime finite. In other words, the modified propagator $\rho^{-1}\mathfrak{L}^{-1}(\mathbf{p}_1)$ can be considered to be a measure of the mean free time between collisions of particle 1. It is well known that $\mathfrak{L}(\mathbf{p}_1)$, the linearized Boltzmann collision operator, is positive definite except when operating on the collision invariants.[18]

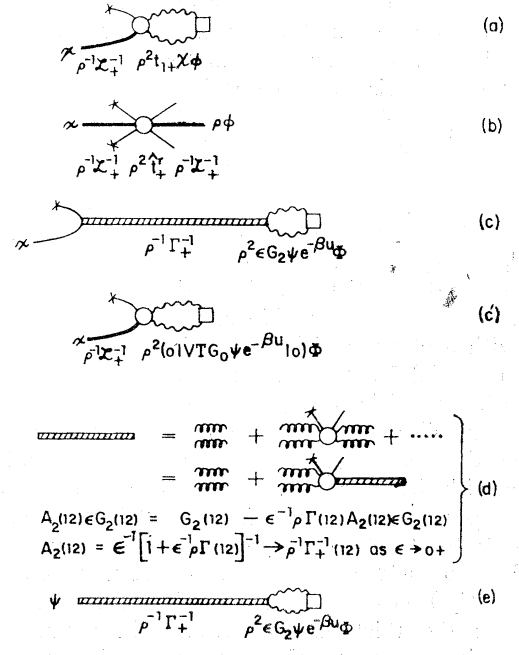

FIG. 6. The various processes contributing to the first-density correction to the shear viscosity.

[18] L. Waldmann, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. XII, p. 365.

Turning now to the first-order density correction, similar considerations enable us to construct the diagrams for $\eta^{(1)}$ as we see in Fig. 6. $\eta_{KK1}{}^{(1)}$ is represented by Fig. 6(a), where a pair of wavy lines represents the propagation of a freely moving, spatially correlated pair of particles created by $F_0(r_{12})$ in t_{1+} (3.6). The square represents the source of the spatial correlation, here, $F_0(r_{12})$. Figure 6(b) describes $\eta_{KKr}{}^{(1)}$ where the circle represents the triple collision. $\eta_{KU}{}^{(1)}$ is represented by Fig. 6(c) where the hatched part is the modified propagator of the pair of interacting particles which is represented in Fig. 6(d). There a pair of helical lines represents the unmodified propagator for the pair of interacting particles. This pair of particles can undergo repeated collisions with other particles (actually triple collisions) giving rise to the modified propagator for the pair in just the same way as we obtained the modified single-particle propagator in Fig. 5(b). The modified propagator for the pair is again the measure of the mean free time between collisions for the pair. Finally Fig. 6(e) describes $\eta_{UU}{}^{(1)}(\epsilon)$. The ρ dependence of $\eta^{(1)}$ again becomes apparent by multiplying the factors appearing in each diagram.

Let us now go briefly to the case of repulsive intermolecular forces. Figure 5 and Fig. 6(a), (b) remain unchanged. Since two particles cannot stay close together, the modified two particle propagator splits into two lines, and Fig. 6(c) reduces to Fig. 6(c'). For the same reason, no contribution is expected from Fig. 6(e) representing $\eta_{UU}{}^{(1)}$ in agreement with I.

7. CONCLUSION AND SOME REMARKS

In the foregoing sections we obtained an explicit expression for the first density correction to the shear viscosity for systems with attractive forces including the bound states. We assume that at densities of interest the number of bound clusters is small (becoming smaller as the size of the clusters becomes larger) compared to N. We have seen that only the bound pairs contribute to the first density correction. In higher density corrections, bound states involving more particles contribute. In the nth density correction the largest bound cluster involved consists of $n+1$ particles.

In the present work, we have defined the bound states in such a way that they have infinite lifetimes when left isolated. However, recently Kim and Ross[9] have pointed out that the states in which the particles stay close together for a long but finite time, the so-called "quasibound" and "metastable" states, cannot be ignored in understanding the temperature dependence of the first density correction to the shear viscosity. In our theory, we have classified these clusters with finite lifetimes as unbound states. Such a classification is justified in obtaining the entire density expansion of $\eta(\rho)$ in a strictly mathematical sense. In practice, however, we are more interested in the

density expansion as an approximation for $\eta(\rho)$ for a small but finite ρ. Then our classification, in effect, completely neglects the collisions of these clusters (while they form "quasi" or "metastable" bound states) with other particles. This is only justified if the average lifetime of these clusters is sufficiently small compared to the mean free time between their collisions with other particles. In the opposite case, these clusters behave as though they are true bound states because they undergo a great many collisions before spontaneous disintegration.[8] This situation can be treated if we relax the definition of bound clusters so as to include those clusters whose lifetimes are very large compared to the mean free time between collisions.

If these two time scales are of the same order of magnitude, the situation becomes more subtle. As an illustration, we consider the contribution of these "metastable" or "quasi" bound states with natural lifetime τ_0 to η_{UU}. Roughly speaking this contribution would have a form

$$\text{const.}\times\rho^2(\alpha\rho+\tau_0^{-1})^{-1}, \tag{7.1}$$

where $(\alpha\rho)^{-1}$ designates the mean lifetime of the bound states due to collisions with other particles. In a strictly mathematical sense there is no first density correction arising from these bound states. However, for $\alpha\rho\gtrsim\tau_0^{-1}$, the convergence of the density-expansion series will become very poor and may, in fact, diverge. Thus in this case a separate treatment which does not make use of density expansions is required. When $\alpha\rho\gg\tau_0^{-1}$, (7.1) is proportional to the density and produces a contribution to the first density correction to η (see Refs. 8 and 9). It is clear that the resulting term cannot be looked upon as part of an analytic expansion in powers of the density since (7.1) is proportional to ρ^2 for small enough ρ.

APPENDIX A: SOME PROPERTIES OF THE BINARY COLLISION OPERATORS

Here we discuss the properties of the binary-collision operator T_{12} in the limit $\epsilon\to 0+$. In I, we have shown by using the formula

$$T_{12}=-\theta_{12}-\theta_{12}G_2(12)\theta_{12} \tag{A1}$$

that in the absence of bound states, T_{12} is nonsingular as $\epsilon\to 0+$ simply because the two particles 1 and 2 initially within the range of mutual interactions will find themselves far apart after a sufficient lapse of time. Obviously, one cannot expect this if one allows for bound molecular clusters, and thus a separate investigation is necessary.

We shall start with an alternative formula for T_{12}

$$T_{12}=-\int_0^\infty dt e^{-\epsilon t}G_0^{-1}[S_{-t}^{(2)}(12)-S_{-t}^{(0)}]G_0^{-1}, \tag{A2}$$

which follows from I(2.25) and the definitions of the resolvent operators. The general matrix element of (A2) is [see I(3.2), I(3.7), and I(3.8)]

$$VT_{12}(\mathbf{k}^N|\mathbf{k}'^N)=-\int_0^\infty dt e^{-\epsilon t}\left[\epsilon+i\frac{\mathbf{p}^N\cdot\mathbf{k}^N}{m}\right]\times(\mathbf{k}^N|V[S_{-t}^{(2)}-S_{-t}^{(0)}]|\mathbf{k}'^N)\times[\epsilon+i(\mathbf{p}^N\cdot\mathbf{k}'^N/m)]. \tag{A3}$$

Since interactions exist only between the particles 1 and 2, we can separate out the relative motion of the particles 1 and 2 from the rest. The rest consists of the motion of the noninteracting particles $3\cdots N$ and the center of mass motion of the particles 1 and 2, and gives rise to a factor e^{-itl} in the integrand, where

$$l\equiv(\mathbf{k}_1+\mathbf{k}_2)\cdot(\mathbf{p}_1+\mathbf{p}_2)/2+\sum_{i=3}^N\mathbf{k}_i\cdot\mathbf{p}_i.$$

Note that $\mathbf{k}_1'+\mathbf{k}_2'=\mathbf{k}_1+\mathbf{k}_2$ and $\mathbf{k}_i'=\mathbf{k}_i$, $i=3, 4, \cdots N$. Therefore, when $l\neq 0$, the integrand has an oscillating factor in time, and no singularity appears as $\epsilon\to 0+$. This enables us to limit our consideration to the case $l=0$, and to the relative motion of the particles 1 and 2. Writing explicitly only the relative wave vector $\mathbf{k}\equiv(\mathbf{k}_1-\mathbf{k}_2)/2$, and introducing the relative momentum $\mathbf{p}\equiv(\mathbf{p}_1-\mathbf{p}_2)/2$ and the reduced mass $\mu=m/2$, we have

$$VT_{12}(\mathbf{k}|\mathbf{k}')=-\int_0^\infty dt e^{-\epsilon t}(\epsilon+i\mathbf{p}\cdot\mathbf{k}/\mu)\times(\mathbf{k}|V[S_{-t}^{(2)}-S_{-t}^{(0)}]|\mathbf{k}')(\epsilon+i\mathbf{p}\cdot\mathbf{k}'/\mu). \tag{A4}$$

According to the definition of the matrix element [see I(3.2)], the above expression actually involves an integral over the relative coordinates $\mathbf{r}_{12}$. For small enough values of the relative momentum $\mathbf{p}$, the region of $\mathbf{r}_{12}$ splits into the region in which the particles 1 and 2 form a bound cluster and that in which these particles remain unbound. Corresponding to these two regions we write

$$VT_{12}(\mathbf{k}|\mathbf{k}')=VT_{12}{}^b(\mathbf{k}|\mathbf{k}')+VT_{12}{}^u(\mathbf{k}|\mathbf{k}'), \tag{A5}$$

where

$$VT_{12}{}^b(\mathbf{k}|\mathbf{k}')\equiv-\int_0^\infty dt e^{-\epsilon t}(\epsilon+i\mathbf{p}\cdot\mathbf{k}/\mu)\times(\mathbf{k}|E_b(12)V[S_{-t}^{(2)}-S_{-t}^{(0)}]|\mathbf{k}')\times(\epsilon+i\mathbf{p}\cdot\mathbf{k}'/\mu), \tag{A6}$$

where $E_b(12)$ is a function of the relative coordinates and momenta of particles 1 and 2 which takes the value 1 when these particles form a bound pair and is zero otherwise. $VT_{12}{}^u(\mathbf{k}|\mathbf{k}')$ has the same form as (A6) except that $E_b(12)$ is replaced by $1-E_b(12)$. Since $VT_{12}{}^u(\mathbf{k}|\mathbf{k}')$ is nonsingular, we need examine only the

various matrix elements of $VT_{12}{}^{b}(\mathbf{k}|\mathbf{k}')$.

(a) $VT_{12}{}^{b}(0|0)$

$$=-\epsilon^2\left(0\left|V\int_0^\infty dte^{-\epsilon t}E_b(12)\times V[S_{-t}{}^{(2)}-S_{-t}{}^{(0)}]\right|0\right), \quad \text{(A7)}$$

$$=-\epsilon(0|VE_b(12)[\bar{S}_\epsilon{}^{(2)}-\bar{S}_\epsilon{}^{(0)}]|0), \quad \text{(A8)}$$

where we have introduced the notation

$$\bar{S}_\epsilon\equiv\int_0^\infty dte^{-\epsilon t}S_{-t}\Big/\int_0^\infty dte^{-\epsilon t}=\epsilon G(\epsilon). \quad \text{(A9)}$$

For the unbound states, $\bar{S}_\epsilon$ reduces to $S_{-\infty}$ as $\epsilon\to 0+$, whereas for bound states $\bar{S}_\epsilon$ reduces to the average of S_{-t} over a period of the relative motion. Since bound states come from a finite region in the relative coordinate space, the operator in the bracket in (A8) is nonsingular as $\epsilon\to 0+$, and in this limit $VT_{12}{}^{b}(0|0)$ vanishes. We note that only $VT_\alpha(0|0)$ appears in the Boltzmann collision operator, and therefore the bound states do not contribute to the Boltzmann collision operator, as was first noted explicitly by Kirkwood.[19]

(b) $VT_{12}{}^{b}(0|\mathbf{k})$

$$=-(0|VE_b(12)[\bar{S}_\epsilon{}^{(2)}(12)-S_\epsilon{}^{(0)}]|\mathbf{k})\times(\epsilon+i\mathbf{p}\cdot\mathbf{k}/\mu), \quad (\mathbf{k}\neq 0). \quad \text{(A10)}$$

As in (a), the operator in the bracket is finite as $\epsilon\to 0+$, and the bound states give a finite contribution to the matrix element $VT_{12}{}^{b}(0|\mathbf{k})$. The same is true for $VT_{12}{}^{b}(\mathbf{k}|0)$. This property also follows from (A1).

(c) $VT_{12}{}^{b}(\mathbf{k}|\mathbf{k}')$

$$=-\epsilon^{-1}(\epsilon+i\mathbf{p}\cdot\mathbf{k}/\mu)(\mathbf{k}|VE_b(12)\times[\bar{S}_\epsilon{}^{(2)}(12)-\bar{S}_\epsilon{}^{(0)}]\mathbf{k}')(\epsilon+i\mathbf{p}\cdot\mathbf{k}'/\mu), \quad (\mathbf{k},\mathbf{k}'\neq 0). \quad \text{(A11)}$$

Here again the operator in the bracket is nonsingular and is finite in general as $\epsilon\to 0+$, thus we should expect a singularity of the form $1/\epsilon$ for $VT_{12}{}^{b}(\mathbf{k}|\mathbf{k}')$ as $\epsilon\to 0+$. As one notes from (A1), this is a consequence of the fact that in the bound states, particles stay close together for indefinite lengths of time.

APPENDIX B: SURFACE INTEGRAL FORMS FOR THE TRIPLE COLLISION OPERATOR

Here we shall rewrite the triple-collision operator which appeared in Sec. 3 in terms of the streaming operators and surface integrals.

[19] J. G. Kirkwood, J. Chem. Phys. **15**, 72 (1947).

Consider the operator on the momenta $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{p}_3$,

$$J(\mathbf{p}^3)\equiv\int\int d\mathbf{r}_2d\mathbf{r}_3\epsilon^2[G_3(123)-G_0+\sum_\alpha G_0T_\alpha G_0-\sum_\alpha\sum_\beta{}' G_0T_\alpha G_0T_\beta G_0]\exp\{-\beta U(123)\}, \quad \text{(B1)}$$

where the summations have the same meaning as in (3.19). First we eliminate T_α in terms of $G_2(\alpha)$ to obtain

$$J(\mathbf{p}^3)=\int\int d\mathbf{r}_2d\mathbf{r}_3\epsilon^2[G_3-\sum_\alpha\sum_\beta{}' G_2(\alpha)G_0{}^{-1}G_2(\beta)+3\sum_\alpha G_2(\alpha)-4G_0]\exp\{-\beta U(123)\}. \quad \text{(B2)}$$

Expressing the resolvent operators in terms of the corresponding streaming operators, (B2) becomes

$$J(\mathbf{p}^3)=\int\int d\mathbf{r}_2d\mathbf{r}_3\epsilon^2\int_0^\infty dt\exp(-\epsilon t)S_{-t}{}^{r}(123)\times\exp\{-\beta U(123)\}=\epsilon^2\int_0^\infty dt\exp(-\epsilon t)B(\mathbf{p}^3;t), \quad \text{(B3)}$$

where

$$S_{-t}{}^{r}(123)\equiv S_{-t}{}^{(3)}(123)-\sum_\alpha\sum_\beta{}'\int_0^t S_{-t+\tau}{}^{(2)}(\alpha)\times(\epsilon+iL_0)S_{-\tau}{}^{(2)}(\beta)d\tau+3\sum_\alpha S_{-t}{}^{(2)}(\alpha)-4S_{-t}{}^{(0)} \quad \text{(B4)}$$

and $B(\mathbf{p}^3;t)$ is given by (3.21). In Sec. 3 we have seen that $B(\mathbf{p}^3;t)$ has the form

$$B(\mathbf{p}^3;t)=tC(\mathbf{p}^3;t)+D(\mathbf{p}^3;t), \quad \text{(B5)}$$

where $C(\mathbf{p}^3;t)$ and $D(\mathbf{p}^3;t)$ stay finite for large values of t, and that only the first term contributes to (B3) in the limit $\epsilon\to 0+$. Therefore, neglecting $D(\mathbf{p}^3;t)$, we can write (B3) as

$$J(\mathbf{p}^3)=\langle C(\mathbf{p}^3;t)\rangle^\epsilon, \quad \text{(B6)}$$

where the symbol $\langle\ \rangle^\epsilon$ indicates a certain time average defined by

$$\langle C(\mathbf{p}^3;t)\rangle^\epsilon\equiv\int_0^\infty dtte^{-\epsilon t}C(\mathbf{p}^3;t)\Big/\int_0^\infty dtte^{-\epsilon t}. \quad \text{(B7)}$$

When no bound states are involved, $C(\mathbf{p}^3;t)$ has a well-defined limit at $t=+\infty$, and we obtain

$$\lim_{\epsilon\to 0+}J(\mathbf{p}^3)=\lim_{t\to\infty}C(\mathbf{p}^3;t). \quad \text{(B8)}$$

When there are bound states at large t, $C(\mathbf{p}^3;t)$ contains contributions oscillating in time, and (B7) implies that the time average should be taken over such oscillating contributions as in Appendix A.

Explicit expressions for $C(\mathbf{p}^3;t)$ are obtained by transforming the six-dimensional coordinate integral over $\mathbf{r}_2$ and $\mathbf{r}_3$ into a five-dimensional surface integral as has been done by Green for the case of repulsive interactions.[17] Since different transformations are necessary for the regions of configuration space with and without bound states, we shall discuss these two separately.

We first consider the contribution from the regions with no bound states at the time $t=0$. Here the transformation is exactly the same as in Green's paper. The volume element for $\mathbf{r}_2$ and $\mathbf{r}_3$ can be rewritten as

$$d\mathbf{r}_2 d\mathbf{r}_3 = (|\mathbf{p}_2-\mathbf{p}_1|/m)dt_{21}d\mathbf{b}_{21} \times(|\mathbf{p}_3-\mathbf{p}_1|/m)dt_{31}d\mathbf{b}_{31}, \quad \text{(B9)}$$

where t_{21} and $\mathbf{b}_{21}$ are the time of collision and the collision parameter for the pair 12 and t_{31} and $\mathbf{b}_{31}$ have a similar meaning for the pair 13.[20] We now write $dt_{21}dt_{31}$ as $dtd\tau$ where $t\equiv t_{21}$ and $\tau\equiv t_{31}-t_{21}$. Changing t with fixed τ, $\mathbf{b}_{21}$, $\mathbf{b}_{31}$ merely changes the time at which the whole event occurs. Thus the integration with respect to t produces a term proportional to t plus a term which stays finite for large t and is of no interest to us. Therefore, by (B3), (B5), and (B6) we obtain the desired surface integral form for $J(\mathbf{p}^3)$ in the absence of bound states,

$$\lim_{\epsilon\to 0+} J_u(\mathbf{p}^3) = \int E_u(123)\frac{|\mathbf{p}_2-\mathbf{p}_1|}{m}\frac{|\mathbf{p}_3-\mathbf{p}_1|}{m}d\mathbf{b}_{21}d\mathbf{b}_{31} \times d\tau \lim_{t\to\infty} S_{-t}{}^r(123)\exp\{-\beta U(123)\}, \quad \text{(B10)}$$

where $J_u(\mathbf{p}^3)$ is the part of $J(\mathbf{p}^3)$ in which no bound states are involved at $t=0$ and $E_u(123)$ is a function of x_1, x_2, and x_3 which takes the value unity when the point (x_1,x_2,x_3) involves no bound states, and otherwise vanishes.

Next we consider the cases where bound states are involved. Since the three-particle bound states give only vanishing contributions, it is sufficient to consider the case when one of the pairs, say (12), forms a bound state at the time $t=0$. Since for fixed $\mathbf{r}_1$, $\mathbf{r}_2$ describes the internal configuration of the bound pair, we have to consider the transformation of $\mathbf{r}_3$, which can be done by considering the process as a binary collision of 3 with the bound pair (12). That is

$$d\mathbf{r}_3 = |\mathbf{p}_3/m-(\mathbf{p}_1+\mathbf{p}_2)/2m|d\mathbf{b}_3 dt_3, \quad \text{(B11)}$$

where $\mathbf{b}_3$ is the collision parameter and t_3 is the collision time.[21] The integration over t_3 again produces a term proportional to t and a term finite at large t. Thus by (B3), (B5), and (B6), we obtain

$$\lim_{\epsilon\to 0+} J_b(\mathbf{p}^3) = \int E_b(12:3)\left|\frac{\mathbf{p}_3}{m}-\frac{\mathbf{p}_1+\mathbf{p}_2}{2m}\right|d\mathbf{b}_3 d\mathbf{r}_2 \times\langle S_{-t}{}^r(123)\rangle^{0+}\exp\{-\beta U(123)\}, \quad \text{(B12)}$$

where $J_b(\mathbf{p}^3)$ is the part of $J(\mathbf{p}^3)$ involving the bound pair (12) at $t=0$ and $E_b(12:3)$ is a function of x_1, x_2, and x_3 which is equal to unity for those points (x_1,x_2,x_3) in which only the pair (12) forms a bound state and vanishes for other points.

When the intermolecular forces are repulsive and of short range, $\exp\{-\beta U(123)\}$ in (B2) can be replaced by unity (see I Sec. III). Then, we can replace G_0^{-1} by ϵ, and (B2) becomes

$$J(\mathbf{p}^3) = \int\int d\mathbf{r}_2 d\mathbf{r}_3 \epsilon^2[G_3' - \epsilon\sum_\alpha{\sum_\beta}' G_2'(\alpha)G_2'(\beta)], \quad \text{(B13)}$$

where

$$G_3' \equiv G_3 - \sum_\alpha G_2(\alpha) + 2G_0, \qquad G_2'(\alpha)\equiv G_2(\alpha)-G_0. \quad \text{(B14)}$$

Introducing appropriate streaming operators U_{-t} by

$$G_3' = \int_0^\infty dt e^{-\epsilon t}U_{-t}(123), \qquad G_3'(\alpha) = \int_0^\infty dt e^{-\epsilon t}U_{-t}(\alpha). \quad \text{(B15)}$$

Equation (B13) can also be written as

$$J(\mathbf{p}^3) = \epsilon^2\int_0^\infty dt e^{-\epsilon t}\int\int d\mathbf{r}_2 d\mathbf{r}_3\Big\{U_{-t}(123) - \epsilon\sum_\alpha{\sum_\beta}'\int_0^t d\tau U_{-t+\tau}(\alpha)U_{-\tau}(\beta)\Big\}. \quad \text{(B16)}$$

The second term can be transformed by integrating by parts with respect to time and by making use of the fact that $U_{-t}=0$ for $t=0$ to yield

$$J(\mathbf{p}^3) = \epsilon^2\int_0^\infty dt e^{-\epsilon t}\int\int d\mathbf{r}_2 d\mathbf{r}_3\tilde{S}_{-t}{}^r(123), \quad \text{(B17)}$$

where

$$\tilde{S}_{-t}{}^r(123)\equiv U_{-t}(123) - \sum_\alpha{\sum_\beta}'\int_0^t d\tau\frac{d}{dt}U_{-t+\tau}(\alpha)U_{-\tau}(\beta). \quad \text{(B18)}$$

By making use of the same transformation that leads us to (B10), we obtain from (B17)

$$\lim_{\epsilon\to 0+} J(\mathbf{p}^3) = \int\int\int\frac{|\mathbf{p}_2-\mathbf{p}_1|}{m}\frac{|\mathbf{p}_3-\mathbf{p}_1|}{m}d\mathbf{b}_{21}d\mathbf{b}_{31} \times d\tau\lim_{t\to\infty}\tilde{S}_{-t}{}^r(123). \quad \text{(B19)}$$

[20] For the precise meaning of these new coordinates, see Ref. 17.

[21] $\mathbf{b}_3$ and t_3 can be conveniently defined by replacing the pair (12) by a single particle at the center-of-mass point of the pair.

If we note that (B18) can be also written as

$$\tilde{S}_{-t}{}^{r}(123)=U_{-t}(123)$$
$$-\sum_{\alpha}\sum_{\beta}{}'\int_{-t/2}^{t/2}d\tau\left[\frac{d}{d\tau}U_{-\tau-t/2}(\alpha)\right]U_{\tau-t/2}(\beta), \quad \text{(B20)}$$

we see that our result (B19) is equivalent to the expression obtained by Green.[17]

APPENDIX C: SOME PROPERTIES OF $\Gamma(12)$

Here we shall first discuss $\Gamma(12)$ for the case with repulsive pair intermolecular forces of a finite range and consider η_{KU} given by (4.22) and (4.23). As we have discussed in Sec. 2, in obtaining these results we first replaced $1-\epsilon^{-1}\rho\Gamma(12)$ by

$$[1+\epsilon^{-1}\rho\Gamma(12)]^{-1}=1+\sum_{n=1}^{\infty}(-\rho/\epsilon)^{n}\Gamma^{n}(12) \quad \text{(C1)}$$

assuming that the higher order terms in ρ/ϵ in the operator appearing in $\eta_{KU}(\epsilon)$ could be represented by the above expression. Thus, we have to consider the operators

$$\gamma_{n}(\mathbf{p}_1)\equiv\int d\mathbf{p}_2 V(0|\Gamma^{n}(12)\epsilon G_2(12)\psi(12)\times\exp\{-\beta u(12)\}|0)\varphi(p_2)$$
$$=\int d\mathbf{p}_2 V\sum_{\mathbf{k}}(0|\Gamma^{n}(12)|\mathbf{k},-\mathbf{k})(\mathbf{k},-\mathbf{k}|\times\epsilon G_2(12)\psi(12)\exp\{-\beta u(12)\}|0)\varphi(p_2). \quad \text{(C2)}$$

The matrix element

$$(\mathbf{k},-\mathbf{k}|\epsilon G_2(12)\psi(12)\exp\{-\beta u(12)\}|0)=\epsilon g(\mathbf{k},-\mathbf{k})(\mathbf{k},-\mathbf{k}|[1-T_{12}G_0]\psi(12)\times\exp\{-\beta u(12)\}|0)$$

and since the coefficient of ϵ is nonsingular for $\mathbf{k}\neq 0$, this expression vanishes as $\epsilon\to 0+$ for $\mathbf{k}\neq 0$. Thus (C2) becomes

$$\gamma_{n}(\mathbf{p}_1)=\int d\mathbf{p}_2(0|\Gamma^{n}(12)|0)V(0|\epsilon G_2(12)\psi(12)\times\exp\{-\beta u(12)\}|0)\varphi(p_2)+O(\epsilon). \quad \text{(C3)}$$

Next we consider $(\mathbf{k},-\mathbf{k}|\Gamma(12)|0)$ which according to (4.14) and (4.18) contains an expression of the form:

$$\epsilon(\mathbf{k},-\mathbf{k}|G_2(ij)T(ij:l)|0)=\epsilon g(\mathbf{k},-\mathbf{k})\times(\mathbf{k},-\mathbf{k}|\{\sum_{\alpha}^{\alpha\neq ij}T_{\alpha}-\sum_{\alpha}^{\alpha\neq ij}\sum_{\beta}{}'T_{\beta}G_0T_{\alpha}+\cdots\}|0), \quad \text{(C4)}$$

where (i,j,l) is a permutation of (1,2,3) and the summations are over the pairs (12), (13), and (23) with the restrictions indicated. For $\mathbf{k}\neq 0$, this term does not contribute as $\epsilon\to 0+$, since the number of terms which contains $G_0=\epsilon^{-1}$ is smaller by a factor N^{-1}. Thus (C3) reduces to

$$\gamma_{n}(\mathbf{p}_1)=\int d\mathbf{p}_2(0|\Gamma(12)|0)^{n}V(0|\epsilon G_2(12)\psi(12)\times\exp\{-\beta u(12)\}|0)\Phi(\mathbf{p}^2)+O(\epsilon). \quad \text{(C5)}$$

We now consider the case $\mathbf{k}=0$ of (C4) with $(i,j,l)=(1,2,3)$ which is,

$$\epsilon V(0|G_2(12)T(12:3)|0)$$
$$=V(0|\{\sum_{\alpha}^{\alpha\neq 12}T_{\alpha}-\sum_{\alpha}^{\alpha\neq 12}\sum_{\beta}{}'T_{\beta}G_0T_{\alpha}+\sum_{\alpha}^{\alpha\neq 12}\sum_{\beta}{}'\sum_{\gamma}{}'T_{\gamma}G_0T_{\beta}G_0T_{\alpha}-\cdots\}|0)$$
$$=\sum_{\alpha}^{\alpha\neq 12}VT_{\alpha}(0|0)-\epsilon^{-1}\sum_{\alpha}^{\alpha\neq 12}\sum_{\beta}{}'VT_{\beta}(0|0)T_{\alpha}(0|0)+\sum_{\alpha}^{\alpha\neq 12}\sum_{\beta}{}'\sum_{\gamma}{}'V(0|\{T_{\gamma}G_0T_{\beta}G_0T_{\alpha}-\cdots\}|0). \quad \text{(C6)}$$

If we remember the properties of $T_{\alpha}(0|0)$ and $(0|T_{\gamma}G_0T_{\beta}G_0T_{\alpha}|0)$, the second and the third terms of (C6) are of relative order of N^{-1} compared with the first term and can be ignored. Thus we obtain by (4.18)

$$(0|\Gamma(12)|0)=\frac{1}{2}\int d\mathbf{p}_3 V(1+\mathcal{P}_{23}+\mathcal{P}_{13})\times\{T_{13}(0|0)+T_{23}(0|0)\}\varphi(p_3). \quad \text{(C7)}$$

We now consider

$$\int d\mathbf{p}_2(0|\Gamma(12)|0)a(12)\Phi(\mathbf{p}^2)$$
$$=\frac{1}{2}\int\int d\mathbf{p}_2 d\mathbf{p}_3 V\{T_{13}(0|0)+T_{23}(0|0)+[T_{12}(0|0)+T_{23}(0|0)]\mathcal{P}_{23}+[T_{13}(0|0)+T_{12}(0|0)]\mathcal{P}_{13}\}a(12)\Phi(\mathbf{p}^3), \quad \text{(C8)}$$

where $a(12)$ is a function of $\mathbf{p}_1$ and $\mathbf{p}_2$ and has the property $a(12)=a(21)$. If we further note that

$$\int\int d\mathbf{p}_2 d\mathbf{p}_3 VT_{23}(0|0)\cdots=0 \quad \text{I(3.15)}$$

and use the symmetry property of $a(12)$, (C8) reduces to

$$\int d\mathbf{p}_2(0|\Gamma(12)|0)a(12)\Phi(\mathbf{p}^2)=\int d\mathbf{p}_2\mathfrak{L}(\mathbf{p}_1)a(12)\Phi(\mathbf{p}^2), \quad \text{(C9)}$$

where $\mathfrak{L}(\mathbf{p}_1)$ is the Boltzmann collision operator defined by (3.5). This result can be applied repeatedly to (C5) to yield

$$\gamma_n(\mathbf{p}_1)=\int d\mathbf{p}_2[\mathfrak{L}(\mathbf{p}_1)]^n V(0|\epsilon G_2(12)\psi(12) \times\exp\{-\beta u(12)\}|0)\Phi(\mathbf{p}^2)+O(\epsilon). \quad \text{(C10)}$$

Thus, in η_{KU} we can replace $\Gamma(12)$ by $\mathfrak{L}(\mathbf{p}_1)$ and obtain

$$\eta_{KU}=\frac{\rho}{KT}\int\int d\mathbf{p}_1 d\mathbf{p}_2 \mathfrak{L}_+^{-1}(\mathbf{p}_1)\int d\mathbf{r}_2[\epsilon G_2(12)]_+ \times\psi(12)\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2) \quad \text{(C11)}$$

which reduces to I(4.16) and I(4.17) if we notice that $\epsilon G_2(12)$ here can be replaced by $-T_{12}G_0$ because of (4.12).

We now turn to the case with attractive intermolecular forces. Since we need $\Gamma(12)$ in (4.20), (4.21), (4.23), (5.8), and (5.9), and also considering the remarks made at the beginning of this Appendix, we must consider $\Gamma(12)$ operating on expressions of the form:

$$\Gamma^n(12)\epsilon G_2(12)\psi(12)\exp\{-\beta u(12)\}\Phi(\mathbf{p}^2). \quad \text{(C12)}$$

We shall denote these operands in general by a symbol $Z(12)$. We now divide $Z(12)$ into two terms: one having contributions only from the bound states of the pair 12 at the time $t=0$, the other from unbound states at the time $t=0$. The former can be generally expressed in the form:

$$\epsilon G_2(12)Z_b(12) \quad \text{(C13)}$$

since in this case the interaction between the pair persists after collisions. Here $Z_b(12)$ is nonvanishing only in the region of bound pairs, and we have ignored the three-particle bound states because they do not contribute to (C12) for $n=1$ as $\epsilon\to 0+$. That this is also true for $n>1$ can be seen by repeated application of the result we shall obtain for $\Gamma(12)$ below. Then, we can write

$$Z(12)=\epsilon G_2(12)Z_b(12)+Z_u(12), \quad \text{(C14)}$$

where $Z_u(12)$ is the contribution from the unbound states.

Now, we can show that

$$\Gamma(12)\epsilon G_2(12)Z_b(12)$$

is nonsingular as $\epsilon\to 0+$ in exactly the same way as we have shown the finiteness of $\epsilon^2\eta_{KU}{}^r(\epsilon)$ in Sec. 4. Next, we consider

$$\Gamma(12)Z_u(12).$$

This contains two kinds of processes as typified by Figs. 1(a) and 1(b_4), respectively. The former involves no bound states and can be treated as though no attractive forces exist. This case was discussed earlier in this Appendix, and no singularity appears for $\Gamma(12)$ as $\epsilon\to 0+$. In the latter kind of processes which accompany formations of bound pairs, for fixed $\mathbf{p}_3$, the contributing region of $\mathbf{r}_3$ is confined to a finite volume and no singularity is expected in $\Gamma(12)$ as $\epsilon\to 0+$. Thus, we have been able to show that in each case of interest $\Gamma(12)$ remains finite as $\epsilon\to 0+$. As a consequence of these results, we can express $X(12)$ introduced in (4.22) and (4.23) in the same form as (C14) namely, by (4.24).