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Rutger A. van Santen

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Quantum Mechanical Derivation of the Correction to the Boltzmann Equation Due to the Duration of Collisions

RUTGER A. VAN SANTEN*,†
Stanford Research Institute, Menlo Park, California 94025
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Expressions are studied for the rate of change of momentum distribution that result from using a recent formulation of a quantum mechanical derivation of the Boltzmann equation obtained by Snider and Sanctuary. The gas is supposed to consist of spherical and structureless particles. If the distribution function is restricted so as initially to be spatially uniform, it will remain spatially uniform and the rate of change of momentum distribution is as given by the Boltzmann collision term. In case the distribution function initially is spatially nonuniform, the nonuniformity persists in the Boltzmann equation, and in addition to drift terms, a term appears containing the duration of the collisions. This can be related to the Enskog modification of dense gases in the case of hard sphere particles. A new quantum mechanical expression of this correction is presented.

INTRODUCTION

It is well known that the Boltzmann equation is valid if one assumes binary collisions and molecular chaos and neglects contributions resulting from collisions with the wall. The condition of molecular chaos can be defined as the velocity of a molecule being uncorrelated with its position.[1]

If one takes into account the finite extension of the particles, one has to replace this condition by assuming that the distribution function does not change appreciably in times of the order of the duration of the collision or in distances of the order of a molecular diameter.[2,3a] Correcting for the finite dimensions of hard sphere particles, Enskog[3b,4] gives a contribution to the Boltzmann equation that depends on the spatial gradient of the distribution function. The objective of this paper is to calculate the correction to the Boltzmann equation, which includes the effects of the finite dimensions, as well as the duration of the collisions.

The quantum mechanical definition of the duration of a collision, or time delay, in the case of single-channel scattering is $2\hbar(\partial\eta/\partial E)$,[5,6] where η is the phase shift. This definition can easily be generalized for multichannel scattering.[7] In this case, it becomes the single-channel time delay averaged by the S matrix. The important feature of those lifetime definitions is that they can have positive as well as negative values. The time delay can become positive as well as negative, if the particles attract one another and negative if they repulse one another.

In the case of hard spheres for example, the s-wave lifetime becomes negative and is of the order of $-a/v$, where a is the distance of the centers of mass of the particles at collision and v their velocity. The classical limit of the lifetime has been given by Smith,[8] who has shown in a calculation of the second virial coefficient for a hard sphere gas that this reproduces the excluded volume effect.[9]

Therefore, we expect that a generalization of the Enskog modification for more than hard sphere collisions can be found that depends on the duration of the collisions. This then will provide the modification of the Boltzmann equation for particles that interact with a reasonable well behaved potential, attractive as well as repulsive. In an accompanying paper,[10] an intuitive approach is used, which applies this classical definition of the lifetime to study the modification of the Boltzmann equation.

Here a derivation will be given, based on the quantum mechanical Liouville equation, which gives the modification resulting from the lifetime in quantum mechanics. To derive the standard Boltzmann collision term in quantum mechanics one has to reformulate the assumptions of molecular chaos. The assumptions that replace it are the following:

(1) The system is studied for times that are long compared with the duration of the collisions. This implies that the time of free flight is long compared with the duration of the collisions.

(2) Initially, no correlations between the particles are present.

(3) The distribution function can be considered as independent of position in the collision region. The system can be considered spatially uniform.

In our calculation, we relax the last condition and calculate the first order correction to the Boltzmann equation resulting from it. This correction contains the spatial derivatives of the velocity distributions in the same way as do Enskog's corrections. Therefore, its density dependence is of the same order as the one for three-particle collisions. Thus, for a consistent application one should include those contributions.

It has been mentioned[11,12] that the correction to nonuniformity should be more important. However, it also has been pointed out that three-particle collisions depend on the collision time.[13] Therefore, only if the spatial gradient of the momentum distribution is large can the neglect of the three-particle collisions possibly be justified.[14]

Here we consider only the case of two-particle

collisions. Whereas Enskog used an intuitive approach, a rigorous derivation of the Enskog result based on the classical Liouville equation had been given by Boguliubov[15] and Green.[11,16]

Our derivation will start with the quantum mechanical Liouville equation. The method used is analogous to the one of Boguliubov. We reduce the Liouville equation to the BBKGY hierarchy of equations. This is a coupled set of equations that express the one-particle distribution function in terms of the two-particle distribution function, the two-particle distribution function in terms of the three-particle distribution function, and so on. Those equations are truncated to exclude more than two-particle equations. The difference between our method and the methods of Boguliubov and Green is that we do not introduce a two-particle correlation function, which implicitly depends on the one-particle distribution function to solve those equations. This method has been used by Tip[17] in a quantum mechanical derivation of the Boltzmann equation, but it has been criticized by Snider and Sanctuary,[18] because it ignores the free particle evolution in time, which has to compensate for the center of mass motion. Instead, the method of Snider and Sanctuary will be used to solve the two equations for the one- and two-particle distribution functions.

REVIEW OF THE DERIVATION

The BBKGY set of equations which is derived from the quantum-mechanical Liouville equation, is truncated to exclude three-particle collisions. The equation for the two-particle distribution function $\rho_{12}(t)$ is solved, with the initial condition that it describes the scattering process of two particles initially at an infinite distance from one another. $\rho_{12}(t)$ is then calculated for a time that is long compared with the collision time, so that the usual methods of scattering theory can be used to evaluate it. This solution is given by Eq. (7) later in the discussion. It means that the value of $\rho_{12}(t)$ can be calculated from the product of the two one-particle distribution functions at the same time, evaluated in time from their initial values as if no collision has occurred, but transformed by Møller wave operators, which describe the scattering process.

The use of this solution for $\rho_{12}(t)$ in the equation for the one-particle distribution function (1a) implies that the solution of this equation is valid only on a time scale that is large compared with the duration of the collision. Notice that this equation now is independent of the initial value of $\rho_{12}(t)$. The one-particle distribution functions are then transformed to their momentum representation so that substitution of (7) into (1a) results in a set of nonlinear equations for the density matrix $f(\mathbf{k}_1, \mathbf{k}_2; t)$ of one particle (9). Because the differential cross section is proportional to the absolute square of the transition matrix. Eq. (8) is transformed to Eq. (14), which contains the transition matrices explicitly. If the density matrix elements $f(\mathbf{k}_1, \mathbf{k}_2; t)$ are restricted to be diagonal, (14) gives the Boltzmann equation (16) immediately. Because $\mathbf{k}_1$ and $\mathbf{k}_2$ are continuous variables, one has to assume that they are proportional to a δ function in $\mathbf{k}_1$ and $\mathbf{k}_2$ (15). Study of the Wigner distribution function $P(\mathbf{k}_1; \mathbf{R}, t)$, which is the quantum mechanical analog of the classical distribution function, shows that the functions $P(\mathbf{k}_1; \mathbf{R}, t)$ become independent of the spatial coordinate $\mathbf{R}$. Thus, Assumption (15) corresponds to the assumption that the system is spatially uniform. Therefore, Eq. (14) is the one that has to be solved in the general case that the system is nonuniform.

The remainder of the paper is devoted to finding a first approximation to the Boltzmann equation, derived from (14) as a result of nonuniformity. The Wigner distribution functions are convenient for a study of this approximation, because they depend on the position variables. Thus, Eq. (14) is transformed to an equation for the Wigner distribution functions. The successive terms are given by Eqs. (18), (19), and (21). Equation (18) gives the contribution to the rate of change of $P(\mathbf{k}_1; \mathbf{R})$ because of the flow of the particles. In the derivation of (19) and (21), another assumption has been introduced. The Wigner distribution function of the particle i, whose change in momentum distribution is studied, is assumed to be independent of the position, whereas the distribution functions of the particles which collide with it are unrestricted in their space dependence. As a consequence, the value of $\mathbf{R}$, for which one has to evaluate the value of $P(\mathbf{k}_1; \bar{\mathbf{R}}_i, t)$, is arbitrary. The actual value of $P(\mathbf{k}_1; \mathbf{R}_i, t)$ at position R_i was chosen for it.

Only the distribution functions of the colliding particles are chosen to be $\mathbf{R}$ dependent, because the expression (20) for the average force the particles experience due to nonuniformity is then the same as is found in the work of other authors[19] and has the same form as expected in the classical case.[11] Also, the resulting expression for the correction term has the same form as the one of Enskog. Equation (21) reduces to the Boltzmann collision term, if the function $P(\mathbf{k}_1; \mathbf{R})$ is assumed to be independent of position, as it should. The first order contribution due to spatial nonuniformity turns out to be dependent on off-energy shell values of the transition matrix. Expanding those to first order in momentum, one finds that they give rise to terms that contain the first order derivative to position of the distribution function and are only nonzero if the energy derivative of the phase shift is nonzero.

In the Introduction, it was pointed out that this derivative is directly related to the duration of the

collision. The final result is given by (35), which contains a term similar to the Enskog correction, although now it contains Q, an average time delay, defined in (32), instead of the diameters of the particles. Q, the average time delay, has a very transparent interpretation. From (32) it is seen that it consists of the energy derivative of the phase shift averaged over the contributions for different values of l to the differential cross section. In the transition to classical mechanics, the interference terms have to disappear and the result is simply a sum like (31), where $\hbar(\partial\eta_l/\partial E)$ is averaged over the cross section for each value of l.

This is reminiscent of the generalized Ehrenfest theorem from Lippmann,[20] which gives the change of the expectation values of observables by a collision of wave packets. In the classical case, therefore, Q has to be replaced by the classical expression of the lifetime and is to be averaged over the classical cross section.

DERIVATION OF THE COLLISION TERM

Triple and higher order collisions can be excluded by converting the Liouville equation for N particles to the BBKGY hierarchy of equations.[15,21] One truncates this set so as to include only two-particle collisions. The equations to solve with appropriate initial conditions are[17]

$$i\hbar(\partial\rho_1/\partial t)=\mathfrak{L}_1\rho_1+Tr_2\mathfrak{V}_{12}\rho_{12}^{(2)}, \tag{1a}$$

$$i\hbar(\partial\rho_{12}/\partial t)=\mathfrak{L}_{12}^{(2)}\rho_{12}^{(2)}. \tag{1b}$$

The one-particle density matrix ρ_1 is related to the two-particle density matrix by

$$\rho_1=Tr_2\rho_{12}^{(2)}. \tag{2}$$

$\mathfrak{L}_1$ and $\mathfrak{L}_{12}^{(2)}$ are Liouville operators of one and two particles:

$$\mathfrak{L}_{12}^{(2)}=\mathfrak{L}_1+\mathfrak{L}_2+\mathfrak{V}_{12}. \tag{3}$$

The solution of (2) is

$$\rho_{12}^{(2)}(t)=\exp[-(i/\hbar)\mathfrak{L}_{12}^{(2)}(t-t_0)]\rho_{12}^{(2)}(t_0). \tag{4}$$

The appropriate choice of the initial condition[18] at $t=t_0$ is that $\rho_{12}^{(2)}(t_0)$ represents two free particles outside their range of interaction. If

$$i\hbar(\partial\rho_{12}^{(1)}/\partial t)=(\mathfrak{L}_1+\mathfrak{L}_2)\rho_{12}^{(1)}(t), \tag{5}$$

it means that

$$\rho_{12}^{(1)}(t_0)=\rho_{12}^{(2)}(t_0). \tag{6}$$

One calculates (4) after scattering and then substitutes this into (1). The resulting equation has to be evaluated on a time scale that is large compared with the duration of the collisions. The results of Jauch, Misra, and Gibson[22] can be used to calculate

$$\lim_{t-t_0\to\infty}\rho_{12}^{(2)}(t-t_0).$$

If the potentials are sufficiently well behaved and there are no bound states, it gives

$$\lim_{t-t_0\to\infty}\rho_{12}(t)=\Omega\rho_{12}^{1}(t)\Omega^{\dagger}, \tag{7}$$

where Ω is the Møller wave operator. Defining the momentum-space representation density functions $f(\mathbf{k}_1,\mathbf{k}_2;i,t)$ of the one-particle correlation function of particle i by

$$\rho_1(t,\mathbf{r}_i;\mathbf{r}_i')=\int d^3\mathbf{k}_1\int d^3\mathbf{k}_2 f(\mathbf{k}_1,\mathbf{k}_2;i,t)\exp[i(\mathbf{k}_1\mathbf{r}_i-\mathbf{k}_2\mathbf{r}_i')], \tag{8}$$

and assuming that the particles are distinguishable and are interacting with a potential $V_{ij}(\mathbf{r}_i-\mathbf{r}_j)$, one finds the following equation for $f(\mathbf{k}_1,\mathbf{k}_2;i,t)$:

$$\begin{aligned}i\hbar\dot{f}(\mathbf{k}_1,\mathbf{k}_2;i,t)&=(\hbar^2/2m_i)(\mathbf{k}_1^2-\mathbf{k}_2^2)f(\mathbf{k}_1,\mathbf{k}_2;i,t)+\sum_{j\neq i}\int d^3\mathbf{r}_i\int d^3\mathbf{r}_i'\exp[-i(\mathbf{k}_1\mathbf{r}_i-\mathbf{k}_2\mathbf{r}_i')]\\&\times\int d^3\mathbf{r}_j\{V_{ij}(\mathbf{r}_{ij})-V_{ij}(\mathbf{r}_{ij'})\}\int d^3\mathbf{k}\int d^3\mathbf{k}_4\int d^3\mathbf{k}_5\int d^3\mathbf{k}_6\int d^3\mathbf{k}_7\int d^3\mathbf{k}_8\exp[i(\mathbf{k}_7\mathbf{r}_{ij}-\mathbf{k}_8\mathbf{r}_{ij}')]\\&\times\Omega(\mathbf{k}_7,\mathbf{k}_8;ij)\Omega^{\dagger}(\mathbf{k}_5,\mathbf{k}_8;ij)f(\tfrac{1}{2}\mathbf{k}_3+\mathbf{k}_4,\tfrac{1}{2}\mathbf{k}_5+\mathbf{k}_6;i,t)f(\tfrac{1}{2}\mathbf{k}_3-\mathbf{k}_4,\tfrac{1}{2}\mathbf{k}_5-\mathbf{k}_6;j,t)\exp[i(\mathbf{k}_3\mathbf{R}_{ij}-\mathbf{k}_5\mathbf{R}_{ij'})],\end{aligned} \tag{9}$$

where

$$\mathbf{r}_{ij}=\mathbf{r}_i-\mathbf{r}_j$$

and

$$\mathbf{R}_{ij}=\tfrac{1}{2}(\mathbf{r}_i+\mathbf{r}_j). \tag{10}$$

The particles are assumed to be identical. One now uses the relationships that express Ω in terms of the transition matrix T and the one that relates T with interaction potential V:

$$\Omega(\mathbf{k}_1,\mathbf{k}_2)=\delta(\mathbf{k}_1-\mathbf{k}_2)+(GT^{*})(\mathbf{k}_1,\mathbf{k}_2), \tag{11}$$

$$(V\Omega)(\mathbf{k}_1,\mathbf{k}_2)=T(\mathbf{k}_1,\mathbf{k}_2). \tag{12}$$

G is defined by

$$G=\lim_{\epsilon\to 0}(E-H+i\epsilon)^{-1}, \tag{13}$$

where H is the Hamiltonian of two particles in the center of mass coordinate system. Equation (9) then becomes

$$i\hbar\dot{f}(\mathbf{k}_1, \mathbf{k}_2; i, t) = (\hbar^2/2m_i)(\mathbf{k}_1^2-\mathbf{k}_2^2)f(\mathbf{k}_1, \mathbf{k}_2; i, t) + \sum_{j\neq i}\int d^3\mathbf{k}_3 \int d^3\mathbf{k}_4 \int d^3\mathbf{k}_5 \int d^3\mathbf{k}_6 \delta(\mathbf{k}_2-\mathbf{k}_1+\mathbf{k}_3-\mathbf{k}_5)$$
$$\times\{T^{ij}[\tfrac{1}{2}(\mathbf{k}_2+\mathbf{k}_1)-\tfrac{1}{2}\mathbf{k}_3, \mathbf{k}_4]\delta(\mathbf{k}_6-\mathbf{k}_2+\tfrac{1}{2}\mathbf{k}_5)+T^{ij}[\tfrac{1}{2}(\mathbf{k}_2+\mathbf{k}_1)-\tfrac{1}{2}\mathbf{k}_5, \mathbf{k}_4](T^{ij}G^{ij})^\dagger(\mathbf{k}_6, \mathbf{k}_2-\tfrac{1}{2}\mathbf{k}_5)$$
$$-T^{*ij}[\tfrac{1}{2}(\mathbf{k}_2+\mathbf{k}_1)-\tfrac{1}{2}\mathbf{k}_3, \mathbf{k}_6]\delta(\mathbf{k}_1-\tfrac{1}{2}\mathbf{k}_3-\mathbf{k}_4)-(T^{ij}G^{ij})(\mathbf{k}_1-\tfrac{1}{2}\mathbf{k}_3, \mathbf{k}_4)T^{ij\dagger}[\mathbf{k}_6, \tfrac{1}{2}(\mathbf{k}_1+\mathbf{k}_2)-\tfrac{1}{2}\mathbf{k}_3]\}$$
$$\times f(\tfrac{1}{2}\mathbf{k}_3+\mathbf{k}_4, \tfrac{1}{2}\mathbf{k}_5+\mathbf{k}_6; i, t)f(\tfrac{1}{2}\mathbf{k}_3-\mathbf{k}_4, \tfrac{1}{2}\mathbf{k}_5-\mathbf{k}_6; j, t). \quad (14)$$

In the spatially uniform case, the functions $f(\mathbf{k}_1, \mathbf{k}_2)$ have the form

$$f(\mathbf{k}_1, \mathbf{k}_2) = f(\mathbf{k}_1)\delta(\mathbf{k}_1-\mathbf{k}_2). \quad (15)$$

If one fixes the initial condition (6) such that (14) holds at $t=t_0$, it is found that it holds for all times. If one introduces (15) into (14) one finds

$$i\hbar\dot{f}(\mathbf{k}_1; i, t) = -2\pi i\sum_{j\neq i}\int d^3\mathbf{k}_3[\{T^{ij}\delta[E(\mathbf{k}_1-\tfrac{1}{2}\mathbf{k}_3)-H^{ij}]T^{ij*}\}(\mathbf{k}_1-\tfrac{1}{2}\mathbf{k}_3, \mathbf{k}_1-\tfrac{1}{2}\mathbf{k}_3)f(\mathbf{k}_1; i, t)f(\mathbf{k}_3-\mathbf{k}_1; j, t)$$
$$-\int d^3\mathbf{k}_4 \mid T(\mathbf{k}_1-\tfrac{1}{2}\mathbf{k}_3, \mathbf{k}_4)\mid^2 \delta\{(\hbar^2\mathbf{k}_4^2/2\mu_{ij})-[\hbar^2(\mathbf{k}_1-\tfrac{1}{2}\mathbf{k}_3)^2/2\mu_{ij}]\}f(\tfrac{1}{2}\mathbf{k}_3+\mathbf{k}_4; i, t)f(\tfrac{1}{2}\mathbf{k}_3-\mathbf{k}_4; j, t)]. \quad (16)$$

One finds no drift term, and the rate of change of the momenta is given by the Boltzmann collision term.

THE SPATIALLY NONUNIFORM CASE

Since the general solution of (13) is extremely difficult, we will calculate the first order correction to (16). We introduce the Wigner distribution function $P^i(\mathbf{k}_7; \mathbf{R}, t)$, which in the classical limit represents the momentum distribution of particle i at position $\mathbf{R}$ and time t. If $P^i(\mathbf{k}_7; \mathbf{R}, t)$ has to be considered as a function of $\mathbf{R}$, the distribution is spatially nonuniform:

$$P^i(\mathbf{k}_7; \mathbf{R}_i, t) = \int d^3\mathbf{k}_8 f(\mathbf{k}_7+\tfrac{1}{2}\mathbf{k}_8, \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8; i, t)\exp(i\mathbf{k}_8\mathbf{R}_i), \quad (17a)$$

with

$$\mathbf{k}_8 = \mathbf{k}_1-\mathbf{k}_2,$$
$$\mathbf{k}_1 = \tfrac{1}{2}(\mathbf{k}_1+\mathbf{k}_2). \quad (17b)$$

The first term of the rhs of (14) is found to give

$$\hbar^2\mathbf{k}_7/im_i\cdot\nabla_{\mathbf{R}_i}P^i(\mathbf{k}_7; \mathbf{R}_i, t). \quad (18)$$

This is simply the contribution due to the flow of the particles divided by $-\hbar/i$. The collision term in (14) will be calculated, assuming that $f(\mathbf{k}_1, \mathbf{k}_2; i, t)$ satisfies (15) but that the density functions of particles j do not. The contribution of the terms first order in V is then

$$\sum_{j\neq i}\int d^3\mathbf{R}_{j'}\int d^3\mathbf{k}_8\int d^3\mathbf{k}_3 \exp[i\mathbf{k}_8(\mathbf{R}_i-\mathbf{R}_{j'})]V^{ij}(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3+\tfrac{1}{2}\mathbf{k}_8, \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3-\tfrac{1}{2}\mathbf{k}_8)P^j(\mathbf{k}_3-\mathbf{k}_7; \mathbf{R}_{j'}, t)$$
$$\times P^i(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8; \bar{\mathbf{R}}_i, t)-V^{ij*}(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3-\tfrac{1}{2}\mathbf{k}_8, \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3+\tfrac{1}{2}\mathbf{k}_8)P^j(\mathbf{k}_3-\mathbf{k}_7; \mathbf{R}_{j'}, t)P^i(\mathbf{k}_7+\tfrac{1}{2}\mathbf{k}_8; \bar{\mathbf{R}}_i, t). \quad (19)$$

The P^i's have to be calculated for some average value of $\mathbf{R}_i$. One chooses the same values as in (18). Expanding P^i to $\tfrac{1}{2}\mathbf{k}_8$, one finds the first contributing term to (19) to be

$$i\sum_{j\neq i}\nabla_{\mathbf{R}_i}\int d^3\mathbf{R}_{j'}\int d^3\mathbf{k}_8\int d^3\mathbf{k}_3 \exp[i\mathbf{k}_8(\mathbf{R}_i-\mathbf{R}_{j'})]V(\mathbf{k}_8)P^j(\mathbf{k}_3-\mathbf{k}_7; \mathbf{R}_{j'}, t)\nabla(\mathbf{k}_7)P^i(\mathbf{k}_7; \mathbf{R}_i, t). \quad (20)$$

Multiplying this with $-i/\hbar$, this expression is found to be equal to the contribution to the drift term because of the average potential of the other particles.[19]

The calculation of the other terms is straightforward, if one rewrites the remaining terms of the rhs of (14) as

$$2i\sum_{j\neq i}\int d^3\mathbf{R}_{j'}\int d^3\mathbf{k}_3\int d^3\mathbf{k}_7\{\cos\mathbf{k}_8(\mathbf{R}_i-\mathbf{R}_{j'})\{\mathrm{Im}(T^{ij}G^{ij}T^{ij*})(\mathbf{k}_7+\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3, \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3)P^i(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8; \mathbf{R}_i, t)$$
$$\times P^j(\mathbf{k}_3-\mathbf{k}_7; \mathbf{R}_{j'}, t)+\int d^3\mathbf{k}_4\,\mathrm{Im}T^{ij}(\tfrac{1}{2}\mathbf{k}_8+\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3, \mathbf{k}_4-\tfrac{1}{2}\mathbf{k}_8; T^{ij}G^{ij})^\dagger(\mathbf{k}_4, \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3)$$
$$\times P^i(\tfrac{1}{2}\mathbf{k}_3+\mathbf{k}_4-\tfrac{1}{2}\mathbf{k}_8; \bar{\mathbf{R}}_i, t)P^j(\tfrac{1}{2}\mathbf{k}_3-\mathbf{k}_8; \mathbf{R}_{j'}, t)\}+\sin\mathbf{k}_8(\mathbf{R}_i-\mathbf{R}_{j'})\{\mathrm{Re}(T^{ij}G^{ij}T^{ij*})$$
$$(\mathbf{k}_7+\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3, \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3)P^i(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8; \bar{\mathbf{R}}_i, t)P^j(\mathbf{k}_3-\mathbf{k}_7; \mathbf{R}_{j'}, t)+\int d^3\mathbf{k}_4$$
$$\times\mathrm{Re}T^{ij}(\tfrac{1}{2}\mathbf{k}_8+\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3, \mathbf{k}_4-\tfrac{1}{2}\mathbf{k}_8; T^{ij}G^{ij})^\dagger(\mathbf{k}_4, \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3)P^i(\tfrac{1}{2}\mathbf{k}_3+\mathbf{k}_4-\tfrac{1}{2}\mathbf{k}_7; \bar{\mathbf{R}}_i, t)P^j(\tfrac{1}{2}\mathbf{k}_3-\mathbf{k}_4; \mathbf{R}_{j'}, t)]\}. \quad (21)$$

The term within the braces is now real. The first term of (21) contributes if the dependence of the function within

the braces is symmetric in $\mathbf{k}_8$. If one neglects the $\mathbf{k}_8$ dependence, the contribution of this term is simply the Boltzmann collision term. The next contribution has to be proportional to $\mathbf{k}_7^2$ and therefore gives a contribution dependent on $\nabla_{\mathbf{R}_i}{}^2\tilde{P}^j(\mathbf{R}_i)$. We will confine our attention to terms of the first order in $\nabla_{\mathbf{R}_i}$ and we will ignore the higher terms. The second term of (21) contributes only if the function within the braces is antisymmetric in $\mathbf{k}_8$.

Therefore the zero-order term disappears. Expanding the functions P^i, one finds the first order:

$$i\sum_{j\neq i}\nabla_{\mathbf{R}_i}\int d^3\mathbf{k}_3\int d^3\mathbf{R}_{j'}\int d^3\mathbf{k}_8\exp[i\mathbf{k}_8(\mathbf{R}_i-\mathbf{R}_{j'})]\Big\{\mathrm{Re}(T-V)(\mathbf{k}_7+\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3,\ \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3)$$

$$\times P^j(\mathbf{k}_3-\mathbf{k}_7;\mathbf{R}_{j'},t)\nabla(\mathbf{k}_7)P^i(\mathbf{k}_7;\tilde{\mathbf{R}}_i,t)+\int d^3\mathbf{k}_4\,|\,T^{ij}(-\tfrac{1}{2}\mathbf{k}_3+\mathbf{k}_7,\mathbf{k}_4)\,|^2\,\frac{\text{Pr. P.}}{(\hbar^2\mathbf{k}_4^2/2\mu_{ij})-(\hbar^2(\mathbf{k}_7-\frac{1}{2}\mathbf{k}_3)^2/2\mu_{ij})}$$

$$\times P^j(\tfrac{1}{2}\mathbf{k}_3-\mathbf{k}_4;\mathbf{R}_{j'},t)\nabla(\tfrac{1}{2}\mathbf{k}_3+\mathbf{k}_4)P^i(\tfrac{1}{2}\mathbf{k}_3+\mathbf{k}_4;\tilde{\mathbf{R}}_i,t)\Big\}. \quad (22)$$

Pr. P. means taking the principal part of the integral in (22). Expanding the P's in the second term around $\mathbf{k}_4=\mathbf{k}_7-\frac{1}{2}\mathbf{k}_3$ shows that their sum cancels in zero order. Because higher order terms entail higher derivatives of P^i and P^j, it is found that in a first approximation (22) vanishes.

Until now our results contain nothing new. However, a contribution to the second term of (21) exists if the $\mathbf{k}_8$ dependence of the P's is neglected. We calculate first the contribution from the term TGT^*. It has already been used in (22) that

$$\mathrm{Re}(T^{ij}G^{jj}T^{ij*})(\mathbf{k}_7+\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3,\ \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_4-\tfrac{1}{2}\mathbf{k}_3)=\mathrm{Re}(T-V)(\mathbf{k}_7+\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3,\ \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3). \quad (23)$$

Expansion to $\mathbf{k}_8$ gives only a first order correction due to T, because V is symmetric in $\mathbf{k}_8$. If $\mathrm{Re}T$ is antisymmetric in $\mathbf{k}_8$, then

$$\mathrm{Re}T(\mathbf{k}_7+\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3,\ \mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3)\neq\mathrm{Re}T(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3,\ \mathbf{k}_7+\tfrac{1}{2}\mathbf{k}_8-\tfrac{1}{2}\mathbf{k}_3). \quad (24)$$

The difference of the terms can be evaluated by using the identity

$$\mathrm{Re}(T_{\alpha\beta}-T_{\beta\alpha})=\mathrm{Re}\tfrac{1}{2}\{(T_{\alpha\beta}-T_{\beta\alpha}^*)-(T_{\beta\alpha}-T_{\alpha\beta}^*)\}. \quad (25)$$

It is learned from the theory of off-energy shell matrix elements[23] that

$$T_{\alpha\beta}-T_{\beta\alpha}^*=\sum_\gamma\int_0^\infty dE_\gamma T_{\alpha\gamma}T_{\beta\gamma}^*\lim_{\epsilon\to0}[(E_\beta-E_\gamma+i\epsilon)^{-1}-(E_\alpha-E_\gamma-i\epsilon)^{-1}]. \quad (26)$$

It follows from (26) that, if $\alpha=\beta$, (25) vanishes. To the first order in $(\alpha-\beta)$, one can express (26) as a function of on-energy-shell matrix elements. Those are the ones we need. One finds

$$\mathrm{Re}(T_{\alpha\beta}-T_{\beta\alpha}^*)=-2\pi i\,\mathrm{Im}\sum_\gamma T_{\alpha\gamma}(\partial T_{\alpha\gamma}^*/\partial\alpha)(\beta-\alpha). \quad (27)$$

In the spherical symmetric case, one can express T into the phase shift δ_l, characterized by the magnitude of its angular momentum l[23]:

$$T=k^{-1}\sum_{l=0}(2l+1)\exp(i\delta_l)\sin\delta_l P_l(\cos\theta). \quad (28)$$

Here k is the relative momentum and θ the angle over which one scatters. The derivative of the phase shift gives an imaginary contribution. This is related to Δt_l, the time delay, which is the duration of the scattering process in channel l[7] by

$$\Delta t_l=2\hbar(\partial\delta_l/\partial E). \quad (29)$$

Using (28) and (29), one finds for (27) after integrating over θ

$$-\frac{\pi\hbar}{k\mu}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_l\Delta t_l. \quad (30)$$

Before integrating over θ, one finds a modified differential cross section, the sum over l not being weighted over $(2l+1)$ but

$$-\tfrac{1}{2}\hbar k(2l+1)\Delta t_l, \quad (31)$$

whereas a second term appears. We define the average time delay per unit angle by

$$Q(\mathbf{k}_1\mathbf{v}\mathbf{k}_2,|\,k\,|)=\tfrac{1}{2}\,\mathrm{Re}\sum_{l,l'}(2l+1)(2l'+1)\exp[-i(\delta_l-\delta_{l'})]\sin\delta_l\sin\delta_{l'}\Delta t_l P_l\{\cos(\mathbf{k}_1\mathbf{v}\mathbf{k}_2)\}P_{l'}\{\cos(\mathbf{k}_1\mathbf{v}\mathbf{k}_2)\}$$

$$-\tfrac{1}{2}\mathrm{Im}\sum_{l,l'}(2l+1)(2l'+1)\exp[-i(\delta_l-\delta_{l'})]\cos\delta_l\sin\delta_{l'}\Delta t_l P_l\{\cos(\mathbf{k}_1\mathbf{v}\mathbf{k}_2)\}P_{l'}\{\cos(\mathbf{k}_1\mathbf{v}\mathbf{k}_2)\}, \quad (32)$$

where $\mathbf{k}_1 v \mathbf{k}_2$ is the angle between $\mathbf{k}_1$ and $\mathbf{k}_2$. The contribution resulting from expansion of (27) is

$$-i\hbar \sum_{j\neq i} (2\hbar/\mu_{ij}) \int d^3\mathbf{k}_3 \int d\mathbf{k}_4 \delta\{(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3)^2-\mathbf{k}_4^2\}[\hbar(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3)/\mu_{ij}] Q\{\mathbf{k}_4 v(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3), |\,\mathbf{k}_4\,|\}$$
$$\times P^i(\mathbf{k}_7; \bar{\mathbf{R}}_i, t)\, \nabla_{\mathbf{R}_i} P^j(\mathbf{k}_3-\mathbf{k}_7; R_i, t). \quad (33)$$

It is now clear how to calculate the contribution of the last term in the second half of (21). This is found to be

$$-i\hbar \sum_{j\neq i} (2\hbar/\mu_{ij}) \int d^3\mathbf{k}_3 \int d\mathbf{k}_4 \delta(\mathbf{k}_3^2-\mathbf{k}_4^2)(\hbar\mathbf{k}_4/\mu_{ij}) \cdot Q\{\mathbf{k}_4 v(\mathbf{k}_7-\tfrac{1}{2}\mathbf{k}_3), |\,\mathbf{k}_4\,|\} P^i(\tfrac{1}{2}\mathbf{k}_3+\mathbf{k}_4; \bar{\mathbf{R}}_i, t) \cdot \nabla_{\mathbf{R}_i} P^j(\tfrac{1}{2}\mathbf{k}_3-\mathbf{k}_4; \mathbf{R}_i, t). \quad (34)$$

We neglected corrections due to change in angular distribution. Their contribution will be small as long as the time delay is large.

RESULTS

Putting together the results derived in (10), (20), (33), and (34), the equation giving the rate of change of $P^i(\mathbf{p}; \mathbf{R}_i, t)$, where $\mathbf{p}=\hbar\mathbf{k}$, is

$$(\partial/\partial t) P^i(\mathbf{p}; \mathbf{R}_i, t) + (\mathbf{p}/m_i) \cdot \nabla_{\mathbf{R}_i} P(\mathbf{p}; \mathbf{R}_i, t) - \sum_{j\neq i} \nabla_{\mathbf{R}_i} \int d^3\mathbf{R}_{j'} \int d^3\mathbf{p}_1 \int d^3\mathbf{p}_2 \exp[i\mathbf{p}_2(\mathbf{R}_i-\mathbf{R}_{j'})]$$
$$\times V^{ij}(\mathbf{p}_2) P^j(\mathbf{p}_1-\mathbf{p}; \mathbf{R}_{j'}, t)\, \nabla(\mathbf{p}) P^i(\mathbf{p}; \mathbf{R}_i, t) = -\sum_{j\neq i} (2/\mu_{ij}) \int d^3\mathbf{p}_1 \int d^3\mathbf{p}_2 \delta(\mathbf{p}_1^2-\mathbf{p}_2^2)(\partial\sigma/\partial\Omega)$$
$$\times \{P^i(\mathbf{p}; \mathbf{R}_i, t) P^j(\mathbf{p}_1-\mathbf{p}; \mathbf{R}_i, t) - P^i(\tfrac{1}{2}\mathbf{p}_1+\mathbf{p}_2; \bar{\mathbf{R}}_i, t) P^j(\tfrac{1}{2}\mathbf{p}_1-\mathbf{p}_2; \mathbf{R}_i, t)\} - \sum_{j\neq i} (2/\mu_{ij}) \int d^3\mathbf{p}_1 \int d\mathbf{p}_2$$
$$\times Q\{\mathbf{p}_2 v(\mathbf{p}-\tfrac{1}{2}\mathbf{p}_1), |\,\mathbf{p}_2\,|\} \delta\{(\mathbf{p}-\tfrac{1}{2}\mathbf{p}_1)^2-\mathbf{p}_2^2)\} \{P^i(\mathbf{p}_1; \bar{\mathbf{R}}_i, t)[(\mathbf{p}-\tfrac{1}{2}\mathbf{p}_1)/\mu_{ij}] \cdot \nabla_{\mathbf{R}_i} P^j(\mathbf{p}_1-\mathbf{p}; \mathbf{R}_i, t)$$
$$+ P^i(\tfrac{1}{2}\mathbf{p}_1+\mathbf{p}_2; \bar{\mathbf{R}}_i, t)(\mathbf{p}_2/\mu_{ij}) \cdot \nabla_{\mathbf{R}_i} P^j(\tfrac{1}{2}\mathbf{p}_1-\mathbf{p}_2; \mathbf{R}_i, t)\}, \quad (35)$$

where $(\partial\sigma/\partial\Omega)$ denotes the differential cross section.

The last term of (35) gives our correction. This expression is related to the Enskog modification of dense gases.[3a] For the case of hard spheres, Enskog calculated the correction due to the excluded volume. Then Q is found to be negative[7] and of the order $\mathbf{k}_3^2 a^3/v$, where a is the radius of the spheres and v the relative velocity.

Therefore, our Expression (35) can be considered as a generalization of the Enskog modification to the Boltzmann equation for particles that interact by a general potential under the restriction that this potential is not allowed to support bound states.

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† Present address: Koninklijke/Shell-Laboratorium, Amsterdam, The Netherlands.

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