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Binary Collision Expansion for the Kinetic Equation of Time-Displaced Correlation Functions*

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Using the binary collision expansion of the time-displacement operator, a kinetic equation for the Van Hove correlation functions is derived. The method differs from those already in the literature by the fact that equilibrium correlations are taken into account fully. This permits us to recover the exact "short-time" kinetic equations developed recently by various authors, from the lowest-order term in our expansion. Indeed, when the interaction between the particles is due entirely to their hard cores, then our lowest-order term is identical with the short-time kinetic operator, yielding an Enskog-type correction to the low-density equation. In the particular case of a system of hard rods in one dimension we get the exact kinetic equation found by Lebowitz, Percus, and Sykes. For non-hard-core potentials our lowest-order term represents a natural extension of the Boltzmann-Enskog type equation obtained in the case of hard spheres. The resulting kinetic operator can be put, for sufficiently short collision times, into a form similar to the hard-core case, albeit with a velocity-dependent collision diameter.

1. INTRODUCTION

There has been much work done recently on obtaining reasonable approximations for the time-displaced distribution functions, i.e., the Van Hove correlation functions, of a classical fluid. A great stimulation for this work has been the beautiful molecular dynamic machine computations of Rahman[1] and Verlet.[2] One of the theoretical approaches used by many authors has been the kinetic-equation method which works so well for dilute gases. The difficulties of this method for dense fluids are well known and may be divided, in some sense, into the problem of the correlations and the problem of dynamics. The division hinges on the fact that in considering the time-displaced distribution functions we are dealing with a system, that is, in a well-defined sense, only slightly removed from equilibrium. Hence, the problem may be put in a form in which the correlations required are those of the equilibrium state, which are assumed to be known; in principle, at least. It may then be hoped that even when the dynamics of the problem is dealt with approximately, the final results may be reasonably good. This has been the philosophy of many authors[3-5] going back to the work of Enskog on the modification of the Boltzmann equation for a system of dense hard spheres. The results, when compared to the experiment, have been in general quite encouraging.

It is the purpose of this paper to describe a systematic development for the kinetic equation of the self- and total-time-displaced distribution functions of a classical fluid in which the equilibrium correlations are taken into account exactly at each step. Our procedure is based on the "binary collision" expansion formalism of Siegert and Teramoto[6] as used in transport theory by Zwanzig.[7] This method has been used recently for the investigation of the kinetic equation and transport coefficients of gases at low density, i.e., expansions in powers of the density ρ. Our variation and hopeful improvement of this procedure will consist of keeping intact, i.e., not expanding in the density, the full equilibrium correlations.

One of our motivations was the desire to understand from this general point of view the exact results obtained by Lebowitz, Percus, and Sykes[8] for the time-displaced distribution functions of a one-dimensional system of hard rods. Their methods depend on the particular simplicity of the system studied and cannot be directly extended to three-dimensional systems. Our methods, however, are valid in any dimensions, and we can, therefore, use their exact results both as a check and as a test of different approximations.

We begin by defining the problem: Consider a system of N particles of mass m interacting via a pair potential $\phi(|\vec{r}|)$. The particles are confined to a periodic box of volume V with a density

ρ. At $t=0$ the Gibbs ensemble in the $6N$-dimensional phase space has the form of an equilibrium distribution with one labeled test particle (particle number one) out of equilibrium

$$\mu(\vec{x}_1, \ldots, \vec{x}_N; 0) = N\mu_0(\vec{x}_1, \ldots, \vec{x}_N) W(\vec{x}_1)[\rho h_0(\vec{v}_1)]^{-1} = F_0(\vec{x}_2, \vec{x}_3, \ldots, \vec{x}_N | \vec{x}_1) W(\vec{x}_1). \quad (1.1)$$

Here $\vec{x}_i = (\vec{r}_i, \vec{v}_i)$ represents the position and velocity of the ith particle, $\mu_0(\vec{x}_1, \ldots, \vec{x}_N) \sim \exp(-\beta H_N)$ is the equilibrium canonical distribution function at reciprocal temperature β and

$$h_0(\vec{v}) = (2\pi m/\beta)^{-3/2} e^{-\beta m v^2/2} \quad (1.2)$$

is the equilibrium velocity distribution function. $W(\vec{x})$ is the distribution function of the labeled particle (the test particle) and the function $F_0(\vec{x}_2, \ldots, \vec{x}_N | \vec{x}_1)$ is the conditional probability of $\vec{x}_2, \ldots, \vec{x}_N$, relative to $\vec{x}_1$ in the equilibrium ensemble. We now define the self- and total-one-particle distribution functions f_S and f at time t obtained from the ensemble density μ whose initial value is given in (1.1),

$$f_S(\vec{x}_1, t) = \int d\vec{x}_2 \cdots d\vec{x}_N \mu(\vec{x}_1, \ldots, \vec{x}_N; t), \quad (1.3)$$

$$f(\vec{x}_1, t) = \int d\vec{x}_2 \cdots d\vec{x}_N [1 + (N-1)P_{12}] \times \mu(\vec{x}_1, \ldots, \vec{x}_N; t) = \eta(\vec{x}_1, t) + \rho h_0(\vec{v}_1), \quad (1.4)$$

where P_{12} is the permutation operator which interchanges $\vec{x}_1$ and $\vec{x}_2$. From (1.1), we have

$$f_S(\vec{x}_1, 0) = W(\vec{x}_1), \quad (1.5)$$

$$\eta(\vec{x}_1, 0) = W(\vec{x}_1) + \rho h_0(\vec{v}_1) \times \int d\vec{x}_2 [g(\vec{r}_{12}) - 1] W(\vec{x}_2). \quad (1.6)$$

Since $\mu(t)$ and thus f_S and f are linear functionals of W, we may also write

$$f_S(\vec{x}, t) = \int d\vec{y} T_S(\vec{x}, \vec{y}, t) W(\vec{y}), \quad (1.7)$$

$$\eta(\vec{x}, t) = \int d\vec{y} T(\vec{x}, \vec{y}, t) W(\vec{y}), \quad (1.8)$$

where $T_S(\vec{x}, \vec{y}, t)$ and $T(\vec{x}, \vec{y}, t)$ are the functions f_S and η corresponding to

$$W(\vec{x}) = \delta(\vec{x} - \vec{y}).$$

The kernels $T_S(\vec{x}, \vec{y}, t)$ and $T(\vec{x}, \vec{y}, t)$ can be written explicitly in terms of the Koopmann operators,[7] which can be expanded in terms of the binary collision operators.[6] This allows us to get a "closed" kinetic equation for both $f_S(\vec{x}, t)$ and $\eta(\vec{x}, t)$. A formal series expansion for these equations is given in Sec. 2. Section 3 is devoted to the discussion of the lowest-order terms of these equations in some detail; it is shown that only connected diagrams contribute to the series at each order. In Sec. 4, we check our equations with the exact equations for one-dimensional hard-core systems. Also the short-time approximations[9,10] and other limiting expressions can be obtained from our formal expansion. Finally, in Sec. 5, we give a brief discussion of the general equation for long times.

Let us say, finally, that the binary collision expansion is not the essential feature of our analysis. An alternative procedure would be to use the Ursell function expansion of Green and Cohen,[11] which leads to the same results for the lowest-order terms for a general potential, and for the whole series in the case of hard-core potentials.

2. BINARY COLLISION EXPANSION

Let us consider a system with binary interactions only. The Hamiltonian of such a system is

$$H = H_0 + U, \quad H_0 = \tfrac{1}{2} m \sum_{i=1}^{N} v_i^2, \quad U = \sum_{i>j}^{N} \phi_{ij}, \quad \phi_{ij} = \phi(|\vec{r}_{ij}|), \quad \vec{r}_{ij} = \vec{r}_i - \vec{r}_j. \quad (2.1)$$

We have

$$\mu(t) = e^{-tL} \mu(0) = \mu[\vec{x}_1(-t), \ldots, \vec{x}_N(-t); 0], \quad (2.2)$$

where we have used the notation

$$L = L_0 + \sum_{i>j}^{N} \theta_{ij}, \quad (2.3)$$

$$L_0 = \sum_{i=1}^{N} \vec{v}_i \cdot \frac{\partial}{\partial \vec{r}_i}, \quad (2.4)$$

$$\theta_{ij} = -\frac{1}{m} \frac{\partial \phi_{ij}}{\partial \vec{r}_{ij}} \cdot \frac{\partial}{\partial \vec{v}_{ij}}, \quad (2.5)$$

with $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$.

Going back to Eqs. (1.7) and (1.8), we note that the operators $T_S(t)$ and $T(t)$ may be defined by

$$T_S(t) = \int d\vec{x}_2 \cdots d\vec{x}_N e^{-tL_N} F_0(\vec{x}_2 \cdots | \vec{x}_1), \quad (2.6)$$

$$T(t) = \int d\vec{x}_2 \cdots d\vec{x}_N e^{-tL_N} \times [1 + (N-1)P_{12}] F_0(\vec{x}_2 \cdots | \vec{x}_1) . \quad (2.7)$$

The treatment of both these operators is very similar, so that we will outline the procedure for the first, which will give us a kinetic equation for the self-distribution function, and only quote the results for the total.

Let us first define the Laplace transforms of the Koopmann operators

$$G = \int_0^\infty dt\, e^{-t(s+L)} = (s+L)^{-1}, \quad (2.8)$$

$$G_0 = \int_0^\infty dt\, e^{-t(s+L_0)} = (s+L_0)^{-1}, \quad (2.9)$$

$$Gij = \int_0^\infty dt\, e^{-t(s+L_0+\theta_{ij})} = (s+L_0+\theta_{ij})^{-1} . \quad (2.10)$$

Using the binary collision expansion we get[6]

$$G = G_0\left[1 + \sum_\alpha T_\alpha G_0 + \sum_\alpha \sum_{\beta \neq \alpha} T_\alpha G_0 T_\beta G_0 + \cdots\right], \quad (2.11)$$

where α, β, ... are shorthand notations for the pairs ij, kl, ... and the binary collision operator is defined by

$$T_\alpha = G_0^{-1}(G_\alpha - G_0)G_0^{-1} = -\theta_\alpha G_\alpha G_0^{-1} = -\theta_\alpha(1 + G_0 T_\alpha). \quad (2.12)$$

In time-dependent form, (2.11) is

$$G(t) = G_0(t) + \int_0^t dt_1 \int_0^{t_1} dt_2 \sum_\alpha G_0(t-t_1) \times T_\alpha(t_1 - t_2) G_0(t_2) + \cdots . \quad (2.13)$$

(We shall generally use the same symbol for a function of the time t and for its Laplace transform which is a function of s frequently omitting the argument in the latter.)

Our method may now be summarized as follows: Replacing (2.13) into (2.6) we may write

$$\mathcal{T}(t) = \mathcal{T}_0(t) + \sum_{n=1}^\infty \int_0^t dt'\, \mathcal{T}_0(t-t') K_n(t') = \mathcal{T}_0(t)\left[1 + \int_0^t dt' \mathcal{T}_0(-t') K(t')\right], \quad (2.14)$$

where

$$\mathcal{T}_0(t) = \int d\vec{x}_2, \ldots, d\vec{x}_N G_0(t) = \exp\left[-t\vec{v}_1 \cdot \frac{\partial}{\partial \vec{r}_1}\right] \quad (2.15)$$

is just the free-particle evolution operator. The multiple collision operators $K_n(t)$ contain the product of exactly n binary collision operators T_α and are defined below. Taking the time derivative of (2.14) applied to the initial value of $f_s(t)$, $f_s(0) = W(\vec{x}_1)$, we get

$$\frac{\partial f_s(t)}{\partial t} + \vec{v}_1 \cdot \frac{\partial f_s(t)}{\partial \vec{r}_1} = \sum_{n=1}^\infty K_n(t) W(\vec{x}_1) . \quad (2.16)$$

The Laplace transforms of Eqs. (2.14) and (2.16) have the forms

$$f_s(s) = \mathcal{T}_0(s)\left[1 + \sum_{n=1}^\infty K_n(s)\right] W(\vec{x}_1), \quad (2.17)$$

$$\left[s + \vec{v}_1 \cdot \frac{\partial}{\partial \vec{r}_1}\right] f_s(s) = \left[1 + \sum_{n=1}^\infty K_n(s)\right] W(\vec{x}_1) = \left[\sum_{n=1}^\infty K_n(s)\right]\left[\sum_{m=0}^\infty D_m(s)\right] f_s(s) + W(\vec{x}_1) = \left[\sum_{l=1}^\infty M_l(s)\right] f_s(s) + W(\vec{x}_1), \quad (2.18)$$

where we have written

$$W(\vec{x}_1) = \left[1 + \sum_{n=1}^\infty K_n(s)\right]^{-1} \mathcal{T}_0(s)^{-1} f_s(s) = \sum_{m=0}^\infty D_m(s) f_s(s), \quad (2.19)$$

and $$M_l(s) = \sum_{n+m=l} K_n(s) D_m(s). \quad (2.20)$$

Here again, D_j and M_j contain precisely j collision operators T_α. In time-dependent form, our basic equation (2.18) is

$$\left[\frac{\partial}{\partial t} + \vec{v}_1 \cdot \frac{\partial}{\partial \vec{r}_1}\right] f_s(s) = \sum_{l=1} \int_0^t dt' M_l(t-t') f_s(t') = \int_0^t dt' M(t-t') f_s(t'), \quad (2.21)$$

where $M_l(t)$ is the inverse Laplace transform of $M_l(s)$, and the first equality in (2.21) is a binary collision expansion of the memory operator (or kernel) $M(t)$ (cf. Ref. 9).

The formal expressions for the operators K_j, D_j, and M_j are readily obtained. Thus

$$\mathcal{T}(s) = \mathcal{T}_0(s)\left[1 + \sum_{n=1} K_n(s)\right] = \sum_n \int d\vec{x}_2, \ldots, d\vec{x}_N G_0$$

$$\times\left[\sum_{\alpha_1}\sum_{\alpha_2\neq\alpha_1}\cdots\sum_{\alpha_n\neq\alpha_{n-1}}T_{\alpha_1}G_0\cdots T_{\alpha_n}G_0\right]\times F_0(\vec{x}_2\cdots|\vec{x}_1)\,, \tag{2.22}$$

whose inverse is[12]

$$\mathcal{T}(s)^{-1}=\left[1+\sum_{n=1}s_n(s)\right]\mathcal{T}_0(s)^{-1}\,, \tag{2.23}$$

where

$$s_m(s)=(-)^m\begin{vmatrix} K_1 & 1 & 0 & . & . & 0\\ K_2 & K_1 & 1 & . & . & 0\\ K_3 & K_2 & K_1 & . & . & 0\\ . & . & . & . & . & .\end{vmatrix}\,. \tag{2.24}$$

This yields $M_1=K_1\mathcal{T}_0^{-1}$, (2.25)

$$M_2=[K_2-K_1^2]\mathcal{T}_0^{-1}\,, \tag{2.26}$$

$$M_3=[K_3-K_2K_1-K_1K_2+K_1^3]\mathcal{T}_0^{-1}\,. \tag{2.27}$$

The series on the right-hand side of (2.18) and (2.19) is a number of collisions expansion in the sense that M_n contains exactly n binary collision operators. Note, however, that in this formal procedure the triple, quadruple, etc., collisions are also expanded in terms of binary collision operators. This could be avoided if the similar expansion using the Ursell function method would have been used.[11] For hard cores there are no multiple collision events, and both methods yield exactly the same results. A density expansion can be obtained from (2.21) by expanding the correlation functions that appear in each of the operators M_n.

For the total distribution function the expansion procedure is entirely similar. The final result is also formally similar but the meaning of the operators changes in that there is a factor $[1+(N-1)P_{12}]$ multiplying the integrand in Eq. (2.22). This means that instead of the operators K_n we will get the new operators Q_n defined by

$$Q_n=\int d\vec{x}_2,\ldots,d\vec{x}_N[1+(N-1)P_{12}]\sum_{\alpha_1}\sum_{\alpha_2\neq\alpha_1}\cdots\sum_{\alpha_n\neq\alpha_{n-1}}T_{\alpha_1}G_0\cdots T_{\alpha_n}G_0F_0(\vec{x}_2\cdots|\vec{x}_1) \tag{2.28}$$

for $n\geq 1$. For $n=0$ we have

$$Q_0=\{1+\rho h_0(\vec{v}_1)\int d\vec{x}_2\,[g(\vec{r}_{12})-1]P_{12}\}\mathcal{T}_0\,. \tag{2.29}$$

The kinetic equation for the total distribution function is then

$$\left[\frac{\partial}{\partial t}+\vec{v}_1\cdot\frac{\partial}{\partial\vec{r}_1}\right]\eta(\vec{x}_1,t)=\sum_{n=1}^{\infty}\int_0^t dt'\gamma_n(t')\eta(\vec{x}_1,t-t')\,, \tag{2.30}$$

where $\gamma_n(t)$ is the inverse Laplace transform of $\gamma_n(s)$ defined in a similar way as M_n in Eq. (2.20). The first few terms are

$$\gamma_1(s)=Q_1Q_0^{-1}\,, \tag{2.31}$$

$$\gamma_2(s)=Q_2Q_0^{-1}-Q_1Q_0^{-1}\mathcal{T}_0Q_1Q_0^{-1}\,. \tag{2.32}$$

As in the case of the self-distribution function, (2.30) corresponds to the binary collision expansion of the kernels of the "master equation" for $\eta(\vec{x}_1,t)$.[9]

3. REDUCTION TO CONNECTED TERMS

A. Self-Operator

Let us now consider the operators M_n [Eq. (2.18)] in more detail. It will be convenient to use the Fourier transforms of these operators. We define

$$\langle\vec{k}_1',\vec{k}_2',\ldots,\vec{k}_n'|\mathcal{O}|\vec{k}_1,\vec{k}_2,\ldots,\vec{k}_n\rangle=\int d\vec{r}_1\,d\vec{r}_2\cdots d\vec{r}_N\exp[-i\textstyle\sum_1^n\vec{k}_j'\cdot\vec{r}_j]\,\mathcal{O}\,\exp[i\sum_1^n\vec{k}_j\cdot\vec{r}_j]\,. \tag{3.1}$$

Hence, we get for (2.18)

$$(s+i\vec{k}_1\cdot\vec{v}_1)f_s(\vec{k}_1,\vec{v}_1,s)=\sum_{n=1}^{\infty}M_n(\vec{k}_1)f_s(\vec{k}_1,\vec{v}_1,s)+W(\vec{k}_1,\vec{v}_1)\,, \tag{3.2}$$

with $$f_s(\vec{k}_1,\vec{v}_1,s)=\langle\vec{k}_1|f_s(\vec{x}_1,s)|0\rangle\,, \tag{3.3}$$

$$M_n(\vec{k}_1)=\langle\vec{k}_1|M_n|\vec{k}_1\rangle\,. \tag{3.4}$$

In deriving (3.2), we have taken into account the translational invariance of the collision operators M_n, so that only diagonal operators (3.4) are different from zero. Using

$$\langle \vec{k}_1' | \mathcal{T}_0^{-1} | \vec{k}_1 \rangle = 8\pi^3 \delta(\vec{k}_1' - \vec{k}_1)(s + i\vec{k}_1 \cdot \vec{v}_1), \tag{3.5}$$

we get for the one-collision term [Eq. (2.25)]

$$M_1(\vec{k}_1) = (8\pi^3)^{-1} \langle \vec{k}_1 | \int d\vec{v}_2, \ldots, d\vec{v}_N \sum_\alpha T_\alpha G_0 F_0(\vec{x}_2 \cdots | \vec{x}_1) | \vec{k}_1 \rangle (s + i\vec{k}_1 \cdot \vec{v}_1). \tag{3.6}$$

It is easy to see that the only nonzero contributions are those in which the pair α involves particle 1 (cf. Ref. 7), so that in the thermodynamic limit, $N \to \infty$, $V \to \infty$ $N/V \to$ finite,

$$M_1(\vec{k}_1, \vec{v}_1, s) = [8\pi^3]^{-1} \rho \int d\vec{v}_2 \langle \vec{k}_1 | T_{12} G_0 g(\vec{r}_{12}) | \vec{k}_1 \rangle (s + i\vec{k}_1 \cdot \vec{v}_1) h_0(\vec{v}_2). \tag{3.7}$$

It is shown in Appendix A that M_1 can be written in the form of a modified linear Boltzmann collision operator in ordinary space time [cf. Eq. (A17)]

$$M_1 = \rho \int d\Lambda \epsilon(\vec{r}_{12} \cdot \vec{v}_{12}) [J_{12}'(t) - J_{12}'(-t)] g(\vec{r}_{12}) h_0(\vec{v}_2), \tag{3.8}$$

where ϵ is the unit-step function, $J_{12}'(t)$ is essentially a time-evolution operator for two interacting particles, $d\vec{\Lambda}$ is a volume element in phase space (cf. Appendix A), and we have written the integrand in terms of positions and velocities to avoid the necessity of writing the rather complicated transformation functions to the Hamilton-Jacobi variables explicitly.

Let us now consider the next term, Eq. (2.26). Note first that in K_2 the only nonvanishing sequences are

$$T_{1j} T_{ij} \quad \text{and} \quad T_{1j} T_{1i}. \tag{3.9}$$

Hence,

$$M_2 = \rho^2 \int d\vec{v}_2 \, d\vec{v}_3 \langle \vec{k}_1 | [(T_{12} G_0 T_{23} G_0 + T_{12} G_0 T_{13} G_0) g(\vec{r}_1, \vec{r}_2, \vec{r}_3) - T_{12} G_0 g(\vec{r}_{12}) T_{13} G_0 g(\vec{r}_{13})] G_0^{-1} | \vec{k}_1 \rangle h_0(\vec{v}_2) h_0(\vec{v}_3). \tag{3.10}$$

As was first shown by Zwanzig,[7] the uncorrelated part of this contribution vanishes.

The third-order term Eq. (2.27) has two types of nonvanishing terms. The first type has sequences that involve only three particles:

$$T_{12} T_{13} T_{12}, \quad T_{12} T_{13} T_{23}, \quad T_{12} T_{23} T_{12}, \quad T_{13} T_{23} T_{12}. \tag{3.11}$$

The second type contains sequences involving four particles:

$$T_{12} T_{13} T_{14}, \quad T_{12} T_{13} T_{34}, \quad T_{12} T_{23} T_{14}, \quad T_{12} T_{13} T_{24}. \tag{3.12}$$

The terms in the first group are doubly connected and will occur only in the operator K_3, so that no possible cancellation can occur. The total contribution of these terms is

$$M_3(\text{conn}) = \rho^2 \int d\vec{v}_2 d\vec{v}_3 \langle \vec{k}_1 | [T_{12} G_0 T_{13} G_0 (T_{12} + T_{23}) + (T_{12} + T_{13}) G_0 T_{23} G_0 T_{12}] G_0 g(\vec{r}_1, \vec{r}_2, \vec{r}_3) G_0^{-1} | \vec{k}_1 \rangle h_0(\vec{v}_2) h_0(\vec{v}_3). \tag{3.13}$$

The uncorrelated sequences (3.12) cancel out also in this case. The correlated terms are at least of order ρ^3.[7]

It is interesting to note that our expansion holds also for the case when particle one, the labeled particle, is physically different from the other particles in the system. In particular, we may consider the case of a "Rayleigh gas", in which a "test" particle moves in a gas of noninteracting particles, i.e., $\phi_{ij} = T_{ij} = 0$, unless $i = 1$ or $j = 1$. Now it was noted by Lebowitz and Percus,[13] that the self-distribution function $f_S(\vec{x}, t)$ for a one-dimensional system of hard rods of diameter σ at density ρ is identical to the distribution function of a particle with "zero diameter" moving among noninteracting particles of density $n = \rho/(1 - \rho\sigma)$. For this case, M_2 [Eq. (3.10)] vanishes, and (3.13) can be evaluated explicitly (cf. Appendix B) to yield,

$$M_3 f_S(\vec{k}_1, \vec{v}_1, s) = n^2 \int dv_2 dv_3 |v_{12}| (P_{12} - 1) P_{13} |v_{12}| \epsilon(v_{12} v_{23}) \times (s + ik_1 v_2)^{-1} (P_{12} - 1) h_0(v_2) h_0(v_3) f_S(k_1, v_1, s). \tag{3.14}$$

This is just the Fourier-Laplace transform of (5.2) of Ref. 13, which is the n^2 term in the expansion of the exact kinetic equation

B. Total Operator

The formalism in this case is very similar to the one of the self-distribution function. The main difference is the structure of the operator Q_0. The inverse of this operator can be obtained from the Fourier transform of (2.29) and is

$$Q_0^{-1}(\vec{k}_1) = (s + i\vec{k}_1 \cdot \vec{v}_1)[1 - \rho h_0(\vec{v}_1)C(\vec{k}_1)\int d\vec{v}_2 P_{12}], \tag{3.15}$$

where $C(\vec{k}_1)$ is the Fourier transform of the direct correlation function.[14]

The first term in the expansion of the kinetic equation (2.31) can be written

$$\gamma_1 = \langle \vec{k}_1 | \int d\vec{v}_2, \ldots, d\vec{v}_N [1 + (N-1)P_{12}] \sum_\alpha T_\alpha G_0 F_0(\vec{x}_2 \cdots | \vec{x}_1) Q_0^{-1} | \vec{k}_1 \rangle . \tag{3.16}$$

As in the case of the self-distribution function, the only nonvanishing contributions are those in which the pair α contains particles 1 or 2. In this case, however, a new term essentially due to the nonlocal nature of the collision operator, and which involves three-particle correlations appears. Using (3.15), we get

$$\gamma_1 = \rho \langle \vec{k}_1 | \int d\vec{v}_2 d\vec{v}_3 [(1 + P_{12})T_{12}G_0 g(\vec{r}_{12}) + \rho \int d\vec{r}_3 T_{12}G_0 P_{13} g(\vec{r}_1, \vec{r}_2, \vec{r}_3)]$$
$$\times | \vec{k}_1 \rangle h_0(\vec{v}_2) h_0(\vec{v}_3)(s + i\vec{k}_1 \cdot \vec{v}_1)[1 - \rho h_0(\vec{v}_1)C(\vec{k}_1)\int d\vec{v}_4 P_{14}]. \tag{3.17}$$

Since $$\int d\vec{v}_3 P_{13}[1 - \rho h_0(\vec{v}_1)C(\vec{k}_1)\int d\vec{v}_4 P_{14}]\psi(\vec{v}_1) = [1 - \rho C(\vec{k}_1)]\int d\vec{v}_4 P_{14}\psi(\vec{v}_1), \tag{3.18}$$

where $\psi(\vec{v}_1)$ is any function of the velocity $\vec{v}_1$. Equation (3.17) can be written in the more compact form

$$\gamma_1 = \rho\Gamma_1 + \rho^2\Gamma_2, \tag{3.19}$$

$$\Gamma_1 = \langle \vec{k}_1 | \int d\vec{v}_2 (1 + P_{12})T_{12}G_0 g(\vec{r}_{12})G_0^{-1} | \vec{k}_1 \rangle h_0(\vec{v}_1), \tag{3.20}$$

$$\Gamma_2 = \langle \vec{k}_1 | \int d\vec{v}_2 (1 + P_{12})T_{12}G_0 g(\vec{r}_{12})C(\vec{k}_1)h_0(\vec{v}_1)h_0(\vec{v}_2)G_0^{-1} + \int d\vec{r}_3 T_{12}G_0 g(\vec{r}_1, \vec{r}_2, \vec{r}_3)$$
$$\times h_0(\vec{v}_1)h_0(\vec{v}_2)[1 - \rho C(\vec{k}_1)]G_0^{-1}P_{13} | \vec{k}_1 \rangle \int d\vec{v}_4 P_{14}. \tag{3.21}$$

The first term is the linearized Boltzmann term with the Enskog correction. The second term Γ_2 is essentially a mean field contribution and depends on the equilibrium correlations in a quite involved manner. However, in some limiting cases, it can be reduced to simple expressions: This will be discussed in Sec. 4.

4. DISCUSSION OF THE LOWEST-ORDER TERM OF THE TOTAL KINETIC EQUATION

We want to discuss now Eq. (3.19) in more detail. It can be shown that for very short times and for arbitrary potentials the correlation term Γ_2 reduces to a simple form. Let us consider first the case of soft potentials. In the limit $s \to \infty$ the collision operator T_{12} approaches θ_{12}

$$\theta_{12} = -m^{-1}(\partial\phi_{12}/\partial\vec{r}_{12}) \cdot \partial/\partial\vec{v}_{12} \tag{4.1}$$

Using this limit (which corresponds to looking at the kinetic equation for very short times) in (3.20) and (3.21), we find

$$\Gamma_1 = -\langle \vec{k}_1 | g(\vec{r}_{12}) \frac{\partial\phi_{12}}{\partial\vec{r}_{12}} \cdot \frac{\partial}{\partial\vec{p}_1} + \frac{\partial\phi_{12}}{\partial\vec{r}_{12}} \cdot \frac{\partial}{\partial\vec{p}_1} h_0(\vec{v}_1) \int d\vec{v}_2 P_{12} | \vec{k} \rangle, \tag{4.2}$$

$$\Gamma_2 = \left[\frac{\partial}{\partial\vec{p}_1} h_0(\vec{v}_1)\right] \cdot \langle \vec{k} | g(\vec{r}_{12}) \frac{\partial\phi_{12}}{\partial\vec{r}_{12}} (1 + P_{12}) C(\vec{k}_1)$$

$$- \int d\vec{r}_3\, g(\vec{r}_1, \vec{r}_2, \vec{r}_3) \frac{\partial \phi_{12}}{\partial \vec{r}_{12}} [1 - \rho C(\vec{k}_1)]\, P_{13} | \vec{k}_1 \rangle \int d\vec{v}_4\, P_{14} \,. \tag{4.3}$$

Using the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) relation[15]

$$\beta^{-1} \frac{\partial}{\partial \vec{r}_1} g(\vec{r}_{13}) + g(\vec{r}_{13}) \frac{\partial \phi_{13}}{\partial \vec{r}_{13}} = - \rho \int d\vec{r}_2 \frac{\partial \phi_{12}}{\partial \vec{r}_{12}} g(\vec{r}_1, \vec{r}_2, \vec{r}_3) \,, \tag{4.4}$$

and noting that $$\int d\vec{r}_2 \frac{\partial \phi_{12}}{\partial \vec{r}_{12}} g(\vec{r}_{12}) = 0 \,, \tag{4.5}$$

we get $$\Gamma_1 = \left[\frac{\partial}{\partial \vec{p}_1} h_0(\vec{v}_1) \right] \cdot \langle \vec{k}_1 | g(\vec{r}_{12}) \frac{\partial \phi_{12}}{\partial \vec{r}_{12}} P_{12} | \vec{k}_1 \rangle \int d\vec{v}_4 P_{14} \,, \tag{4.6}$$

$$\Gamma_2 = \left[\frac{\partial}{\partial \vec{p}_1} h_0(\vec{v}_1) \right] \cdot \langle \vec{k}_1 | - g(\vec{r}_{12}) \frac{\partial \phi_{12}}{\partial \vec{r}_{12}} P_{12} C(\vec{k}_1)$$

$$- \frac{1}{\rho} \left[\frac{1}{\beta} \frac{\partial}{\partial \vec{r}_{12}} g(\vec{r}_{12}) + g(\vec{r}_{12}) \frac{\partial \phi_{12}}{\partial \vec{r}_{12}} P_{12} \right] [1 - \rho C(\vec{k}_1)] | \vec{k}_1 \rangle \int d\vec{v}_4 P_{14} \,. \tag{4.7}$$

Replacing in (3.19) and using the fact that for Maxwell-Boltzmann distributions

$$\frac{\partial}{\partial \vec{p}_1} h_0(\vec{v}_1) = - \vec{v}_1 \beta h_0(\vec{v}_1) \,, \tag{4.8}$$

we get, in time-dependent form, valid for $t = 0+$,

$$\left[\frac{\partial}{\partial t} + i\vec{k}_1 \cdot \vec{v}_1 \right] \eta(\vec{k}_1, \vec{v}_1, t) = - i\vec{k}_1 \cdot \vec{v}_1 h_0(\vec{v}_1) C(\vec{k}_1) \int d\vec{v}_2\, \eta(\vec{k}_1, \vec{v}_2, t) \,, \tag{4.9}$$

which is a collisionless Vlasov-type equation. This equation was derived and discussed using different procedures by many authors.[9, 10, 14, 16]

A similar reduction occurs in the case of hard cores. In this case, however, no *ad hoc* short-time reduction of the collision operator is necessary, since the collision is already instantaneous. The suitable BBGKY equation is, in this case,

$$\frac{\partial}{\partial \vec{r}_{13}} g(\vec{r}_{13}) + \hat{\vec{r}}_{13} g(\vec{r}_{13}) \delta(|\vec{r}_{13}| - \sigma) = - \rho \int d\vec{r}_2\, \hat{\vec{r}}_{12}\, \delta(|\vec{r}_{12}| - \sigma) g(\vec{r}_1, \vec{r}_2, \vec{r}_3) \,, \tag{4.10}$$

where $\hat{\vec{r}}_{12}$ is the versor of the vector $\vec{r}_{12}$.

Let us first discuss the one-dimensional case. The BBGKY equation is then reduced to

$$\frac{\partial}{\partial r_1} g(r_{13}) + g(r_{13}) [\delta(r_{13} - \sigma) + \delta(r_{13} + \sigma)] = - \rho [g(r_1, r_1 - \sigma, r_3) - g(r_1, r_1 + \sigma, r_3)] \,. \tag{4.11}$$

The collision operators Γ_1 and Γ_2 are then

$$\Gamma_1 = g(\sigma) \int dv_2 | v_{12} | (1 - P_{12}) \{ [\epsilon(v_{12}) e^{i\sigma k_1} + \epsilon(- v_{12}) e^{-i\sigma k_1}] - 1 \} h_0(v_2) \,, \tag{4.12}$$

$$\Gamma_2 = - g(\sigma) \int dv_2 (v_{12}) h_0(v_1) h_0(v_2) \{ 2i \sin(\sigma k_1) C(k_1) + \int dr_{13} e^{-ik_1 r_{13}} [g(r_1, r_1 - \sigma, r_3)$$

$$- g(r_1, r_1 + \sigma, r_3)] \} [1 - \rho C(k_1)] \int dv_4 P_{14} \,. \tag{4.13}$$

Using these results in (3.19), we get after some algebra,

$$\gamma_1 = \rho g(\sigma) [\mu(v_1) (\cos k_1 \sigma - 1) + i v_1 \sin k_1 \sigma + h_0(v_1) \int dv_2 \{ | v_{12} | (\cos k_1 \sigma - 1) - i v_{12} \sin k_1 \sigma \} P_{12}]$$

$$- 2i v_1 h_0(v_1) \rho^2 g^2(\sigma) k_1^{-1} (1 - \cos k_1 \sigma) \int dv_2 P_{12} \,, \tag{4.14}$$

where $$\mu(v_1) = \int dv_2 | v_{12} | h_0(v_2) \,. \tag{4.15}$$

This result is identical with the exact kinetic equation for the total distribution function for hard rods found by Lebowitz, Percus, and Sykes.[8] Here there is a question of why the higher-order terms of the expansion (2.30) are not present in the exact equation: This could be answered by evaluating the higher-order terms in the kinetic equation. We conjecture that these terms vanish in the thermodynamic limit.

In the three-dimensional case a similar procedure can be used. Let us first split the operator (3.21) into two parts:

$$\Gamma_2 = (\Gamma_{21} + \Gamma_{22}) \int d\vec{v}_4 P_{14} , \tag{4.16}$$

$$\Gamma_{21} = - \int d\vec{v}_2 \langle \vec{k}_1 | (1 + P_{12}) T_{12} G_0 g(\vec{r}_{12}) G_0^{-1} | \vec{k}_1 \rangle h_0(\vec{v}_1) h_0(\vec{v}_2) C(\vec{k}_1) , \tag{4.17}$$

$$\Gamma_{22} = \int d\vec{v}_2 \langle \vec{k}_1 | T_{12} G_0 g(\vec{r}_1, \vec{r}_2, \vec{r}_3) G_0^{-1} P_{13} | \vec{k}_1 \rangle P_{13} h_0(\vec{v}_1) h_0(\vec{v}_2) [1 - \rho C(\vec{k}_1)] . \tag{4.18}$$

Using the explicit form of the collision operator (A23), we get for the first term

$$\Gamma_{21} = \int d\vec{v}_2 d\hat{\sigma} \sigma^2 g(\vec{\sigma}) \vec{v}_{12} \cdot \hat{\sigma} e^{i\vec{k}_1 \cdot \vec{\sigma}} h_0(\vec{v}_1) h_0(\vec{v}_2) C(\vec{k}_1) . \tag{4.19}$$

Similarly,

$$\Gamma_{22} = \int d\vec{v}_2 d\hat{\sigma} \int d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 e^{-i\vec{k}_1 \cdot \vec{r}_{13}} \delta(\vec{r}_{12} - \vec{\sigma}) \vec{v}_{12} \cdot \hat{\sigma} g(\vec{r}_1, \vec{r}_2, \vec{r}_3) h_0(\vec{v}_1) h_0(\vec{v}_2) [1 - \rho C(\vec{k}_1)] . \tag{4.20}$$

Using (4.10), we get

$$\Gamma_{22} = - \rho^{-1} \int d\vec{v}_2 [i\vec{k}_1 \cdot \vec{v}_{12} g(\vec{k}_1) + \int d\hat{\sigma} \sigma^2 g(\vec{\sigma}) e^{-i\vec{k}_1 \cdot \vec{\sigma}} \vec{v}_{12} \cdot \hat{\sigma}] h_0(\vec{v}_1) h_0(\vec{v}_2) [1 - \rho C(\vec{k}_1)] . \tag{4.21}$$

Performing the indicated integrations in (4.17) and (4.20), and adding them up, we get

$$\rho \Gamma_2 = - i\vec{k}_1 \cdot \vec{v}_1 h_0(\vec{v}_1) \tilde{C}(\vec{k}_1) \int d\vec{v}_2 P_{12} , \tag{4.22}$$

where $\tilde{C}(\vec{k}_1)$ is the Fourier transform of

$$\tilde{C}(\vec{r}) = C(\vec{r}) - g(\vec{\sigma}) \epsilon(|r| - \sigma) . \tag{4.23}$$

This result can be substituted into the transport equation (2.30),

$$\left[\frac{\partial}{\partial t} + i\vec{k}_1 \cdot \vec{v}_1\right] \eta(\vec{k}_1, \vec{v}_1, t) = \rho g(\vec{\sigma}) \int d\vec{v}_2 d\hat{\sigma} \sigma^2 |\vec{v}_{12} \cdot \hat{\sigma}| \epsilon(\vec{v}_{12} \cdot \vec{\sigma}) \{[h_0(\vec{v}'_2) \eta(\vec{k}_1, \vec{v}_1, t) - h_0(\vec{v}_2) \eta(\vec{k}_1, \vec{v}_1, t)]$$

$$+ [e^{-i\vec{k}_1 \cdot \vec{\sigma}} h_0(\vec{v}'_1) \eta(\vec{k}_1, \vec{v}_2, t) - h_0(\vec{v}_1) \eta(\vec{k}_1, \vec{v}_2, t) e^{i\vec{k}_1 \cdot \vec{\sigma}}]\} \quad - i\vec{k}_1 \cdot \vec{v}_1 h_0(\vec{v}_1) \tilde{C}(\vec{k}_1) \int d\vec{v}_2 \eta(\vec{k}_1, \vec{v}_2, t) , \tag{4.24}$$

where $\vec{v}'_1$ and $\vec{v}'_2$ are the velocities after collision (see Appendix A). This equation was first derived by Lebowitz, Percus, and Sykes,[9] using a different and more intuitive method.

A similar equation, also derived first by these authors, can be obtained using a potential which is the sum of a hard-core potential plus a soft part. The equation is formally equal to (4.23), but now the correlations correspond to the full interaction.

Equation (4.24) is the first term of a number of collisions expansion, and is exact only at $t = 0^+$, except for the one-dimensional system of hard rods where, as already mentioned, it is exact at all times. We expect that even in three dimensions Eq. (4.24) already contains much of the essential physics of the problem, and should therefore, like the Enskog equation, give reasonably good results for moderately dense "hard-sphere" fluids. To obtain an analogous Enskog-type equation for real systems with short range, but not hard core, interactions we have to look at the form of the kinetic operator in (3.19) for times which are large compared to the duration of a collision. We shall discuss this in Sec. 5.

5. FIRST-ORDER-COLLISION TERM FOR LONG TIMES

Let us first consider the case of the self-part equation (2.21). For times longer than the duration of a collision, we can write, up to the first order,

$$\frac{\partial}{\partial t} + i\vec{k}_1 \cdot \vec{v}_1 \, f_S(\vec{k}_1, \vec{v}_1, t) = [\int_0^\infty dt' \, M_1(t')] f_S(\vec{k}_1, \vec{v}_1, t) , \tag{5.1}$$

where we have used the approximation that during the duration of one collision, $f_S(\vec{k}_1, \vec{v}_1, t)$ does not change appreciably. Using the explicit form of M_1 [Eq. (3.8)], and provided that there are no "orbiting" trajectories, the integral on the right-hand side can be replaced by its average.

Note that the scattering operator $J'_{12}(t)$ acting on a reasonably smooth function of the positions and velocities, will give a finite contribution only inside the sphere which defines the range of the interparticle potential. If this potential becomes steeper and the range shorter, in the limit of hard-core potentials, the resulting function will contain a $\delta(t)$ function. Therefore, it seems reasonable to assume for the time dependence of $J'_{12}(t)$ some sort of a smeared Dirac δ function. The exact shape of this function will depend on the quantities which originally were on the right of the operator $J'_{12}(t)$. We may then approximate $\vec{r}_{12}(-t)$ by its average $\bar{\sigma}$. The direction of $\bar{\sigma}$ is going to be the same as the one of $\sigma_{\min}$, which is the relative position at the distance of closest approach, but the magnitude will not be the same, in general. As a first approximation, it would seem reasonable to take $\bar{\sigma}$ just proportional to $\sigma_{\min}$. Note here that the angle of deflection will not depend on the form of the smeared Dirac δ, but simply on the initial collision parameters. Using these approximations, we get for the self-distribution function

$$\left[\frac{\partial}{\partial t} + i\vec{k}_1 \cdot \vec{v}_1\right] f_S(\vec{k}_1, \vec{v}_1, t) = \int d\Lambda\, \epsilon(\vec{v}_{12} \cdot \bar{\sigma}) g(\bar{\sigma}) (\bar{J}_{12} - 1) h_0(\vec{v}_2) f_S(\vec{k}_1, \vec{v}_1, t)\,, \tag{5.2}$$

where $\bar{J}_{12}$ is analogous to the operator J_{12} defined by (A21), but with the velocity-dependent $\bar{\sigma}$ instead of σ.

The kinetic equation for the total distribution function is similarly,

$$\left[\frac{\partial}{\partial t} + i\vec{k}_1 \cdot \vec{v}_1\right] \eta(\vec{k}_1, \vec{v}_1, t) = \rho \int d\Lambda\, (\vec{v}_{12} \cdot \bar{\sigma}) g(\bar{\sigma}) \{[\bar{J}_{12} - 1] + [e^{-i\vec{k}_1 \cdot \bar{\sigma}} \bar{J}_{12} - e^{i\vec{k}_1 \cdot \bar{\sigma}}] P_{12}\} h_0(\vec{v}_2) \eta(\vec{k}_1, \vec{v}_1, t) + \rho^2 h_0(\vec{v}_1)$$

$$\times \int d\Lambda \{h_0(\vec{v}_2) g_{12}(\bar{\sigma}) e^{-i\vec{k}_1 \cdot \bar{\sigma}} C(\vec{k}_1) + \int d\vec{r}_{13}\, e^{-i\vec{k}_1 \cdot \vec{r}_{13}} g(\vec{r}_1, \vec{r}_1 - \bar{\sigma}, \vec{r}_3)[1 - \rho C(\vec{k}_1)]\} \int d\vec{v}_3\, \eta(\vec{k}_1, \vec{v}_3, t)\,. \tag{5.3}$$

In this expression, the last term represents the mean field contribution of the particles of the media to the relaxation towards equilibrium of the test particle.

No approximation like the ones discussed in Sec. 4 is possible here. First, the fact that $\bar{\sigma}$ is velocity-dependent, generally, in a quite complicated manner, makes the evaluation of the integral over $d\Lambda$ very difficult. Also the appearance of the three-particle correlation function makes the evaluation of this term difficult, and some approximation scheme in which the three-particle correlation function is expressed in terms of two-particle correlations is needed. We hope to come back to this point in future work.

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APPENDIX A: BINARY COLLISION OPERATOR

A complete derivation of the explicit form of the binary collision operator can not be found in the literature. The reason for this is that in the current method,[17] not the operators but their Laplace transforms are calculated. For a general potential, the Laplace transform of the binary collision Green's function cannot be obtained explicitly. Hence, an alternative procedure which avoids this step has to be used.

In time-dependent form, the collision operator is

$$\tilde{T}_{12}(t) = \int_0^t dt_1 \int_0^{t_1} dt_2\, G_0^{-1}(t - t_1)[\, G_{12}(t_1 - t_2) - G_0(t_1 - t_2)\,]\, g(\vec{r}_{12}) G_0^{-1}(t_2)\,, \tag{A1}$$

where $G_0^{-1}(t)$ is the inverse Laplace transform of G_0^{-1}. This operator can be represented by

$$G_0^{-1}(t) = e^{-tL_0} \delta'(t)\,,$$

where $\delta'(t)$ is the first derivative of the Dirac δ function, and is understood as referring to $t = 0^+$. Using this representation, the Fourier transform of (A1) is, after transforming to the new set of variables

$$\vec{r}_{12} = \vec{r}_1 - \vec{R}_2\,; \qquad \vec{R} = \tfrac{1}{2}(\vec{r}_1 + \vec{r}_2)\,, \tag{A2}$$

$$\langle \vec{k}_1', \vec{k}_2' | \tilde{T}_{12} | \vec{k}_1, \vec{k}_2 \rangle = 8\pi\delta(\vec{k}_1' + \vec{k}_2' - \vec{k}_1 - \vec{k}_2)(A_1 - A_2) , \tag{A3}$$

$$A_1 = \int_0^t dt_1 \int_0^{t_1} dt_2 \int d\vec{r}_{12} \exp\{-\tfrac{1}{2} i \vec{k}_{12}' \cdot [\vec{r}_{12} + (t - t_1)\vec{v}_{12}]\}$$
$$\times \delta'(t - t_1) G_{12}(t_1 - t_2) g(\vec{r}_{12}) \exp[\tfrac{1}{2} i \vec{k}_{12} \cdot (\vec{r}_{12} - t_2 \vec{v}_2)] \delta'(t_2) , \tag{A4}$$

$$A_2 = \int_0^t dt_1 \int_0^{t_1} dt_2 \int d\vec{r}_{12} \exp\{-\tfrac{1}{2} i \vec{k}_{12}' \cdot [\vec{r}_{12} + (t - t_1)\vec{v}_{12}]\}$$
$$\times \delta'(t - t_1) G_0(t_1 - t_2) g(\vec{r}_{12}) \exp[\tfrac{1}{2} i \vec{k}_{12} \cdot (\vec{r}_{12} - t_2 \vec{v}_{12})] \delta'(t_2) , \tag{A5}$$

where we used the notation $\vec{k}_{12}' = \vec{k}_1' - \vec{k}_2'$; $\vec{k}_{12} = \vec{k}_1 - \vec{k}_2$. (A6)

Let us now proceed with the term A_1. Note first that

$$G_{12}(t)\vec{r}_{12} = \vec{r}_{12}(-t) = \vec{r}_{12} + \int_0^{-t} dt' \, \vec{v}_{12}(t') , \quad G_{12}(t)\vec{v}_{12} = \vec{v}_{12}(-t) , \tag{A7}$$

where $G_{12}(t)$, $\vec{r}_{12}(-t)$, and $\vec{v}_{12}(-t)$ are also functions of the initial relative velocity and position.

Hence, $$A_1 = \int_0^t dt_1 \int_0^{t_1} dt_2 \int d\vec{r}_{12} \exp\{-\tfrac{1}{2} i \vec{k}_{12}' \cdot [\vec{r}_{12} + (t - t_1)\vec{v}_{12}]\} \delta'(t - t_1)$$
$$\times \exp[\tfrac{1}{2} i \vec{k}_{12} \cdot \vec{r}_{12}(t_2 - t_1) - t_2 \vec{v}_{12}(t_2 - t_1)] G_{12}(t_1 - t_2) \delta'(t_2) g(\vec{r}_{12}) . \tag{A8}$$

Using the well-known relation

$$\delta'(x) f(x) = -\delta(x) f'(0) , \tag{A9}$$

we get $$A_1 = -\int d\vec{r}_{12} \exp\{-\tfrac{1}{2} i [\vec{k}_{12}' \cdot \vec{r}_{12} - \vec{k}_{12} \cdot \vec{r}_{12}(-t)]\}$$
$$\times \{\tfrac{1}{2} i [\vec{k}_{12}' \cdot \vec{v}_{12} - \vec{k}_{12} \cdot \vec{v}_{12}(-t)] G_{12}'(t) + G_{12}''(t)\} g(\vec{r}_{12}) , \tag{A10}$$

where $G_{12}'(t)$ and $G_{12}''(t)$ are the first and second time derivatives of the operator $G_{12}(t)$.

Let us now introduce a different set of coordinates for the system, in which every point in phase space is defined by a trajectory and a timelike parameter, which we will call τ_{12} and which defines a fixed initial position of the particles. This transformation corresponds to the well-known Hamilton Jacobi (HJ) canonical transformation.[18] In the case of hard-core potentials, this is just the collision time

$$\tau_{12} = (|\vec{r}_{12} - \vec{\sigma}|)/|\vec{v}_{12}| \operatorname{sgn}(\vec{r}_{12} \cdot \vec{v}_{12}) , \tag{A11}$$

where $\vec{\sigma}$ is the relative position of the particles at the collision and $\operatorname{sgn}(x)$ is the sign function of x. For an arbitrary potential this becomes

$$\tau_{12} = \int_{\vec{r}_{12}(0)}^{\vec{r}_{12}(-t)} |d\vec{r}_{12}| (|\vec{v}_{12}(-t)|)^{-1} \operatorname{sgn}(\vec{r}_{12} \cdot \vec{v}_{12}) . \tag{A12}$$

Both in (A11) and (A12), the sign of τ_{12} means that we are before (+) or after (–) an inverse collision. Note now that the collision operator always appears in the form of a velocity integral, so that instead of (A10), we will have the velocity integral of that expression. Using the variable τ_{12}, (A10) can be written in the more compact form

$$\int d\vec{v}_{12} A_1 = \int d\vec{v}_{12} d\vec{r}_{12} \frac{\partial}{\partial \tau_{12}} \exp\{-\tfrac{1}{2} i [\vec{k}_{12}' \cdot \vec{r}_{12} - \vec{k}_{12} \cdot \vec{r}_{12}(-t)]\} [G_{12}'(t - \tau_{12})] g(\vec{r}_{12}) . \tag{A13}$$

This equation is more conveniently expressed in terms of direct and inverse collisions by splitting the integrand according to whether $\tau \gtrless 0$. The term with $\tau_{12} < 0$ is then expressed in terms of the inverse-collision variables

$$\vec{r}_{12} \to \vec{r}_{12} ; \quad t \to -t, \quad \vec{v}_{12} \to \vec{v}_{12} . \tag{A14}$$

The result is

$$\int d\vec{v}_{12} A_1 = \int d\vec{v}_{12} d\vec{r}_{12} \frac{\partial}{\partial \tau_{12}} \epsilon(\vec{r}_{12}\cdot\vec{v}_{12}) \Big[\exp\{-\tfrac{1}{2} i[\vec{k}'_{12}\cdot\vec{r}_{12} - \vec{k}_{12}\cdot\vec{r}_{12}(-t)]\}$$

$$\times G'_{12}(t-\tau_{12}) - \exp\{\tfrac{1}{2} i[\vec{k}'_{12}\cdot\vec{r}_{12} - \vec{k}_{12}\cdot\vec{r}_{12}(-t)]\} G'_{12}(\tau_{12}-t) \Big] g(\vec{r}_{12}) \ . \tag{A15}$$

Furthermore, since the HJ transformation is canonical, the Jacobian of the transformation is one, so that

$$\int d\vec{v}_{12} A_1 = \int d\vec{\Lambda} \int_0^\infty d\tau_{12} \frac{\partial}{\partial \tau_{12}} \epsilon(\vec{r}_{12}\cdot\vec{v}_{12}) \Big[\exp\{-\tfrac{1}{2} i[\vec{k}'_{12}\cdot\vec{r}_{12} - \vec{k}_{12}\circ\vec{r}_{12}(-t)]\} G'_{12}(t-\tau_{12})$$

$$- \exp\{\tfrac{1}{2} i[\vec{k}'_{12}\cdot\vec{r}_{12} - \vec{k}_{12}\cdot\vec{r}_{12}(-t)]\} G'_{12}(\tau_{12}-t) \Big] g(\vec{r}_{12}) \ , \tag{A16}$$

where $d\vec{\Lambda}$ is the differential of the five remaining HJ variables. Now the integration over τ_{12} is trivial.

For the second part of $T_{12}(t)$, A_2 (A5), the analysis is entirely similar, since G_0 can be considered as a limiting case of G_{12} when the interaction vanishes. Outside the collision region A_1 and A_2 will cancel out each other. If we call $J_{12}(t)$ the difference. then we get as our final result

$$\int d\vec{v}_2 \langle \vec{k}'_1, \vec{k}'_2 | \, T_{12}(t) | \vec{k}_1, \vec{k}_2 \rangle = 8\pi^3 \delta(\vec{k}'_1 + \vec{k}'_2 - \vec{k}_1 - \vec{k}_2) \int d\vec{\Lambda} \, \epsilon(\vec{r}_{12}\circ\vec{v}_{12})$$

$$\times \{ \exp[-i\vec{q}\cdot\vec{r}_{12}(-t)] \, J'_{12}(t) - \exp[i\vec{q}\circ\vec{r}_{12}(t)] \, J'_{12}(-t) \} g(\vec{r}_{12}) \ , \tag{A17}$$

where $2\vec{q} = \vec{k}'_{12} - \vec{k}_{12}$ (A18)

and $J'_{12}(t)$ is the time derivative of $J_{12}(t)$.

In a similar way, we get for the "different" particle operator

$$\int d\vec{v}_2 \langle \vec{k}'_1, \vec{k}'_2 | \, T_{12}(t) P_{12} | \vec{k}_1, \vec{k}_2 \rangle = 8\pi^3 \delta(\vec{k}'_1 + \vec{k}'_2 - \vec{k}_1 - \vec{k}_2) \int d\vec{\Lambda} \, \epsilon(\vec{r}_{12}\circ\vec{v}_{12})$$

$$\times \{ \exp[-i(\vec{k}_{12} + \vec{q})\cdot\vec{r}_{12}(-t)] \, J'_{12}(t) - \exp[i(\vec{k}_{12} + \vec{q})\cdot\vec{r}_{12}(t)] \, J'_{12}(-t) \} g(\vec{r}_{12}) P_{12} \ . \tag{A19}$$

These operators reduce to simpler forms in the case of hard cores. For hard spheres the operator $J_{12}(t)$ in HJ variables is

$$J_{12}(t) = \epsilon(t)\epsilon(|\sigma| - |\vec{r}_{12}\cdot\vec{n}|) J_{12} \ , \tag{A20}$$

where $\vec{n}$ is the unit vector normal to $\vec{v}_{12}$ in the $\vec{v}_{12}$, $\vec{r}_{12}$ plane and J_{12} is an operator that transforms the velocities before collision into velocities after collision

$$J_{12}\vec{v}_{12} = \vec{v}'_{12} = \vec{v}_{12} + 2\hat{\sigma}(\vec{v}_{12}\circ\hat{\sigma}) \ , \tag{A21}$$

where $\hat{\sigma}$ is the unit vector in the direction of $\vec{\sigma}$, and $\vec{\sigma}$ is $\vec{r}_{12}$ at the collision. For $J_{12}(-t)$ we get a similar expression to (A20) but, since this operator gives essentially the velocities "before" a direct (or more properly "after" an inverse) collision, this operator does not cause any change in the velocities, and the identity operator will appear in the place of J_{12}. Replacing in (A17) and (A19), we get at once

$$\langle \vec{k}'_1, \vec{k}'_2 | \, T_{12}(t) | \vec{k}_1, \vec{k}_2 \rangle = 8\pi^3 \delta(\vec{k}'_1 + \vec{k}'_2 - \vec{k}_1 - \vec{k}_2) \delta(t) \int d\hat{\sigma} \, \sigma^2 \epsilon(\vec{v}_{12}\cdot\vec{\sigma}) |\vec{v}_{12}\cdot\hat{\sigma}| [e^{-i\vec{q}\cdot\vec{\sigma}} J_{12} - e^{i\vec{q}\cdot\vec{\sigma}}] g(\vec{q}) \ , \tag{A22}$$

$$\langle \vec{k}'_1, \vec{k}'_2 | \, T_{12}(t) P_{12} | \vec{k}_1, \vec{k}_2 \rangle = 8\pi^3 \delta(\vec{k}'_1 + \vec{k}'_2 - \vec{k}_1 - \vec{k}_2) \delta(t)$$

$$\times \int d\hat{\sigma} \, \sigma^2 \epsilon(\vec{v}_{12}\circ\hat{\sigma}) |\vec{v}_{12}\cdot\hat{\sigma}| [e^{-i(\vec{k}_{12} + \vec{q})\cdot\vec{\sigma}} J_{12} - e^{i(\vec{k}_{12} + \vec{q})\cdot\vec{\sigma}}] P_{12} g(\vec{q}). \tag{A23}$$

When, instead of the two-particle correlation function, a different function of the position appears, e.g., the three-particle correlation function, an entirely similar procedure can be used. The correct form of a related collision operator for hard spheres was first obtained by Hiroike. [19]

For one-dimensional hard rods, the particles simply exchange their momenta on collision, so that $J_{12} = P_{12}$. Hence,

$$\langle k_1', k_2' | (1+P_{12}) T_{12}(t) | \mathbf{k}_1, \mathbf{k}_2 \rangle = 2\pi\delta(\mathbf{k}_1'+\mathbf{k}_2'-k_1-k_2)\delta(t)|v_{12}|$$
$$\times\{[\epsilon(v_{12})e^{-iq\sigma}+\epsilon(-v_{12})e^{iq\sigma}]P_{12}-\epsilon(-v_{12})e^{-iq\sigma}+\epsilon(v_{12})e^{iq\sigma}+\epsilon(-v_{12})e^{-i(k_{12}+q)\sigma}$$
$$+\epsilon(v_{12})e^{i(k_{12}+q)\sigma}-[\epsilon(-v_{12})e^{i(k_{12}+q)\sigma}+\epsilon(v_{12})e^{-i(k_{12}+q)\sigma}]P_{12}\}g(q) \ . \tag{A24}$$

APPENDIX B: ONE-DIMENSIONAL RECOLLISION TERM

Note first that in the kinetic equation (2.21), the term M_3 is going to be the only contribution to the order ρ^2, since after the first three collisions occurred, in a sequence like $T_{12}T_{13}T_{12}T_{13}$, particles two and three fly apart from particle one after the first three collisions, and the fourth collision will take place after a time $L|v_{13}|^{-1}\to\infty$ for $L\to\infty$, where L is the length of the system and we have assumed periodic boundary conditions. We have then

$$M_3 = \int dv_2 dv_3 \langle k_1 | G_0^{-1}(G_{12}-G_0)G_0^{-1}(G_{13}-G_0)G_0^{-1}(G_{12}-G_0)G_0^{-1}|k_1\rangle h_0(v_3)h_0(v_2) \ . \tag{B1}$$

For this particular case the operator $G_{12}-G_0$ can be written

$$G_{12}-G_0 = \int_0^\infty dt\, e^{-st}\epsilon(r_{12}v_{12})\epsilon(|v_{12}|t-|r_{12}|)(P_{12}-1)e^{-tL_0} \ . \tag{B2}$$

Using this equation in (B1), after some algebra, we get

$$M_3 = (2\pi)^{-1}\int dv_2 dv_3 |v_{12}|(P_{12}-1)Ah_0(v_2)h_0(v_3) \ , \tag{B3}$$

$$A = \int dr_{12}dr_{13}dq e^{-ir_{13}(k_1-q)/2}(P_{13}-1)\epsilon(r_{13}v_{13})\exp[\tau_{13}(-s-ik_1v_1+iqv_{12})$$
$$+\tfrac{1}{2}ir_{13}(k_1-q)-\tfrac{1}{2}ir_{12}(k_1-2q)]\epsilon(r_{12}v_{12})(P_{12}-1)\exp[-\tau_{12}(s+ik_1v_1)+\tfrac{1}{2}ik_1r_{12}] \ . \tag{B4}$$

The q integration yields

$$A = 2\pi\int dr_{12}dr_{13}[P_{13}\delta(\tau_{13}v_{12}-r_{13}+r_{12})-\delta(\tau_{13}v_{12}+r_{12})$$
$$\times\epsilon(r_{13}v_{13})\exp[-\tau_{13}(s+ik_1v_1)+ik_1r_{23}](P_{12}-1)\epsilon(r_{12}v_{12})\exp[-\tau_{12}(s+ik_1v_1)] \ . \tag{B5}$$

The term with $\delta(\tau_{13}v_{12}+r_{12})$ vanishes identically. Carrying out the r_{12} and r_{13} integrations in the other term, we get

$$A = 2P_{13}|v_{13}|(|v_{23}|)^{-1}v_{12}v_{23}(v_{13})^{-1}\epsilon(v_{12}v_{23})(s+ik_1v_2)^{-1}(P_{12}-1) \ . \tag{B6}$$

If the Heaviside function is satisfied then

$$|v_{13}|v_{23}(|v_{23}|v_{13})^{-1}=1 \ . \tag{B7}$$

So, that going back to (B3) we get (3.14).

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Laser-Induced Breakdown in Liquid He^4

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The threshold power for laser-induced breakdown in liquid helium was studied as a function of temperature between 4 and 1.1 °K. Above the λ point, it was found to be temperature-independent. In He II, however, the threshold increases rapidly by one order of magnitude on cooling between the λ temperature and 1.5 °K. This behavior is interpreted in terms of a rapidly increasing mobility of free electrons in the energy range of several electron volts if the liquid is cooled below the λ point.

Laser-induced breakdown in compressed gaseous helium was investigated in a number of previous experiments.[1-4] The pressure dependence of the threshold clearly demonstrated the basic role of collisions between electrons and atoms for attaining the observed high degree of ionization.[5,6] It seemed, therefore, that a measurement of the threshold power for breakdown in superfluid helium would provide valuable information about the collision rate of free electrons in this quantum liquid. Furthermore, in view of the recent application of stimulated Brillouin scattering techniques to liquid helium,[7] a knowledge of the threshold for optical breakdown in this liquid seemed desirable. The experiments reported here demonstrate the basic importance of the collective excitations for the breakdown phenomenon and lead to the expectation that the breakdown behavior of liquid He^3 and liquid He^4 may be rather different.

The beam of a Q-switched ruby laser (peak power 50 MW, pulse duration 25 nsec) was directed from the top into a helium Dewar and was focused inside the liquid. Breakdown was evident by a bright spark in the focal volume which could be easily observed. The threshold power was determined by successively attenuating the laser pulses until suddenly no spark was detectable anymore. The temperature dependence of the threshold intensity[8] observed in this way is presented in Fig. 1. There are three temperature regions of interest: In He I, the threshold remains constant including the vicinity of the λ point. In He II, however, it increases rapidly by one order of magnitude when the liquid is cooled from the λ point to 1.5 °K. Below 1.5 °K, the threshold becomes almost temperature-independent, attaining a value which is higher than the damage threshold of any solid studied so far.[9]

The breakdown intensities reported here for liquid helium are several orders of magnitude lower than the estimated threshold for multiphoton ionization of unexcited helium atoms.[10,11] Multiphoton ionization also fails to account for the rapid