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Hard-Sphere Binary-Collision Operators

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The time displacement operator is described for a system of hard-sphere particles. We show how to avoid needing a representation for this operator in unphysical regions of phase space, and how to construct a useful representation in terms of binary collision operators in the physical region. The various binary collision operators used for hard-sphere systems are derived for the case of a system of two spheres, and the results are generalized to N-particle systems.

KEY WORDS: Binary collision operator; hard spheres; kinetic theory; Liouville operator.

1. INTRODUCTION

Recent developments in the kinetic theory of neutral gases and fluids with short-ranged forces have allowed a wide variety of different nonequilibrium phenomena to be described. For example, the short-, intermediate-, and long-time behavior of various time correlation functions can be calculated and the results compared with experiment or with molecular dynamics results.[1,2] The glass–fluid transition is at present an area of study in which kinetic theory makes substantial contributions.[3] The basis of kinetic theory is a very careful analysis of the dynamical events that can take place among small numbers of particles in infinite space or inside a container. In either case, one must have some model for the interaction of the particles, and, in the latter case, for their interactions with the walls of the container. In selecting such interaction models, one tries to simplify the dynamics as

Dedicated to Prof. E. G. D. Cohen on the occasion of his 65th birthday.

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much as possible without losing the essential physics of the phenomena under discussion. Under these circumstances, a hard-sphere model for the particles that comprise the system seems very natural, provided one is not interested in effects due to attractive forces or to particles in contact over some period of time. The advantage of a hard-sphere model is that all dynamical events taking place among the particles in the system can be described by sequences of instantaneous binary collision separated by intervals of time in which all the particles are either moving freely or colliding with the walls.

Despite the simplicity of this dynamics, the development of a useful mathematical description of it proved to be difficult. The basic problem is that statistical averages of dynamical quantities involve an integration over the phase space volume of an N-particle system. Such an integration includes regions where two or more hard-sphere particles overlap, and for such regions the dynamics is undefined. While it seems obvious that such physical situations can never occur, it was not at all obvious how to develop a mathematical formalism where such configurations never appear. This problem was carefully formulated and solved in 1969, with the development of a carefully defined binary collision expansion for the so-called N-particle time-displacement operator.[4] One of the remarkable points of the analysis was that the time displacement operator has to be used in conjunction with the configurational part of the N-particle equilibrium distribution function for hard spheres. Further, the precise structure of the binary collision operator depends on whether or not the time-displacement operator acts on the equilibrium distribution function together with the dynamical variables of interest.

The purpose of this paper is to clarify these various issues, to show for a simple example involving two particles in infinite space how the various hard-sphere binary-collision operators arise naturally, and how they are to be used. Our aim is to provide a clear derivation so that other workers interested in nonequilibrium hard-sphere dynamics will be able to work easily and correctly with the appropriate binary-collision operators. It was at the urging of Prof. E. G. D. Cohen that we worked out this simple approach, and it has proved to be of value to other workers as well. Therefore, we are happy to dedicate this paper to Professor Cohen on the occasion of his 65th birthday.

In Section 2 we discuss the time-displacement operator for hard spheres, and outline the problem of and approach to the proper representation of these operators. In Section 3 we construct explicit representations of these operators for a simple system consisting of two hard spheres, and we discuss the generalization to N hard spheres in Section 4.

2. TIME-DISPLACEMENT OPERATORS

Time-dependent quantities of interest in statistical mechanics generally appear as statistical averages over an N-particle distribution function $f_N(\Gamma, t)$, which obeys the Liouville equation, or an equilibrium time-correlation function. In the former case we are led to consider integrals of the form

$$\langle F(t)\rangle = \int d\Gamma\, F(\Gamma)\, f_N(\Gamma, t) = \int d\Gamma\, f_N(\Gamma, 0)\, F(\Gamma(t)) \tag{2.1}$$

and in the latter, integrals of the form

$$\begin{aligned}\langle A(0)\, B(t)\rangle_{\text{eq}} &= \int d\Gamma\, f_{\text{eq}}(\Gamma)\, A(\Gamma)\, B(\Gamma(t)) \\ &= \int d\Gamma\, f_{\text{eq}}(\Gamma)\, B(\Gamma)\, A(\Gamma(-t))\end{aligned} \tag{2.2}$$

In Eqs. (2.1) and (2.2), the angular brackets denote ensemble averages, Γ is a point in N-particle phase space, $F(\Gamma)$, $A(\Gamma)$, and $B(\Gamma)$ are dynamical functions of the phase variables, and t is the time. We have used Liouville's theorem and the stationary properties of the equilibrium ensemble averages to obtain the second equality in Eqs. (2.1) and (2.2), respectively. It is often convenient to express time-dependent dynamical quantities such as those appearing in the integrand in Eqs. (2.1) and (2.2) in terms of a time-displacement operator $S_t(\Gamma)$ that has the following properties:

$$S_t(\Gamma)\, F(\Gamma) = F(\Gamma(t)) \tag{2.3a}$$

$$f_N(\Gamma, t) = S_{-t}(\Gamma)\, f_N(\Gamma, 0) = f_N(\Gamma(-t), 0) \tag{2.3b}$$

for any dynamical function $F(\Gamma)$, and for solutions of the Liouville equation, $f_N(\Gamma, t)$, with initial value $f_N(\Gamma, 0)$. Here $\Gamma(t)$ represents the phase point that evolves in time t starting at the point Γ. Similarly, $\Gamma(-t)$ is the phase point that evolves to Γ after a time t. For systems of monatomic particles that interact with two-body, central forces determined by a continuous potential function $\phi(r)$, the time-displacement operator has a very simple form,

$$S_t(\Gamma) = e^{tL(\Gamma)} \tag{2.4}$$

where $L(\Gamma)$ is the Liouville operator

$$L(\Gamma) = L_0(\Gamma) + L_I(\Gamma) \tag{2.5}$$

with

$$L_0(\Gamma) = \sum_{i=1}^{N} \frac{\mathbf{p}_i}{m} \cdot \nabla_{r_i} \tag{2.6a}$$

and

$$L_I = -\sum_{i<j} \frac{\partial \phi(r_{ij})}{\partial \mathbf{r}_i} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \tag{2.6b}$$

Here $\mathbf{r}_i$, $\mathbf{p}_i$ are the position and momentum of particle i, respectively, and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and we have assumed that there are N particles, each with mass m. For continuous potentials, there are no obvious difficulties in defining $S_{\pm t}(\Gamma)$ for all points $\Gamma = (\mathbf{r}_1, \mathbf{p}_1, ..., \mathbf{r}_N, \mathbf{p}_N)$, except for sets of measure zero, where the centers of two or more particles coincide.

However, if we consider systems of hard-sphere particles, the problems of defining $S_{\pm t}(\Gamma)$ become clear. That is, if we suppose that the particles are all hard spheres with diameter a, then $S_{\pm t}(\Gamma)$ is not defined for all points Γ where $r_{ij} < a$ for any i and j. We can avoid ever having to consider these regions of configuration space if we can manage to consider $W_N(\Gamma)\, S_{\pm t}(\Gamma)$, where

$$W_N(\Gamma) = \begin{cases} 0 & \text{if } r_{ij} < a \quad \text{for any } i, j \\ 1 & \text{otherwise} \end{cases} \tag{2.7}$$

By examining the integrand appearing in the right-hand sides of Eqs. (2.1) and (2.2) we see that this is possible in Eq. (2.1) if the initial N-particle distribution function $f_N(\Gamma, 0)$ is proportional to $W_N(\Gamma)$, and it is possible in Eq. (2.2) because $f_{\text{eq}}(\Gamma)$ is proportional to $W_N(\Gamma)$. This latter point follows because

$$f_{\text{eq}}(\Gamma) = C_N e^{-\beta H_N(\Gamma)} = C'_N W_N(\Gamma) \prod_{i=1}^{N} \phi_0(\mathbf{p}_i) \tag{2.8}$$

Here C_N and C'_N are normalization constants containing the canonical partition function, $\phi_0(\mathbf{p}_i)$ is the single-particle Maxwell–Boltzmann momentum distribution function, and $H_N(\Gamma)$ is the Hamiltonian function for the system of N particles. The second equality on the right-hand side of Eq. (2.8) holds only for hard spheres, of course.

Therefore, under the circumstances outlined above, we need only consider quantities of the form $W_N(\Gamma)\, S_{\pm t}(\Gamma)$ when computing statistical averages. In the next section we will find an explicit form for $W_N(\Gamma)\, S_{\pm t}(\Gamma)$ for the simple case of two particles, and thereby define the binary collision operators $T_{\pm}(i, j)$ for two particles i and j. We will also show how the quantity $S_{\pm t}(\Gamma)\, W_N(\Gamma)$ can be defined by constructing the adjoint of $W_N(\Gamma)\, S_{\mp t}(\Gamma)$.

3. THE BINARY-COLLISION OPERATORS

In order to develop a useful representation of the time-displacement operator for hard spheres, we consider first the case of two particles and study the quantity $W(1,2)\,S_t(1,2)$, where

$$W(1,2)=\begin{cases}0 & \text{if } r_{12}<a\\ 1 & \text{otherwise}\end{cases} \tag{3.1}$$

and where $S_t(1,2)$ is the time-displacement operator for a system of two hard spheres. Rather than consider this quantity directly, it is more convenient when visualizing the geometry of hard-sphere motion to eliminate the trivial region of two-particle phase space where the spheres do not collide, and where no questions of definition of $S_t(1,2)$ arise. Therefore, the quantity of interest to us is $I_t(1,2)F$

$$I_t(1,2)F=W(1,2)[S_t(1,2)-S_t^0(1,2)]\,F(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2) \tag{3.2}$$

where $F(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2)$ is some arbitrary function, and $S_t^0(1,2)$ is a free-particle time-displacement operator that acts on F to produce

$$S_t^0(1,2)\,F(\mathbf{r}_1,\mathbf{p}_1,\mathbf{r}_2,\mathbf{p}_2)=F(\mathbf{r}_1+\mathbf{v}_1t,\mathbf{p}_1,\mathbf{r}_2+\mathbf{v}_2t,\mathbf{p}_2)=e^{tL_0}F \tag{3.3}$$

for all phases of particles 1 and 2, and $\mathbf{v}_i=\mathbf{p}_i/m$. To compute $I_t(1,2)F$ we set up a coordinate system at the center of particle 2, with z axis in the direction of $\mathbf{v}_{12}=\mathbf{v}_1-\mathbf{v}_2$ (Fig. 1). In this coordinate system the initial phase of particle 1 is located by the vector $\mathbf{r}_{12}$, given by

$$\mathbf{r}_{12}=\mathbf{r}_\perp+r_{||}\hat{z} \tag{3.4}$$

where $\mathbf{r}_\perp$ is the projection of $\mathbf{r}_{12}$ onto the plane through the origin perpendicular to the z axis, $\hat{z}$ is a unit vector in the z direction, and $r_{||}$ is the projection of $\mathbf{r}_{12}$ onto the z axis. Here $r_{||}$ is a negative quantity. Since $W(1,2)$ ensures that $I_t(1,2)F$ is only defined for phases where $r_{12}>a$, we have that

$$\begin{aligned}I_t(1,2)F&=W(1,2)[S_t(1,2)-S_t^0(1,2)]F=0\\ &\text{unless}\quad |\mathbf{r}_\perp|<a\quad\text{and}\quad -\gamma-v_{12}t<r_{||}<-\gamma\end{aligned} \tag{3.5}$$

where $\gamma=(a^2-r_\perp^2)^{1/2}$. Therefore we may write

$$\begin{aligned}I_t(1,2)F=\Theta(a-|\mathbf{r}_\perp|)[\Theta(\gamma+v_{12}t+r_{||})-\Theta(\gamma+r_{||})]\\ \times\,[F(\mathbf{r}_1(t),\mathbf{p}_1(t),\mathbf{r}_2(t),\mathbf{p}_2(t))\\ -\,F(\mathbf{r}_1+\mathbf{v}_1t_1,\mathbf{p}_1,\mathbf{r}_2+\mathbf{v}_2t,\mathbf{p}_2)]\end{aligned} \tag{3.6}$$

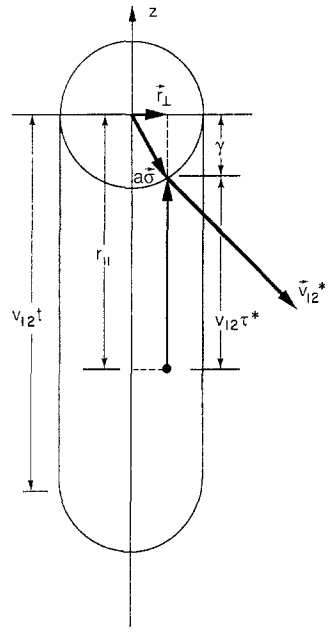

Fig. 1. Collision cylinder for the (1, 2) binary collision. The z axis is in the direction of the relative velocity $\mathbf{v}_1 - \mathbf{v}_2 = \mathbf{v}_{12}$.

Here $\Theta(x) = 1$ if $x > 0$, and $\Theta(x) = 0$ for $x < 0$. Also, $\mathbf{r}_i(t)$, $\mathbf{p}_i(t)$ are the phases of particle i at time t, determined by the dynamics of two bodies. Using the fact that the derivative of $\Theta(x)$ is $\delta(x)$, and that particle 1 will collide with particle 2 at time τ^* given by

$$\tau^* = \frac{-r_{||} - \gamma}{v_{12}} \tag{3.7}$$

we can compute $\mathbf{r}_1(t)$, $\mathbf{p}_1(t)$ and $\mathbf{r}_2(t)$, $\mathbf{p}_2(t)$ in Eq. (3.6) and then express $I_t(1, 2)F$ as

$$\begin{aligned} I_t(1,2)F = \Theta(a - |\mathbf{r}_\perp|) \int_0^t d\tau\, |v_{12}|\, \delta(r_{||} + v_{12}\tau + \gamma) \\ \times [F(\mathbf{r}_1 + \mathbf{v}_1\tau + \mathbf{v}_1^*(t-\tau), \mathbf{p}_1^*, \mathbf{r}_2 + \mathbf{v}_2\tau + \mathbf{v}_2^*(t-\tau), \mathbf{p}_2^*) \\ - F(\mathbf{r}_1 + \mathbf{v}_1 t, \mathbf{p}_1, \mathbf{r}_2 + \mathbf{v}_2 t, \mathbf{p}_2)] \end{aligned} \tag{3.8}$$

Here $(\mathbf{v}_1^*, \mathbf{v}_2^*)$ or $(\mathbf{p}_1^*, \mathbf{p}_2^*)$ are the velocities or momenta of the two particles after the collision. They are given by

$$\mathbf{v}_1^* = \frac{\mathbf{p}_1^*}{m} = \mathbf{v}_1 - (\mathbf{v}_{12} \cdot \hat{\sigma})\hat{\sigma} \tag{3.9a}$$

$$\mathbf{v}_2^* = \frac{\mathbf{p}_2^*}{m} = v_2^* + (\mathbf{v}_{12} \cdot \hat{\sigma})\hat{\sigma} \tag{3.9b}$$

Here $\hat{\sigma}$ is a unit vector in the direction of the point of contact of particles 1 and 2 at the instant of collision. In the coordinate system we are using

$$\hat{\sigma} = \frac{1}{a}\left[\mathbf{r}_\perp - (a^2 - r_\perp^2)^{1/2}\,\hat{z}\right] \tag{3.10}$$

It is now obvious by inspection of the right-hand side of Eq. (3.8) that it can be expressed simply as

$$I_t(1,2)F = \int_0^t d\tau\; S_\tau^0(1,2)\, T_+(1,2)\, S_{(t-\tau)}^0(1,2)\, F(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2) \tag{3.11a}$$

where

$$T_+(1,2) = |v_{12}|\,\Theta(a - |\mathbf{r}_\perp|)\,\delta(r_{||} + \gamma)(P_\sigma - 1) \tag{3.11b}$$

Here P_σ is a substitution operator that replaces $\mathbf{v}_1$, $\mathbf{v}_2$ by $\mathbf{v}_1^*$, $\mathbf{v}_2^*$ whenever these quantities appear to the right of it. The quantity $T_+(1,2)$ is a binary collision operator. It can easily be transformed to the expression usually given in the literature,

$$T_+(1,2) = a^{d-1} \int_{\mathbf{v}_{12}\cdot\hat{\sigma} < 0} d\hat{\sigma}\; |\mathbf{v}_{12} \cdot \hat{\sigma}|\; \delta(a\hat{\sigma} - \mathbf{r}_{12})(P_\sigma - 1) \tag{3.12}$$

where d is the number of dimensions of the system. We have thus proved that

$$W(1,2)\, S_t(1,2) = W(1,2)\left[S_t^0(1,2) + \int_0^t d\tau\; S_\tau^0(1,2)\, T_+(1,2)\, S_{t-\tau}^0(1,2) \right] \tag{3.13}$$

This expression can be further simplified if we note that

$$T_+(1,2)\, S_\tau^0(1,2)\, T_+(1,2) = 0 \qquad \text{for any} \quad \tau > 0 \tag{3.14}$$

since the two hard spheres cannot collide more than once. Then Eq. (3.13) can be put in the form

$$W(1,2)\,S_t(1,2) = W(1,2)\exp\{t[L_0(1,2)+T_+(1,2)]\} \tag{3.15}$$

Similarly, we can show that

$$W(1,2)\,S_{-t}(1,2) = W(1,2)\exp\{-t[L_0(1,2)-T_-(1,2)]\} \tag{3.16}$$

where

$$T_-(1,2) = a^{d-1}\int_{\mathbf{v}_{12}\cdot\hat{\sigma}>0} d\hat{\sigma}\,|\hat{v}_{12}\cdot\hat{\sigma}|\,\delta(\mathbf{r}_{12}-a\hat{\sigma})(P_\sigma - 1) \tag{3.17}$$

Let us return to Eq. (3.13) and represent the streaming operator in (2.13) as

$$S_t(1,2) = S_t^0(1,2) + S_+^0 * T_+(1,2)S_+^0 \tag{3.18}$$

where the asterisk denotes a convolution product, such that

$$f * g = \int_0^t d\tau\, f_\tau\, g_{t-\tau} = \int_0^t d\tau\, f_{t-\tau}\, g_\tau \tag{3.19}$$

We consider for the moment how the various terms on the right-hand side behave for different initial configurations of particles 1 and 2. We consider nonoverlapping configurations for which $W(1,2)=1$. Suppose there is no (1, 2) collision during the interval $(0, t)$. Then $S_t(1,2)$ reduces to $S_t^0(1,2)$, and the second term on the right-hand side of Eq. (3.18) vanishes, since the particles are never in contact during the interval. Suppose instead that there is a (1, 2) collision during the interval. If we note that $T_+(1,2)$ can be written

$$T_+(1,2) = T_+^{\mathrm{r}} + T_+^{\mathrm{v}}$$

where T^{r} denotes the first term on the right-hand side of Eq. (3.12) proportional to P_σ, and T^{v} denotes the second term, without the P_σ, and the superscripts denote "real" and "virtual," respectively, then the right-hand side of Eq. (3.19) reduces to

$$S_t(1,2) = S_+^0 * T_+^{\mathrm{r}}(1,2)S_+^0 \tag{3.20}$$

as expected. That is, the "virtual" collision contribution to $S_+^0 * TS_+^0$ cancels the free streaming term S_t^0, and a correct description of the "real" (1, 2) collision remains. A similar description of $S_{-t}(1,2)$ can be shown to hold as well.

To complete our discussion of the binary collision operators, we ask if there is any way to generate a binary collision operator representation of the time-displacement operator $S_t(1, 2)$ when it appears to the left of the function $W(1, 2)$. This can in fact be given a positive answer in terms of the adjoint of well-defined operators. To do this, we consider the well-defined integral

$$J_t = \int dx_1 \int dx_2 \, g(1, 2) \, W(1, 2) \, S_{-t}(1, 2) \, f(1, 2) \tag{3.21}$$

where $dx_1 \, dx_2 = d\mathbf{r}_1 \, d\mathbf{p}_1 \, d\mathbf{r}_2 \, d\mathbf{p}_2$, and f and g are arbitrary functions. Now, using Eq. (3.16), we can express J_t as

$$J_t = \int dx_1 \int dx_2 \, g(1, 2) \, W(1, 2) \times \left[S^0_{-t}(1, 2) + \int_0^t d\tau \, S^0_{-\tau}(1, 2) \, T_-(1, 2) \, S^0_{-(t-\tau)}(1, 2) \right] f(1, 2) \tag{3.22}$$

With the aid of the free-particle Liouville theorem, we can write the right-hand side of Eq. (3.22) as

$$J_t = \int dx_1 \int dx_2 \left\{ f(1, 2)[S^0_{+t}(1, 2) \, g(1, 2) \, W(1, 2)] + \int_0^t d\tau \, [S^0_\tau(1, 2) \, g(1, 2) \, W(1, 2)] \times a^{d-1} \int_{\mathbf{v}_{12} \cdot \hat{\sigma} > 0} d\hat{\sigma} \, |\mathbf{v}_{12} \cdot \hat{\sigma}| \, \delta(\mathbf{r}_{12} - a\hat{\sigma})(P_\sigma - 1) \, S^0_{-(t-\tau)}(1, 2) \, f(1, 2) \right\} \tag{3.23}$$

The integral involving the real collision, i.e.,

$$\int dx_1 \int dx_2 \int_{\mathbf{v}_{12} \cdot \sigma > 0} d\hat{\sigma} \times [S^0_\tau(1, 2) \, g(1, 2) \, W(1, 2)] \, |\mathbf{v}_{12} \cdot \boldsymbol{\sigma}| \, \delta(\mathbf{r}_{12} - a\hat{\sigma}) \, P_\sigma \times S^0_{-(t-\tau)}(1, 2) \, f(1, 2)$$

can be transformed to

$$\int dx_1 \int dx_2 \int_{\mathbf{v}_{12} \cdot \hat{\sigma} < 0} d\hat{\sigma} \times f(1, 2) \, S^0_{(t-\tau)}(1, 2) \, |\mathbf{v}_{12} \cdot \hat{\sigma}| \, \delta(\mathbf{r}_{12} - a\hat{\sigma}) \, P_\sigma \times S^0_\tau(1, 2) \, g(1, 2) \, W(1, 2)$$

by means of the one-particle Liouville theorem, the identities

$$d\mathbf{p}_1\, d\mathbf{p}_2 = d\mathbf{p}_1^*\, d\mathbf{p}_2^* \tag{3.24a}$$

$$\mathbf{v}_{12}\cdot\hat{\sigma} = -(\mathbf{v}_{12}^*\cdot\hat{\sigma}) \tag{3.24b}$$

and finally relabeling the "starred" and "unstarred" momentum variables. Similarly, the integral involving the virtual collision

$$\int dx_1 \int dx_2 \int_{\mathbf{v}_{12}\cdot\hat{\sigma}>0} d\hat{\sigma}$$
$$\times [S_\tau^0(1,2)\, g(1,2)\, W(1,2)]\, |\mathbf{v}_{12}\cdot\hat{\sigma}|\, \delta(\mathbf{r}_{12}-a\hat{\sigma})\, S^0_{-(t-\tau)}(1,2)\, f(1,2)$$

may be written as

$$\int dx_1 \int dx_2 \int_{\mathbf{v}_{12}\cdot\sigma<0} d\hat{\sigma}$$
$$\times f(1,2)\, S^0_{+(t-\tau)}(1,2)\, |\mathbf{v}_{12}\cdot\hat{\sigma}|\, \delta(\mathbf{r}_{12}+a\hat{\sigma})\, S_\tau^0(1,2)\, W(1,2)\, g(1,2)$$

where we have let $\hat{\sigma}\to -\hat{\sigma}$, and used the free particle Liouville theorem. Therefore, J_t may be written

$$J_t = \int dx_1 \int dx_2\, f(1,2)\left[S^0_{+t}(1,2) + \int_0^t d\tau\, S^0_{(t-\tau)}(1,2)\, \bar{T}_+(1,2)\, S_\tau^0(1,2)\right]$$
$$\times\ W(1,2)\, g(1,2) \tag{3.25}$$

with the binary collision operator $\bar{T}_+$ defined as

$$\bar{T}_+ = a^{d-1}\int_{\mathbf{v}_{12}\cdot\hat{\sigma}<0} d\hat{\sigma}\, |\mathbf{v}_{12}\cdot\hat{\sigma}|\, [\delta(\mathbf{r}_{12}-a\hat{\sigma})\, P_\sigma - \delta(\mathbf{r}_{12}+a\hat{\sigma})] \tag{3.26}$$

We may therefore conclude that $S_t(1,2)\, W(1,2)$ can be defined if we use the representation

$$S_t(1,2)\, W(1,2) = (\exp\{t[L_0(1,2)+\bar{T}_+(1,2)]\})\, W(1,2) \tag{3.27}$$

Here we have used the fact that the $\bar{T}_+$ operators can be shown to have the property

$$\bar{T}_+(1,2)\, S_\tau^0(1,2)\, \bar{T}_+(1,2) = 0 \qquad \text{for all} \quad \tau>0 \tag{3.28}$$

In a similar way we can define the operator $S_{-t}(1,2)\, W(1,2)$ by

$$S_{-t}(1,2)\, W(1,2) = (\exp\{-t[L_0-\bar{T}_-(1,2)]\})\, W(1,2) \tag{3.29}$$

with

$$\bar{T}_-(1,2) = a^{d-1} \int_{\mathbf{v}_{12}\cdot\hat{\sigma}>0} d\hat{\sigma}\, |\mathbf{v}_{12}\cdot\hat{\sigma}|\, [\delta(\mathbf{r}_{12} - a\hat{\sigma})\, P_\sigma - \delta(\mathbf{r}_{12} + a\hat{\sigma})] \quad (3.30)$$

This completes our discussion of the binary-collision operator representation of the time-displaced operators for a system of two hard spheres. In the next section we discuss the generalization to a system of N hard spheres, and make some general comments on the binary-collision expansion of the time-displacement operators for such systems.

4. CONCLUSION

In the previous section we derived expressions for the two-body time-dependent operators appropriate for use either to the left or to the right of the configurational distribution function $W(1,2)$. These results immediately suggest the generalization to N-particle displacement operators of the form

$$W(1,\ldots,N)\, S_{\pm t}(1,\ldots,N) = W(1,\ldots,N) \exp\left\{ \pm t \left[L_0(N) \pm \sum_{i<j} T_\pm(i,j) \right] \right\} \quad (4.1)$$

and

$$S_{\pm t}(1,\ldots,N)\, W(1,\ldots,N) = \exp\left\{ \pm t \left[L_0(N) \pm \sum_{i<j} \bar{T}_\pm(i,j) \right] W(1,\ldots,N) \right\} \quad (4.2)$$

where $T_\pm(i,j)$ are given by Eqs. (3.12) and (3.17), and $\bar{T}_\pm(i,j)$ by Eqs. (3.26) and (3.30), with (1, 2) replaced by (i,j). It is not at all obvious that expressions (4.1) and (4.2) correctly represent the dynamics of N hard spheres moving in infinite space. However, this result can be established by means of a rather direct, but lengthy argument, which we outline briefly here.[4]

Consider some arbitrary N-particle phase point Γ for which $W(\Gamma) = 1$, and some time interval t during which the particles collide in the sequence α_1 at t_1^*, α_2 at t_2^*, and so on. Here α_i represents a particular pair of particles. From the geometrical meaning of the T_+^r operator it follows that a proper representation of the time-displacement operator S_+ is given by

$$S_+ = S_+^0 * T_+^r(\alpha_1)\, S_+^0 * T_+^r(\alpha_2)\, S_+^0 \cdots * T_+^r(\alpha_n)\, S_+^0 \quad (4.3)$$

We need to prove that for this phase point, the representation of S_+ given by Eq. (4.1) reduces to (4.3). We proceed by an induction proof. First, we expand S_+ in (3.11) in powers of T_+ operators as

$$S_+ = S_+^0 + \sum_\alpha S_+^0 * T_+(\alpha)\, S_+^0 + \sum_\alpha \sum_\beta S_+^0 * T_+(\alpha)\, S_+^0 * T_+(\beta)\, S_+^0 \cdots \quad (4.4)$$

Now, for $t < t_1^*$ all but the first term on the right-hand side will vanish. Consider $t > t_1^*$ and rewrite Eq. (4.4) as

$$S_+ = R_+(\alpha_1) + S_+^0 * T_+(\alpha_1)\, R_+(\alpha_1) \tag{4.5}$$

$$R_+(\alpha_1) = S_+^0 + \sum_{\beta \neq \alpha_1} S_+^0 * T_+(\beta)\, S_+^0 + \sum_{\beta \neq \alpha_1} \sum_{\gamma} S_+^0 * T_+(\beta)\, S_+^0 * T_+(\gamma)\, S_+^0 \tag{4.6}$$

that is, $R_+(\alpha_1)$ consists of all of the terms in the binary collision expansion of S_+ except those for which the *first* binary collision operator involves the pair α_1. We now decompose $T_+(\alpha_1)$ in Eq. (4.5) into its real and virtual parts $T_+^{\mathrm{r}}(\alpha_1)$ and $T_+^{\mathrm{v}}(\alpha_1)$ to write

$$S_+ = R_+(\alpha_1) + S_+^0 * T_+^{\mathrm{r}}(\alpha_1)\, R_+(\alpha_1) + S_+^0 * T_+^{\mathrm{v}}(\alpha_1)\, R_+(\alpha_1) \tag{4.7}$$

As in the previous section, we can show that for $t > t_1^*$ the first and third terms on the right-hand side of Eq. (4.7) cancel each other and we obtain

$$S_+ = S_+^0 * T_+^{\mathrm{r}}(\alpha_1)\, R_+(\alpha_1), \qquad t > t_1^* \tag{4.8}$$

To complete the induction proof, we suppose $t > t_{n-1}^*$ and that Eq. (4.4) reduces to

$$S_+ = S_+^0 * T_+^{\mathrm{r}}(\alpha_1)\, S_+^0 * T_+^{\mathrm{r}}(\alpha_2)\, S_+^0 * \cdots T_+^{\mathrm{r}}(\alpha_{n-1})\, R_+(\alpha_{n-1}) \tag{4.9}$$

Then rewrite $R_+(\alpha_{n-1})$ or

$$\begin{aligned} R_+(\alpha_{n-1}) &= R_+(\alpha_n) - S_+^0\, T_+(\alpha_{n-1}) * R_+(\alpha_{n-1}) + S_+^0\, T_+(\alpha_n) * R_+(\alpha_n) \\ &= R_+(\alpha_n) + S_+^0\, T_+^{\mathrm{r}}(\alpha_n) * R_+(\alpha_n) + S_+^0\, T_+^{\mathrm{v}}(\alpha_n) * R_+(\alpha_n) \\ &\quad - S_+^0\, T_+(\alpha_{n-1}) * R_+(\alpha_{n-1}) \end{aligned} \tag{4.10}$$

Now for the phase point that we consider and for $t > t_n^*$, the first and third terms on the right-hand side of (4.10) will cancel when substituted in (4.9), the fourth term will vanish, while the second term will give exactly what is needed to establish Eq. (4.3). Therefore, expressions (4.1) and (4.2) represent the solution to the problem stated initially, to find a convenient representation of the dynamics of a system of hard spheres that can be used to explicitly compute quantities of interest for the statistical mechanics of irreversible processes.

We mention in conclusion that Eqs. (4.1) and (4.2) form very convenient starting points for the calculation of the transport properties of hard-sphere systems and they have been applied to a description of a broad

range of phenomena, ranging from a study of Stokes' law for a macroscopic sphere in a hard-sphere fluid,[5] to a study of the hard-sphere glass–fluid phase transition.[3] It is, of course, of considerable interest to find a similarly convenient representation of the time-displaced operator for systems that interact with continuous, central potentials, for systems that interact with noncentral forces, for molecular systems, and so on. It is not clear whether such representations exist in general, but various approximate expressions can be very useful in many instances. As a simple example, many results obtained for hard-sphere systems can be easily generalized to apply to systems of particles with short-ranged central forces in those cases where the duration of the binary collisions can be neglected, and where the gas is dilute enough so that triple and higher order collisions can also be neglected (see, e.g., ref. 6).

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