Binary Collision Expansion of the Classical N-Body Green's Function

JEROME WEINSTOCK
National Bureau of Standards, Washington, D. C.
(Received November 29, 1961)

The explicit time integrations in the formal binary collision expansion of the classical N-body Green's function are performed to obtain a product of binary collision operators which bears a strong resemblance to the Mayer product of f_{ij}'s. These integrations are exact for hard-sphere interactions and are expected to be a good approximation for finite but short-range pair interactions. The resulting expansion can be averaged over configuration space to obtain a transport equation for a dense gas in analogy with the cluster expansion of the classical partition function.

I

An expansion of the quantum partition function in terms of binary collision operators, which is applicable to systems of pair interacting particles, has been obtained by Lee and Yang.[1] Starting with the Bloch equation, Siegert and Teramoto[2] later obtained a simple and direct derivation of this "binary collision expansion." It is generally known that a similar binary collision expansion may be obtained for the classical Green's function solution of Liouville's equation. These expansions in binary collision operators are analogous to the expansion of the classical partition function in terms of Mayer f_{ij}'s.[3] They are suited to the study of systems with infinite repulsive interactions, such as hard spheres, since the terms of these expansions are bounded functions of the interaction strength. For such systems of infinite interactions, the binary collision expansion is preferable to expansions in powers of the interaction strength as proposed by Prigogine *et al.*[4] In the latter expansions one must perform complicated summations (summations of Born approximations) in order to remove the divergencies at infinite interaction strength. Indeed, if these summations were performed (and they have been done only in the limit of zero particle density), the result would be similar to the binary collision expansion. It would thus be simpler to start with the binary collision expansion in the first place.

Tempting as it is to apply the binary collision expansion to the Green's function solution of Liouville's equation, little has been forthcoming because the expansion is quite complicated. It involves time-convoluted products of binary propagators interspersed with interaction terms, and does not resemble the analogous Mayer f_{ij} expansion in any obvious way.

In this article we shall perform an exact time integration of the binary collision expansion of the classical Green's function for a system of hard spheres. The result [Eq. (26) or (27)] is an unconvoluted product of propagators which bears a strong resemblance to the Mayer product of f_{ij}'s. This time-integrated expansion can be averaged over all the initial coordinates of the system to obtain a transport equation to all orders in the density in the same way as was done by Brout[5] (to the lowest order in the density) for a similar but less rigorous expansion.

The time integrations of the binary collision expansion are based upon the fact that, for hard spheres, the interaction terms which appear in the integrand of the expansion are delta functions of the integration variables. The explicit dependence of these delta functions upon the integration variables is then determined after which the integrations are trivial. Although exact only for hard-sphere interactions, the integrations may be a good approximation for finite but short-range interactions.

II

We begin by writing Liouville's equation for the time dependence of any function f of the phase of a system of N particles with pair interactions:

$$i\partial f(t)/\partial t = -Lf(t). \tag{1}$$

This has the formal solution

$$f(t) = e^{itL}f(0) \equiv G(t)f(0), \tag{2}$$

in terms of the initial value of $f(t)$. The Liouville operator L is given by

$$L = -i\sum_{k<s} m^{-1}\mathbf{F}_{ks}(0)\cdot[\partial/\partial\mathbf{v}_k(0) - \partial/\partial\mathbf{v}_s(0)] - i\sum_k \mathbf{v}_k(0)\cdot\partial/\partial\mathbf{R}_k(0), \tag{3}$$

where $\mathbf{R}_k(0)$ and $\mathbf{v}_k(0)$ are the initial vector position and vector velocity, respectively, of the kth particle, $\mathbf{F}_{ks}(0)$ is the force between particles k and s, and the summation extends over all the particles of the system. In order to obtain the binary collision expansion of the classical propagator (Green's function) $G(t)$, we must define a free-particle propagator $G_0(t)$ and a

[1] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959).

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

[3] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940).

[4] I. Prigogine and R. Balescu, Physica **25**, 281, 302 (1959). This paper refers to related work.

[5] R. Brout, Physics **22**, 509 (1956).

binary collision propagator $G_\alpha(t)$:

$$G_0(t)\equiv e^{itL_0},\qquad G_\alpha(t)\equiv e^{it(L_0+L_\alpha)},\tag{4}$$

where

$$L_0=-i\sum_k \mathbf{v}_k(0)\cdot\partial/\partial\mathbf{R}_k(0),$$
$$L_\alpha\equiv L_{ks}=-im^{-1}\mathbf{F}_{ks}(0)\cdot[\partial/\partial\mathbf{v}_k(0)-\partial/\partial\mathbf{v}_s(0)],\tag{5}$$

and the single index α denotes the double index ks so that

$$\mathbf{R}_\alpha(0)\equiv\mathbf{R}_k(0)-\mathbf{R}_s(0),\quad \mathbf{v}_\alpha(0)\equiv\mathbf{v}_k(0)-\mathbf{v}_s(0).$$

With this notation, the binary collision expansion is given by[4]

$$G(t)=G_0(t)+\sum_{n=1}^{\infty}\sum_{\{\alpha\}}\int_0^t dt_1\int_0^{t_1}dt_2\cdots\int_0^{t_{n-1}}dt_n \times G_{\alpha_1}(t_n)iL_{\alpha_1}G_{\alpha_2}(t_{n-1}-t_n)iL_{\alpha_2}\cdots \times G_{\alpha_n}(t_1-t_2)iL_{\alpha_n}G_0(t-t_1),\tag{6}$$

where the sum extends over all values of $\alpha_1,\cdots,\alpha_n$ such that

$$\alpha_1\neq\alpha_2,\ \alpha_2\neq\alpha_3,\ \cdots,\ \alpha_{n-1}\neq\alpha_n;$$

i.e., such that no consecutive pair of α's are identical.

It is the above expression that will be integrated. In order to perform the implied integrations in (6) it will be necessary to understand some of the formal properties of the propagators $G_0(t)$ and $G_\alpha(t)$. The propagator $G_0(t)$ describes the time evolution of a system of free particles, and $G_\alpha(t)$ describes the time evolution of a system in which the interaction between the pair of particles α is turned on, and all the other particles are moving freely. Hence, if

$$f[\mathbf{R}_1(0),\mathbf{R}_2(0),\cdots;\mathbf{v}_1(0),\mathbf{v}_2(0),\cdots]$$

is any funtion of the initial phase point and if α denotes the pair ks, then

$$G_0(t)f=f[\mathbf{R}_1(0)+t\mathbf{v}_1(0),\cdots;\mathbf{v}_1(0),\cdots],$$
$$G_\alpha(t)=f[\mathbf{R}_1(0)+t\mathbf{v}_1(0),\cdots\mathbf{R}_k(1)+t\mathbf{v}_k(1),\cdots\mathbf{R}_s(1)+t\mathbf{v}_s(1),\cdots;\mathbf{v}_1(0),\cdots\mathbf{v}_k(1),\cdots\mathbf{v}_s(1),\cdots],\tag{7}$$

where $\mathbf{v}_k(1)$ and $\mathbf{v}_s(1)$ are the velocities of particles k and s after they have interacted with each other (we assume that all interactions are instantaneous as for hard spheres), and $[\mathbf{R}_k(1)+t\mathbf{v}_k(1)]$ and $[\mathbf{R}_s(1)+t\mathbf{v}_s(1)]$ are the positions of particles k and s at time t (assuming that a collision between k and s has taken place). Here $\mathbf{R}_s(1)$ is given by

$$\mathbf{R}_s(1)=\mathbf{R}_s(0)+t^*[\mathbf{v}_s(0)-\mathbf{v}_s(1)],\tag{8}$$

where t^* is the time at which the collision between k and s takes place. The time of collision t^* of two hard spheres of diameter a with initial relative position $\mathbf{R}_{ks}(0)$ and relative velocity $\mathbf{v}_{ks}(0)$ is given by the solution of

$$|\mathbf{R}_{ks}(0)+t^*\mathbf{v}_{ks}(0)|=a.\tag{9}$$

The position of particle s at the time t has been written in the form $[\mathbf{R}_s(1)+t\mathbf{v}_s(1)]$ because this form displays the explicit time dependence of the position of s and will be useful later on. The dependence will be generally as simple as shown only if the collisions are either complete or instantaneous. The time dependence will be complicated otherwise. If no collision takes place between k and s in the time t, then we simply have

$$\mathbf{R}_s(1)=\mathbf{R}_s(0),\quad \mathbf{R}_k(1)=\mathbf{R}_k(0),$$
$$\mathbf{v}_s(1)=\mathbf{v}_s(0),\quad \mathbf{v}_k(1)=\mathbf{v}_k(0),$$

so that

$$G_\alpha(t)f=G_0(t)f.$$

We have seen that the propagator $G_\alpha(t)$ prescribes the evolution of a system of particles from time zero to time t, with only the α interaction turned on. In general, the product of propagators

$$G_{\alpha_1}(t_1)G_{\alpha_2}(t_2-t_1)\cdots G_{\alpha_n}(t_n-t_{n-1}),\tag{10}$$

means that the system of particles evolves from time zero to time t_1 with only the α_1 interaction turned on, and then the system evolves from t_1 to t_2 with only the α_2 interaction turned on, etc. Consequently, if $f[\mathbf{R}_k(0);\mathbf{v}_k(0)]$ is any function of $\mathbf{R}_k(0)$ and $\mathbf{v}_k(0)$, then

$$\begin{aligned}G_{\alpha_1}(t_1)G_{\alpha_2}(t_2-t_1)\cdots G_{\alpha_n}(t_n-t_{n-1})f[\mathbf{R}_k(0);\mathbf{v}_k(0)]\\ =f[\mathbf{R}_k(0)+t_1{}^*\mathbf{v}_k(0)+(t_2{}^*-t_1{}^*)\mathbf{v}_k(1)+\cdots\\ +(t_n{}^*-t_{n-1}{}^*)\mathbf{v}_k(n-1)+(t_n-t_n{}^*)\mathbf{v}_k(n);\mathbf{v}_k(n)]\\ \equiv f[\mathbf{R}_k(n)+t_n\mathbf{v}_k(n);\mathbf{v}_k(n)],\end{aligned}\tag{11}$$

where $t_s{}^*$ is the time at which the pair α_s collide, given that the system evolves up to time t_1 with only the α_1 interaction turned on, and then evolves from t_1 to t_2 with only the α_2 interaction turned on, and so on up to time t_s. The quantity $\mathbf{v}_k(s)$ is the velocity of particle k after the collision of the pair α_s in the above sequence of consecutive collisions. If, in the above sequence, the pair α_s are not aimed to collide in the time interval t_s to t_{s-1} then, $\mathbf{v}_k(s)=\mathbf{v}_k(s-1)$ and the quantity $t_s{}^*$ disappears from (11). The quantities $t_s{}^*$ and $\mathbf{v}_k(s)$ are unique functions of the initial phase point and may be calculated in a straightforward manner by successive solutions of the two-body problem. Fortunately, it will be sufficient for our ends to understand these quantities in merely a formal way.

III

With the above understanding of the formal properties of the propagators, we are in a position to perform the integrations in (6). For convenience, we let

$$t_1=t_n,\ t_2=t_{n-1},\ \cdots,\ t_n=t_1,$$

and then change the order of integration in (6) to get

$$I_n(t)=\int_0^t dt_1\int_{t_1}^t dt_2\cdots\int_{t_{n-2}}^t dt_{n-1}\int_{t_{n-1}}^t dt_n \times G_{\alpha_1}(t_1)iL_{\alpha_1}G_{\alpha_2}(t_2-t_1)iL_{\alpha_2}\cdots \times G_{\alpha_{n-1}}(t_{n-1}-t_{n-2})iL_{\alpha_{n-1}}G_{\alpha_n}(t_n-t_{n-1})iL_{\alpha_n} \times G_0(t-t_n), \quad (12)$$

where $I_n(t)$ is the integral in (6). The integration over t_n is immediate, since, as a special case of (6),

$$\int_{t_{n-1}}^t dt_n\, G_{\alpha_n}(t_n-t_{n-1})iL_{\alpha_n}G_0(t-t_n) = G_{\alpha_n}(t-t_{n-1})-G_0(t-t_{n-1}), \quad (13)$$

and we thus have

$$I_n(t)=\int_0^t dt_1\cdots\int_{t_{n-2}}^t dt_{n-1} \times G_{\alpha_1}(t_1)iL_{\alpha_1}\cdots G_{\alpha_{n-1}}(t_{n-1}-t_{n-2})iL_{\alpha_{n-1}} \times[G_{\alpha_n}(t-t_{n-1})-G_0(t-t_{n-1})]. \quad (14)$$

The integration over t_{n-1} is more difficult but may be done exactly for a hard sphere interaction. In this case the force is a delta function and, hence, the positional dependence of $L_{\alpha_{n-1}}$ is given by

$$L_{\alpha_{n-1}}\propto\delta(|\mathbf{R}_{\alpha_{n-1}}|-a), \quad (15)$$

where a is the hard-sphere diameter, so that [see (11)] the integrand of $I_n(t)$ contains the delta function:

$$G_{\alpha_1}(t_1)G_{\alpha_2}(t_2-t_1)\cdots G_{\alpha_{n-1}}(t_{n-1}-t_{n-2})L_{\alpha_{n-1}} \propto\delta(|\mathbf{R}_{\alpha_{n-1}}(n-1)+t_{n-1}\mathbf{v}_{\alpha_{n-1}}(n-1)|-a). \quad (16)$$

Consequently, the integrand of $I_n(t)$ contains a delta function of t_{n-1} and this integrand will be nonzero for only that value of t_{n-1} which satisfies

$$|\mathbf{R}_{\alpha_{n-1}}(n-1)+t_{n-1}\mathbf{v}_{\alpha_{n-1}}(n-1)|-a=0, \quad (17)$$

so that

$$t_{n-1}=-[v_{\alpha_{n-1}}(n-1)]^{-1}\{\mathbf{R}_{\alpha_{n-1}}(n-1)\cdot\hat{v}_{\alpha_{n-1}}(n-1) -[a^2-(\mathbf{R}_{\alpha_{n-1}}(n-1)\times\hat{v}_{\alpha_{n-1}}(n-1))^2]^{\frac{1}{2}}\} \equiv t_{n-1}^*=-[v_{\alpha_{n-1}}(n-2)]^{-1}\{\mathbf{R}_{\alpha_{n-1}}(n-2) \times\hat{v}_{\alpha_{n-1}}(n-2)+[a^2-(\mathbf{R}_{\alpha_{n-1}}(n-2) \times\hat{v}_{\alpha_{n-1}}(n-2))^2]^{\frac{1}{2}}\}, \quad (18)$$

[the time at which pair α_{n-1} collide, see (11)], where $\hat{v}$ denotes the unit vector in the direction of $\mathbf{v}$.

Since there will be a contribution to the t_{n-1} integration only for $t_{n-1}=t_{n-1}^*$ we may replace any function of t_{n-1} which appears to the right of $L_{\alpha_{n-1}}$, in $I_n(t)$, by its value at t_{n-1}^* and then take this function of t_{n-1}^* out of the t_{n-1} integral. We then have, with the identity

$$G_0(t-t_{n-1})G_0(t_{n-1}-t)=1,$$

$$I_n(t)=\int_0^t dt_1\cdots\int_{t_{n-2}}^t dt_{n-1}\,G_{\alpha_1}(t_1)iL_{\alpha_1}\cdots \times G_{\alpha_{n-2}}(t_{n-2}-t_{n-3})iL_{\alpha_{n-2}}G_0(t-t_{n-2})G_0(t_{n-2}-t) \times G_{\alpha_{n-1}}(t_{n-1}-t_{n-2})iL_{\alpha_{n-1}}G_0(t-t_{n-1}) \times G_0(t_{n-1}-t)[G_{\alpha_n}(t-t_{n-1})-G_0(t-t_{n-1})]$$

$$=\int_0^t dt_1\cdots\int_{t_{n-2}}^t dt_{n-1}\,G_{\alpha_1}(t_1)iL_{\alpha_1}\cdots G_{\alpha_{n-2}}(t_{n-2}-t_{n-3})iL_{\alpha_{n-2}}G_0(t-t_{n-2}) \times\lim_{\tau_{n-1}\to -t^0{}_{n-1}} G_0(t_{n-2}-t) \times G_{\alpha_{n-1}}(t_{n-1}-t_{n-2})iL_{\alpha_{n-1}}G_0(t-t_{n-1}) \times G_0(-\tau_{n-1})[G_{\alpha_n}(\tau_{n-1})-G_0(\tau_{n-1})], \quad (19)$$

where

$$t^0{}_{n-1}=-[v_{\alpha_{n-1}}(0)]^{-1}\{\mathbf{R}_{\alpha_{n-1}}(0)\cdot\hat{v}_{\alpha_{n-1}}(0) +[a^2-(\mathbf{R}_{\alpha_{n-1}}(0)\times\hat{v}_{\alpha_{n-1}}(0))^2]^{\frac{1}{2}}\} \quad (20)$$

and we have used, for any function f,

$$G_{\alpha_1}(t_1)G_{\alpha_2}(t_2-t_1)\cdots G_{\alpha_{n-2}}(t_{n-2}-t_{n-3}) \times G_0(t-t_{n-2})f(-t^0{}_{n-1})=f(t-t_{n-1}^*). \quad (21)$$

The t_{n-1} integration in (19) is now similar to (13) and may be done immediately to obtain

$$I_n(t)=\int_0^t dt_1\cdots\int_{t_{n-3}}^t dt_{n-2}\,G_{\alpha_1}(t_1)iL_{\alpha_1}\cdots \times G_{\alpha_{n-2}}(t_{n-2}-t_{n-3})iL_{\alpha_{n-2}} \times G_0(t-t_{n-2})\lim_{\tau_{n-1}\to -t^0{}_{n-1}} G_0(t_{n-2}-t) \times[G_{\alpha_{n-1}}(t-t_{n-2})-G_0(t-t_{n-2})] \times G_0(-\tau_{n-1})[G_{\alpha_n}(\tau_{n-1})-G_0(\tau_{n-1})]. \quad (22)$$

(If the interaction in $L_{\alpha_{n-1}}$ were of finite duration, the t_{n-1} integrand would be nonzero for a finite range and $G_0(t_{n-1}-t)[G_{\alpha_n}(t-t_{n-1})-G_0(t-t_{n-1})]$ could not ordinarily be replaced by its value at t_{n-1}^*. However, the preceding term is a relatively slowly varying function of t_{n-1} so that for an interaction of finite but short duration about the time t_{n-1}^* it would still be a good approximation to replace

$$G_0(t_{n-1}-t)[G_{\alpha_n}(t-t_{n-1})-G_0(t-t_{n-1})]$$

by its value at t_{n-1}^* and then complete the t_{n-1} integration as above.)

We may perform the remaining integrations similarly by noting that for hard spheres the integrand of $I_n(t)$

contains the delta functions,

$$\delta(|\mathbf{R}_{\alpha_k}(k)+t_k\mathbf{v}_{\alpha_k}(k)|-a), \quad (1\leq k\leq n-1) \quad (23)$$

and, thus, there will be a nonzero contribution to the integration over t_k only for real and positive t_k given by

$$t_k=-\{\mathbf{R}_{\alpha_k}(k)\cdot\hat{v}_{\alpha_k}(k)-[a^2-(\mathbf{R}_{\alpha_k}(k)\times\hat{v}_{\alpha k}(k))^2]^{\frac{1}{2}}\}\times[v_{\alpha_k}(k)]^{-1} \quad (24)$$
$$\equiv t_k^*, \quad (1\leq k\leq n-1).$$

We then proceed in the same way as for the t_{n-1} integration to obtain

$$I_n(t)=G_0(t)\lim_{\tau_1\to -t^0_1}G_0(-t)[G_{\alpha_1}(t)-G_0(t)]\times\lim_{\tau_2\to -t^0_2}G_0(-\tau_1)[G_{\alpha_2}(\tau_1)-G_0(\tau_1)]\cdots\times G_0(-\tau_{n-1})[G_{\alpha_n}(\tau_{n-1})-G_0(\tau_{n-1})], \quad (25)$$

so that the binary collision expansion becomes

$$G(t)-G_0(t)=\sum_{n=1}^{\infty}\sum_{\{\alpha\}}G_0(t)\lim_{\tau_1\to -t^0_1}G_0(-t)[G_{\alpha_1}(t)-G_0(t)]\times\lim_{\tau_2\to -t^0_2}G_0(-\tau_1)[G_{\alpha_2}(\tau_1)-G_0(\tau_1)]\cdots\times G_0(-\tau_{n-1})[G_{\alpha_n}(\tau_{n-1})-G_0(\tau_{n-1})], \quad (26)$$

which is the desired result. Equation (26) is exact for hard spheres and is expected to be a good approximation for finite but short range interactions.

It is important to note that t_k^* will be real and positive and, hence, $I_n(t)$ will be nonzero for only those initial phase points which lead to a collision between the pair α_k. This is reflected in the integrated form, (26), of the expansion by the appearance of propagators in the combination

$$[G_{\alpha k}(\tau_{k-1})-G_0(\tau_{k-1})],$$

which, when operating on any function of the initial phase point, will be nonzero for only those phase points which lead to a collision between the pair α_k within the time τ_{k-1}.

In view of (21) we may interpret any term in (26) as follows: Reading from left to right the propagators in the first bracketed term "operate" from time zero to time t, i.e., the propagators displace phase points along their paths in phase space from time zero to time t, and this term will be zero unless the pair α_1 are aimed to collide within the time t. The next term prescribes a free motion backwards in time from time t to that time t_1^* at which the pair α_1 were aimed to collide. The propagators in the next bracketed term then operate from time t_1^* to t and will be zero unless the pair α_2 are aimed to collide, and so on. Since each term $[G_{\alpha_k}(\tau_{k-1})-G_0(\tau_{k-1})]$ will be zero unless the pair α_k are aimed to collide the initial relative coordinate of α_k must lie within a collision cylinder.[5] The term $I_n(t)$ will thus be nonzero for only those small regions (collision cylinders) in the space of $\mathbf{R}_{\alpha_1}(0), \cdots, \mathbf{R}_{\alpha_n}(0)$ which lead to a collision between α_1 followed by a collision between α_2 and so on.

The analogy between the terms of the integrated binary collision expansion (26) and the Mayer f_{ij}'s is now clear. The formal analogy is seen by noting that

$$G_0(-\tau)[G_\alpha(\tau)-G_0(\tau)]=e^{-i\tau L_0}e^{i\tau(L_0+L_\alpha)}-1,$$

so that if the interaction term L_α were to commute with the free-particle term L_0 (as the kinetic-energy term commutes with the interaction term in the classical-partition function), then we would have

$$G_0(-\tau)[G_\alpha(\tau)-G_0(\tau)]=e^{i\tau L_\alpha}-1.$$

This has the same form as the Mayer f_α. A more significant similarity between $G_0(-\tau)[G_\alpha(\tau)-G_0(\tau)]$ and the Mayer f_α is that both are nonzero for only a small region in $\mathbf{R}_\alpha$ space. The latter similarity should prove useful in performing the integration of (26) over coordinate space.

In view of the analogy with the Mayer f_{ij}'s it would be useful to define a new f_{ij} by

$$f_{\alpha k}\equiv\lim_{\tau_k\to t^0_k}G_0(-\tau_{k-1})[G_{\alpha_k}(\tau_{k-1})-G_0(\tau_{k-1})],$$

so that (26) may be written in the form

$$G(t)-G_0(t)=\sum_{n=1}^{\infty}\sum_{\{\alpha\}}G_0(t)f_{\alpha 1}f_{\alpha 2}f_{\alpha 3}\cdots f_{\alpha u}, \quad (27)$$

where

$$\tau_0\equiv t.$$

Equation (27) can be integrated over all coordinates to obtain a generalization of Brout's derivation of a master equation. The integration over coordinates introduces "cluster" integrals for multiplet collisions analogous to the cluster integrals of equilibrium theory. The cluster integrals can then be summed to obtain density expansions of transport equations analogous to the density expansion of the classical partition function. This work will be reserved for a future article.

ACKNOWLEDGMENT

The author wishes to thank Dr. M. S. Green, Dr. R. A. Piccirelli, and Dr. R. Zwanzig for many helpful discussions.