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Derivation of Kinetic Equations for Slow-Neutron Scattering*

J. M. J. VAN LEEUWEN†
Department of Chemistry, Cornell University, Ithaca, New York

AND

SIDNEY YIP
Department of Engineering Physics and Materials Science, Cornell University, Ithaca, New York

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It is shown that for moderately dense classical gases Van Hove's correlation functions $G(r,t)$ and $G_s(r,t)$ can be calculated from kinetic equations. The kinetic equations are derived from the cluster expansion of a one-particle distribution function which describes the propagation of a density-momentum impulse. For times short compared with the time between collisions, the density series can be used directly. But for longer times a different treatment is necessary because of the increasing importance of multiple collisions. Considering only the dominant terms, the series is shown to be the iterated solution of an integral equation. In lowest order, this equation has the form of a linearized Boltzmann equation in which the collision kernel is nonlocal because of the finite extent of the particles, and is non-Markoffian if the duration of a collision is finite. The present approach permits a systematic treatment of coherent as well as incoherent scattering. In particular, we demonstrate an earlier assertion that the appropriate equations for studying the two kinds of scattering are, respectively, the linearized Boltzmann equation and the neutron transport equation. The effects of statistical correlation are introduced approximately in the kinetic equations in lowest order.

I. INTRODUCTION

IN recent years a great deal of interest has been generated in the use of slow neutrons as microscopic probes of molecular dynamics in matter. While this technique has yielded much useful information on phonon frequency distributions and dispersion relations in solids,[1] progress in the study of liquids has been more limited and less well defined. In a well known work Van Hove[2] has shown that slow-neutron scattering is completely described by the double Fourier transform of the space-time functions $G(r,t)$ and $G_s(r,t)$. These functions are defined as the equilibrium ensemble average of products of appropriate time-dependent density operators. When treated quantum mechanically they are in general complex and therefore have no simple physical meanings. However, when treated classically, $G(r,t)$ is real and gives the probability of finding a particle at (r,t) given that initially a particle was at the origin; similarly, $G_s(r,t)$ gives the analogous probability in which both particles are the same. Because in this special context the functions are obviously time-displaced density correlation functions, the classical limit of Van Hove's formalism has been widely used in analyzing liquid data.[3–5] Aside from slow-neutron scattering, $G(r,t)$ or $G_s(r,t)$ is known to play a similarly fundamental role in other dynamical processes such as Rayleigh scattering of light,[6] broadening of Mössbauer lines,[7] and the scattering of conduction electrons by lattice oscillations.[8] It therefore appears that the behavior of these correlation functions are general dynamical properties of any interacting system.

It is generally recognized that the nonequilibrium linear response of a system is closely related to its time-dependent equilibrium correlation functions. This connection has been useful in obtaining exact formal expressions for transport coefficients,[9] but it is equally well suited for studying correlation phenomena in terms of relaxation processes.[10] In the case of $G(r,t)$, the corresponding dynamical process is that of propagating a density impulse produced by a microscopic disturbance. Just as in the kinetic theory of gases where a nonequilibrium process is characterized by the time scale involved, so it is appropriate here to characterize the system relaxation according to the magnitudes of the wavelength and frequency of the disturbance.

For very rapidly varying disturbances (wavelengths of the order of the range of molecular forces and frequencies greater than or comparable to the reciprocal of a collision duration) the relaxation is strongly dependent upon the initial conditions. In any description the

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† On leave from the Catholic University of Nijmegen, The Netherlands.

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[4] See for example, B. N. Brockhouse, Nuovo Cimento Suppl. **9**, 45 (1958); A. Rahman, K. S. Singwi, and A. Sjolander, Phys. Rev. **126**, 997 (1962).

[5] In this paper we restrict our attention only to classical systems. The use of classical $G(r,t)$ and $G_s(r,t)$ in analyzing neutron scattering has been discussed by R. Aamodt, K. M. Case, M. Rosenbaum, and P. F. Zweifel, Phys. Rev. **126**, 1165 (1962); see also M. Rosenbaum, dissertation, University of Michigan, 1963 (unpublished).

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collisions should be treated as frequency-dependent processes since such events are likely to be incomplete. On such a short time scale one can also consider a time expansion in which the expansion coefficients are just the frequency moments of the excitation spectrum (or equivalently in scattering terms the energy-transfer moments).[11] The first few moments have been used to show a narrowing of the spectrum at certain wavelengths,[12] an effect due to equilibrium spatial correlations.

At the opposite extreme of very slowly varying disturbances the response is completely described by the spatial relaxation of macroscopic variables. This is the familiar region where the system is effectively in local thermodynamic equilibrium, and it is only here that phenomenological equations[3,13] are known to be applicable. Since the hydrodynamical behavior of density-correlation functions are well known, measurements carried out in the long-wavelength region should be relatively simple to interpret.

In slow-neutron measurements typical wavelengths are of the order of 10^{-8} cm, so it appears that the space-time scales of interest are neither those characteristic of the initial regime nor those of the hydrodynamical regime. One is then concerned with the so-called kinetic regime, where wavelengths and frequencies are of the order of mean free paths and the reciprocal of mean free times. Thus in contrast to the analysis of Rayleigh scattering or the calculations of transport coefficients where the assumption of long wavelengths or zero frequency is valid, a more general study of the propagation of a microscopic density disturbance is required. From the general standpoint of irreversible processes in fluids, this problem is of interest since it provides a basis for studying the extension of existing molecular theories of transport.

Recently, it has been proposed that molecular descriptions of $G(r,t)$ and $G_s(r,t)$ can be formulated using single-particle kinetic equations.[14–16] The basic assumption was that the correlation functions can be expressed as momentum integrals of the appropriate one-particle distribution functions (or conditional probability densities). These descriptions have been applied only to dilute fluids; consequently, the results do not take into account of the effects of statistical correlation. In an earlier work, Vineyard[17] has derived kinetic equations for two-time molecular distributions, thus far the procedure has yielded only formal results. More recently a kinetic equation suitable for the study of $G_s(r,t)$ has been derived by Nossal.[18] This description is presumably more realistic at short times, but further clarification of the validity of this approach seems necessary.

The aim of this paper is to supply a theoretical basis for the earlier calculations[14,15] and to show in what directions the equations should be modified to take into account time-dependent collision effects and effects of statistical correlation. The present method uses a cluster expansion for the correlation functions similar to those used by Mazo and Zemach.[19] Such an expansion is restricted to times small compared to the mean free time. By considering only the dominant terms for large times, the expansion can be effectively extended to the whole time domain by a summation of the dominant terms. This technique is the same as that used in recent transport theory[20,21]; however, the equations in this case are more involved since one has to retain the information for short times as well. In the following description only binary collisions and pairwise statistical correlation are considered. The approach is therefore limited only by the density of the system.

In Sec. II the definition of $G(r,t)$ is generalized to a correlation function f in phase space to emphasize the symmetry in configuration and momentum coordinates. On the basis of dynamical and statistical considerations f is decomposed into two parts, one of which f_b vanishes if statistical effects are completely ignored. An Ursell series is developed for the more fundamental part f_a, and a convolution relation connecting f_a and f_b is derived in the approximation of only pairwise spatial correlations. In order to treat the divergent terms in the series at long times the concept of dominant terms is introduced in Sec. III. Graphical representation is discussed, and it is shown that the dominant terms correspond to a set of connected graphs with no cycles known as Cayley trees. The formal derivation of a kinetic equation for f_a in the Cayley tree approximation is carried out in Sec. IV. The validity of this equation for both short and long times is discussed. The derivation establishes unambiguously the relationship between the density-correlation functions and the various kinetic equations, and also clarifies the basic difference in the calculation of $G(r,t)$ and $G_s(r,t)$. Finally in Sec. VI some concluding remarks are given.

II. PROPAGATION OF A DENSITY-MOMENTUM IMPULSE

We consider a one-component system of N monatomic particles which is characterized by the Hamiltonian function

$$H(x^N)=\sum_{i=1}^{N}\frac{p_i^2}{2m}+\sum_{i<j}\Phi(q_{ij}), \tag{2.1}$$

where $x^N=(x_1\cdots x_N)$ is a vector in Γ space specifying

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the phase coordinates of the N particles, $x_i=(\mathbf{q}_i,\mathbf{p}_i)$ is a vector in μ space specifying the position $\mathbf{q}_i$ and momentum $\mathbf{p}_i$ of the ith particle, m is the particle mass, and Φ is the pair potential which depends only on the relative displacement $q_{ij}=|\mathbf{q}_i-\mathbf{q}_j|$. For simplicity we consider no external potentials, in particular, the wall potential will have no effect since ultimately we take N and V, the volume of the system, to be infinite. Once the system is specified at some initial time, its trajectory in Γ space is formally determined by applying Koopman's time displacement operator $\exp(tL_N)$. The Liouville operator L_N is given by

$$L_N=L(1\cdots N)=\sum_{i=1}^{N}\left(\frac{\partial H}{\partial \mathbf{p}_i}\cdot\frac{\partial}{\partial \mathbf{q}_i}-\frac{\partial H}{\partial \mathbf{q}_i}\cdot\frac{\partial}{\partial \mathbf{p}_i}\right)$$
$$=L^0(1\cdots N)+\sum_{i<j}L'(ij)\,,\qquad(2.2)$$

with

$$L^0(1\cdots N)=\sum_{i=1}^{N}L^0(i)=\sum_{i}^{N}\frac{\mathbf{p}_i}{m}\cdot\frac{\partial}{\partial \mathbf{q}_i}\,,\qquad(2.3)$$

$$L'(ij)=\left(\frac{\partial}{\partial \mathbf{p}_j}-\frac{\partial}{\partial \mathbf{p}_i}\right)\cdot\frac{\partial}{\partial \mathbf{q}_i}\Phi(q_{ij})\,.\qquad(2.4)$$

Thus if $f(x^N)$ is any function of the phase coordinates of the system, at a time t later it will have the value

$$f(x^N(t))=\exp(tL)f(x^N)\,.\qquad(2.5)$$

The time-dependent density correlation function is defined by

$$G(r,t)=n^{-1}\langle\sum_{i,j=1}^{N}\delta(\mathbf{q}_i-\mathbf{q})\delta(\mathbf{q}_j(t)-\mathbf{q}')\rangle\,,\qquad(2.6)$$

where n is the density, $\langle\ \rangle$ denotes an ensemble average over an N-particle equilibrium distribution (assumed henceforth to be the canonical distribution), and the system is assumed to be homogeneous and isotropic so that G depends only the relative separation $r=|\mathbf{q}-\mathbf{q}'|$. Since we will be concerned with the evolution of the system in phase space, there is no need to restrict our attention to an impulse only in configuration space. We can therefore consider the more general correlation function

$$f(xx';t)=n^{-1}\langle\sum_{i,j=1}^{N}\delta(x_i-x)\delta(x_j(t)-x')\rangle\,.\qquad(2.7)$$

It is obvious that $f(xx';t)$ describes the propagation of a density-momentum impulse from x to x' during time t. Once it is determined, $G(r,t)$ follows immediately upon integrations,

$$G(r,t)=\int d^3p\,d^3p'f(xx';t)\,.\qquad(2.8)$$

One also has the momentum correlation function,

$$\Phi(\mathbf{p}\mathbf{p}';t)=\langle\sum_{i,j=1}^{N}\delta(\mathbf{p}_i-\mathbf{p})\delta(\mathbf{p}_j(t)-\mathbf{p}')\rangle$$
$$=n\int d^3q\,d^3q'f(xx';t)\,.\qquad(2.9)$$

The normalization valid for all times is

$$\int dx'f(xx';t)=V\langle\sum_{i=1}^{N}\delta(x_i-x)\rangle=N\phi(p)\,,\qquad(2.10)$$

where

$$\phi(p)=(\beta/2\pi m)^{3/2}\exp(-\beta p^2/2m)\,,\qquad(2.11)$$

and $\beta=(k_BT_0)^{-1}$, with k_B the Boltzmann constant and T_0 the equilibrium temperature.

Similarly, corresponding to the self-correlation function

$$G_s(r,t)=n^{-1}\langle\sum_{i=1}^{N}\delta(\mathbf{q}_i-\mathbf{q})\delta(\mathbf{q}_i(t)-\mathbf{q}')\rangle\,,\qquad(2.12)$$

we can define

$$f_s(xx';t)=n^{-1}\langle\sum_{i=1}^{N}\delta(x_i-x)\delta(x_i(t)-x')\rangle\,,\qquad(2.13)$$

$$\Phi_s(\mathbf{p}\mathbf{p}';t)=\langle\sum_{i=1}^{N}\delta(\mathbf{p}_i-\mathbf{p})\delta(\mathbf{p}_i(t)-\mathbf{p}')\rangle\,,\qquad(2.14)$$

with normalization

$$\int dx'f_s(xx';t)=\phi(p)\,.\qquad(2.15)$$

In order to obtain density expansions for f and f_s we make use of the Ursell expansion of Koopman's time-displacement operator,

$$\exp[tL(1\cdots N)]$$
$$=U_t(j)\exp[tL(1\cdots j-1,\,j+1\cdots N)]+\sum_{j'}{}'\,U_t(jj')$$
$$\times\exp[tL(1\cdots j-1,\,j+1\cdots j'-1,\,j'+1\cdots N)]$$
$$+\cdots,\qquad(2.16)$$

with

$$U_t(1)=e^{tL(1)}=e^{tL^0(1)}\,,\qquad(2.17)$$

$$U_t(12)=e^{tL(12)}-e^{tL^0(12)}\,,\qquad(2.18)$$

$$U_t(123)=e^{tL(123)}-e^{t[L(12)+L^0(3)]}-e^{t[L(13)+L^0(2)]}$$
$$-e^{t[L(23)+L^0(1)]}+2e^{tL^0(123)}\,.\qquad(2.19)$$

The prime over the summation sign indicates that the summation indices must not equal j and that they must not equal to each other. Thus in (2.7) one can write

$$\delta(x_j(t)-x')=\Big[U_t(j)+\sum_{j'}{}' U_t(jj')+\tfrac{1}{2}\sum_{j'j''}{}' U_t(jj'j'')+\cdots\Big]\delta(x_j-x') \qquad (2.20)$$

and obtain

$$f(xx';t)=V\Big\langle\sum_{i,j=1}^{N}\delta(x_i-x)\Big[U_t(j)+\sum_{m=1}^{\infty}\frac{1}{m!}\times\sum_{\{j_m\}}{}' U_t(jj_1\cdots j_m)\Big]\delta(x_j-x')\Big\rangle . \qquad (2.21)$$

The factor $m!$ is inserted to avoid double counting. The first term in the square bracket corresponds to a development in the specified time interval t with particle j streaming freely. Each term in the m sum describes the phase-space trajectory of particle j resulting from dynamical interactions with only those particles in the set $\{j_m\}=(j_1\cdots j_m)$. In other words, the particles j, j_1, $\cdots$, j_m form a dynamically independent cluster so that their trajectories are entirely determined by their mutual interactions. If we speak of particles as being dynamically correlated if they appear in the argument of the U_t operator, then clearly unless i is equal to j or is contained in $\{j_m\}$ there is no way for the particle at x to be dynamically correlated with the particle at x' at a time t later. This observation suggests a decomposition of $f(xx';t)$ in the form of

$$f(xx';t)=f_a(xx';t)+f_b(xx';t), \qquad (2.22)$$

with

$$f_a(xx';t)=V\sum_{m=0}^{\infty}\int dx^N\phi_1\cdots\phi_N\frac{e^{-\beta U(q^N)}}{Q_N}\times\Big[\delta(x_j-x)+\sum_{i=1}^{m}\delta(x_{j_i}-x)\Big]\times\frac{1}{m!}\sum_{\{j_m\}}{}' U_t(jj_1\cdots j_m)\delta(x_j-x'), \qquad (2.23)$$

$$Q_N=\int dq^N\exp[-\beta U(q^N)],$$

$$U(q^N)=\sum_{i<j}\Phi(q_{ij}).$$

Since (2.23) is symmetric in the indices j, j_1, $\cdots$, j_m we can label particle j as particle 1, particle j_1 as particle 2, $\cdots$, particle j_m as particle $m+1$. Moreover, since there are $(N-1)$ ways of choosing j_1, $\cdots$, $(N-m)$ ways of choosing j_m, the sum over $\{j_m\}$ produces merely a factor of $(N-1)(N-2)\cdots(N-m)$. The integrations over the phases of particles $m+2$, $\cdots$, N can be carried out and one finds

$$f_a(xx';t)=n^{-1}\sum_{m=1}^{\infty}\frac{1}{m!}\int dx^m n(1\cdots m)\times\sum_{i=1}^{m}\delta(x_i-x)U_t(1\cdots m)\sum_{j=1}^{m}\delta(x_j-x'), \qquad (2.24)$$

where

$$n(1\cdots m)=\phi_i\cdots\phi_m n^m g(\mathbf{q}_i\cdots\mathbf{q}_m) \qquad (2.25a)$$

and

$$n^m g(\mathbf{q}_i\cdots\mathbf{q}_m)=\frac{N(N-1)\cdots(N-m+1)}{Q_N}\times\int d^3q_{m+1}\cdots d^3q_N\exp[-\beta U(q^N)] \qquad (2.25b)$$

is the usual m-particle density function in the equilibrium theory of distribution functions. Equation (2.24) shows that in f_a the particles at x and $x'(t)$ are not only dynamically correlated but also statistically correlated through the distribution function $g(\mathbf{q}_1\cdots\mathbf{q}_m)$.

The second term in (2.22) represents the contributions in which the particles at x and $x'(t)$ are not correlated by dynamical interactions. This term consists of all the terms in (2.21) for which index i is not among j, j_1, $\cdots$, j_m. In a similar way it can be written as

$$f_b(xx';t)=n^{-1}\sum_{m=1}^{\infty}\frac{1}{m!}\int dx^{m+1}\delta(x_{m+1}-x)n(1\cdots m+1)\times U_t(1\cdots m)\sum_{j=1}^{m}\delta(x_j-x'). \qquad (2.26)$$

Because x and x' are dynamically independent the dependence on $\mathbf{p}$ is always Maxwellian. To give a more explicit interpretation of f_b let us take

$$f_b(xx';t)=\phi(p)\bar{f}_b(qx';t), \qquad (2.27)$$

and after a few manipulations one has

$$f_b(qx';t)=Zn^{-1}\Big\langle\exp\Big[-\beta\sum_{i=1}^{N}\Phi(|\mathbf{q}-\mathbf{q}_i|)\Big]\times\sum_{j=1}^{N}\delta(x_j(t)-x')\Big\rangle. \qquad (2.28)$$

Here $Z=(N+1)Q_N/Q_{N+1}$ is the activity. Equation (2.28) can be verified by making a density expansion and comparing with (2.26). According to (2.28) the system is initially in equilibrium with an extraneous particle fixed at $\mathbf{q}$, and that upon the removal of this particle at $t=0$ the system develops in time with the expected number of particles at x' at time t being given by $\bar{f}_b$. At $t=0$,

$$\bar{f}_b(qx';0)=n\phi(p')g(\mathbf{q}\mathbf{q}'). \qquad (2.29)$$

On the other hand, from (2.21)

$$f_a(xx';0)+f_b(xx';0)=\phi(p)\delta(x-x')+n\phi(p)\phi(p')g(\mathbf{q}\mathbf{q}'). \qquad (2.30)$$

Therefore one has the relationship

$$f_b(qx';0)=n\int dx''g(\mathbf{q}\mathbf{q}'')f_a(x''x';0). \qquad (2.31)$$

We now give an argument that (2.31) is approximately valid for all times. Going back to (2.26) we write

$$n(1\cdots m+1) = n(1\cdots m)\phi_{m+1}\Big[n + n\sum_{i=1}^{m} G(\mathbf{q}_{m+1}-\mathbf{q}_i)+\cdots\Big], \qquad (2.32)$$

where $G(\mathbf{q}-\mathbf{q}')$ is the equilibrium pair-correlation function. By keeping only the terms shown in (2.32) we are considering the case in which the particle $m+1$ is either not correlated at all with the complex of particles $(1\cdots m)$ or correlated in the weakest possible way, i.e., via two-particle correlation only. Inserting this into (2.26) leads to

$$\begin{aligned} f_b(qx';t) &\simeq \sum_{m=1}^{\infty}\frac{1}{m!}\int dx^m n(1\cdots m)U_t(1\cdots m)\sum_{j=1}^{m}\delta(x_j-x') \\ &\quad + \int d^3q'' G(\mathbf{q}-\mathbf{q}'')\sum_{m=1}^{\infty}\frac{1}{m!}\int dx^m n(1\cdots m) \\ &\qquad \times \sum_{i,\,j=1}^{m}\delta(\mathbf{q}_i-\mathbf{q}'')U_t(1\cdots m)\delta(x_j-x') \\ &= \langle\sum_{j=1}^{N}\delta(x_j(t)-x')\rangle + n\int dx'' G(\mathbf{q}-\mathbf{q}'')f_a(x''x';t) \end{aligned}$$

or

$$f_b(qx';t) - n\phi(p') = n\int dx'' G(\mathbf{q}-\mathbf{q}'')f_a(x''x';t)\,. \qquad (2.33)$$

Since

$$g(\mathbf{q}\mathbf{q}') = 1 + G(\mathbf{q}-\mathbf{q}')\,, \qquad (2.34)$$

(2.33) is just the extension of (2.31) to all times. The terms ignored in (2.32) describe higher order statistical correlations. We shall see below that at long times these effects will be relatively unimportant compared to the terms already retained.

III. ASYMPTOTIC TEMPORAL BEHAVIOR OF THE URSELL SERIES

The function $f(xx';t)$ was introduced in the preceding section to describe the correlation of particles (or the same particle) at two time-displaced phase points. By expressing the ensemble average as an Ursell series the many-body calculation is formally transformed to a consideration of dynamical and statistical correlations in clusters of particles of definite size. The number of particles in a cluster depends on the number of particles involved in the dynamical operator $U_t(1\cdots m)$. If the particle initially localized also belongs to this cluster then $f(xx';t)$ is given by (2.24). Otherwise a different function, $f_b(xx';t)$, given by (2.28) must also be considered. On the basis of this approach a number of correlation functions can be calculated, in particular the Van Hove density correlation function $G(r,t)$ is just given by the double momentum integral of $f(xx';t)$. In this section we shall investigate the asymptotic temporal behavior of the Ursell series. Because each term in the series represents all possible interactions among the fixed number of particles, a large number of collision sequences will have to be examined. These collision sequences will be analyzed by the so called binary expansion method. Although this is a formal technique applicable, in principle, to all situations, it becomes particularly effective when the duration of a collision is small compared to the time between two successive events.

We shall be primarily concerned with a discussion of the Ursell series for $f_a(xx';t)$. When only pairwise statistical effects are considered this function is the fundamental quantity in the present description, and a knowledge of it is sufficient to determine $G(r,t)$. Writing out the first two terms in (2.24) more explicitly we have

$$\begin{aligned} f_a(xx';t) &= \int dx_1\delta(x_1-x)\phi(p_1)\exp[tL^0(1)]\delta(x_1-x') \\ &\quad + \frac{n}{2!}\int dx_1dx_2\phi(p_1)\phi(p_2)g(\mathbf{q}_1\mathbf{q}_2) \\ &\quad \times[\delta(x_1-x)+\delta(x_2-x)]U_t(12) \\ &\qquad \times[\delta(x_1-x')+\delta(x_2-x')]+\cdots. \end{aligned} \qquad (3.1)$$

The zeroth-order term in this expression is independent of the density, and is just the free-particle contribution

$$f_a{}^0(xx';t) = \phi(p)\delta(\mathbf{p}-\mathbf{p}')\delta(\mathbf{q}-\mathbf{q}'-\mathbf{v}t)\,, \qquad (3.2)$$

with $\mathbf{v}=\mathbf{p}/m$. The first-order terms, proportional to n, have implicit density dependence in $g(\mathbf{q}_1\mathbf{q}_2)$. They represent the contribution due to all possible collision sequences involving two particles, and to the lowest order in the density they are linear in the density. Similarly, the jth-order terms account for the dynamical and statistical effects of a $(j+1)$-particle cluster, and to the lowest order in n they are proportional to n^j.

The operator $U_t(12)$ given in (2.18) is the difference of two propagators with and without dynamical interaction. The asymptotic time dependence of this operator at long times is perhaps best described in terms of the relative spatial configurations of particles 1 and 2 which will lead to a 12 collision. Since $U_t(12)$ vanishes unless the particles collide during time interval t, the relevant configurations must either lie within the interaction sphere or in a collision cylinder with length $|\mathbf{v}_1-\mathbf{v}_2|t$. The interaction sphere contains all the configurations in which the particles collide at $t=0$, and the cylinder contains all those which lead to a collision within time t. The important point is that the volume of these configurations increases linearly with t; hence the first-order terms in (3.1) will vary asymptotically like t at long times. This conclusion tacitly assumes that the range of the pair potential $\Phi(q_{12})$ is finite, a requirement consistent with the assumption of the existence of a mean free time. The asymptotic behavior of the higher order terms are more difficult to visualize in the same way, but qualitative arguments show that among the jth-order terms the most singular contribution varies asymptotically as t^j.[22]

Since the Ursell series diverges asymptotically like a power series in t, it is clear that any description of the correlation functions derived from a truncated series will not be suitable at long times. As already emphasized by Zwanzig this property implies that a straightforward density expansion in the calculation of transport coefficients does not exist.[20] Stated simply it means that the dominant effects at long times are those due to multiple collisions, and that to derive an acceptable description valid for all times the Ursell series must be appropriately summed to all orders. On the other hand, one can expect a truncated series to be useful for those times during which the particles either have not collided at all or have collided only a few times. Simple dimensional consideration suggests that this should be the case whenever t is smaller than the mean free time.

In order to deal with the higher order terms in the Ursell series we introduce the concept of dominant terms. We have already remarked that the most singular contribution from the jth-order terms behave at long times like t^j. In the Laplace transform

$$f_a{}^j(xx';z)=\int_0^\infty dte^{-zt}f_a{}^j(xx';t)\,, \tag{3.3}$$

there will appear singularities of the type $1/z^{j+1}$ for small z and one can then expect a Maclaurin series in z for $f_a{}^j(xx';z)$ to start with the power $1/z^{j+1}$. The dominant terms in (2.24) are just these leading terms from each Maclaurin series. To the lowest order in the density, these terms are therefore characterized by a dependence of the type $(n/z)^j z^{-1}$.

To illustrate more explicitly how the set of dominant terms arises from the Ursell series we consider further expansions of the operators $U_t(1\cdots j)$ and the statistical factors $n(1\cdots j)$. Using the Lee and Yang's binary collision expansion, we have[23]

$$U_t(1\cdots j)=\sum\int_{t>t_1>\cdots>t_n>0} dt_1\cdots dt_n$$
$$\times\prod \exp[(t_h-t_i)L^0(k)]B_{t_r-t_s}(mn)\,, \tag{3.4}$$

where the sum runs over all connected j graphs and the product runs over all elements of the graph under consideration. A j graph consists of j vertical (particle) lines which represent the streaming operators $\exp[(t_h-t_i)L^0(k)]$, and which are connected to each other by collision blocks (crossed squares in Fig. 1) representing the binary kernels $B_t(mn)$. The latter are defined by

$$B_t(mn)=e^{tL(mn)}L'(mn)\,. \tag{3.5}$$

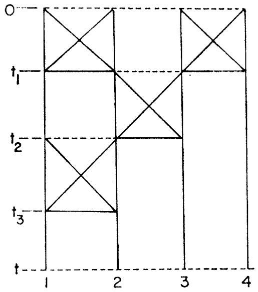

FIG. 1. A typical 4-graph with 4 collision blocks.

A typical graph for $j=4$ is shown in Fig. 1. This graph has three intermediate time levels, t_1, t_2, t_3. To each block corresponds a factor $B_{t_r-t_s}(mn)$ in the product, where m and n are the connected particle lines and t_r and $t_s\,(n\geqslant r>s>0)$ are the time levels which define the extent of the block. To each segment of the particle line k corresponds a factor $\exp[(t_h-t_i)L^0(k)]$, where again t_h and $t_i\,(n\geqslant h>i>0)$ are the levels which define the extent of the segment. The contribution of the particular graph shown can now be written down by inspection,

$$n^3\int_{t>t_3>t_2>t_1>0} dt_1dt_2dt_3dx_1\cdots dx_4\phi(p_1)\cdots\phi(p_4)$$
$$\times B_{t_1}(12)B_{t_1}(34)e^{(t_2-t_1)L^0(1)}e^{(t-t_1)L^0(4)}$$
$$\times B_{t_3-t_2}(12)e^{(t-t_3)[L^0(1)+L^0(2)]}e^{(t-t_2)L^0(3)}\,. \tag{3.6}$$

As indicated in the figure the blocks may not overlap on any particle line, nor can two consecutive blocks occur between the same pair of lines. Also there must be at least one block extending to the top time level 0, and there must be no block extending to the bottom level t.

In the j-particle function $n(1\cdots j)$ an Ursell type of expansion is made for $g(\mathbf{q}_1\cdots\mathbf{q}_j)$

$$g(\mathbf{q}_1\cdots\mathbf{q}_j)$$
$$=G(\mathbf{q}_1)g(\mathbf{q}_2\cdots\mathbf{q}_j)+\sum_{s=2}^{j}G(\mathbf{q}_1-\mathbf{q}_s)$$
$$\times g(\mathbf{q}_2\cdots\mathbf{q}_{s-1}\mathbf{q}_{s+1}\cdots\mathbf{q}_j)+\cdots+G(\mathbf{q}_1\cdots\mathbf{q}_j)\,, \tag{3.7}$$

where the correlation functions $G(\mathbf{q}_1\cdots\mathbf{q}_j)$ are defined recursivley as

$$\begin{gathered}G(\mathbf{q})=g(\mathbf{q})=1\,,\\ G(\mathbf{q}-\mathbf{q}')=g(\mathbf{q}\mathbf{q}')-g(\mathbf{q})g(\mathbf{q}')\,,\ \text{etc.}\end{gathered} \tag{3.8}$$

The functions $G(\mathbf{q}_1\cdots\mathbf{q}_j)$ are still implicit functions of the density but have a nonvanishing zero-density limit. They can be included in the graphical representation by adding bonds (represented by horizontal lines ending

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[22] M. S. Green, J. Chem. Phys. **25**, 836 (1956).

[23] T. D. Lee and C. N. Yang, Phys. Rev. **113**, 1165 (1959); A. J. F. Siegert and E. Teramoto, *ibid.* **110**, 1232 (1958).

with dots) between the particle lines $1\cdots j$ at the top of each graph. Combining the two expansions (3.4) and (3.7) we obtain a graphical representation of the Ursell series for $f_a(xx';t)$. A typical graph in this representation is shown in Fig. 2(a). A cross is drawn along the time levels 0 and t to denote a specific $\delta(x_i-x)$ and $\delta(x_j-x')$ have been chosen out of the i and j sums in (2.24). The full contribution of this graph reads

$$\frac{n^3}{4!}\int_{t>t_3>t_2>t_1>0} dt_1dt_2dt_3dx_1\cdots dx_4\phi(p_1)\cdots\phi(p_4)$$
$$\times\delta(x_2-x)G(\mathbf{q}_2\mathbf{q}_4)G(\mathbf{q}_1\mathbf{q}_2\mathbf{q}_3)B_{t_1}(12)e^{t_2L^0(3)}$$
$$\times e^{t_1L^0(4)}e^{(t-t_1)L^0(1)}B_{t_2-t_1}(24)B_{t_3-t_2}(23)$$
$$\times e^{(t-t_2)L^0(4)}e^{(t-t_3)[L^0(2)+L^0(3)]}\delta(x_3-x')\,. \quad (3.9)$$

Notice that for an s-particle cluster the factor $1/s!$ can be omitted by considering only one member of the family of $s!$ equivalent graphs obtained from each other by permuting the particle lines.

It is possible to reduce the number of graphs which have to be treated. We first define an isolated section in a graph as a group of at least two lines which are connected *only* to each other by collision blocks or statistical bonds. Then we have the following theorem.

Theorem 1: A graph has zero contribution if it can be separated by a horizontal cut such that the lower portion has an isolated section which does not contain the factor $\delta(x_j-x')$.

Proof: One has only to observe that when $B_t(ij)$ acts on a function independent of x_i or x_j the result is zero. (Notice that as far as Theorem 1 is concerned the isolated section must contain at least one block.)

Applying similar arguments we can therefore ignore those segments of particle lines at the bottom of a graph which do not lead to the factor $\delta(x_j-x')$. In particular, the graph in Fig. 2(a) is equivalent to that shown in Fig. 2(b) which corresponds to setting the factors $\exp[(t-t_1)L^0(1)]$, $\exp[(t-t_2)L^0(4)]$, $\exp[(t-t_3)L^0(2)]$ in (3.9) equal to unity. A theorem can now be proved which will enable us to reduce the number of graphs which ultimately are to be summed. This theorem concerns those graphs which can be separated by a horizontal cut such that the upper portion has an isolated section not containing the factor $\delta(x_i-x)$. Let $\{C_n\}$ be the set of graphs in which the aforementioned isolated section contains n-particle lines common to the remaining part. Let $R(C_n)$ be the contribution of all graphs which belong to $\{C_n\}$ and which all have the same remainder.

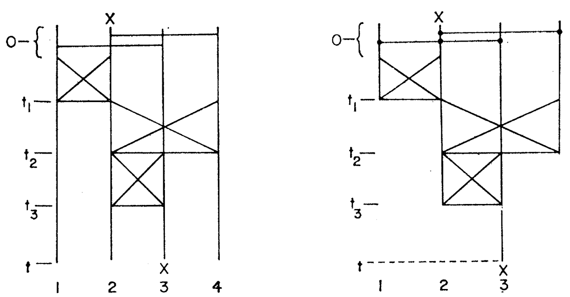

FIG. 2. Typical 4-graphs with 3 collision blocks and 2 statistical bonds. Particle 2 is localized at $t=0$ and particle 3 localized at time t. Comparison of (a) and (b) shows that except for particle 3 the streaming of all other particles after their last interaction is irrelevant in the description.

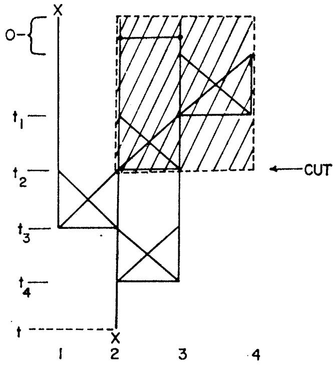

FIG. 3. A 4-graph in which the isolated section (shaded portion) has particle lines 2 and 3 in common with the remainder.

Theorem 2: The contribution $R(C_n)$ is given by the contribution of the remainder with an additional factor of $n^mg(\mathbf{q}_{i_1}\cdots\mathbf{q}_{i_m})$ in the spatial integrals, where $i_1, i_2, \cdots, i_m$ are the particle lines in common with the isolated section.

Proof: We illustrate the general proof by considering a typical graph shown in Fig. 3, where the isolated section is indicated by the shaded portion. In this case the common particle lines are labeled 2 and 3. The total effect of all possible isolated sections which contain 2 and 3 as common particle lines is given by an operator $S(x_2,x_3;t_2)$, where

$$S(x_1,x_2;t)=\lim_{N\to\infty}\frac{N(N-1)}{Q_N}\int dx_3\cdots dx_N\phi(p_3)\cdots$$
$$\times\phi(p_N)\exp[-\beta H(x^N)]\exp[tL_N]\,. \quad (3.10)$$

Thus the contribution $R(C_2)$ is

$$R(C_2)=\int_0^t dt_2\int dx_2dx_3\phi(p_2)\phi(p_3)$$
$$\times S(x_2,x_3;t)R(x_2,x_3;t,t_2)\,, \quad (3.11)$$

where $R(x_2,x_3;t,t_2)$ represents the effect of the remainder,

$$n\int_{t>t_4>t_3>t_2} dt_3dt_4\delta(x-x_1)e^{t_2L^0(1)}B_{t_3-t_2}(12)$$
$$\times e^{(t_3-t_2)L^0(3)}B_{t_4-t_3}(23)e^{(t-t_4)L^0(2)}\delta(x_2-x')\,. \quad (3.12)$$

Now inserting (3.10) into (3.11) gives

$$R(C_2)=\lim_{N\to\infty}N(N-1)\int_0^t dt_2\langle R(x_2(t_2),x_3(t_2);t,t_2)\rangle\,. \quad (3.13)$$

Since the ensemble average is independent of the time variation of the phase points, one has

$$R(C_2)=\int_0^t dt_2\int dx_2dx_3n(23)R(x_2,x_3;t,t_2)\,, \quad (3.14)$$

which proves the theorem. We can graphically represent $R(C_2)$ by the sum of two graphs shown in Figs. 4(a) and 4(b). These graphs correspond to

$$n^3\int_{t>t_4>t_3>t_2>0} dt_2dt_3dt_4dx_1dx_2dx_3\phi(p_1)\phi(p_2)\phi(p_3)$$
$$\times\delta(x_1-x)e^{t_2L^0(1)}B_{t_3-t_2}(12)B_{t_4-t_3}(23)$$
$$\times e^{(t-t_4)L^0(2)}\delta(x_2-x')\,, \quad (3.15)$$

and

$$n^3\int dt_2dt_3dt_4dx_1dx_2dx_3\phi(p_1)\phi(p_2)\phi(p_3)$$
$$\times\delta(x_1-x)G(\mathbf{q}_2\mathbf{q}_3)e^{t_2L^0(1)}e^{(t_3-t_2)L^0(3)}$$
$$\times B_{t_3-t_2}(12)B_{t_4-t_3}(23)e^{(t-t_4)L^0(2)}\delta(x_2-x')\,, \quad (3.16)$$

respectively. We observe that the factor

$$\exp[(t_3-t_2)L^0(3)]$$

is omitted in the first expression [and similarly the corresponding line segment in Fig. 4(a)] because this factor can be removed by a coordinate transformation $q_3'=\exp[(t_3-t_2)L^0(3)]q_3$. This simplification will be carried out wherever applicable in all subsequent graphs. In subsequent sections, reference is made only to graphs of the reduced form as shown in Figs. 4 and 5.

It has been mentioned that the most singular graphs corresponding to a j-particle cluster behave like $1/z^j$. Such graphs may be identified from the series of graphs generated by applying the expansions (3.4) and (3.8) to each term in (2.24). Given j-particle lines the minimum number of collision blocks that any j graph can have is $j-1$. As will be shown later these graphs behave indeed like $1/z^j$ for z small. For j graphs with more than $j-1$ blocks, the additional blocks must necessarily involve lines which already appear in other blocks. As a consequence of the restriction of the available phase space, each additional block introduces a factor of z. For example, a 3-graph with 2 blocks has a dependence of $1/z^2$ whereas the same graph with 3 blocks has a dependence of $1/z$. The presence of statistical factors like $G(\mathbf{q}_i\cdots\mathbf{q}_m)$ also influences the over-all z dependence of a graph. This is because the cluster property of $G(\mathbf{q}_i\cdots\mathbf{q}_m)$ completely suppresses the growth of the configurations of particles $i,\cdots,m$ with time. Roughly speaking, each factor of $G(\mathbf{q}_1\cdots\mathbf{q}_m)$ introduces a factor of z^{m-1}.

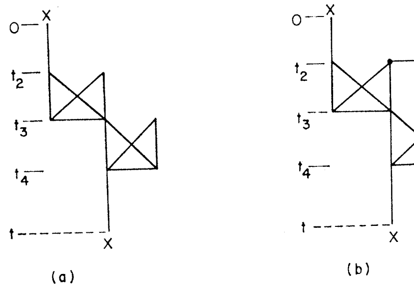

FIG. 4. 3-graphs corresponding to Fig. 3 after application of Theorem 2. Sum of (a) and (b) is equivalent to the graph in Fig. 3.

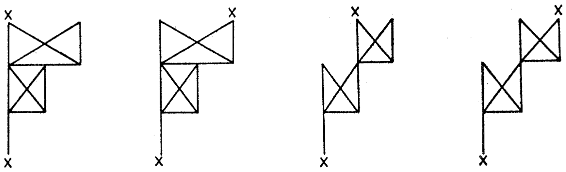

FIG. 5. Four distinct 3-particle Cayley trees. From these one can generate a total of 24 3-graphs with 2 collision blocks.

As far as the set of dominant terms is concerned we have thus to investigate all j graphs $(j=2,3\cdots)$ which contain $j-1$ blocks and no statistical bonds. Following the terminology used in equilibrium theory, we shall call these graphs Cayley trees to denote the class of connected graphs without cycles.[24] Four Cayley trees which would arise in the binary collision expansion of $U_t(123)$ are shown in Fig. 5. These are the only distinct 3-particle Cayley trees in the sense that all others can be obtained from these four by permutation of the particle lines.

IV. DERIVATION OF KINETIC EQUATIONS

Having developed an Ursell series for $f_a(xx';t)$ and discussed the asymptotic temporal behavior of the most singular contributions we are now in a position to derive a kinetic equation for this correlation function. The kinetic equation is valid for all times and is obtained by the use of an inversion technique which is equivalent to the summation of an appropriate class of graphs. It will be convenient to work with the transform of $f_a(xx';t)$ in wavelength and frequency space. Thus we consider

$$f_a(\mathbf{pp}',\mathbf{k}z)=\frac{1}{V}\int_0^\infty dte^{-zt}\int d^3qd^3q'$$
$$\times e^{i\mathbf{k}\cdot(\mathbf{q}'-\mathbf{q})}f_a(xx';t)\,. \quad (4.1)$$

Furthermore we introduce k-space representation of a j-particle dynamical operator

$$(\mathbf{k}_1'\cdots\mathbf{k}_j'|O(1\cdots j)|\mathbf{k}_1\cdots\mathbf{k}_j)$$
$$=\frac{1}{V}\int d^3q_1\cdots d^3q_je^{-i(\mathbf{k}_1'\cdot\mathbf{q}_1+\cdots+\mathbf{k}_j'\cdot\mathbf{q}_j)}$$
$$\times O(1\cdots j)e^{i(\mathbf{k}_1\cdot\mathbf{q}_1+\cdots+\mathbf{k}_j\cdot\mathbf{q}_j)}\,, \quad (4.2)$$

where $O(1\cdots j)$ acts in both the configuration and momentum space of the j particles. Some properties of the binary collision operator in this form have been noted

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[24] G. E. Uhlenbeck and G. W. Ford in *Studies in Statistical Mechanics*, edited by J. deBoer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962), Vol. 1.

recently by Zwanzig.[20] The Ursell series for $f_a(xx';t)$ now becomes

$$h_a(\mathbf{p}\mathbf{p}',\mathbf{k}z)=h_a{}^0(\mathbf{p}\mathbf{p}',\mathbf{k}z)+\sum_{j=1}\frac{n^j}{j!}\times\int d^3p''K^j(\mathbf{p}\mathbf{p}'',\mathbf{k}z)h_a{}^0(\mathbf{p}''\mathbf{p}',\mathbf{k}z)\,,\quad(4.3)$$

where

$$f_a(\mathbf{p}\mathbf{p}',\mathbf{k}z)=\phi(p)h_a(\mathbf{p}\mathbf{p}',\mathbf{k}z)\,,\quad(4.4)$$

the zero-density distribution $h_a{}^0$ is

$$h_a{}^0(\mathbf{p}\mathbf{p}',\mathbf{k}z)=\delta(\mathbf{p}-\mathbf{p}')[z-i\mathbf{k}\cdot\mathbf{v}]^{-1}\quad(4.5)$$

and the kernels $K^j(\mathbf{p}\mathbf{p}'',\mathbf{k}z)$ are given by

$$\begin{aligned}K^j(\mathbf{p}\mathbf{p}'',\mathbf{k}z)=\int d^3p_1\cdots d^3p_{j+1}\delta(\mathbf{p}_1-\mathbf{p})\phi(p_1)\cdots\phi(p_{j+1})\,(\mathbf{k}0\cdots0|g(\mathbf{q}_1\cdots\mathbf{q}_{j+1})B_z(1\cdots j+1)|\mathbf{k}0\cdots0)\\ \times\delta(\mathbf{p}_1-\mathbf{p}'')+(\mathbf{k}0\cdots0|g(\mathbf{q}_1\cdots\mathbf{q}_{j+1})B_z(1\cdots j+1)|0\mathbf{k}0\cdots0)\delta(\mathbf{p}_2-\mathbf{p}'')+\cdots\\ +(\mathbf{k}0\cdots0|g(\mathbf{q}_1\cdots\mathbf{q}_{j+1})B_z(1\cdots j+1)|0\cdots0\mathbf{k})\delta(\mathbf{p}_{j+1}-\mathbf{p}'')\,.\quad(4.6)\end{aligned}$$

The operator $B_z(1\cdots j)$ is defined as

$$U_z(1\cdots j)=B_z(1\cdots j)[z-L^0(1\cdots j)]^{-1}.\quad(4.7)$$

As we have emphasized the series expansion (4.3) of h_a in terms of $h_a{}^0$ is only meaningful for short times (large z). The essential point in the present derivation is that if (4.3) is inverted to give an explicit expression of $h_a{}^0$ in terms of h_a, the result becomes also *valid* for long times (small z). The inverse of (4.3) is

$$h_a{}^0(\mathbf{p}\mathbf{p}',\mathbf{k}z)=h_a(\mathbf{p}\mathbf{p}',\mathbf{k}z)+\sum_{j=1}\frac{n^j}{j!}\times\int d^3p''M^j(\mathbf{p}\mathbf{p}'',\mathbf{k}z)h_a(\mathbf{p}''\mathbf{p}',\mathbf{k}z)\,,\quad(4.8)$$

where the kernels $M^j(\mathbf{p}\mathbf{p}',\mathbf{k}z)$ are related to $K^j(\mathbf{p}\mathbf{p}',\mathbf{k}z)$ by the recurrence relations:

$$\begin{aligned}&M^1(\mathbf{p}\mathbf{p}')=K^1(\mathbf{p}\mathbf{p}')\,,\\&M^2(\mathbf{p}\mathbf{p}')=K^2(\mathbf{p}\mathbf{p}')-2\int d^3p''K^1(\mathbf{p}\mathbf{p}'')K^1(\mathbf{p}''\mathbf{p}')\,,\ \text{etc.}\end{aligned}\quad(4.9)$$

The inversion technique has been used by Zwanzig[20] in finding density expansions for transport coefficients and implicitly by Kohn and Luttinger[25] for the electrical conductivity. The method is exact but quite formal. However, a systematic approximation scheme is readily suggested which, in contrast to (4.3), is not restricted to small times. By carrying out the inversion to the lowest order ($j=1$) we obtain the following equation

$$\begin{aligned}h_a(\mathbf{p}\mathbf{p}',\mathbf{k}z)&=\delta(\mathbf{p}-\mathbf{p}')[(z-i\mathbf{k}\cdot\mathbf{v})]^{-1}+n\int d^3p_1d^3p_2\delta(\mathbf{p}-\mathbf{p}_1)\phi(p_2)\\&\times[(\mathbf{k}0|g(\mathbf{q}_1\mathbf{q}_2)B_z(12)|\mathbf{k}0)h_a(\mathbf{p}_1\mathbf{p}',\mathbf{k}z)\\&+(\mathbf{k}0|g(\mathbf{q}_1\mathbf{q}_2)B_z(12)|0\mathbf{k})h_a(\mathbf{p}_2\mathbf{p}',\mathbf{k}z)].\quad(4.10)\end{aligned}$$

The validity of this equation at long and short times can be established by comparing the diagram series corresponding to (4.3) and the series generated by iterating (4.10). For times sufficiently short that the first two terms of (4.3) are adequate to describe $h_a(\mathbf{p}\mathbf{p}',kz)$ it is obvious that the two descriptions are the same. In Appendix A we present a comparison of the second-order terms [terms proportional to n^2 in (4.3)]. There it is shown that the corresponding diagrams are the same if statistical effects are ignored. When only pairwise spatial correlation is included a number of approximations are then necessary to bring the diagrams into correspondence. To show that (4.10) is appropriate at long times, we show that the dominant terms to all orders in the density arising from the iterated series are just those present in (4.3). For this argument we can neglect statistical correlation, hence $g(\mathbf{q}_1\mathbf{q}_2)$ in (4.10) will be replaced by unity.

Thus far we have not made explicit any spatial effects of the collision operators in the diagrams of Sec. III. The operator $B(12)$ acts on both the relative separation of the two particles and their momenta whereas the matrix element $(\mathbf{k}_1'\mathbf{k}_2'|B(12)|\mathbf{k}_1\mathbf{k}_2)$ is a two-particle momentum operator. The latter form, however, suggests that the dynamical process can be interpreted as the propagation of wave vectors. Because of translational invariance the condition $\mathbf{k}_1'+\mathbf{k}_2'=\mathbf{k}_1+\mathbf{k}_2$ must always be satisfied. Thus in the Cayley tree approximation free particle streaming is represented by a labeled line segment as in Fig. 6(a), and collisions are represented by labeled blocks as in Figs. 6(b) and 6(c). Notice that because of the absence of cycles the wave vector $\mathbf{k}$ can propagate along only one particle line at any time. The

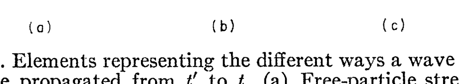

FIG. 6. Elements representing the different ways a wave vector $\mathbf{k}$ can be propagated from t' to t. (a) Free-particle streaming, $\exp[i\mathbf{k}\cdot\mathbf{v}(t-t')]$. (b) Binary collision without transfer of wave vector, $(\mathbf{k}0|B_{t-t'}|\mathbf{k}0)$. (c) Binary collision with wave-vector transfer, $(\mathbf{k}0|B_{t-t'}|0\mathbf{k})$.

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[25] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

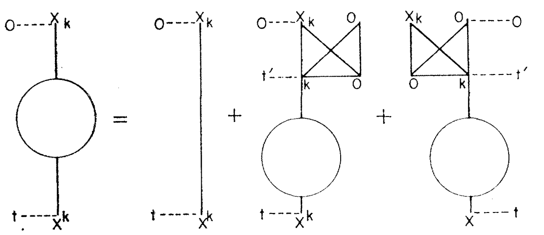

FIG. 7. Graphical representation of Eq. (4.11).

graph elements shown in Fig. 6 constitute the only basic elements in all Cayley trees. If we now represent all the Cayley trees by the graph shown on the left-hand side of Fig. 7, then symbolically this graph can be decomposed into the three components shown on the right-hand side. The first graph on the right-hand side corresponds to free propagation during the entire time interval. The second and third graphs contain collision blocks [Figs. 6(b) and 6(c), respectively] extending to time level t. Figure 7 actually corresponds to an integral equation for h_a in the Cayley tree approximation since except for a factor of $\phi(p)$, h_a is the contribution of all the Cayley trees. The integral equation is

$$h_a(\mathbf{pp}',\mathbf{k}t)$$

$$=\delta(\mathbf{p}-\mathbf{p}')e^{i\mathbf{k}\cdot\mathbf{v}t}+n\int_0^t dt'\int d^3p_1d^3p_2\delta(\mathbf{p}_1-\mathbf{p})\phi(p_2)$$

$$\times[(\mathbf{k}0|B_{t'}(12)|\mathbf{k}0)h_a(\mathbf{p}_1\mathbf{p}',\mathbf{k}t-t')$$

$$+(\mathbf{k}0|B_{t'}(12)|0\mathbf{k})h_a(\mathbf{p}_2\mathbf{p}',\mathbf{k}t-t')]. \quad (4.11)$$

The Laplace transform of this equation is identical to (4.10) in which $g(\mathbf{q}_1\mathbf{q}_2)$ is replaced by unity. Thus the inversion process effectively sums the most dominant terms in the Ursell series to all orders in the density.

Equation (4.10) gives a binary description of the Fourier components of $f_a(xx';t)$ that is valid at both short and long times. This equation is very similar in structure to the linearized Boltzmann equation. To make the connection more explicit we transform the collision matrix elements. We restrict our discussion to hard spheres and the lowest density approximation to $g(\mathbf{q}_1\mathbf{q}_2)$ $(g\simeq\exp[-\beta\Phi(q_{12})])$ because in this case the arguments are quite straight forward and the results are rigorous. It is shown in Appendix B that if $C(\mathbf{p}_1,\mathbf{p}_2)$ is any function of the momenta of particles 1 and 2,

$$(z-i\mathbf{k}\cdot\mathbf{v}_1)(\mathbf{k}0|e^{-\beta\Phi(12)}B_z(12)|\mathbf{k}0)C(\mathbf{p}_1\mathbf{p}_2)$$

$$=v_{12}\int dbd\epsilon b[C(\mathbf{p}_1'\mathbf{p}_2')-C(\mathbf{p}_1\mathbf{p}_2)], \quad (4.12)$$

$$(z-i\mathbf{k}\cdot\mathbf{v}_1)(\mathbf{k}0|e^{-\beta\Phi(12)}B_z(12)|0\mathbf{k})C(\mathbf{p}_1\mathbf{p}_2)$$

$$=v_{12}\int dbd\epsilon be^{i\mathbf{k}\cdot\sigma(b,\epsilon)}[C(\mathbf{p}_1'\mathbf{p}_2')-C(\mathbf{p}_1\mathbf{p}_2)]. \quad (4.13)$$

where $v_{12}=|\mathbf{v}_1-\mathbf{v}_2|$, (b,ϵ) are the conventional impact variables of a binary collision, and $\mathbf{p}_i'$ are the momenta after collision. The difference in the two operators lies in the way the wave vector $\mathbf{k}$ is "scattered" in the collision. In (4.12) $\mathbf{k}$ is associated with 1 throughout the entire process, whereas, in (4.13) $\mathbf{k}$ is originally associated with 1 but is scattered to 2 during the collision. Because the "transfer" can occur only when the particles are a hard-core diameter σ apart, there thus appears a change in phase by the amount $\exp(i\mathbf{k}\cdot\boldsymbol{\sigma})$ which is a function of the impact variables. The presence of the phase factor accounts for the finite extent of the particles. For long times (z small) and wavelengths long compared to the effective range of interaction (k small), one may expect the hard sphere results to be a good approximation for other repulsive two-body forces.

Using the transformations (4.12) and (4.13) and $\phi(p_1)\phi(p_2)=\phi(p_1')\phi(p_2')$ we have from (4.10)

$$(z-i\mathbf{k}\cdot\mathbf{v}_1)f_a(\mathbf{p}_1\mathbf{k}z)$$

$$=\phi(p_1)+n\int d^3p_2v_{12}bdbd\epsilon$$

$$\times\{\phi(p_2')f_a(\mathbf{p}_1'\mathbf{k}z)-\phi(p_2)f_a(\mathbf{p}_1\mathbf{k}z)+e^{i\mathbf{k}\cdot\sigma(b,\epsilon)}$$

$$\times[\phi(p_1')f_a(\mathbf{p}_2'\mathbf{k}z)-\phi(p_1)f_a(\mathbf{p}_2\mathbf{k}z)]\}, \quad (4.14)$$

where

$$f_a(\mathbf{pk}z)=\int d^3p'f_a(\mathbf{pp}'\mathbf{k}z). \quad (4.15)$$

Except for the phase factor this is identical to the appropriately transformed linearized Boltzmann equation with the initial condition $f_a(\mathbf{r}pt=0)=\delta(\mathbf{r})\phi(p)$. That (4.14) has the proper behavior for small k and z is well known from the theory of transport coefficients in dilute systems.[26] Since in the region of slow space and time variation the kinetic description gives essentially the same result as that derived from appropriate hydrodynamic equations, it is then to be expected that any correlation function calculated using (4.14) will have a proper hydrodynamic limit. It is also evident that such a correlation function will exhibit the correct free-particle limit for large k.

V. DISCUSSION

We have investigated the use of kinetic equations for the study of certain generalized correlation functions. The central result of our analysis is an equation describing the time evolution of the function $f_a(xx';t)$. This equation can be considered as a generalization of the linear variant of the equation originally proposed by Boltzmann in two respects. First of all, the collision

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[26] S. Chapman and T. G. Cowling, *The Mathematical Theory oj Non-Uniform Gases* (Cambridge University Press, New York, 1953).

operator is explicitly time-dependent and therefore it is possible to treat incomplete collisions. Secondly, spatial correlation of particles prior to their collision is taken into account through the equilibrium pair-distribution function in the collision integral. The inclusion of $g(r)$ can be compared to Enskog's modification of the Boltzmann equation for moderately dense gases.[26] For short times the effects just mentioned can be significant, and predictions based on Eq. (4.10) can in principle differ appreciably from those based on the ordinary linearized Boltzmann equation. However, no explicit calculations have been carried through thus far to enable a comparison.

The formal technique used in our derivation is the inversion of a truncated series. By ignoring all terms proportional to n^2 and higher in the Ursell series (4.3) we obtain (4.10). Since the latter can be iterated to produce a series in all orders of n, it is possible to study the approximations underlying (4.10) by comparing corresponding terms in the two series. It is obvious that (4.10) treats correctly the single binary collision events with or without statistical correlation, but with regard to successive binary collisions the effect of spatial correlation is different in (4.3) and (4.10). In (4.3) all the particles in a cluster are correlated initially through $n(1\cdots j)$, dynamical correlation is then developed in time according to the collision operator $B_t(1\cdots j)$. On the other hand, in the iterated series corresponding to (4.10) particles are spatially correlated *only* prior to their collision, consequently the system evolves as a result of a series of statistical and dynamical interactions. This difference means that the relevant terms in the two series will not correspond exactly. In Appendix A it is remarked that the effect due to this difference is small for short times. Since it is precisely for short times that spatial correlation of particles is important, the use of (4.10) for all times is not an unreasonable approximation. It should be observed that the use of Cayley tree approximation in the binary expansions of $B_t(1\cdots j)$ and of $g(\mathbf{q}_1\cdots\mathbf{q}_j)$ does not sufficiently reduce the contributions in the Ursell series to those dealing only with purely binary effects. This is because the possibility still exists of a particle colliding with another and yet is spatially correlated to a third.

The inversion technique used to obtain an approximate equation on the binary level can be equally well applied to give kinetic equations on the ternary level, etc. Thus the ternary equation sums at long times the next to dominant terms, those having one higher power of the density than the dominant terms with the same power of z^{-1}. The convergence of these successive approximations is controlled by the density, but nothing is known about the existence of each step in such a sequence.

In this paper we have referred to the hard-sphere interaction as an example. One should realize, however, that the binary collision method cannot be straightforwardly applied to hard spheres since situations in which the particles are inside the interaction sphere are not well defined. Our Eq. (4.10) does not suffer from this difficulty because these unphysical situations are forbidden by the presence of $g(\mathbf{q}_1\mathbf{q}_2)$. The same is true for the more general Eq. (4.8).

Once a description of $f(xx';t)$ is formulated a number of correlation functions can be calculated. In particular, the Van Hove density correlation functions and the momentum correlation function are just appropriate momentum and spatial integrals of $f(xx';t)$. In our analysis we have concentrated on a description for $f_a(xx';t)$ which is only one part of $f(xx';t)$. An expression is given for the remainder, $f_b(xx';t)$, but no equation for it has been derived. However, at the level of (4.10) this is not necessary since one can use the convolution relation (2.33).

When statistical correlation is ignored the Van Hove function $G(r,t)$ is given by the momentum integral of $f_a(r\mathbf{p}t)$, which is a solution of (4.11). Recently Nelkin and co-workers proposed to calculate $G(r,t)$ and $G_s(r,t)$ from kinetic models derived from the linearized Boltzmann equation.[14,15] The theoretical justification for this work is now provided by the derivation of (4.11). The difference in the equations used for G and G_s concerns the collisional invariants of momentum and energy. This difference is readily demonstrated with (4.11) in which the phase factor is again ignored. It is seen that the collision terms in (4.11) are properly symmetrized with respect to the two particles, so that particle number, momentum, and energy are all conserved. On the other hand, in the corresponding equation for $f_s(r\mathbf{p}t)$, where

$$G_s(r,t)=\int d^3p\ f_s(r\mathbf{p}t)=\int d^3p d^3p'\ f_s(xx';t)\,,$$

the collision terms constitute only the first two terms in the integrand of (4.11). Therefore, only particle number is conserved. An important consequence of the difference in collisional invariants in the two descriptions is that G and G_s will exhibit characteristically different hydrodynamical behavior. For long times and long wavelengths (4.10) and (4.11) should give essentially the same results. One can then expect $G(r,t)$ to be characterized by the irreversible processes of thermal diffusion and damped sound propagation whereas $G_s(r,t)$ is characterized by simple diffusion.

With regard to slow-neutron scattering the present formulation provides an appropriate calculation of coherent and incoherent scattering in moderately dense gases without the use of Vineyard's convolution approximation or the so-called Gaussian approximation.[3] Since this approach explicitly incorporates the effect of spatial correlation it can be used to understand the coherent narrowing of the spectrum. It is not known to what extent is (4.10) applicable to the study of density correlations in liquids; nevertheless, it seems worthwhile to pursue further along this line of investigation.

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APPENDIX A

In this Appendix we compare the terms with three particle lines in the graphical representation of f_a and the terms following from the second iteration of the integral Eq. (4.10). The latter are given by (after the appropriate change from h_a to f_a)

$$n^2\int d^3p_1d^3p_2d^3p_3\delta(\mathbf{p}-\mathbf{p}_1)\phi(p_1)\phi(p_2)\phi(p_3)\bigg\{(\mathbf{k}0|g(\mathbf{q}_1\mathbf{q}_2)B_z(12)|\mathbf{k}0)\bigg[(\mathbf{k}0|g(\mathbf{q}_1\mathbf{q}_3)B_z(13)|\mathbf{k}0)\frac{\delta(\mathbf{p}_1-\mathbf{p}')}{z-i\mathbf{k}\cdot\mathbf{v}_1}$$
$$+(\mathbf{k}0|g(\mathbf{q}_1\mathbf{q}_3)B_z(13)|0\mathbf{k})\frac{\delta(\mathbf{p}_3-\mathbf{p}')}{z-i\mathbf{k}\cdot\mathbf{v}_3}\bigg]+(\mathbf{k}0|g(\mathbf{q}_1\mathbf{q}_2)B_z(12)|0\mathbf{k})$$
$$\times\bigg[(\mathbf{k}0|g(\mathbf{q}_2\mathbf{q}_3)B_z(23)|\mathbf{k}0)\frac{\delta(\mathbf{p}_2-\mathbf{p}')}{z-i\mathbf{k}\cdot\mathbf{v}_2}+(\mathbf{k}0|g(\mathbf{q}_2\mathbf{q}_3)B_z(23)|0\mathbf{k})\frac{\delta(\mathbf{p}_3-\mathbf{p}')}{z-i\mathbf{k}\cdot\mathbf{v}_3}\bigg]\bigg\}. \quad \text{(A1)}$$

By setting $g(\mathbf{q}_1\mathbf{q}_2)=1+G(\mathbf{q}_1-\mathbf{q}_2)$ we obtain from (A1) 16 terms which can be compared to the graphs for $f_a(\mathbf{pp}',kz)$ as developed in Sec. III.

It is clear that all the 3-graphs with more than two blocks are not taken into account in Eq. (A1). Also if we consider the Ursell expansion for the 3-particle density distribution function

$$g(\mathbf{q}_1\mathbf{q}_2\mathbf{q}_3)=1+G(\mathbf{q}_1-\mathbf{q}_2)+G(\mathbf{q}_1-\mathbf{q}_3)+G(\mathbf{q}_2-\mathbf{q}_3)$$
$$+G(\mathbf{q}_1-\mathbf{q}_2)G(\mathbf{q}_1-\mathbf{q}_3)+G(\mathbf{q}_1-\mathbf{q}_2)G(\mathbf{q}_2-\mathbf{q}_3)$$
$$+G(\mathbf{q}_1-\mathbf{q}_3)G(\mathbf{q}_2-\mathbf{q}_3)+G(\mathbf{q}_1\mathbf{q}_2\mathbf{q}_3), \quad \text{(A2)}$$

the term containing $G(\mathbf{q}_1\mathbf{q}_2\mathbf{q}_3)$ will not be reproduced by the integral equation. Thus as far as the correspondence between the Ursell expansion for f_a and (4.10) is concerned, the genuine three-particle collisions (three or more blocks) and the genuine three-particle statistical correlations $G(\mathbf{q}_1\mathbf{q}_2\mathbf{q}_3)$ are present in the Ursell expansion but not in the integral equation. For the remaining graphs in the Ursell expansion we show 4 typical examples in Fig. 8 [the particle indices are chosen so as to correspond to the labels in Eq. (A1)]. Each graph shown can be statistically dressed with any of the first seven terms in Eq. (A2), so there are 28 graphs to be considered.

One observes that there are 12 graphs with statistical bonds $G(\mathbf{q}_i-\mathbf{q}_j)$ between particle lines which are not connected by a block. These graphs represent contributions in which two particles interact statistically but not dynamically, and may be viewed as an interference between statistical and dynamical correlations. Such graphs also are not present in Fig. 8. In order to treat these effects one should consider a coupling between f_a and f_b, which is ignored in this paper and which is believed to be small.

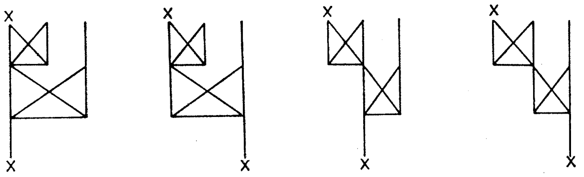


FIG. 8. Four distinct 3-particle Cayley trees which correspond to the terms in Eq. (A1). These graphs are equivalent to those shown in Fig. 5.

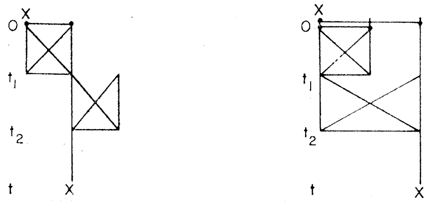
The remaining 16 graphs are reproduced in Fig. 8, the correspondence for the 8 graphs containing either no correlation function or $G(\mathbf{q}_i-\mathbf{q}_j)$ is exact whereas for the other 8 the correspondence is only approximate. We now discuss a typical case for each group. In Fig. 9(a) we show a graph having the following contribution to $f_a(\mathbf{pp}',kt)$

$$n^2\int dx_1dx_2dx_3\phi(p_1)\phi(p_2)\phi(p_3)e^{-i\mathbf{k}\cdot\mathbf{q}_1}\delta(\mathbf{p}_1-\mathbf{p})$$
$$\times G(\mathbf{q}_1-\mathbf{q}_2)\int_0^t dt_1\int_0^{t_1}dt_2B_{t_1}(12)$$
$$\times B_{t_2-t_1}(23)e^{(t-t_2)L^0(2)}\delta(\mathbf{p}_2-\mathbf{p}')e^{i\mathbf{k}\cdot\mathbf{q}_2}. \quad \text{(A3)}$$

The corresponding term from Eq. (A1) is given by

$$n^2\int d^3p_1d^3p_2d^3p_3\phi(p_1)\phi(p_2)\phi(p_3)\delta(\mathbf{p}_1-\mathbf{p})$$
$$\times(\mathbf{k}0|G(\mathbf{q}_1-\mathbf{q}_2)B_z(12)|0\mathbf{k})(\mathbf{k}0|B_z(23)|\mathbf{k}0)$$
$$\times\delta(\mathbf{p}_2-\mathbf{p}')/(z-i\mathbf{k}\cdot\mathbf{v}_2), \quad \text{(A4)}$$

and one sees that Eq. (A4) is indeed the Laplace transform of Eq. (A3). A typical graph in the second group



(a) (b)

FIG. 9. Graphs in the Ursell series for f_a which are taken into account exactly (a) or approximately (b) in Eq. (4.10).

is shown in Fig. 9(b) and has the contribution

$$n^2\int dx_1dx_2dx_3\phi(p_1)\phi(p_2)\phi(p_3)e^{-i\mathbf{k}\cdot\mathbf{q}_1}\delta(\mathbf{p}_1-\mathbf{p})$$
$$\times G(\mathbf{q}_1-\mathbf{q}_2)G(\mathbf{q}_1-\mathbf{q}_3)\int_0^t dt_1\int_0^{t_1} dt_2 B_{t_1}(12)e^{t_1L^0(3)}$$
$$\times B_{t_2-t_1}(13)e^{(t-t_2)L^0(3)}\delta(\mathbf{p}_3-\mathbf{p}')e^{i\mathbf{k}\cdot\mathbf{q}_3}. \quad \text{(A5)}$$

This graph corresponds only approximately to the term from Eq. (A1)

$$n^2\int d^3p_1d^3p_2d^3p_3\phi(p_1)\phi(p_2)\phi(p_3)\delta(\mathbf{p}_1-\mathbf{p})$$
$$\times(\mathbf{k}0|G(\mathbf{q}_1-\mathbf{q}_2)B_z(12)|0\mathbf{k})$$
$$\times(\mathbf{k}0|G(\mathbf{q}_1-\mathbf{q}_3)B_z(13)|0\mathbf{k})$$
$$\times\delta(\mathbf{p}_3-\mathbf{p}')[z-i\mathbf{k}-\mathbf{v}_3]^{-1}. \quad \text{(A6)}$$

The reason that Eq. (A6) is not exactly the Laplace transform of Eq. (A5) lies in the fact that $G(\mathbf{q}_1-\mathbf{q}_3)$ does not commute with $B_{t_1}(12)\exp[t_1L^0(3)]$,

$$G(\mathbf{q}_1-\mathbf{q}_3)B_{t_1}(12)e^{t_1L^0(3)}\neq B_{t_1}(12)e^{t_1L^0(3)}G(\mathbf{q}_1-\mathbf{q}_3). \quad \text{(A7)}$$

However, for small $t-t_1$ the error is small.

APPENDIX B

In this Appendix we discuss some transformation properties[19] of the binary collision operator $B_z(12)$ in the case of hard spheres.

We first show that if $C(\mathbf{p}_1\mathbf{q}_1\mathbf{p}_2\mathbf{q}_2)$ is any function of the phases of particles 1 and 2,

$$B_z(12)C(\mathbf{p}_1\mathbf{q}_1\mathbf{p}_2\mathbf{q}_2)$$
$$=e^{-z\tau_c(12)}[C(\mathbf{p}_1'\mathbf{q}_1'\mathbf{p}_2'\mathbf{q}_2')-C(\mathbf{p}_1\mathbf{q}_1'\mathbf{p}_2\mathbf{q}_2')], \quad \text{(B1)}$$

where $\mathbf{q}_i'=\mathbf{q}_i+\mathbf{v}_i\tau_c(12)$. The function $\tau_c(12)$ is the interval from $t=0$ to the instant of collision, and like the post-collision momenta $\mathbf{p}_i'$ it depends upon $\mathbf{p}_1$, $\mathbf{p}_2$, and $\mathbf{q}_{21}$. To demonstrate (B1), we recall

$$B_z(12)C(\mathbf{p}_1\mathbf{q}_1\mathbf{p}_2\mathbf{q}_2)=\int_0^\infty dte^{-zt}[e^{tL(12)}-e^{tL^0(12)}]$$
$$\times[z-L^0(12)]C(\mathbf{p}_1\mathbf{q}_1\mathbf{p}_2\mathbf{q}_2). \quad \text{(B2)}$$

Now (B2) vanishes unless the initial configuration of the particles is such that a collision occurs during time t. For a given initial configuration we can define a collision time $\tau_c(12)$ so that for all intervals $t<\tau_c$ no collision can occur. For all intervals $t\geqslant\tau_c$ we know that the particles stream freely with their initial velocities for a time $\tau_c(12)$, then a collision takes place and the particles again stream freely but with the post-collision velocities during the remaining interval $t-\tau_c(12)$. Thus one has

$$B_z(12)C(\mathbf{p}_1\mathbf{q}_1\mathbf{p}_2\mathbf{q}_2)=\int d^3\mathbf{p}_1{}^0d^3\mathbf{q}_1{}^0d^3\mathbf{p}_2{}^0d^3\mathbf{q}_2{}^0C(\mathbf{p}_1{}^0\mathbf{q}_1{}^0\mathbf{p}_2{}^0\mathbf{q}_2{}^0)\Lambda, \quad \text{(B3)}$$

$$\Lambda=\int_0^\infty dte^{-zt}[e^{tL(12)}-e^{tL^0(12)}]\left(z-\mathbf{v}_1\cdot\frac{\partial}{\partial\mathbf{q}_1}-\mathbf{v}_2\cdot\frac{\partial}{\partial\mathbf{q}_2}\right)\delta(\mathbf{p}_1-\mathbf{p}_1{}^0)\delta(\mathbf{q}_1-\mathbf{q}_1{}^0)\delta(\mathbf{p}_2-\mathbf{p}_2{}^0)\delta(\mathbf{q}_2-\mathbf{q}_2{}^0)$$
$$=(2\pi)^{-6}\int_{\tau_c(12)}^\infty dte^{-zt}\int d^3yd^3y'\{(z-i\mathbf{v}_1'\cdot\mathbf{y}-i\mathbf{v}_2'\cdot\mathbf{y}')\delta(\mathbf{p}_1'-\mathbf{p}_1{}^0)\delta(\mathbf{p}_2'-\mathbf{p}_2{}^0)e^{i\mathbf{y}\cdot[\mathbf{q}_1+\mathbf{v}_1\tau_c+\mathbf{v}_1'(t-\tau_c)-\mathbf{q}_1{}^0]}$$
$$\times e^{i\mathbf{y}'\cdot[\mathbf{q}_2+\mathbf{v}_2\tau_c+\mathbf{v}_2'(t-\tau_c)-\mathbf{q}_2{}^0]}-(z-i\mathbf{v}_1\cdot\mathbf{y}-i\mathbf{v}_2\cdot\mathbf{y}')\delta(\mathbf{p}_1-\mathbf{p}_1{}^0)\delta(\mathbf{p}_2-\mathbf{p}_2{}^0)e^{i\mathbf{y}\cdot(\mathbf{q}_1+\mathbf{v}_1t-\mathbf{q}_1{}^0)}e^{i\mathbf{y}'\cdot(\mathbf{q}_2+\mathbf{v}_2t-\mathbf{q}_2{}^0)}\}$$
$$=e^{-z\tau_c(12)}\delta(\mathbf{q}_1+\mathbf{v}_1\tau_c-\mathbf{q}_1{}^0)\delta(\mathbf{q}_2+\mathbf{v}_2\tau_c-\mathbf{q}_2{}^0)[\delta(\mathbf{p}_1'-\mathbf{p}_1{}^0)\delta(\mathbf{p}_2'-\mathbf{p}_2{}^0)-\delta(\mathbf{p}_1-\mathbf{p}_1{}^0)\delta(\mathbf{p}_2-\mathbf{p}_2{}^0)]. \quad \text{(B4)}$$

Substituting (B4) into (B3) and performing the indicated integrations one finds the result given in (B1).

Now for any momentum function $C(\mathbf{p}_1\mathbf{p}_2)$ application of (4.4) and (B1) gives, with $g(\mathbf{q}_1\mathbf{q}_2)$ replaced by its lowest density approximation,

$$(\mathbf{k}0|e^{-\beta\Phi(q_{12})}B_z(12)|\mathbf{k}0)C(\mathbf{p}_1\mathbf{p}_2)=\frac{1}{V}\int d^3q_1d^3q_2e^{-(z-i\mathbf{k}\cdot\mathbf{v}_1)\tau_c(12)}e^{-\beta\Phi(q_{12})}[C(\mathbf{p}_1'\mathbf{p}_2')-C(\mathbf{p}_1\mathbf{p}_2)]$$
$$=(z-i\mathbf{k}\cdot\mathbf{v}_1)^{-1}v_{12}\int_0^{2\pi}d\epsilon\int_0^\sigma bdb[C(\mathbf{p}_1'\mathbf{p}_2')-C(\mathbf{p}_1\mathbf{p}_2)], \quad \text{(B5)}$$

where in integrating over relative positions we have chosen the origin at $\mathbf{q}_1$ and the z axis is directed along the relative velocity $\mathbf{v}_2-\mathbf{v}_1$. In using cylindrical coordinates the impact parameter b is the radial coordinate which can range from zero to σ, the hard-core diameter. The azimuthal angle is denoted as ϵ. The length of the collision cylinder is $\mathbf{v}_{12}\tau_c$ so that the volume element becomes

$$d^3q_{21}=v_{12}b\,db\,d\epsilon\,d\tau_c\,,$$

with τ_c ranging from zero to infinity. Similarly,

$$(\mathbf{k}0|e^{-\beta\Phi(q_{12})}B_z(12)|0\mathbf{k})=(z-i\mathbf{k}\cdot\mathbf{v}_1)^{-1}v_{12}\int_0^{2\pi}d\epsilon\int_0^{\sigma}b\,db\,e^{i\mathbf{k}\cdot\boldsymbol{\sigma}(b,\epsilon)}[C(\mathbf{p}_1'\mathbf{p}_2')-C(\mathbf{p}_1\mathbf{p}_2)]\,, \tag{B6}$$

where we have used the relation $\mathbf{q}_2=\mathbf{q}_1+(\mathbf{v}_1-\mathbf{v}_2)\tau_c(12)+\boldsymbol{\sigma}(b,\epsilon)$, with $\boldsymbol{\sigma}(b,\epsilon)$ being the vector from $\mathbf{q}_1$ to $\mathbf{q}_2$ at the instant of contact.

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Theory of Relaxation in a Group of Weakly Coupled Systems

ROBERT L. PETERSON
National Bureau of Standards, Boulder, Colorado

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A general formalism for computing relaxation times characterizing two or more weakly coupled macroscopic systems is presented. The physical nature of the systems is arbitrary, although applications to spin systems are briefly discussed. The main assumptions are that each system is internally in equilibrium with a well-defined temperature, that the systems are weakly coupled to one another, and that the Hamiltonians of the systems form a commuting set. No high-temperature approximations are used. The formalism is presented in an effort to unify in part the approaches which have been developed for many special physical situations, and to show the form some relaxation times take when the high-temperature approximations are not used. It is shown that when one of two coupled systems is a "Zeeman" system, the (spin) relaxation time is proportional to the magnetic adiabatic susceptibility.

INTRODUCTION

FOR many years there has been considerable interest, experimentally and theoretically, in relaxation processes occurring in a group of two or more systems weakly coupled to one another. References 1–12 indicate some of the work concerned with these phenomena. Each of these references is concerned in some way with spin relaxation, and as a rule, treats the spin systems in a high-temperature approximation (that is, the approximation in which Curie's law is perfectly obeyed). An important exception is the work of Orbach.[8] The approach typically is to postulate certain rate equations applicable to the physical systems of interest, and from these to calculate the characteristic relaxation times. The algebra involved is quite similar in most cases.

One of our purposes in this paper is to present a unified treatment of relaxation in a group of loosely coupled systems, the physical nature of which may be left unspecified. The result is a prescription for calculating the relaxation times, namely, finding the roots of a "relaxation time matrix." Of course, general techniques for computing damping constants in electrical circuits are well known and can be found in texts on differential equations and circuit theory. However, we are not aware of any publication containing a prescription for computing relaxation times characterizing a group of macroscopic, thermal systems, and feel that this presentation fills a need.

Perhaps more important is the fact that we have avoided any high-temperature approximation. We discuss in some detail the special cases of two and three coupled systems. We show that the relaxation time characterizing two systems, one of which is a "Zeeman"

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