50 eV, increasing perhaps to a few percent at 1000 eV. It is hard to see why such small amounts of metastables would have had a significant effect on the He-He and He-Ne results, since the Penning ionization cross section is zero in these cases. A small effect might have been present in He-N_2, but it was not apparent. (In the He-H_2 and He-Ar measurements,[20] characteristic structure was present due to metastables.)

The two percent N_2^+ impurity in the He^+ ion beam (before neutralization) had negligible effect on the present measurements. It was found that N_2^+ did not charge transfer in He or Ne, and therefore the neutral beam contained no N_2 in the He-He and He-Ne cases. A similar argument should hold for the water impurity. In the He-N_2 case, the presence of some N_2 in the neutralization chamber did produce one or two percent N_2 in the He neutral beam. However, the N_2-N_2 cross section is not large enough to cause a significant effect on the results.

It appears that structure is present in the He-He ionization cross section versus energy curve. Berry[21] has reported structure in the ionization electron energy distribution for He-He ionizing interactions. It is probable that these effects are related.

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[21] H. W. Berry, Phys. Rev. **121**, 1714 (1961).

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Time-Relaxed Probability Densities and Correlation Functions for Moderately Dense Fluids*

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Kinetic equations are obtained for the purpose of describing the temporal evolution of two-time (conditional) probability densities for locating subsets of particles moving within an equilibrium assembly. The reduction and solution of the equation for the single-particle density is investigated in considerable detail. Information concerning the short-time evolution of the probability densities is explicitly retained, in order that the applicability of the equations for studying the properties of relatively dense systems be preserved. The expressions for probability densities are used to study the properties of certain associated correlation functions. Expressions for the momentum autocorrelation function are derived. Similarly, certain features of the cross sections for the scattering of slow neutrons are investigated.

I. INTRODUCTION

THE statistical mechanical foundations of linear transport processes and irreversible thermodynamics are now firmly established.[1,2] Parameters appearing in the latter macroscopic theories may be related, quite generally, to appropriate time-relaxed correlation functions describing the motions of the constituent particles of a given system of interest. On the other hand, these general relationships are, in a certain sense, only definitions; there yet remains a rather difficult problem, only partially resolved, of how best to evaluate these expressions when performing explicit calculations.

A related difficulty appears in the calculation of cross sections for the scattering of slow neutrons. It has been shown that the latter can be obtained from expressions for time-relaxed probability densities $G(\mathbf{r},t)$ describing the spatial motion of constituent particles of the scattering medium.[3,4] In general, when attempting to calculate $G(r,t)$ by considering *only* the spatial motion of the particles of the system, semiphenomenological kinetic equations or models are employed.[5,6] However, at least in principle, the spatial probability density may be obtained in a more general fashion by performing appropriate integrations over a probability density function defined, as well, over the momentum space of the particles. The advantage of this procedure is that the latter may be obtained by reduction from an n-particle Liouville equation.

Similarly, the correlation functions mentioned in the previous paragraphs, i.e., those appropriate to analyses of macroscopic transport, may also be obtained from generalized time-relaxed probability densities. Although it is often profitable to devise individual calculational programs specifically for the direct calculation of a

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[1] M. S. Green, J. Chem. Phys. **20**, 1287 (1952); **22**, 398 (1954).

[2] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

[3] L. Van Hove, Phys. Rev. **95**, 249 (1954).

[4] R. J. Glauber, Phys. Rev. **98**, 1692 (1955).

[5] A. Rahman, K. S. Singwi, and A. Sjolander, Phys. Rev. **126**, 997 (1962).

[6] S. Yip, dissertation, University of Michigan, 1962 (unpublished).

particular transport quantity,[7,8] greater generality suggests a study of the evolution of the basic probability densities themselves. The latter is the primary concern of this paper.

First, a procedure must be chosen to reduce the Liouville equation to appropriate kinetic equations for the probability densities of interest. There are, of course, a number of methods which have been proposed for the study of the evolution of general probability densities.[9–11] However, these prescriptions are most appropriate for describing the evolution of an assembly for time periods commencing after an interval which is much larger than a representative "collision time" for the system. The theory of dilute gases is, for the most part, predicated upon such assumptions. However, it must be concluded that any procedure which requires imposing asymptotic time limits will be inapplicable to the study of the properties of relatively dense fluids. Indeed, similar objections can be raised even for dilute systems if one is ultimately interested in studying frequency-dependent transport quantities at high frequency. In the latter case, a kinetic description which retains a memory of the initial value of the probability density is essential.[12]

For these reasons, we consider the derivation and solution of kinetic equations which retain information about the short-time behavior of the system. For this purpose, an elaboration and modification of the projection operator procedure introduced by Zwanzig[13] in similar studies of irreversible statistical mechanics is employed. A projection operator is chosen so that the collision integral appearing in the kinetic equations can be expanded in a series which demonstrates successively higher contributions of the internal potential energy of the assembly.

As is well known, difficulties are frequently encountered when performing coupling constant expansions for systems characterized by interaction potentials containing strong short-range repulsive cores. It is often found that the individual terms appearing in the resulting expansions are, strictly speaking, of infinite magnitude. In these circumstances, it is necessary either to sum over an infinite set of expansion terms, or to make various approximations to argue boundedness of a chosen noninfinite subset of expansion terms. However, judicious choice of the projection operator insures that the expansion parameters, in the series appearing below, are convergent even for potentials with strongly repulsive cores. The logical difficulty which might otherwise be associated with expansion in terms of a 'small' parameter characteristic of an infinitely strong interaction is thus eliminated.

Hence, equations are derived in Sec. II to provide the temporal evolution of time-relaxed probability densities for groups of particles moving through an equilibrium assembly of like particles. Detailed investigation is made of the kinetic equation for the one-particle density [that is, for $f_1(\mathbf{x}_1;t|\mathbf{x}_{1_0})$, defined as the probability density for finding a specified particle in the neighborhood of the 6-dimensional phase point, $\mathbf{x}_1\equiv(\mathbf{q}_1,\mathbf{p}_1)$, at time t, given that at $t=0$, the particle was located exactly at $\mathbf{x}_{1_0}$].

In Sec. III, procedures for solving the equation for f_1 are introduced. Expressions for momentum densities and associated correlation functions are obtained. By explicitly retaining terms to fourth order in the forces, one is able to see in what manner negative correlations may be manifest in the autocorrelation function.

Similarly, aspects of the temporal behavior of the configurational probability density $G_s(\mathbf{r},t)$ are investigated in Sec. IV. Consideration is given to related expressions for the incoherent cross section for low-energy neutron scattering.

II. KINETIC EQUATIONS

a. General Considerations

Let us commence by obtaining kinetic equations to describe the temporal evolution of reduced time-relaxed probability densities. First, let

$$f_n(\mathbf{X}_n;t|\mathbf{X}_{s_0}) \tag{2.1}$$

represent the *conditional* probability density for finding a specified n-particle system in the neighborhood of a point $\mathbf{X}_n\equiv(\mathbf{q}_1,\cdots,\mathbf{q}_n;\mathbf{p}_1,\cdots,\mathbf{p}_n)$ of Γ space, at time t, given that at $t=0$, a designated s-dimensional subset of particles was located at the point $\mathbf{X}_{s_0}$ of a pertinent $6s$-dimensional reduced phase space. Marginal densities are to be obtained from $f_n(\mathbf{X}_n;t|\mathbf{X}_{s_0})$ by integrating over extraneous coordinates, i.e.,

$$f_{a,b}(\mathbf{q}_1,\cdots,\mathbf{q}_a;\mathbf{p}_1,\cdots,\mathbf{p}_b;t|\mathbf{X}_{s0})$$
$$\equiv\int d\mathbf{q}_{a+1}\cdots d\mathbf{q}_n d\mathbf{p}_{b+1}\cdots d\mathbf{p}_n f_n(\mathbf{X}_n;t|\mathbf{X}_{s0}). \tag{2.2}$$

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[7] S. A. Rice, J. Chem. Phys. **33**, 1376 (1960).

[8] E.g., S. Fujita and F. Mayné, Physica **29**, 1201 (1963).

[9] N. N. Bogoliubov, in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (English transl. by E. K. Gora) (North-Holland Publishing Company, Amsterdam, 1960), Vol. I.

[10] J. G. Kirkwood, in *Rendiconti della Scuola Internazionale di Fisica "Enrico Fermi," Corso X* (Nicola Zanichelli, Bologna, 1959).

[11] I. Prigogine, *Non-equilibrium Statistical Mechanics* (Interscience Publishers, Inc., New York, 1962).

[12] For example, suppose that the actual temporal behavior of a time-relaxed correlation function were $C(t)=a_1e^{-\lambda_1 t}+a_2e^{-\lambda_2 t}$, with $\lambda_2\gg\lambda_1>0$. An asymptotic kinetic equation might correctly provide the first term on the right-hand side of the latter expression, but would fail to provide the second.

Suppose, also, that the transport quantity appropriate to $C(t)$ were proportional to the real part of its Fourier time transform [such is the case for the incoherent scattering function, cf. Eqs. (4.7) and (4.10), below], the latter being $\bar{C}(\omega)\propto[(a_1\lambda_1/\lambda_1^2+\omega^2)+(a_2\lambda_2/\lambda_2^2+\omega^2)]$. Thus, for $\omega>\lambda_2$, it is seen that the measurement of the transport quantity primarily probes that contribution to $C(t)$ which describes the short-time behavior of the system.

An asymptotic kinetic equation is assumed valid for $t\gg\tau$, where τ is a typical time describing phenomena occurring on a "short-time scale." Thus, at the least, for frequencies $\omega\sim1/\tau$, one would expect an erroneous result to ensue from the use of the asymptotic equation for the calculation of $C(t)$.

[13] R. W. Zwanzig, J. Chem. Phys. **33**, 1338 (1960).

As is well known, once the initial state, $f_n(\mathbf{X}_n;0|\mathbf{X}_{s0})$, is specified, $f_n(\mathbf{X}_n;t|\mathbf{X}_{s0})$ is determined for all time according to the Liouville equation. The latter may be written in the following convenient form:

$$\partial_t f_n(\mathbf{X}_n;t|\mathbf{X}_{s0})=Lf_n(\mathbf{X}_n;t|\mathbf{X}_{s0}), \tag{2.3}$$

where L is the Liouville operator $L=L_0+L_1+L_2$ with

$$L_0\equiv-\sum_{i=1}^{n}\frac{\mathbf{p}_i}{m_i}\cdot\frac{\partial}{\partial\mathbf{x}_i}; \tag{2.4a}$$

$$L_1\equiv\tfrac{1}{2}\sum_{i\neq k}^{n}\sum^{n}\frac{\partial}{\partial\mathbf{q}_j}V(|\mathbf{q}_j-\mathbf{q}_k|)\cdot\left(\frac{\partial}{\partial\mathbf{p}_j}-\frac{\partial}{\partial\mathbf{p}_k}\right); \tag{2.4b}$$

$$L_2\equiv\sum_{i=1}^{n}\frac{\partial}{\partial\mathbf{q}_i}U^{[i]}\cdot\frac{\partial}{\partial\mathbf{p}_i}. \tag{2.4c}$$

To obtain Eqs. (2.4), it has been assumed that all forces be velocity-independent. Also, the internal potential energy is taken to be the sum of two-particle central force interactions, where $V(|\mathbf{q}_i-\mathbf{q}_j|)$ is the potential between the ith and jth particles. $U^{[i]}$ is the external potential acting upon the ith particle.

To obtain a kinetic equation for $f_s(\mathbf{X}_s;t|\mathbf{X}_{s0})$, let us introduce the following operators:

$$\bar{\mathcal{P}}_s\equiv\int d\mathbf{x}_{s+1}\cdots d\mathbf{x}_n;$$
$$\mathcal{P}_s\equiv f_{n|s}(\mathbf{x}_{s+1},\cdots,\mathbf{x}_n|\mathbf{x}_1,\cdots,\mathbf{x}_s;0)\bar{\mathcal{P}}_s, \tag{2.5}$$

where $f_{n|s}$ designates the *stationary* conditional probability density for finding an n-s particle subsystem in the neighborhood of phase point $\{\mathbf{x}_{s+1},\cdots,\mathbf{x}_n\}$ at time t, given that (at the same time) the coordinates of particles $1\rightarrow s$ are $\mathbf{x}_1,\cdots,\mathbf{x}_s$. Notice that $\mathcal{P}_s$ is a projection operator, since $\mathcal{P}_s^2\,\mathrm{Fcn}(\mathbf{X}_n;t)=\mathcal{P}_s\,\mathrm{Fcn}(\mathbf{X}_n;t)$.

Now, following Zwanzig,[13,14] the following identity may be obtained from the Liouville equation:

$$\partial_t[\bar{\mathcal{P}}_sf_n(\mathbf{X}_n;t|\mathbf{X}_{s0})]=\bar{\mathcal{P}}_sL[\mathcal{P}_sf_n]$$
$$+\int_0^t d\tau\bar{\mathcal{P}}_sLe^{\tau(1-\mathcal{P}_s)L}(1-\mathcal{P}_s)Lf_n(t-\tau)$$
$$+\bar{\mathcal{P}}_sLe^{t(1-\mathcal{P}_s)L}(1-\mathcal{P}_s)f_n(\mathbf{X}_n;0|\mathbf{X}_{s0}). \tag{2.6}$$

However (cf. Appendix A),

$$f_n(\mathbf{X}_n;0|\mathbf{X}_{s0})=[f_{\mathrm{eq}}{}^{[n]}(\mathbf{X}_n)/f_{\mathrm{eq}}{}^{[s]}(\mathbf{X}_s)]\prod_{i=1}^{s}\delta^6(\mathbf{x}_i-\mathbf{x}_{i0})$$
$$=f_{n|s}\prod_{i=1}^{s}\delta^6(\mathbf{x}_i-\mathbf{x}_{i0}), \tag{2.7}$$

so that, in virtue of Eq. (2.5), the inhomogeneous term appearing in Eq. (2.6) vanishes. (In the following discussion, it will be assumed that $f_{\mathrm{eq}}{}^{[n]}(\mathbf{X}_n)$ is the canonical density, i.e., that the system, taken as a whole, is in equilibrium.)

As a consequence of Eqs. (2.4), further simplification ensues. The first term on the right-hand side of Eq. (2.6) becomes

$$\bar{\mathcal{P}}_sL\mathcal{P}_sf_n(\mathbf{X}_n;t|\mathbf{X}_{s0})=\left\{-\sum_{i=1}^{s}\frac{\mathbf{p}_i}{m}\cdot\frac{\partial}{\partial\mathbf{q}_i}\right.$$
$$\left.+\tfrac{1}{2}\sum_{i\neq k}^{s}\sum^{s}\frac{\partial}{\partial\mathbf{q}_i}V_{ij}\cdot\left(\frac{\partial}{\partial\mathbf{p}_i}-\frac{\partial}{\partial\mathbf{p}_j}\right)-\sum_{i=1}^{s}\frac{\partial}{\partial\mathbf{q}_i}U^{[i]}\cdot\frac{\partial}{\partial\mathbf{p}_i}\right\}$$
$$\times f_s(\mathbf{X}_s;t|\mathbf{X}_{s0}). \tag{2.8}$$

The latter arises as follows: Remember that L is written as the sum of three terms. From the L_1 term

$$\bar{\mathcal{P}}_sL_1\mathcal{P}_sf_n=\int d\mathbf{x}_{s+1}\cdots d\mathbf{x}_n\left[\tfrac{1}{2}\sum_{i\neq j}^{n}\sum^{n}\frac{\partial}{\partial\mathbf{q}_i}V_{ij}\right.$$
$$\left.\cdot\left(\frac{\partial}{\partial\mathbf{p}_i}-\frac{\partial}{\partial\mathbf{p}_j}\right)\right]f_{n|s}f_s$$
$$=\tfrac{1}{2}\sum_{i\neq j}^{s}\sum^{s}\frac{\partial}{\partial\mathbf{q}_i}V_{ij}\cdot\left(\frac{\partial}{\partial\mathbf{p}_i}-\frac{\partial}{\partial\mathbf{p}_j}\right)f_s(t),$$

where

$$\int d\mathbf{x}_{s+1}\cdots d\mathbf{x}_n\left[\sum_{i=1}^{s}\sum_{j=s+1}^{n}\frac{\partial}{\partial\mathbf{q}_i}V_{ij}\cdot\frac{\partial}{\partial\mathbf{p}_i}\right]f_{n|s}=0$$

by virtue of integration over an odd function of the configurational coordinates. (To ensure that $f_{n|s}$ be a symmetric function of the interparticle coordinates, let it be assumed that the external field be zero for $t\leq0$.) The deduction of the L_0 and L_2 terms in Eqs. (2.8) is straightforward and follows from the assumption that $\bar{\mathcal{P}}$ integration of gradients of f_n yields zero-valued boundary terms.

Hence, in virtue of Eq. (2.8), the kinetic equation describing the evolution of the s-particle density is given by

$$\partial_tf_s(\mathbf{X}_s;t|\mathbf{X}_{s0})-[H_s;f_s]$$
$$=\bar{\mathcal{P}}_s\int_0^t d\tau Le^{\tau(1-\mathcal{P}_s)L}(1-\mathcal{P}_s)Lf_{n|s}$$
$$\times f_s(\mathbf{X}_s;t-\tau|\mathbf{X}_{s0}), \tag{2.9}$$

with initial condition

$$f_s(\mathbf{X}_s;0|\mathbf{X}_{s0})=\prod_{i=1}^{s}\delta(\mathbf{x}_i-\mathbf{x}_{i0}). \tag{2.10}$$

H_s is the reduced s-particle Hamiltonian; the brackets are the Poisson brackets.

The complicated non-Markoffian collision operator

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[14] R. W. Zwanzig, in *Lectures in Theoretical Physics* (*Boulder Lectures*) (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 106.

appearing on the right-hand side of the above equation accounts for the interaction of the s particle subsystem with the remaining n-s particles. Were there no such interaction, the collision integral would, indeed, be equal to zero, and the left-hand side of the equation would describe the temporal evolution of a probability density defined over a reduced, isolated, Γ space of $6s$ dimensions.

The effect of the operator defined by Eq. (2.5) is to project the initial distribution into the collision kernel; although at first glance only the s-particle probability density seems to appear in the collision integral, in reality, a modified n-body problem persists. However, an advantage to obtaining the kinetic information in this way is that, because L operators in the collision integral occur always multiplied by $f_{n|s}$, coefficients appearing in potential energy expansions of the kernel will be finite even for intermolecular potentials containing hard core repulsive terms.

b. Simplification of the Collision Integral for $f_1(x_1;t|x_{1_0})$

Attention shall now be focused upon the kinetic equation for the one-particle time-relaxed density in the absence of external forces. From Eq. (2.9), the temporal evolution of $f_1(\mathbf{x}_1;t|\mathbf{x}_{1_0})$ is seen to be determined by

$$\partial_t f_1(\mathbf{x}_1;t|\mathbf{x}_{1_0})+\frac{\mathbf{p}_i}{m}\cdot\frac{\partial}{\partial\mathbf{q}_i}f_1 =\bar{\mathcal{P}}\int_0^t d\tau e^{+\tau L(1-\mathcal{P})}L(1-\mathcal{P})Lf_{n|1}f_1(t-\tau) \equiv I[f_1], \quad (2.11)$$

where

$$\bar{\mathcal{P}}\equiv\int d\mathbf{x}_2\cdots d\mathbf{x}_n,$$

$$f_{n|1}\equiv(Z_{qn}/\Omega)^{-1}e^{-\beta V(\mathbf{q}_1,\cdots,\mathbf{q}_n)}\prod_{i=2}^n f_{\mathrm{eq}}(\mathbf{p}_i),$$

and

$$\mathcal{P}\equiv f_{n|1}\bar{\mathcal{P}}. \quad (2.12)$$

Also, for the initial condition,

$$f_1(\mathbf{x}_1;0|\mathbf{x}_{1_0})=\delta^6(\mathbf{x}_1-\mathbf{x}_{1_0}). \quad (2.13)$$

The collision integral appearing in Eq. (2.11) may be expanded as a series of terms which successively demonstrate increasing orders of the strength of interactions between particles. First, employ the following identity:

$$e^{\alpha(A+B)}=e^{\alpha A}\left[1+\int_0^\alpha d\beta e^{-\beta A}Be^{+\beta(A+B)}\right] \quad (2.14)$$

to obtain

$$\begin{aligned}I[f_1]=\bar{\mathcal{P}}\int_0^t d\tau_1 e^{\tau_1 L_0(1-\mathcal{P})}L(1-\mathcal{P})Lf_{n|1} &\times f_1(\mathbf{x}_1:t-\tau|\mathbf{x}_{1_0})+\bar{\mathcal{P}}\int_0^t d\tau_1 e^{\tau_1 L_0(1-\mathcal{P})}\\ &\times\int_0^{\tau_1} d\tau_2 e^{-\tau_2 L_0(1-\mathcal{P})}L_1(1-\mathcal{P})e^{\tau_2 L_0(1-\mathcal{P})}\\ &\times L(1-\mathcal{P})Lf_{n|1}f(t-\tau)+\cdots. \quad (2.15)\end{aligned}$$

Next, noticing that[15]

$$\bar{\mathcal{P}}e^{\tau L_0(1-\mathcal{P})}=\bar{\mathcal{P}}, \quad (2.16)$$

$$e^{\tau L_0(1-\mathcal{P})}=[e^{\tau L_0}(1-\mathcal{P})+\mathcal{P}], \quad (2.17)$$

and

$$\mathcal{P}L_1 e^{-\beta V(\mathbf{q}_1,\cdots,\mathbf{q}_n)}f_1(\mathbf{x}_1;t|\mathbf{x}_{1_0})=0, \quad (2.18)$$

after performing the following coordinate transformation

$$\xi_i\equiv(\mathbf{q}_i-\mathbf{q}_1), \quad i\neq 1, \quad (2.19)$$

one finds that the integral can be written as an infinite series of terms,

$$I[f_1]=\sum_{r=1}^{\infty}I^{[r]}[f_1(\mathbf{x}_1:t|\mathbf{x}_{1_0})] \quad (2.20)$$

such that, for $r>1$,

$$\begin{aligned}I^{[r]}\equiv\Big\{\bar{\mathcal{P}}(\Xi)\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2\cdots\int_0^{\tau_{r-1}}d\tau_r\mathcal{L}_1(\Xi)\{\exp[(\tau_2-\tau_3)\mathcal{L}_0^+(\Xi)](1-\mathcal{P}(\Xi))\}\\ \times\mathcal{L}_1\{\exp[(\tau_3-\tau_4)\mathcal{L}_0^+]\mathcal{S}_{-(\tau_3-\tau_4)}(1-\mathcal{P})\}\cdots\mathcal{L}_1\{\exp[(\tau_{r-1}-\tau_r)\mathcal{L}_0^+]\mathcal{S}_{-(\tau_{r-1}-\tau_r)}(1-\mathcal{P})\}\\ \times\mathcal{L}_1[\exp(\tau_r\mathcal{L}_0^+)\mathcal{S}_{-\tau_r}(1-\mathcal{P})]\mathcal{L}(\Xi)\mathcal{L}^+(\Xi)f_{n|1}f_1(t-\tau)\Big\}, \quad (2.21)\end{aligned}$$

and, for $r=1$,

$$I^{[1]}=\bar{\mathcal{P}}(\Xi)\int_0^t d\tau\mathcal{L}(\Xi)\mathcal{L}^+(\Xi)f_{n|1}(\Xi)f_1(\mathbf{x}_1;t-\tau|\mathbf{x}_{1_0}). \quad (2.21a)$$

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[15] The first of these relationships is established as follows: $\bar{\mathcal{P}}e^{\tau L_0(1-\mathcal{P})}=\bar{\mathcal{P}}[1+\tau L_0(1-\mathcal{P})+\frac{1}{2}\tau^2 L_0(1-\mathcal{P})L_0(1-\mathcal{P})+\cdots]$. But $\partial/\partial\mathbf{q}_i$, $i\neq 0$, yields boundary terms which $\rightarrow 0$ as the volume of the system, Ω, $\rightarrow\infty$. Thus, $\bar{\mathcal{P}}L_0(1-\mathcal{P})=\bar{\mathcal{P}}(-(\mathbf{p}_1/m)\cdot(\partial/\partial\mathbf{q}_1))\times(1-\mathcal{P})=0$, in virtue of $\bar{\mathcal{P}}\mathcal{P}=\bar{\mathcal{P}}$. Similarly, $\bar{\mathcal{P}}L_0^n(1-\mathcal{P})=0$. Thus, the identity Eq. (2.16) is established. Equation (2.17) is established in a similar way. Equation (2.18) holds because $V(\mathbf{q}_1,\cdots,\mathbf{q}_n)$ is an even function of the interparticle coordinates, whereas L_1 is an odd function of these variables.

In the above expressions,

$$\mathcal{L}(\boldsymbol{\Xi})\equiv\mathcal{L}_0(\boldsymbol{\Xi})+\mathcal{L}_1(\boldsymbol{\Xi})\,;\quad \mathcal{L}^+(\boldsymbol{\Xi})\equiv\mathcal{L}_0^+(\boldsymbol{\Xi})+\mathcal{L}_1(\boldsymbol{\Xi}) \tag{2.22}$$

with

$$\mathcal{L}_0(\boldsymbol{\Xi})\equiv-\sum_{i=2}^{n}\frac{(\mathbf{p}_i-\mathbf{p}_1)}{m}\cdot\frac{\partial}{\partial\xi_i}-\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}, \tag{2.23a}$$

$$\mathcal{L}_1(\Xi)\equiv-\sum_{j\neq1}\frac{\partial}{\partial\xi_j}\phi(\xi_j)\cdot\left(\frac{\partial}{\partial\mathbf{p}_1}-\frac{\partial}{\partial\mathbf{p}_j}\right)+\tfrac{1}{2}\sum_{i\neq j\neq1}\sum\frac{\partial}{\partial\xi_j}\phi(|\xi_i-\xi_j|)\cdot\left(\frac{\partial}{\partial\mathbf{p}_i}-\frac{\partial}{\partial\mathbf{p}_j}\right), \tag{2.23b}$$

and

$$\mathcal{L}_0^+(\boldsymbol{\Xi})\equiv\mathcal{L}_0(\boldsymbol{\Xi})+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}. \tag{2.23c}$$

It is to be noted that $f_{n|1}(\boldsymbol{\Xi})$ depends only on the coordinates of particles $2\rightarrow n$.

$\mathcal{S}_{-\tau}$ is the streaming operator (Taylor's series operator),

$$\mathcal{S}_{-\tau}\equiv\exp\left(-\tau\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}\right) \tag{2.24}$$

having the property that, when acting upon a function of $\mathbf{q}_1$, $\mathbf{p}_1$, t, $\mathcal{S}_{-\tau}\,\mathrm{fcn}(\mathbf{q}_1;\mathbf{p}_1)=\mathrm{fcn}[\mathbf{q}_1-(\mathbf{p}_1\tau/m);\mathbf{p}_1]$. $\bar{\mathcal{P}}(\boldsymbol{\Xi})$ is defined by

$$\bar{\mathcal{P}}(\boldsymbol{\Xi})\equiv\int d\xi_2\cdots d\xi_n d\mathbf{p}_2\cdots d\mathbf{p}_n, \tag{2.25}$$

there being similar definitions for $\mathcal{P}(\boldsymbol{\Xi})$ and $f_{n|1}(\boldsymbol{\Xi})$. As a consequence of performing the transformation, $f_{n|1}$ is not a function of $\mathbf{x}_1$. This latter property will be of considerable aid in the following analysis.

One must yet determine criteria for grouping various terms in the collision integral series, Eq. (2.20). The identification of necessary expansion parameters is, of course, one of the desired results of this study. In this respect, it may be asserted *a posteriori* that further reduction of interaction terms will demonstrate the intrinsic importance of constants of the following form:

$$\int d\xi_2\cdots d\xi_k g_k(\xi_2,\cdots,\xi_k)\left\{\frac{\partial^{m_{2,1}}}{\partial\xi_2{}^{m_{2,1}}}\phi(\xi_2)\frac{\partial^{m_{2,2}}}{\partial\xi_2{}^{m_{2,2}}}\cdots\frac{\partial^{m_{k,f}}}{\partial\xi_k{}^{m_{k,f}}}\phi(\xi_k)\right\}. \tag{2.26}$$

$\phi(\xi)$ is the pair potential energy expressed as a function of the distance between particles and

$$g_k(\xi_2,\cdots,\xi_k)\equiv\frac{\Omega^{k-1}\int d\xi_{k+1}\cdots d\xi_n\exp[-\beta V(\xi_2,\cdots,\xi_n)]}{\int d\xi_2\cdots d\xi_n\exp[-\beta V(\xi_2,\cdots,\xi_n)]}. \tag{2.27}$$

It may now be asserted that the criterion for grouping terms according to interaction strength is that M, defined as the sum of the differentiation indexes appearing in Eq. (2.26), be the same for all members of the group. In other words, defining

$$M\equiv\sum_{j=2}^{k}\sum_{i=1}^{f}m_{j,i}, \tag{2.28}$$

all terms of the type (2.26) for which M is the same are of equal "strength."

To readily see that all terms in the same group are indeed of equal magnitude, make the approximation $g_k\propto\exp-\beta V(\xi_2,\cdots,\xi_k)$; in this case, simple partial integration shows the equivalence of seemingly different expressions.

Consider further simplification of the collision integral. Because $\mathcal{P}(\boldsymbol{\Xi})\partial/\partial\xi_i$ yields boundary terms in ξ_i which are zero in the limit of volume of the assembly growing large, $\bar{\mathcal{P}}(\boldsymbol{\Xi})\mathcal{L}_0{}^+f_{n|1}=0$, so that, from Eq. (2.21a),

$$I^{[1]}[f_1]=\bar{\mathcal{P}}(\boldsymbol{\Xi})\int_0^t d\tau\left(\mathcal{L}_1-\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}\right)\mathcal{L}f_{n|1}f_1(t-\tau). \tag{2.29}$$

Let us now impose the following lemma (which arises from the fact that $(\partial/\partial\xi_j)\phi(|\xi_j-\xi_k|)$ is an odd function in the variables $(|\xi_j-\xi_k|)$, whereas $f_{n|1}(\boldsymbol{\Xi})$ is an even function of these variables).

Lemma: If

$$Q \equiv \bar{\mathcal{P}}(\boldsymbol{\Xi})[\mathcal{L}_1(\boldsymbol{\Xi})\mathcal{L}_0^+(\boldsymbol{\Xi})\mathcal{L}_0^+\cdots \mathcal{L}_1\mathcal{L}_1\mathcal{L}_0^+\cdots]f_{n|1}(\boldsymbol{\Xi}) \tag{2.30}$$

is to be nonzero, the integer representing the number of times that $\mathcal{L}_1$ terms appear, when added to the integer signifying the number of times $\mathcal{L}_0^+$ appears, must be even.

In virtue of this requirement, noting also that $\bar{\mathcal{P}}\partial/\partial\mathbf{p}_i \Rightarrow 0$ for $i \neq 1$ and remembering that all particles have been assumed to be alike, it can be readily shown that

$$I^{[1]}[f_1(t)] = c\int_0^t d\tau\left[\eta(2)\left(\nabla_{p_1}{}^2 + \frac{\tau}{m}\nabla_{p_1,q_1}{}^2\right) + \frac{\chi(2)}{m}\operatorname{div}_{p_1}\mathbf{p}_1\right]f(t-\tau), \tag{2.31}$$

where

$$\eta(2) \equiv \int d\xi g_2(\xi)\left(\frac{\partial\phi(\xi)}{\partial\xi_x}\right)^2, \tag{2.32}$$

$$\chi(2) \equiv \int d\xi g_2(\xi)\frac{\partial^2}{\partial\xi_x{}^2}\phi(\xi), \tag{2.33}$$

and c is the average density of particles in the assembly.

However, $I^{[1]}[f_1]$ is not the complete first-order contribution to the collision integral. From $I^{[2]}$ one also finds a term

$$^0I_1{}^{[2a]} + {}^0I_2{}^{[2a]} \equiv \bar{\mathcal{P}}(\boldsymbol{\Xi})\int_0^t d\tau_1 \times \int_0^{\tau_1} d\tau_2 \mathcal{L}\mathcal{S}_{-\tau_2}\mathcal{L}_0\mathcal{L}^+(\boldsymbol{\Xi})f_{n|1}f_1(t-\tau). \tag{2.34}$$

Thus, adding Eq. (2.34) to Eq. (2.31) provides the following first-order kinetic equation,

$$\frac{\partial f_1}{\partial t} + \frac{\mathbf{p}_1}{m}\cdot\frac{\partial f_1}{\partial\mathbf{q}_1} = c\int_0^t d\tau\left[\eta(2)\left(\nabla_{p_1}{}^2 + \frac{\tau}{m}\nabla_{p_1,q_1}{}^2\right) + \frac{\chi(2)}{m}\operatorname{div}_{p_1}\mathbf{p}_1\right]\mathcal{S}_{-\tau}f_1(t-\tau). \tag{2.35}$$

Calculation of the second-order contribution to the kinetic integral is considerably more complicated.[16] However, one can observe the general form of higher order terms even if analytic complexity precludes their explicit evaluation. It is found that the expansion of the integral term may be written as

$$I = \sum_{k=1}^{\infty}\mathfrak{M}_{[2k]}\int_0^t d\tau\frac{\tau^{(2k-2)}}{(2k-2)!}\operatorname{Op}^{[k]}\left(\mathbf{p}_1; \frac{\partial}{\partial\mathbf{p}_1}; \frac{\tau}{m}\frac{\partial}{\partial\mathbf{q}_1}\right) \times \mathcal{S}_{-\tau}f_1(t-\tau), \tag{2.36}$$

where $\mathfrak{M}_{[2k]}$ are system constants for which $M=2k$, and $\operatorname{Op}^{[k]}$ are derivative operators similar to those appearing in Eq. (2.31). Powers of τ in the integrals increase directly with increasing powers of M. Terms in the $\operatorname{Op}^{[k]}$ which do not contain derivatives with respect to spatial coordinates do not contain the time τ explicitly. Spatial terms in the operators appear only as powers of derivatives with respect to $\mathbf{q}_1$. Furthermore, every derivative term in $\mathbf{q}_1$ is always coupled with a factor (τ/m).

It is to be remarked that the expansions for probability densities and correlation functions to be obtained in the following sections will not be power series in any single parameter. There is no simple parameter available to characterize the interactions between particles; rather, expressions will contain the complicated parameters of the type defined by (2.26). Notice that the latter, however, exist even for potentials having strong repulsive parts. Due to the presence of the g_k's in the integrand, one need not resort to cutoff procedures to insure the finiteness of these expansion quantities. Consequently, the individual terms in the collision integral expansion will also be finite.

One wishes to apply these calculations to assemblies for which interparticle forces are characterized by a hard repelling core plus short-range attracting "tail." For systems with complex force laws, it is impossible to determine the exact relationships between system constants of successively higher order. However, if one makes the following approximation for $g_2(\rho)$, which corresponds to an infinitely strong repulsive core

$$g_2(\rho) \propto \begin{cases} 0 & \text{for} \quad \rho \leq \rho_0, \\ e^{\beta\phi_a} & \text{for} \quad \rho > \rho_0, \end{cases} \tag{2.37}$$

then, for example, the following typical ratio of a fourth-order term to a second-order term would be[17]:

$$\mu(4,x)/\eta(2) = \int d\xi g_2(\xi)[F_x(\xi)]^4 \bigg/ \int d\xi g_2(\xi)[F_x]^2 = o(\epsilon_0{}^2), \tag{2.38}$$

where ϵ_0 is the depth of the attractive potential well. To be more explicit, in expansions for slow neutron scattering cross sections [cf. Eq. (4.7) below], for example, where it is necessary to compare terms proportional to $\eta(2)$ with those proportional to $\beta^2\mu(4,x)/k^2$, the pertinent expansion parameter is effectively $\beta\epsilon_0$.[18]

III. SOLUTION OF THE KINETIC EQUATION FOR $f_1(x_1;t|x_{1_0})$; RELATED PROBABILITY DENSITIES AND CORRELATION FUNCTIONS

a. Solution of the First-Order Kinetic Equation

It is interesting to see whether the approximate kinetic equation for f_1, i.e., that equation obtained by

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[16] The second-order expression pertinent to an equation for the one-particle *momentum* density is presented in Appendix B, below.

[17] $\mu(4,x)$ is one of the system constants characterizing interaction strengths of fourth order. See Appendix B, below.

[18] $\mathbf{k}$ is the wave-number related to the momentum transfer experienced by the scattered neutron.

retaining only the first-order term in the potential-energy expansion of the collision integral, can properly demonstrate relaxation processes which are expected to occur in the assembly. Specifically, let us consider the behavior of momentum densities and associated correlation functions when obtained from Eq. (2.35).

The time-relaxed momentum density may be obtained from the general μ-space density by integration over spatial coordinates

$$\Phi(\mathbf{p}_1;t|\mathbf{p}_{1_0})=\lim_{\Omega\to\infty}\frac{1}{\Omega}\int_\Omega d\mathbf{q}_1 d\mathbf{q}_{1_0} f_1(\mathbf{x}_1;t|\mathbf{x}_{1_0})\,. \quad (3.1)$$

(Thus, Φ is the conditional probability density that a particle will have its momentum in the neighborhood of $\mathbf{p}_1$ at time t, given that at $t=0$ its momentum was $\mathbf{p}_{1_0}$.) In virtue of Eq. (3.1) and Eq. (2.35), the following kinetic equation for Φ is obtained[19]:

$$\left\{\frac{\partial^2}{\partial t^2}-c\left[\eta(2)\nabla_p{}^2+\frac{\chi(2)}{m}\operatorname{div}_p\mathbf{p}\right]\right\}\Phi(t)=0\,, \quad (3.2)$$

with initial condition

$$\Phi(0)=\delta^3(\mathbf{p}-\mathbf{p}_0)\,. \quad (3.3)$$

The solution of the latter equation provides

$$\Phi(t)=\cosh\{ct^2[\eta(2)\nabla_p{}^2+\chi(2)/m\operatorname{div}_p\mathbf{p}]\}^{1/2} \times\delta^3(\mathbf{p}-\mathbf{p}_0)\,, \quad (3.4)$$

valid for all $t\geq 0$.

One can use this expression to calculate the momentum auto-correlation function, $\pi(t)$, which is defined by

$$\pi(t)\equiv\langle\mathbf{p}_1(0)\cdot\mathbf{p}_1(t)\rangle$$
$$=\int d\mathbf{p}_0 d\mathbf{p}(\mathbf{p}\cdot\mathbf{p}_0)\{(2\pi mkT)^{-3/2}\exp(-\beta p_0{}^2/2m)\} \times\Phi(\mathbf{p};t|\mathbf{p}_0)\,. \quad (3.5)$$

Physical arguments require that, for interacting particles,

$$\lim_{t\to\infty}\pi(t)\to 0\,. \quad (3.6)$$

But, from Eq. (3.4), one obtains

$$\pi(t)=(3m/\beta)\cos\{[c\chi(2)/m]^{1/2}t\} \quad (3.7)$$

which violates the condition given by Eq. (3.6). This suggests that simple coupling-constant expansions suffer not only from the logical difficulties already mentioned in Sec. I but, additionally, may also fail to provide mechanisms necessary to describe the relaxation of the assembly being considered.

b. Kinetic Equation to Higher Orders

Since the truncated equation, Eq. (2.35), is seen to be unsatisfactory for certain applications, there is reason to focus attention on the general kinetic equation. The latter may be written as

$$\left(\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}\right)f_1=\sum_{i=0}^{\infty}J_i[f_1(t)]\,, \quad (3.8)$$

where the J_i are terms of the "potential-energy expansion," ordered according to increasing powers of the ratio of potential to kinetic energies. [$J_0=0$, J_1 is given by the expression on the right-hand side of Eq. (2.35), J_2 appears explicitly in Appendix B, below.]

One may search for an iteration solution to Eq. (3.7) having the form

$$f_1(\mathbf{x}_1;t|\mathbf{x}_{1_0})=f_1{}^{[0]}+f_1{}^{[1]}+f_1{}^{[2]}+\cdots=\sum_{i=0}^{\infty}f_1{}^{[i]}\,, \quad (3.9)$$

where $f_1{}^{[0]}$ is the expression to be obtained if the assembly were an ideal gas, and $f_1{}^{[1]}$, $f_1{}^{[2]}$, $\cdots$ represent successively higher order corrections to account for interactions between members of the assembly.

Thus, the zeroth term of f_1 is given by the solution of

$$\left(\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}\right)f_1{}^{[0]}=J_0[f_1]=0 \quad (3.10)$$

taken with the initial condition

$$f_1{}^{[0]}(0)=\delta^6(\mathbf{x}_1-\mathbf{x}_{1_0})\,. \quad (3.11)$$

The first correction is obtained by solving

$$\left(\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}\right)f_1{}^{[1]}=J_1[f_1{}^{[0]}]\,, \quad (3.12)$$

subject to the initial condition

$$f_1{}^{[1]}(0)\equiv 0\,,\quad \text{for all } \mathbf{x}_1\,. \quad (3.12')$$

Similarly, the second-order correction is provided by

$$\left(\frac{\partial}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial}{\partial\mathbf{q}_1}\right)f_1{}^{[2]}=J_2[f_1{}^{[0]}]+J_1[f_1{}^{[1]}]\,, \quad (3.13)$$

with the initial condition

$$f_1{}^{[2]}(0)\equiv 0\,. \quad (3.13')$$

Higher order terms may be found from similar equations.

These kinetic equations may be solved by taking Fourier-Laplace transforms and then inverting the resulting expressions. For $f_1{}^{[0]}$, one readily finds the expected, ideal-gas result

$$f_1{}^{[0]}(\mathbf{x}_1;t|\mathbf{x}_{1_0})=\delta(\mathbf{q}_1-\mathbf{q}_{1_0}-\mathbf{p}_1t/m)\delta(\mathbf{p}_1-\mathbf{p}_{1_0})\,. \quad (3.14)$$

Of somewhat greater complexity, $f_1{}^{[1]}$ is found to be

$$f_1{}^{[1]}(\mathbf{x}_1;t|\mathbf{x}_{1_0})=ct^2\left\{\eta(2)\left[\delta^q(t)\nabla_p{}^2\delta^p-\frac{t}{m}\nabla_q\delta^q\cdot\nabla_p\delta^p+\frac{t^2}{4m^2}\delta^p\nabla_q{}^2\delta^q\right]+\chi(2)\left[\left(\operatorname{div}_p-\frac{2t}{3m}\operatorname{div}_q\right)\times\mathbf{p}\delta^q\delta^p\right]\right\}\,, \quad (3.16)$$

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[19] In the remainder of this section, the subscript (1) is to be understood.

with

$$\delta^p \equiv \delta^3(\mathbf{p}-\mathbf{p}_0)\,; \quad \delta^q \equiv \delta^3(\mathbf{q}-\mathbf{q}_0)\,.$$

Higher order terms could be calculated in the same way, although it is apparent that they would be quite complicated.

Momentum densities can be found in direct correspondence with the series solution for f_1 [cf., Eq. (3.1)]. It is found that

$$\Phi(\mathbf{p};t|\mathbf{p}_0)=\{1+\tfrac{1}{2}ct^2[\eta(2)\nabla_p{}^2+\chi(2)/m\ \mathrm{div}_p\mathbf{p}] +t^4o(\epsilon_0{}^4)+\cdots\}\delta^3(\mathbf{p}-\mathbf{p}_0)\,. \quad (3.17)$$

The t^4 terms are readily obtained from the collision integrals listed in Appendix B. It is of primary interest that one finds that the t^4 term of the first truncated equation, Eq. (3.4), does not appear in the exact expansion because the contribution from $J_1[f_1{}^{[1]}]$ is just cancelled by a term from $J_2[f_1{}^{[0]}]$.

The momentum autocorrelation function [cf. Eq. (3.5)] is found to be, in correspondence with Eq. (3.17),

$$\pi(t)=3m\beta^{-1}\left\{1-\frac{ct^2}{2m}\chi(2)+\frac{3c^2t^4}{4!m^2}\chi(4)_3+\frac{ct^4}{24m^2} \times[-10\beta^{-1}\chi(4)+6\eta(4,xx)]+o(t^6,\epsilon_0{}^6)+\cdots\right\}, \quad (3.18)$$

with the system constants being defined by

$$\chi(4)_3\equiv\int d\xi_2\int d\xi_3 g_3(\xi_2,\xi_3)\frac{\partial^2}{\partial\xi_{2_x}{}^2}\phi(\xi_2)\frac{\partial^2}{\partial\xi_{3_x}{}^2}\phi(\xi_3)\,,$$

$$\chi(4)=\int d\xi g_2(\xi)\frac{\partial^4}{\partial\xi_x{}^4}\phi(\xi)\,, \quad (3.19)$$

$$\eta(4,xx)\equiv\int d\xi g_2(\xi)\frac{\partial}{\partial\xi_x}\phi(\xi)\frac{\partial^3}{\partial\xi_x{}^3}\phi(\xi)\,.$$

Note that if $\chi(4)_3$ is approximated by $[\chi(2)]^2$, $\pi(t)$ may be represented [to $o(t^4,\epsilon^4)$] by[20]

$$\pi(t)=3m\beta^{-1}\exp\{-ct^2\chi(2)/2m\} \times\cos\{c^{1/2}[\tfrac{5}{6}\beta^{-1}\chi(4)-\tfrac{1}{2}\eta(4,xx)]t^2/m\}\,. \quad (3.20)$$

By performing analyses which correspond to termination of expansion (3.17) at order ϵ^2t^2, other investigators[7,21] have already remarked that

$$\pi(t)\approx 3m\beta^{-1}\exp\{-ct^2\chi(2)/2m\}\,. \quad (3.21)$$

However, it is also known[7] that use of such an expression (purely Gaussian decay) to calculate the self-diffusion constant for simple liquids provides values which have correct orders of magnitude, but which are somewhat higher than experimentally observed quantities. It has been suggested that this discrepancy arises because Eq. (3.21) fails to account for negative correlations. On the other hand, the latter are well represented in Eq. (3.20), which has been obtained by retaining terms to higher order. This new form has the intuitively satisfying property of representing the autocorrelation function by a damped oscillatory decay.[22]

IV. SPATIAL DENSITIES AND CORRELATION FUNCTIONS

Spatial densities can also be obtained in direct correspondence with the expansion for $f_1(\mathbf{x}_1;t|\mathbf{x}_{1_0})$. In this section, consideration shall be given to $G_s(\mathbf{r},t)$, defined as the conditional probability density for finding a specified particle in the neighborhood of the configuration phase point $(\mathbf{q}_{1_0}+\mathbf{r})$ at time t, given that at $t=0$ the *same* particle was at $\mathbf{q}_{1_0}$.

Upon assuming that the systems under study are uniform and isotropic, G_s does not depend on $\mathbf{q}_{1_0}$; furthermore, G_s will be a function only of the absolute value of $\mathbf{r}$. Hence,

$$G_s(\mathbf{r},t)=\int d\mathbf{p}_1 d\mathbf{p}_{1_0}(2\pi mkT)^{3/2}e^{-\beta p_0{}^2/2m} \times f_1(\mathbf{p}_1,\mathbf{q}_{1_0}+\mathbf{r};t|\mathbf{q}_{1_0},\mathbf{p}_{1_0}) =\sum_{i=0}^{\infty}G_s{}^{[i]}(r,t)\,, \quad (4.1)$$

with

$$G_s{}^{[i]}(r,t)\equiv\int d\mathbf{p}_1 d\mathbf{p}_0(2\pi mkT)^{3/2}e^{-\beta p_0{}^2/2m}f_1{}^{[i]}(\mathbf{p}_1,\mathbf{r};t|\mathbf{p}_0,0)\,. \quad (4.2)$$

Thus, for the zeroth (ideal gas) term,

$$G_s{}^{[0]}(r,t)=[m\beta/(2\pi t^2)]^{3/2}e^{-m\beta r^2/(2t^2)}\,. \quad (4.3)$$

The first-order correction, i.e., that through the second power of the forces, is found from Eq. (3.15) to be

$$G_s{}^{[1]}(r,t)=\frac{ct^4}{2m^2}\left[\frac{\eta(2)}{4}-\frac{\chi(2)}{3\beta}\right]\nabla_r{}^2G_s{}^{[0]}(r,t)\,. \quad (4.4)$$

Details of calculations of higher order terms may be found elsewhere.[23] The interesting point, however, is that it has been found that the expansion for $G_s(r,t)$ may be put in the form

$$G_s(r,t)=\sum_{n=0}^{\infty}t^{2n}D_R{}^{[n]}G_s{}^{[0]}(R,t)\,, \quad (4.5)$$

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[20] Further simplification ensues if one notices, particularly at high temperatures or low density, $\chi(4)\approx\beta\eta(4,xx)$. Then,

$$\pi(t)\approx 3m\beta^{-1}e^{-ct^2\chi(2)/(2m)}\cos[0.577c^{1/2}\chi(4)^{1/2}\beta^{-1}t^2/m].$$

[21] P. G. de Gennes, in *Proceedings of the Symposium on Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1960), p. 239.

[22] In a relatively dense medium, one would expect the average behavior of the particles to contain contributions representative of vibration as well as diffusion. After moving away from their initial positions, a certain number of particles would have their directions reversed as a consequence of interaction with the collective force field of neighboring particles. Such effects are clearly present in cell models of liquids. [For a more thorough discussion of these points, see the article by Rice (Ref. 7)].

[23] R. J. Nossal, dissertation, University of Michigan, 1963 (unpublished).

where

$$R\equiv(m\beta)^{1/2}r/t\,,\quad G_s^{[0]}(R,t)\equiv[m\beta/(2\pi t^2)]^{3/2}e^{-R^2/2} \tag{4.6}$$

and the $D_R^{[n]}$ are purely differential operators in R and are not explicit functions of t. The differential order of $D^{[n]}$ is $\leq 2n$.

One can use Eq. (4.5) to obtain an asymptotic inverse temperature expansion for the incoherent cross section for the scattering of low-energy neutrons. The quantum mechanical incoherent scattering function, $S_{\text{inc}}(\mathbf{k},\omega)$, is defined by

$$S_{\text{inc}}(\mathbf{k},\omega)=(2\pi)^{-1}\int d\mathbf{r}dte^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\mathcal{G}_s(\mathbf{r},t)\,, \tag{4.7}$$

with

$$\mathcal{G}_s(\mathbf{r},t)\equiv n^{-1}\Big\langle\sum_{j=1}^{n}\int d\mathbf{r}'\delta(\mathbf{r}+\mathbf{q}_j(0)-\mathbf{r}')\times\delta(\mathbf{r}'-\mathbf{q}_j(t))\Big\rangle\,. \tag{4.8}$$

Difficulty arises when trying to evaluate Eq. (4.7) because the delta functions in Eq. (4.8) do not commute. However, a classical approximation to the incoherent scattering function, denoted by $S_{\text{inc}}^{\text{cl}}(\mathbf{k},\omega)$, may be obtained from Eq. (4.7) by replacing $\mathcal{G}_s(\mathbf{r},t)$ by $G_s(\mathbf{r},t)$. Correspondingly, the classical approximation to the "intermediate scattering function" is defined as

$$\mathcal{I}_{\text{inc}}^{\text{cl}}(\mathbf{k},t)\equiv\int d\mathbf{r}e^{i\mathbf{k}\cdot\mathbf{r}}G_s(\mathbf{r},t)\,. \tag{4.9}$$

From Eq. (4.5) it is determined that

$$\mathcal{I}_{\text{inc}}^{\text{cl}}(\mathbf{k},t)=e^{-t^2k^2/(2m\beta)}\sum_{n=0}^{\infty}t^{2n}w^{[n]}(tk/(m\beta)^{1/2})\,, \tag{4.10}$$

where the $w^{[n]}(tk/(m\beta)^{1/2})$ are polynomials in $tk/(m\beta)^{1/2}$ which correspond to the $D^{[n]}$. For example, $w^{[n]}\sim -t^2k^2/(m\beta)$ corresponds to the differential operator $D_R^{[n]}\sim\nabla_R^2$.

It has been suggested that one of the reasons for investigating slow neutron scattering is to facilitate a deduction of the form of $G(r,t)$ for particular scattering systems. However, almost all analytic studies of this phenomenon[24,25] have provided expansions for $\mathcal{I}_{\text{inc}}(\mathbf{k},t)$ or $S_{\text{inc}}(\mathbf{k},\omega)$ and have not yielded $G_s(\mathbf{r},t)$ directly. Perhaps Eq. (4.5) and Eq. (4.10) will aid in the deduction of the latter from calculations already available for the scattering functions.

A number of studies[26,27] have been made in order to obtain the exact quantum scattering function in terms of corrections to the expression given by the classical approximation. Rosenbaum[26] has succeeded in expressing corrections to the classical scattering function as a power series in $\hbar^2$, having shown that

$$S_{\text{inc}}(\mathbf{k},\omega)=e^{\beta\hbar^2\omega/2}e^{-\beta\hbar k^2/(8m)}\times\bigg[S_{\text{inc}}^{\text{cl}}(\mathbf{k},\omega)+\frac{c\hbar^2\beta^2\chi(2)}{48}\Big(\frac{\beta}{2\pi mk^2}\Big)^{1/2}e^{-m\beta\omega^2/(2k^2)}\times\Big(1-\frac{\omega^2m\beta}{k^2}+\frac{\hbar^2k^2\beta}{8m}\Big)+o(\hbar^4)\bigg]\,. \tag{4.11}$$

Further investigation may now be made of the conditions under which Eq. (4.11) may be useful for the analysis of experiments. The expansion has not yet been explicitly developed beyond the second power in $\hbar$. However, it may be surmised that the exact scattering function can probably be expressed as a sum of terms, each of which is proportional to one of the system constants defined by (2.26), so that

$$\begin{aligned}S_{\text{inc}}(\mathbf{k},\omega)=e^{\beta\hbar\omega/2}e^{-\beta\hbar^2k^2/8m}[S_{\text{inc}}^{\text{cl}}(k,\omega)&\\+a_1(k,\hbar,\omega)\chi(2)+a_2(k,\hbar,\omega)\eta(2)&\\+a_3(k,\hbar,\omega)\chi(4)+\cdots\text{etc.}]\,.&\end{aligned} \tag{4.12}$$

Thus, for example, using Eq. (4.5) and Eq. (4.8), one finds

$$S_{\text{inc}}^{\text{cl}}(\chi,\omega)=\bigg[\frac{m}{(2\pi k^2)}\bigg]^{1/2}e^{-m\beta\omega^2/2k^2}\times\bigg[1+\frac{c}{24k^2}\Big(3-\frac{10m\beta\omega^2}{k^2}+\frac{m^2\beta^2\omega^4}{k^4}\Big)\chi(2)+\text{terms in the ``fourth power of the forces''}\bigg]\,. \tag{4.13}$$

[Here, the high-temperature limit has been taken, i.e., it has been assumed that $\eta(2)\approx\beta^{-1}\chi(2)$.] Hence, it is seen that the same system constants which demonstrate the deviation of $S_{\text{inc}}^{\text{cl}}$ from the form for an ideal gas are also intimately involved in expressing the intrinsic quantum nature of the scattering process. To be consistent, one must keep terms in the $\hbar$ series expansion to the same order in coupling constant as is needed to express $G_s^{\text{cl}}(r,t)$ to a given accuracy.

Consequently, it must be concluded that generally it is impossible to separate quantum effects in the cross section from contributions due to interactions between particles. For example, upon inserting Eq. (4.12) into

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[24] P. Schofield, in *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1960), p. 39.

[25] M. Nelkin, in *Proceedings of the Symposium on Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1960) p. 3.

[26] M. Rosenbaum, dissertation, University of Michigan, 1963 (unpublished); see also, R. Aamodt, K. M. Case, M. Rosenbaum, and P. F. Zweifel, Phys. Rev. **126**, 1165 (1962).

[27] K. Singwi and A. Sjölander, Phys. Rev. **120**, 1093 (1960).

Eq. (4.11), it is found that

$$S_{\mathrm{inc}}(\mathbf{k},\omega)=[m\beta/(2\pi k^2)]^{1/2}e^{\beta\hbar\omega/2}e^{-\beta\hbar^2k^2/8m}$$

$$\times\left[1+\frac{c\beta\chi(2)}{24k^2}\left(3-\frac{10m\beta\omega^2}{k^2}+\frac{m^2\beta^2\omega^4}{k^4}\right)\Delta_2(k,\omega,\beta)\right.$$

$$\left.+o(\hbar^4,\omega^4)+\cdots\right].\quad(4.14)$$

In the above expression,

$$\Delta_2(k,\omega,\beta)\equiv\left\{1+\frac{\beta\hbar^2k^2}{2m}\left[\frac{1-\omega^2m\beta/(k^2)+\hbar^2k^2\beta/8m}{3-10m\beta\omega^2/(k^2)+m^2\beta^2\omega^4/k^4}\right]\right\}\quad(4.15)$$

represents the quantum deviation of the second term in the scattering function. It would be unity only if no correction were necessary.

Yet, it is also seen from Eq. (4.15) that for small momentum and energy transfer, for which $\beta\hbar^2k^2/2m\ll1$, quantum corrections to the scattering function are much less significant than the normal corrections due to interactions between particles. Under those conditions, Eq. (4.11) offers a useful approximation.

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APPENDIX A: INITIAL CONDITIONS

In the preceding analysis, the following expression was asserted as the initial condition for the n-particle density [cf., Eq. (2.7)]:

$$f_n(\mathbf{X}_n;0|\mathbf{X}_{s0})=[f_{\mathrm{eq}}{}^{[n]}(\mathbf{x}_1,\cdots,\mathbf{x}_n)/f_{\mathrm{eq}}{}^{[s]}(\mathbf{x}_1,\cdots,\mathbf{x}_s)]\times\prod_{i=1}^{s}\delta(\mathbf{x}_i-\mathbf{x}_{i0}).\quad(\mathrm{A1})$$

The choice of this function shall now be justified.

It is certainly true that

$$f_n(\mathbf{X}_n;0|\mathbf{X}_{n0})=\prod_{i=1}^{n}\delta(\mathbf{x}_i-\mathbf{x}_{i0}).\quad(\mathrm{A2})$$

Hence, as a consequence of the following general relationship for conditional probability densities

$$f_{X|Y}(x|y)=\int f_{X|Y,Z}(x|y,z)f_{Z|Y}(z|y)dz,\quad(\mathrm{A3})$$

it follows that

$$f_n(\mathbf{X}_n;0|\mathbf{X}_{s0})=\int d\mathbf{x}_{s+1_0}\cdots d\mathbf{x}_{n0}f_n(\mathbf{X}_n;0|\mathbf{X}_{n0})\times f_{n|s}{}^{[\mathrm{eq}]}(\mathbf{x}_{s+1_0},\cdots,\mathbf{x}_{n0}|\mathbf{X}_{s0}).\quad(\mathrm{A4})$$

$f_{n|s}{}^{[\mathrm{eq}]}(\mathbf{x}_{s+1},\cdots,\mathbf{x}_n|\mathbf{X}_s)$ is the equilibrium conditional full-system probability density for finding particles $(s+1,\cdots,n)$ in the neighborhood of $(\mathbf{x}_{s+1},\cdots,\mathbf{x}_n)$, given that particles $(1,\cdots,s)$ are located at $(\mathbf{x}_1,\cdots,\mathbf{x}_s)$, respectively.

But,

$$f_{n|s}{}^{[\mathrm{eq}]}(\mathbf{x}_{s+1_0},\cdots,\mathbf{x}_{n0}|\mathbf{X}_{s0})=f_{\mathrm{eq}}{}^{[n]}(\mathbf{X}_{n0})/f_{\mathrm{eq}}{}^{[s]}(\mathbf{X}_{s0}),\quad(\mathrm{A5})$$

where $f_{\mathrm{eq}}{}^{[s]}(\mathbf{X}_{s0})$ is defined by

$$f_{\mathrm{eq}}{}^{[s]}(\mathbf{X}_{s0})\equiv\int d\mathbf{x}_{s+1_0}\cdots d\mathbf{x}_{n0}f_{\mathrm{eq}}{}^{[n]}(\mathbf{X}_{n0}).\quad(\mathrm{A6})$$

Therefore, in virtue of Eq. (A2) and Eq. (A5),

$$f_n(\mathbf{X}_n;0|\mathbf{X}_{s0})=[f_{\mathrm{eq}}{}^{[n]}(\mathbf{x}_{1_0},\cdots,\mathbf{x}_{s0},\mathbf{x}_{s+1},\cdots,\mathbf{x}_n)/f_{\mathrm{eq}}{}^{[s]}(\mathbf{X}_{s0})]\prod_{i=1}^{s}\delta(\mathbf{x}_i-\mathbf{x}_{i0}).\quad(\mathrm{A7})$$

But the delta function really has meaning only as a distribution, i.e., as a weight factor in a definite integral taken over the space on which the argument of the delta function is defined. Consequently,

$$f(x)\delta(x-a)=f(a)\delta(x-a)\quad(\mathrm{A8})$$

which, when taken with Eq. (A7), is justification for the choice of the expression given by Eq. (A1).

APPENDIX B: SECOND-ORDER COLLISION TERMS

The kinetic equation for the one-particle momentum density may be written as follows:

$$\partial_t\Phi(\mathbf{p}_1;t|\mathbf{p}_{1_0})=\sum_{i=0}^{\infty}\bar{J}_i(\Phi;t),\quad(\mathrm{B1})$$

where [cf., Eq. (3.10), Eq. (2.35)],

$$\bar{J}_0=0\quad(\mathrm{B2a})$$

$$\bar{J}_1=c\int_0^t d\tau(\eta(2)\nabla_{p1}{}^2+\chi(2)/m\,\mathrm{div}_{p1}\mathbf{p}_1]\Phi_1(t-\tau).\quad(\mathrm{B2b})$$

The second-order terms have been found to be[28]

$$\bar{J}_2 = m^{-3}\int_0^t d\tau\left(\tfrac{1}{2}\tau^2\right)\left[c\mathcal{A}_2 + c^2\mathcal{B}_2\right]\Phi(t-\tau)\,, \tag{B3}$$

where $\mathcal{A}_2$ and $\mathcal{B}_2$ are defined as follows:

If one designates

$$\theta_1 \equiv \mathrm{div}_{p_1}\mathbf{p}_1\,;\quad \theta_2 \equiv \nabla_{p_1}{}^2\,;\quad \theta_3 \equiv (5m\beta^{-1}+p_1{}^2)\,, \tag{B4}$$

then $\mathcal{A}_2$ and $\mathcal{B}_2$ can be expressed as

$$\begin{aligned}\mathcal{A}_2 = {} & \chi(4)[\theta_1\theta_3] + \tfrac{2}{3}\eta(4,xx)[2\theta_2\theta_3 + 4\theta_1{}^2 - 5\theta_1] \\ & + \chi(2,xy;2,xy)[3\theta_2\theta_3 - 3m\beta^{-1}\theta_2 + 3\theta_1{}^2 - \theta_1] \\ & + \chi(2,xx;2,xx)[3m\beta^{-1}\theta_2 + 3\theta_1{}^2 + \theta_1] \\ & + m^2\Psi(4,xx)[7\theta_2\theta_1 - 24\theta_2] - m^2\Psi(4,xy,xy)[2\theta_1\theta_2] \\ & + m^2\mu(4,x)\theta_2{}^2\end{aligned} \tag{B5}$$

and

$$\begin{aligned}\mathcal{B}_2 = {} & \chi(4)_3[3\theta_1{}^2] + m^2\Psi(4)_3[6\theta_2\theta_1] - 3\theta_2] \\ & + m^2\mu(4)_3[3\theta_2{}^2] - m[\chi(2)\theta_1 + m\eta(2)\theta_2]^2\,.\end{aligned} \tag{B6}$$

The system constants appearing in the above expressions have the following definitions:

$$\begin{aligned}\chi(2,xy;2,xy) &\equiv \int d\xi g_2(\xi)\left[\frac{\partial^2\phi(\xi)}{\partial\xi_x\partial\xi_y}\right]^2 \\ \chi(2,xx;2,xx) &\equiv \int d\xi g_2(\xi)\left[\frac{\partial^2\phi(\xi)}{\partial\xi_x{}^2}\right]^2 \\ \Psi(4;xx) &\equiv \int d\xi g_2(\xi)\frac{\partial^2\phi}{\partial\xi_x{}^2}[F_x(\xi)]^2 \\ \Psi(4,xy;4,xy) &\equiv \int d\xi g_2(\xi)\frac{\partial^2\phi}{\partial\xi_x{}^2}[F_y(\xi)]^2 \\ \mu(4,x) &\equiv \int d\xi g_2(\xi)[F_x(\xi)]^4 \\ \Psi(4)_3 &\equiv \int d\xi_2 d\xi_3 g_3(\xi_2,\xi_3)\frac{\partial^2\phi(\xi_2)}{\partial\xi_{2_x}{}^2}[F_x(\xi_3)]^2 \\ \mu(4)_3 &\equiv \int d\xi_2 d\xi_3 g_3(\xi_2,\xi_3)[F_x(\xi_2)]^2[F_x(\xi_3)]^2\,,\end{aligned} \tag{B7}$$

and $\eta(2)$, $\chi(2)$, $\chi(4)$, $\eta(4,xx)$, $\chi(4)_3$ are defined in the text above by Eqs. (2.32), (2.33), and (3.19).

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[28] Details of the methods of reduction to integrals of this type may be found elsewhere (cf., footnote 22).

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Hall Coefficients of Liquid Metals[*][†]

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The Hall coefficients R of 9 liquid metals were accurately measured using an alternating-current–alternating-magnetic-field method. Four of these metals have $R = R_0 \equiv 1/nec$, which is the value predicted by the free-electron model of liquid metals. The Hall coefficients of these metals (in units of 10^{-5} cm^3/C) are Hg, −7.6; Cd, −7.2; Zn, −5.2; and Sn, −4.4. The other five metals were found to have $R/R_0 < 1$, with Ga, −3.83; In, −5.3; Tl, −4.8; Pb, −3.7; and Bi, −3.0. The absolute experimental error for Ga is ±2.5%. The experimental error for all other metals relative to Ga is approximately ±1.5% except for Pb (±12%). The free-electron model of liquid metals is discussed. The value of R/R_0 is compared with the magnitude of the mean free path. Comparison is also made with the Hall coefficients of other allotropic forms of these metals.

INTRODUCTION

ONE of the best means for gaining information about the electronic properties of liquid metals is the measurement of the Hall coefficient. The importance of the Hall coefficient R lies in the fact that the free-electron theory predicts Hall coefficients equal to the free-electron value $R_0 \equiv 1/nec$, where n is the concentration of valence electrons. A careful study of the deviations of the Hall coefficient from R_0 is therefore a sensitive tool for testing the validity of the assumptions underlying the free-electron theory.

Early attempts to measure the Hall coefficient of liquid metals failed because of magnetohydrodynamic circulating currents and secondary thermal effects, as well as insensitive detecting equipment. In measurements of the Hall coefficient of Hg, for example, des Coudres[1] in 1901 found a nonzero Hall coefficient, but two subsequent workers in[2] 1914 and[3] 1931 failed to find any measurable Hall coefficient. Indeed, until 1960

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