[4]S. V. Tyablikov and Pu-Fu-Ch'o, Fiz. Tverd. Tela 3, 142 (1961) [Sov. Phys. Solid State 3, 102 (1961)].
[5]S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum, New York, 1967), Chap. VII, Sec. 31.
[6]T. Tanaka, K. Moorjani, and T. Morita, Phys. Rev. 155, 388 (1967).
[7]E. Madsen and T. Tanaka, Phys. Rev. 184, 527 (1969).
[8]W. H. Louisell, in *Quantum Optics*, edited by S. M. Kay and A. Maitland (Academic, London, 1970), pp. 177–200.
[9]J. R. Senitzky, Phys. Rev. 119, 670 (1960).
[10]J. R. Senitzky, Phys. Rev. 124, 642 (1961).
[11]R. Graham and H. Haken, Z. Physik 210, 276 (1968).
[12]H. Haken, in Ref. 8, pp. 201–321.
[13]C. W. Haas and H. B. Callen, in *Magnetism*, Vol. I, edited by G. T. Rado and H. Suhl (Academic, London, 1963), Chap. 10, Sec. VI–VII.
[14]M. Lax, in *Dynamical Processes in Solid State Optics*, edited by R. Kubo and H. Kamimura (Benjamin, New York, 1967), pp. 195–245.
[15]R. Graham, Z. Physik 210, 319 (1968).
[16]It is worthwhile to note that, as in usual cases, magnon-magnon interactions due to surface inhomogeneities are present [M. Sparks, R. Loudon, and C. Kittel, Phys. Rev. 122, 791 (1961)], and the expressions (4.1) and (4.2) for H_s and H_1 are derived with a Bogolyubov-Tyablikov transformation which takes into account this interaction. This means that η_k is determined only by the heat bath, while η_0 is determined by the heat bath and by the inhomogeneity. This last effect is generally the most important one (C. W. Haas and H. B. Callen, in Ref. 13, Sec. IX).
[17]F. Keffer, *Encyclopedia of Physics* (Springer, Berlin, 1966), Vol. XVIII/2, Chap. E, Sec. 86.

PHYSICAL REVIEW A VOLUME 5, NUMBER 1 JANUARY 1972

Incoherent Neutron Scattering by Simple Classical Liquids for Large Momentum Transfer

V. F. Sears

Atomic Energy of Canada Limited, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada
(Received 19 July 1971)

The general form for the moments of the Van Hove incoherent scattering function is derived for a simple classical liquid with velocity-independent interatomic forces. With the additional assumption of additive central forces, explicit expressions are obtained for the coefficients which determine the asymptotic behavior of the moments at large momentum transfer κ. This enables one to obtain an exact asymptotic expansion of the scattering function in inverse powers of κ. The theory is applied in detail to the Lennard-Jones liquid at the triple point and to the hard-sphere fluid at arbitrary density. The results for these two cases are qualitatively different as a consequence of the fact that the atomic velocities are continuous functions of time in the former case and discontinuous in the latter. For example, the leading correction to the impulse approximation due to final-state interactions is proportional to κ^{-2} for the Lennard-Jones potential and to κ^{-1} for hard spheres. With decreasing κ the scattering function changes from the Gaussian shape, characteristic of the impulse approximation at large κ, to the Lorentzian shape characteristic of simple diffusion at small κ. This change occurs in the hard-sphere fluid when $\kappa l \sim 1$, where l is the mean free path (including the Enskog factor).

I. INTRODUCTION

In the limit of large momentum transfer κ the scattering of neutrons by a liquid can be described in terms of the impulse approximation, in which the scattering atom recoils as if it were free, and the energy distribution of the scattered neutrons is the Doppler profile characteristic of the velocity distribution of the atoms in the initial state. The velocity distribution in a classical liquid is Maxwellian so that the scattering cross section in the limit $\kappa \to \infty$ is the same as that of an ideal gas at the same temperature.

The scattering atom is inhibited by intermolecular forces from recoiling freely so that, for a finite value of κ, the effect of final-state interactions is to produce a narrowing of the energy distribution of the scattered neutrons. For a liquid which scatters neutrons incoherently, the narrowing is characteristic of the single-particle motion of the atoms in the liquid and, in the limit $\kappa \to 0$, is determined by the macroscopic coefficient of self-diffusion. For coherent scatterers interference effects are important and the above-mentioned narrowing is sensitive to both the spatial arrangement of the atoms and their collective motion.

The present work is concerned with incoherent neutron scattering by simple classical liquids and, in particular, with the development of an exact expansion of the scattering cross section in inverse powers of κ. Such an expansion is useful for describing the scattering at large momentum transfer where departures from the impulse approximation due to final-state interactions are small. In practice this means, for example, $\kappa \gtrsim 4$ Å^{-1} in the case of liquid argon at the triple point or $\kappa \gtrsim l^{-1}$ for a hard-sphere fluid with mean free path l.

We begin in Sec. II by defining the incoherent scattering function and reviewing briefly some of its relevant properties. The general form for the moments of the scattering function is deduced in Sec. III under the assumption that the interatomic forces are velocity independent. With the additional assumption of additive central forces explicit expressions are obtained for the coefficients which determine the asymptotic behavior of the moments at large κ. The expansion of the scattering function in inverse powers of κ is derived in Sec. IV and the results are applied to the Lennard-Jones fluid in Sec. V and to the hard-sphere fluid in Sec. VI.

II. CLASSICAL INCOHERENT SCATTERING FUNCTION

A. Definition

Consider a system of N identical atoms of mass m enclosed in a volume of space Ω and in thermodynamic equilibrium with a heat bath at temperature T. The cross section for the scattering of a neutron by this system from a state with wave vector $\vec{k}_0$ to one with wave vector $\vec{k}$ is given by[1,2]

$$\frac{d^2\sigma}{d\Omega\, d\omega} = N\left(\frac{k}{k_0}\right)\{a_{\text{coh}}^2 S_{\text{coh}}(\kappa,\ \omega) + a_{\text{inc}}^2 S_{\text{inc}}(\kappa,\ \omega)\}\ , \tag{2.1}$$

where a_{coh} and a_{inc} denote, respectively, the bound coherent and incoherent scattering lengths of a nucleus, $\vec{\kappa} = \vec{k}_0 - \vec{k}$ is the momentum, and $\omega = (\hbar/2m')(k_0^2 - k^2)$ the energy, in units of $\hbar$, which are transferred to the system in the scattering process, m' being the neutron mass. The scattering functions can each be expressed as

$$S(\kappa,\ \omega) = (1/2\pi)\int_{-\infty}^{\infty} e^{-i\omega t} F(\kappa,\ t)\, dt\ , \tag{2.2}$$

where, for incoherent scattering,

$$F(\kappa,\ t) = \langle e^{-i\vec{\kappa}\cdot\vec{r}(0)}\, e^{i\vec{\kappa}\cdot\vec{r}(t)}\rangle\ , \tag{2.3}$$

in which $\vec{r}(t)$ is the position of one particular atom at time t and the brackets $\langle\cdots\rangle$ denote a thermal average. It is assumed at the outset that the system is macroscopically isotropic, e.g., is a gas or liquid, so that the scattering function is independent of the direction of $\vec{\kappa}$.

In the classical limit $F(\kappa,\ t)$ is a real even function of t and $S(\kappa,\ \omega)$ a real even function of ω. In addition (2.3) can be expressed as

$$F(\kappa,\ t) = \langle e^{i\kappa d(t)}\rangle\ , \tag{2.4}$$

where

$$d(t) = x(t) - x(0) = \int_0^t v(t')\, dt'\ , \tag{2.5}$$

in which x denotes the component of $\vec{r}$ in the direction of $\vec{\kappa}$ and $v = \dot{x}$. Expression (2.4) is the basic starting point for the work described in this article.

B. Cumulant Expansion

If the exponential in (2.4) is expanded in powers of κ, the terms can be rearranged to give a cumulant expansion of the form[2-4]

$$F(\kappa,\ t) = \exp\left(\sum_{n=1}^{\infty} (-)^n \kappa^{2n} \rho_n(t)\right)\ , \tag{2.6}$$

where

$$\rho_1(t) = (1/2!)\langle d(t)^2\rangle\ ,$$
$$\rho_2(t) = (1/4!)[\langle d(t)^4\rangle - 3\langle d(t)^2\rangle^2]\ , \tag{2.7}$$

etc. Only even powers of κ occur in (2.6) because $\langle d(t)^n\rangle$ vanishes identically when n is odd.

The velocity autocorrelation function and its spectral density are defined by the relations

$$\chi(t) = \int_{-\infty}^{\infty} e^{i\omega t}\, \hat{\chi}(\omega)\, d\omega = (m/3kT)\langle\vec{v}(0)\cdot\vec{v}(t)\rangle\ . \tag{2.8}$$

One can easily verify that

$$\ddot{\rho}_1(t) = (kT/m)\chi(t)\ , \tag{2.9}$$

so that, with $\rho_1(0) = 0$ and $\dot{\rho}_1(0) = 0$, we have

$$\rho_1(t) = (kT/m)\int_0^t (t-t')\chi(t')\, dt'$$
$$= \frac{2kT}{m}\int_0^{\infty} \frac{1-\cos\omega t}{\omega^2}\, \hat{\chi}(\omega)\, d\omega\ . \tag{2.10}$$

The remaining quantities $\rho_n(t)$ are similarly expressible in terms of multitime velocity correlation functions.[2]

It is sometimes convenient to consider as well the force autocorrelation function,[5]

$$\Phi(t) = \int_{-\infty}^{\infty} e^{i\omega t}\, \hat{\Phi}(\omega)\, d\omega = \langle\vec{F}(0)\cdot\vec{F}(t)\rangle\ , \tag{2.11}$$

in which $\vec{F} = m\dot{\vec{v}}$ is the total force on the atom. Since

$$\Phi(t) = -3mkT\ddot{\chi}(t)\ , \tag{2.12}$$

it follows that

$$\hat{\Phi}(\omega) = 3mkT\omega^2\hat{\chi}(\omega)\ , \tag{2.13}$$

and, with $\chi(0) = 1$ and $\dot{\chi}(0) = 0$, that

$$\chi(t) = 1 - (1/3mkT)\int_0^t (t-t')\Phi(t')\, dt'\ . \tag{2.14}$$

Hence, we have

$$\rho_1(t) = (ut)^2 - (1/18m^2)\int_0^t (t-t')^3\Phi(t')\, dt'\ , \tag{2.15}$$

where $u = (kT/2m)^{1/2}$.

C. Behavior at Large κ

It will be shown later[6] that for the case in which the interatomic potential is smooth we have

$$\rho_1(t) = (ut)^2 + O(t^4)\ ,$$
$$\rho_2(t) = O(t^8)\ , \tag{2.16}$$
$$\rho_3(t) = O(t^{12})\ ,$$

whereas for a hard-sphere fluid we have

$$\rho_1(t)=(ut)^2+O(|t|^3)\ ,$$
$$\rho_2(t)=O(|t|^5)\ , \quad (2.17)$$
$$\rho_3(t)=O(|t|^7)\ .$$

In either case it is evident from (2.6) that in the limit $\kappa\to\infty$, $t\to 0$ with $\kappa t=$ const, we have

$$F(\kappa,\ t)\to e^{-(\kappa u t)^2}\ . \quad (2.18)$$

Hence, in the limit $\kappa\to\infty$, $\omega\to\infty$ with $\kappa/\omega=$ const,

$$S(\kappa,\ \omega)\to(1/2\sqrt{\pi}\,\kappa u)\,e^{-(\omega/2\kappa u)^2}\ , \quad (2.19)$$

so that the scattering function is Gaussian with a full width at half-maximum given by

$$\Delta\omega=4(\ln 2)^{1/2}\kappa u\ . \quad (2.20)$$

The asymptotic relation (2.19) is the classical limit of the impulse approximation[7] and is the same as the scattering function for an ideal gas.[8]

D. Behavior at Small κ

The asymptotic behavior at small κ cannot be established as rigorously as it can at large κ. Formally, one can argue[4] from (2.10) that

$$\rho_1(t)\to Dt-C\quad \text{as } t\to\infty\ , \quad (2.21)$$

where D is by definition the coefficient of self-diffusion and

$$D=(kT/m)\int_0^\infty \chi(t)\,dt\ ,$$
$$C=(kT/m)\int_0^\infty t\chi(t)\,dt\ . \quad (2.22)$$

Similarly one can argue in general that[2]

$$\rho_n(t)\to D_n t-C_n\quad \text{as } t\to\infty\ , \quad (2.23)$$

so that in the limit $\kappa\to 0$, $t\to\infty$ with $\kappa^2 t=$ const, we have

$$F(\kappa,\ t)\to e^{-D\kappa^2 t}\ , \quad (2.24)$$

and in the limit $\kappa\to 0$, $\omega\to 0$ with $\kappa^2/\omega=$ const, we have

$$S(\kappa,\ \omega)\to\frac{D\kappa^2}{\pi}\,\frac{1}{\omega^2+(D\kappa^2)^2}\ , \quad (2.25)$$

so that the scattering function is Lorentzian with a full width at half-maximum given by

$$\Delta\omega=2D\kappa^2\ . \quad (2.26)$$

The weakness of the above argument lies in the fact that there is as yet no proof that the quantities D_n and C_n are finite. The possibility that these quantities may diverge must be taken seriously because it has recently been established[9–13] that at long times $\chi(t)$ is proportional to $t^{-3/2}$ so that, while D is finite, C diverges as $t^{1/2}$. On the other hand, the asymptotic relation (2.23) is more stringent than necessary to establish the validity of (2.25). Even if D_n were to diverge for $n\geq 2$, (2.25) would still be correct as long as it diverges slower than t^n.

E. Behavior at Intermediate κ

With decreasing κ the scattering function changes continuously from the Gaussian shape characteristic of the impulse approximation at large κ to (presumably) the Lorentzian shape characteristic of simple diffusion at small κ. The main purpose of the present article is to derive an expansion of the form

$$S(\kappa,\ \omega)=\frac{1}{2\sqrt{\pi}\,\kappa u}\,e^{-(\omega/2\kappa u)^2}\left[1+\sum_{s=1}^{\infty}\frac{1}{\kappa^{2s}}\,G_{2s}\!\left(\frac{\omega}{2\kappa u}\right)\right], \quad (2.27)$$

in which the quantities $G_{2s}(x)$ describe the effect of final-state interactions which are neglected in the impulse approximation. To obtain the above expansion it is first necessary to calculate the moments of the scattering function. This problem is dealt with in Sec. III.

III. MOMENTS OF CLASSICAL INCOHERENT SCATTERING FUNCTION

A. General Expression for Moments

We exclude for the time being the possibility of hard-sphere interactions in order that $\vec{r}(t)$ can be regarded as a smooth function of t. In this case the quantity $F(\kappa,\ t)$ defined by (2.3) can reasonably be assumed to have, at least asymptotically, an expansion in powers of t of the form

$$F(\kappa,\ t)=\sum_{n=0}^{\infty}\frac{(it)^n}{n!}\,S_n(\kappa)\ , \quad (3.1)$$

where $S_n(\kappa)$ is the nth moment of the scattering function:

$$S_n(\kappa)=(-i)^n\,\frac{\partial^n F(\kappa,\ 0)}{\partial t^n}=\int_{-\infty}^{\infty}\omega^n S(\kappa,\ \omega)\,d\omega\ . \quad (3.2)$$

If the velocity $v(t')$ in (2.5) is expanded in powers of t' it follows from (2.4) and (3.1) that

$$S_0(\kappa)=1\ ,$$
$$S_n(\kappa)=\sum_{m=1}^{n}S_{nm}\,\kappa^m\ ,\quad n=1,\ 2,\ 3,\ldots \quad (3.3)$$

in which

$$S_{nm}=i^{m-n}\,\frac{n!}{m!}\sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_m=0}^{\infty}\delta_{n,\,n_1+n_2+\cdots+n_m+m}\times S_m(n_1 n_2\cdots n_m)\ , \quad (3.4)$$

where

$$S_m(n_1 n_2\cdots n_m)=\frac{\langle v^{(n_1)}v^{(n_2)}\cdots v^{(n_m)}\rangle}{(n_1+1)!\,(n_2+1)!\cdots(n_m+1)!}\ , \quad (3.5)$$

and $v^{(n)}$ denotes the nth time derivative of v. For an isotropic classical system S_{nm} is nonvanishing only if n and m are both even.

Since $S_m(n_1 n_2 \cdots n_m)$ is invariant under any permutation of $n_1 n_2 \cdots n_m$, it follows from (3.4) that, for $n = 2, 4, 6, \cdots$,

$$S_{n,n} = S_n(0\cdots 0) ,$$

$$S_{n,n-2} = -\frac{n!}{(n-3)!} S_{n-2}(20\cdots 0) - \frac{n!}{(n-4)!2!} S_{n-2}(110\cdots 0) ,$$

$$S_{n,n-4} = \frac{n!}{(n-5)!} S_{n-4}(40\cdots 0) + \frac{n!}{(n-6)!} S_{n-4}(310\cdots 0) + \frac{n!}{(n-6)!2!} S_{n-4}(220\cdots 0) + \theta(n-8)$$
$$\times \left(\frac{n!}{(n-7)!2!} S_{n-4}(2110\cdots 0) + \frac{n!}{(n-8)!4!} S_{n-4}(11110\cdots 0) \right) ,$$

$$S_{n,n-6} = -\frac{n!}{(n-7)!} S_{n-6}(60\cdots 0) - \frac{n!}{(n-8)!} S_{n-6}(510\cdots 0) - \frac{n!}{(n-8)!} S_{n-6}(420\cdots 0) \tag{3.6}$$
$$- \frac{n!}{(n-8)!2!} S_{n-6}(330\cdots 0) - \theta(n-10) \left(\frac{n!}{(n-9)!2!} S_{n-6}(4110\cdots 0) + \frac{n!}{(n-9)!} S_{n-6}(3210\cdots 0) \right.$$
$$\left. + \frac{n!}{(n-10)!3!} S_{n-6}(31110\cdots 0) + \frac{n!}{(n-9)!3!} S_{n-6}(2220\cdots 0) + \frac{n!}{(n-10)!(2!)^2} S_{n-6}(22110\cdots 0) \right)$$
$$- \theta(n-12) \left(\frac{n!}{(n-11)!4!} S_{n-6}(211110\cdots 0) + \frac{n!}{(n-12)!6!} S_{n-6}(1111110\cdots 0) \right) ,$$

$$S_{n,2} = i^{2-n} \frac{n!}{2!} \sum_{n_1=0}^{n-2} S_2(n_1, n-n_1-2) ,$$

in which

$$\theta(n) = 0 , \quad n < 0$$
$$= 1 , \quad n \geq 0 . \tag{3.7}$$

The number of independent coefficients in (3.6) can be reduced with the help of the relation $\langle \dot{A} B \rangle = -\langle A \dot{B} \rangle$ and one finds that

$$S_{n,n} = \langle v^n \rangle ,$$

$$S_{n,n-2} = \frac{n!}{(n-4)!4!} \langle \dot{v}^2 v^{n-4} \rangle ,$$

$$S_{n,n-4} = \frac{n!}{(n-6)!6!} \langle \ddot{v}^2 v^{n-6} \rangle$$
$$- \theta(n-8) \frac{7n!}{(n-8)!8!} \langle \dot{v}^4 v^{n-8} \rangle ,$$

$$S_{n,n-6} = \frac{n!}{(n-8)!8!} \langle \dddot{v}^2 v^{n-8} \rangle - \theta(n-10) \tag{3.8}$$
$$\times \left(\frac{10n!}{(n-9)!9!} \langle \ddot{v}^3 v^{n-9} \rangle \right.$$
$$\left. + \frac{90n!}{(n-10)!10!} \langle \ddot{v}^2 \dot{v}^2 v^{n-10} \rangle \right)$$
$$+ \theta(n-12) \frac{297n!}{(n-12)!12!} \langle \dot{v}^6 v^{n-12} \rangle ,$$

$$S_{n,2} = \langle \{ v^{n/2-1} \}^2 \rangle ,$$

where the last line follows from the identity

$$\sum_{n_1=0}^{n-2} \frac{(-)^{n_1}}{(n_1+1)!(n-n_1-1)!} = \frac{2}{n!} , \quad n = 2, 4, 6, \ldots . \tag{3.9}$$

B. Velocity-Independent Interatomic Forces

It is now assumed that the atoms interact via velocity-independent forces so that the total potential energy of the system, V, is a function only of the positions of the atoms, $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N$. The Cartesian components of these vectors will be denoted

$$\vec{r}_1 = (q_1, q_2, q_3) ,$$
$$\vec{r}_2 = (q_4, q_5, q_6) , \tag{3.10}$$
$$\vec{r}_N = (q_{3N-2}, q_{3N-1}, q_{3N}) ,$$

so that, with $v_i = \dot{q}_i$, we have

$$\dot{v}_i = -(1/m) V_i ,$$
$$\ddot{v}_i = -(1/m) V_{ij} v_j , \tag{3.11}$$
$$\dddot{v}_i = -(1/m) V_{ijk} v_j v_k + (1/m^2) V_{ij} V_j ,$$

where

$$V_i = \frac{\partial V}{\partial q_i} , \quad V_{ij} = \frac{\partial^2 V}{\partial q_i \partial q_j} , \quad \text{etc.}, \tag{3.12}$$

and summation over repeated indices is implied. The velocity components v_i are statistically independent both of each other and of the quantities $V_{ij\cdots k}$. Moreover, the velocity distribution is Maxwellian so that

$$\langle v_i^{2n}\rangle = \frac{(2n)!}{n!}u^{2n}, \quad n=0, 1, 2, \ldots \tag{3.13}$$

where $u=(kT/2m)^{1/2}$ as before. On substituting (3.11) into (3.8), with $v=v_1$, and with the help of (3.13) and the relation[3]

$$\left\langle A\frac{\partial V}{\partial q_i}\right\rangle = kT\left\langle\frac{\partial A}{\partial q_i}\right\rangle, \tag{3.14}$$

it follows that

$$\begin{aligned}
S_{2n,2n} &= (2n)!u^{2n}\left(\frac{1}{n!}\right),\\
S_{2n,2n-2} &= (2n)!u^{2n}\left(\frac{\theta(n-2)}{(n-2)!}J_{24}\right),\\
S_{2n,2n-4} &= (2n)!u^{2n}\left(\frac{\theta(n-3)}{(n-3)!}J_{46}+\frac{\theta(n-4)}{(n-4)!}J_{48}\right),\\
S_{2n,2n-6} &= (2n)!u^{2n}\left(\frac{\theta(n-4)}{(n-4)!}J_{68} + \frac{\theta(n-5)}{(n-5)!}J_{6,10}+\frac{\theta(n-6)}{(n-6)!}J_{6,12}\right),\\
S_{2n,2} &= (2n)!u^{2n}(J_{2n-2,2n}),
\end{aligned} \tag{3.15}$$

where $n=1, 2, 3, \ldots$ and

$$\begin{aligned}
J_{24} &= (1/3!)(\beta\langle V_{11}\rangle),\\
J_{46} &= (1/5!)(\tfrac{4}{3}\beta^2\langle V_{1i}^2\rangle),\\
J_{48} &= (1/5!)(\tfrac{5}{3}\beta^2\langle V_{11}^2\rangle - \beta\langle V_{1111}\rangle),\\
J_{68} &= (1/7!)(2\beta^3\langle V_{1i}V_{1j}V_{ij}\rangle + 6\beta^2\langle V_{1ij}^2\rangle),\\
J_{6,10} &= (1/7!)\left[\tfrac{28}{3}\beta^3\langle V_{11}V_{1i}^2\rangle + 8\beta^2(\langle V_{11i}^2\rangle - 2\langle V_{111i}V_{1i}\rangle)\right],\\
J_{6,12} &= (1/7!)(\tfrac{35}{9}\beta^3\langle V_{11}^3\rangle - 7\beta^2\langle V_{1111}V_{11}\rangle + \beta\langle V_{111111}\rangle),
\end{aligned} \tag{3.16}$$

and $\beta = 1/kT$. Hence it is evident that in general

$$S_{2n,2(n-s)} = (2n)!u^{2n}\sum_{r=1}^{s}\frac{\theta(n-s-r)}{(n-s-r)!}J_{2s,2(s+r)} \tag{3.17}$$

for $s=1, 2, \ldots, (n-1)$. It follows from (3.3) that for velocity-independent interatomic forces the moments of the classical incoherent scattering function for an isotropic system are of the form

$$\begin{aligned}
&S_0(\kappa)=1, \qquad S_2(\kappa)=2u^2\kappa^2,\\
&S_{2n}(\kappa) = (2n)!u^{2n}\times\left(\sum_{m=1}^{n-1}\sum_{r=1}^{n-m}\frac{\theta(m-r)}{(m-r)!}J_{2(n-m),2(n-m+r)}\kappa^{2m} + \frac{\kappa^{2n}}{n!}\right),
\end{aligned} \tag{3.18}$$

where $n=2, 3, 4, \ldots$.

C. Additive Central Forces

We now assume that the atoms interact via additive central forces so that

$$V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum_{i>j=1}^{N}\phi(r_{ij}), \tag{3.19}$$

where $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ and $\phi(r)$ is the pair potential. In the thermodynamic limit, $N\to\infty$, $\Omega\to\infty$ with $\rho = N/\Omega$ = const, it follows on substituting (3.19) into (3.16) that

$$J_{sp} = J'_{sp} + J''_{sp}, \tag{3.20}$$

where

$$\begin{aligned}
J'_{24} &= \tfrac{2}{9}\pi\rho(\beta L_1), & J''_{24} &= 0,\\
J'_{46} &= \tfrac{4}{135}\pi\rho(\beta^2 L_2), & J''_{46} &= \tfrac{4}{135}\pi^2\rho^2(\beta^2 M_1),\\
J'_{48} &= \tfrac{1}{270}\pi\rho(\beta^2 L_3 - \tfrac{9}{5}\beta L_4), & J''_{48} &= \tfrac{1}{135}\pi^2\rho^2(\beta^2 M_2),\\
J'_{68} &= \tfrac{32}{3}(\pi/7!)\rho(\beta^3 L_5 + 3\beta^2 L_6), & &\\
J'_{6,10} &= \tfrac{32}{15}(\pi/7!)\rho[\tfrac{7}{3}\beta^3 L_7 + 2\beta^2(L_8 - 2L_9)], & &\\
J'_{6,12} &= \tfrac{4}{35}(\pi/7!)\rho[\tfrac{35}{9}\beta^3 L_{10} - 7\beta^2 L_{11} + \beta L_{12}]. & &
\end{aligned} \tag{3.21}$$

The quantities L_j are integrals of the form

$$L_j = \int_0^\infty L_j(r)g(r)\,dr, \tag{3.22}$$

in which $g(r)$ is the pair correlation function and

$$\begin{aligned}
L_1(r) &= r^2\phi'' + 2r\phi', \qquad L_2(r) = r^2\phi''^2 + 2\phi'^2,\\
L_3(r) &= 3r^2\phi''^2 + 4r\phi''\phi' + 8\phi'^2, \qquad L_4(r) = r^2\phi'''' + 4r\phi''',\\
L_5(r) &= r^2\phi''^3 + (2/r)\phi'^3, \qquad L_6(r) = r^2\phi'''^2 + 6[\phi'' - (1/r)\phi']^2,\\
L_7(r) &= 3r^2\phi''^3 + 2r\phi''^2\phi' + 2\phi''\phi'^2 + (8/r)\phi'^3,\\
L_8(r) &= 3r^2\phi'''^2 + 4r\phi'''[\phi'' - (1/r)\phi'] + 16[\phi'' - (1/r)\phi']^2,\\
L_9(r) &= 3r^2\phi''''\phi'' + 6r\phi'''[\phi'' + (1/r)\phi'] - 12[\phi'' - (1/r)\phi']^2,\\
L_{10}(r) &= 5r^2\phi''^3 + 6r\phi''^2\phi' + 8\phi''\phi'^2 + (16/r)\phi'^3,\\
L_{11}(r) &= r^2\phi''''[5\phi'' + (2/r)\phi'] + r\phi'''[12\phi'' + (16/r)\phi'] - 16[\phi'' - (1/r)\phi']^2,\\
L_{12}(r) &= 5r^2\phi'''''' + 30r\phi''''',
\end{aligned} \tag{3.23}$$

where the primes denote differentiation with respect to r. The quantities M_j in (3.21) involve the triplet correlation function $g(r, s, t)$, in which $\vec{r}$, $\vec{s}$ and $\vec{t}=\vec{s}-\vec{r}$ denote the relative positions of three atoms:

$$M_j=\int_0^\infty dr\int_0^\infty ds\int_{|r-s|}^{r+s} t\,dt\,M_j(r, s, t)g(r, s, t)\ , \tag{3.24}$$

in which

$$\begin{aligned}M_1(r, s, t)&=\cos^2\theta\, r\phi''(r)s\phi''(s)\\&\quad+2(1-\cos^2\theta)r\phi''(r)\phi'(s)\\&\quad+(1+\cos^2\theta)\phi'(r)\phi'(s)\ ,\\M_2(r, s, t)&=(1+2\cos^2\theta)r\phi''(r)s\phi''(s)\\&\quad+4(2-\cos^2\theta)r\phi''(r)\phi'(s)\\&\quad+2(3+\cos^2\theta)\phi'(r)\phi'(s)\ ,\end{aligned} \tag{3.25}$$

and θ is the angle between $\vec{r}$ and $\vec{s}$ so that

$$\cos\theta=(r^2+s^2-t^2)/2rs\ . \tag{3.26}$$

The remaining quantities J''_{68}, $J''_{6,10}$, and $J''_{6,12}$ depend on both the triplet and quadruplet correlation functions but have not been calculated explicitly.

IV. CLASSICAL INCOHERENT SCATTERING FUNCTION AT LARGE MOMENTUM TRANSFER

A. Series Expansion in Inverse Powers of κ

Since the odd moments vanish identically, (3.1) can be expressed as

$$\begin{aligned}F(\kappa, t)&=\sum_{n=0}^{\infty}\frac{(-)^n t^{2n}}{(2n)!}S_{2n}(\kappa)\\&=e^{-(\kappa ut)^2}\sum_{p=0}^{\infty}(-)^p(\kappa ut)^{2p}\epsilon_{2p}(\kappa)\ ,\end{aligned} \tag{4.1}$$

where

$$\epsilon_{2p}(\kappa)=\sum_{n=0}^{p}\frac{(-)^{p-n}}{(p-n)!(2n)!}\frac{S_{2n}(\kappa)}{(\kappa u)^{2n}}\ . \tag{4.2}$$

Hence, one obtains from (2.2) the following Gram-Charlier expansion of the incoherent scattering function[7,14–17]:

$$S(\kappa, \omega)=\frac{1}{2\sqrt{\pi}\,\kappa u}e^{-(\omega/2\kappa u)^2}\sum_{p=0}^{\infty}\epsilon_{2p}(\kappa)H_{2p}\left(\frac{\omega}{2\kappa u}\right), \tag{4.3}$$

in which $H_n(x)$ denotes the Hermite polynomials,

$$H_n(x)=\frac{(-)^n}{2^n}e^{x^2}\frac{d^n e^{-x^2}}{dx^n}\ . \tag{4.4}$$

On substituting (3.18) into (4.2) one finds, with the help of the identity

$$\delta_{p,q}=\theta(p-q)\sum_{n=q}^{p}\frac{(-)^{p-n}}{(p-n)!(n-q)!}\ , \tag{4.5}$$

derived in the Appendix, that

$$\begin{aligned}&\epsilon_0(\kappa)=1\ ,\quad \epsilon_2(\kappa)=0\ ,\\&\epsilon_{2p}(\kappa)=\sum_{s=1}^{p-1}\frac{\theta(2s-p)}{\kappa^{2s}}J_{2s,2p}\ ,\end{aligned} \tag{4.6}$$

in which $p=2, 3, 4, \ldots$. The above expression for $\epsilon_{2p}(\kappa)$ allows the terms in (4.3) to be rearranged as a series in inverse powers of κ of the form shown in (2.27) with

$$G_{2s}(x)=\sum_{p=s+1}^{2s}J_{2s,2p}H_{2p}(x)\ . \tag{4.7}$$

In particular, we have

$$\begin{aligned}G_2(x)&=J_{24}H_4(x)\ ,\\G_4(x)&=J_{46}H_6(x)+J_{48}H_8(x)\ ,\\G_6(x)&=J_{68}H_8(x)+J_{6,10}H_{10}(x)+J_{6,12}H_{12}(x)\ .\end{aligned} \tag{4.8}$$

The above correction terms to the impulse approximation due to final-state interactions have the following structure as is clear from the results of Sec. III C: $G_2(x)$ is determined entirely by the pair correlation function; $G_4(x)$ involves in addition the triplet correlation function, $G_6(x)$ the quadruplet correlation function, and so on.

B. Full Width at Half-Maximum

The full width at half-maximum of $S(\kappa, \omega)$ can be expressed in the form

$$\Delta\omega=4(\ln 2)^{1/2}\kappa u[1-\Gamma(\kappa)]\ , \tag{4.9}$$

in which $\Gamma(\kappa)$ represents the narrowing due to final-state interactions. The expansion of this quantity in inverse powers of κ takes the form

$$\Gamma(\kappa)=\sum_{s=1}^{\infty}\frac{(-)^{s+1}}{\kappa^{2s}}\Gamma_{2s}\ , \tag{4.10}$$

where

$$\begin{aligned}\Gamma_2&=1.1534J_{24}\ ,\\\Gamma_4&=3.2659J_{46}-11.2515J_{48}+1.1390J_{24}^2\ ,\\\Gamma_6&=11.2515J_{68}-45.3975J_{6,10}+206.8121J_{6,12}\\&\quad+3.5393J_{24}J_{46}-1.5423J_{24}J_{48}-1.5783J_{24}^3\ ,\end{aligned} \tag{4.11}$$

in which the numerical values of the coefficients are determined from the relations

$$1.1534=-\tfrac{1}{2}Z+\tfrac{3}{2}\ ,$$

$$3.2659=\tfrac{1}{2}Z^2-\tfrac{15}{4}Z+\tfrac{45}{8}\ ,$$

$$11.2515=-\tfrac{1}{2}Z^3+7Z^2-\tfrac{105}{4}Z+\tfrac{105}{4}\ ,$$

$$1.1390=-\tfrac{1}{4}Z^3+\tfrac{19}{8}Z^2-\tfrac{51}{8}Z+\tfrac{9}{2}\ ,$$

$$45.3975=\tfrac{1}{2}Z^4-\tfrac{45}{4}Z^3+\tfrac{315}{4}Z^2-\tfrac{1575}{8}Z+\tfrac{4725}{32}\ ,$$

$$\begin{aligned}206.8121&=-\tfrac{1}{2}Z^5+\tfrac{33}{2}Z^4-\tfrac{1485}{8}Z^3\\&\quad+\tfrac{3465}{4}Z^2-\tfrac{51975}{32}Z+\tfrac{31185}{32}\ ,\end{aligned}$$

$$3.5393=\tfrac{1}{2}Z^4-\tfrac{15}{2}Z^3+\tfrac{285}{8}Z^2-\tfrac{1005}{16}Z+\tfrac{1035}{32}\ ,$$

$$1.5423=-\tfrac{1}{2}Z^5+\tfrac{45}{4}Z^4-\tfrac{687}{8}Z^3+\tfrac{2205}{8}Z^2-\tfrac{11655}{32}Z+\tfrac{4725}{32}\ ,$$
$$1.5783=\tfrac{1}{6}Z^5-\tfrac{23}{8}Z^4+\tfrac{273}{16}Z^3-\tfrac{87}{2}Z^2+\tfrac{1467}{32}Z-\tfrac{459}{32}\ , \qquad (4.12)$$

where $Z=\ln 2$.

Since, in practice, only the first two or three terms in (4.10) can be determined explicitly, the usefulness of this series is restricted to large values of κ. For small values of κ, on the other hand, (2.26) yields the asymptotic relation

$$\Gamma(\kappa)\to 1-\frac{D\kappa}{2(\ln 2)^{1/2}u} \quad \text{as } \kappa\to 0\ , \qquad (4.13)$$

C. Cumulant Expansion

When (4.1) is rearranged with the help of (4.6) to give a cumulant expansion of the form (2.6) it is found that, with $J_{02}\equiv 1$,

$$\rho_1(t)=\sum_{n=0}^{\infty}(-)^n J_{2n,2n+2}(ut)^{2n+2}\ ,$$
$$\rho_2(t)=(J_{48}-\tfrac{1}{2}J_{24}^2)(ut)^8-(J_{6,10}-J_{24}J_{46})(ut)^{10}+(J_{8,12}-\tfrac{1}{2}J_{46}^2-J_{24}J_{68})(ut)^{12}-\cdots\ , \qquad (4.14)$$
$$\rho_3(t)=(-J_{6,12}+J_{24}J_{48}-\tfrac{1}{3}J_{24}^3)(ut)^{12}-\cdots\ .$$

Hence it follows from (2.9) and (2.12) that the time expansions of the velocity and force autocorrelation functions are

$$\chi(t)=\sum_{n=0}^{\infty}(-)^n(n+1)(2n+1)J_{2n,2n+2}(ut)^{2n}\ ,$$
$$\Phi(t)=3(kT)^2\sum_{n=0}^{\infty}(-)^n(n+1)(n+2)(2n+1)\times(2n+3)J_{2n+2,2n+4}(ut)^{2n}\ . \qquad (4.15)$$

Some years ago Schofield[4] calculated the terms up to t^8 in the expansion of $\rho_1(t)$. In the present notation he obtained J_{24}, J_{46}, and J_{68}. The calculation was later repeated by Nijboer and Rahman,[16] who found the same expressions for J_{24} and J_{46} but a different one for J_{68}. The present results, shown in (3.16), agree with Nijboer and Rahman and we conclude that it is Schofield's expression for J_{68} which is incorrect. Schofield also evaluated the leading term in $\rho_2(t)$ and his result for J_{48} agrees with that given in (3.16). The remaining two quantities in (3.16), $J_{6,10}$ and $J_{6,12}$, have not previously been calculated.

V. LENNARD-JONES LIQUID

The results obtained above are applied in this section to a system for which $\phi(r)$ is represented by the Lennard-Jones potential,[18]

$$\phi(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]\ . \qquad (5.1)$$

In this case the quantities J_{sp} obey a law of corresponding states of the form

$$J_{sp}(\rho,\ T)=(1/\sigma^s)J^*_{sp}(\rho^*,\ T^*)\ , \qquad (5.2)$$

in which $\rho^*=\rho\sigma^3$ is the reduced number density and $T^*=kT/\epsilon$ the reduced temperature.

Verlet[19] has performed a molecular dynamics calculation of the pair correlation function $g(r)$ for the Lennard-Jones fluid for a wide range of densities and temperatures. His results for $\rho^*=0.850$ and $T^*=0.719$, corresponding to a state of the liquid near the triple point, have been used in (3.22) to determine the values for $J^{*\prime}_{sp}$ shown in Table I. Also shown in this table are values of $J^{*\prime\prime}_{46}$ and $J^{*\prime\prime}_{48}$ obtained from (3.21) and (3.24) using the Kirkwood superposition approximation,[20]

$$g(r,\ s,\ t)=g(r)g(s)g(t)\ . \qquad (5.3)$$

This approximation generally overestimates the magnitude of $g(r,\ s,\ t)$ for nearest-neighbor triplet configurations by an amount which is typically 10–15% at liquid densities.[21–24] One further approximation was also employed, based on the fact that the integrand of (3.24) is appreciably different from zero only when $r\simeq s\simeq\sigma$. In evaluating M_j we therefore put $\cos\theta=1-\frac{1}{2}(t/\sigma)^2$ and let the integration over t run from 0 to 2σ. This latter approximation greatly simplifies matters since the expression for M_j then reduces to a sum of products of single quadratures.

The value 65.1, which we have found for J^*_{24}, is in good agreement with the empirical value 62 obtained by Nijboer and Rahman[16] from an analysis of phase equilibrium isotope separation data for liquid argon.[25] The remaining values of J^*_{sp} shown in Table I were obtained by Nijboer and Rahman from molecular dynamics data for a Buckingham potential with $\rho^*=0.830$ and $T^*=0.714$. The discrepancies between these values and those we have calculated for the Lennard-Jones potential are presumably due in large part to the fact that the integrals

TABLE I. Values of J^*_{sp} for a Lennard-Jones liquid with reduced number density $\rho^*=0.850$ and reduced temperature $T^*=0.719$.

sp	$J^{*\prime}_{sp}$	$J^{*\prime\prime}_{sp}$ ($\times 10^3$)	$J^{*\prime}_{sp}+J^{*\prime\prime}_{sp}$ ($\times 10^3$)	J^*_{sp} (Ref. 16)			
2, 4	65.1	0	65.1	45[a]	49[b]	55[c]	62[d]
4, 6	4.20×10^3	1.03	5.23		3.2×10^3 [b]		
4, 8	1.02×10^3	1.53	2.55				
6, 8	4.65×10^5						
6, 10	2.20×10^5						
6, 12	1.98×10^4						

[a]From (3.21).
[b]From (4.15).
[c]From the second moment of the velocity spectrum.
[d]From isotope separation measurements on liquid argon (Ref. 25).

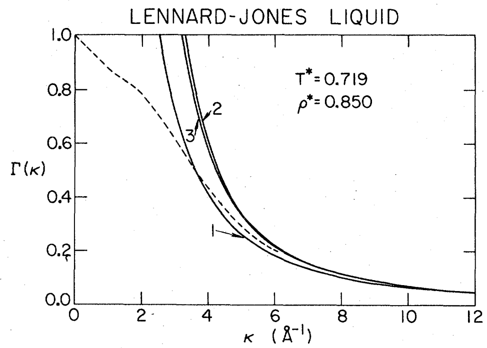

FIG. 1. Comparison of the approximants for $\Gamma(\kappa)$ calculated from (5.4) (full lines) with the molecular dynamics result of Nijboer and Rahman (Ref. 16) (dashed line).

(3.22) and (3.24) are very sensitive to the values of the pair potential and correlation functions in a small neighborhood of the point $r=\sigma$.

The calculated values of J^*_{sp} shown in Table I were used in (4.11) to obtain the following expansion of $\Gamma(\kappa)$ in inverse powers of κ:

$$\Gamma(\kappa)=0.751(10/\kappa\sigma)^2+0.678(10/\kappa\sigma)^4 -0.147(10/\kappa\sigma)^6+\cdots . \quad (5.4)$$

The coefficient of κ^{-6} was calculated with $J_{sp}=J'_{sp}$ for $sp=6$, 8; 6, 10; and 6, 12 and is therefore to be regarded simply as an estimate of the order of magnitude of this quantity. The curves labeled 1, 2, and 3 in Fig. 1 were computed from (5.4), with σ given the value 3.405 Å appropriate to argon,[18] by truncating the series after the first, second, and third terms, respectively. The dashed curve was obtained by Nijboer and Rahman[16] directly from their molecular dynamics data and merges nicely with the approximants calculated from (5.4). It will be noted that for most purposes one need retain only the leading term in (5.4) if $\kappa \gtrsim 4$ Å^{-1} or, more generally, if $\kappa\sigma \gtrsim 14$.

VI. HARD-SPHERE FLUID

A. Equation of State and Enskog Factor

The theory developed above cannot be applied directly to the hard-sphere fluid because it is based on the assumption made in Sec. III A that the positions of the atoms are smooth functions of time. To discuss the hard-sphere fluid we therefore consider first a pair potential of the form

$$\phi(r)=\phi(\sigma)e^{-(r-\sigma)/a} , \quad (6.1)$$

and later take the limit $a\to 0$ in which

$$\phi(r)\to\begin{cases}+\infty , & r<\sigma\\ 0 , & r>\sigma .\end{cases} \quad (6.2)$$

The integrals (3.22) are similar to that which occurs in the virial theorem,[18]

$$P=\rho kT-\tfrac{2}{3}\pi\rho^2\int_0^\infty r^3\phi'(r)g(r)\,dr , \quad (6.3)$$

where P is the pressure. To evaluate such integrals it is convenient to express $g(r)$ in the form

$$g(r)=e^{-\beta\phi(r)}\tilde{g}(r) , \quad (6.4)$$

in which the quantity $\tilde{g}(r)$, unlike $g(r)$, remains continuous at $r=\sigma$ in the limit $a\to 0$.[26] Substituting (6.1) and (6.4) into (6.3), and noting that in the limit $a\to 0$ the integrand is nonvanishing only at $r=\sigma$, one can show that for the hard-sphere fluid,

$$P=\rho kT[1+\rho b\tilde{g}(\sigma)] , \quad (6.5)$$

where $b=(\tfrac{2}{3}\pi)\sigma^3$ is the second virial coefficient and $\tilde{g}(\sigma)$ is the Enskog factor.[18,27]

B. Calculation of J_{sp}

The integrals (3.22) and (3.24) can be evaluated in a similar way and, keeping only the dominant term as $a\to 0$, one finds that

$$J'_{24}=\tfrac{1}{3}(\eta/\sigma a) , \qquad J'_{46}=\tfrac{2}{45}(\eta/\sigma a^3) ,$$
$$J'_{48}=\tfrac{1}{150}(\eta/\sigma a^3) , \qquad J'_{68}=\tfrac{1}{63}(\eta/\sigma a^5) , \quad (6.6)$$
$$J'_{6,10}=\tfrac{8}{1575}(\eta/\sigma a^5) , \quad J'_{6,12}=\tfrac{2}{6615}(\eta/\sigma a^5) ,$$

in which

$$\eta=\rho b\tilde{g}(\sigma)=P/\rho kT-1 , \quad (6.7)$$

and

$$J''_{24}=0 ,$$

$$J''_{46}=\frac{4\pi^2}{135}\frac{\rho^2\sigma^4}{a^2}\int_1^2(z-z^3+\tfrac{1}{4}z^5)g(\sigma,\sigma,\sigma z)\,dz , \quad (6.8)$$

$$J''_{48}=\frac{\pi^2}{135}\frac{\rho^2\sigma^4}{a^2}\int_1^2(3z-2z^3+\tfrac{1}{2}z^5)g(\sigma,\sigma,\sigma z)\,dz .$$

In the limit $a\to 0$, the quantities J''_{46} and J''_{48} are negligible compared with J'_{46} and J'_{48} because the former are proportional to a^{-2} and the latter to a^{-3}. Physically, this is a reflection of the fact that three-body collisions occur with vanishing frequency in the limit of a hard-sphere fluid. Since this is true of n-body collisions in general, we infer that $J_{sp}=J'_{sp}$ for a hard-sphere fluid.

The fact that the quantities J_{sp} all diverge in the limit $a\to 0$ means, according to (3.18), that the fourth- and higher-order moments of the scattering function are infinite. Hence, we have

$$S(\kappa,\omega)\sim 1/\omega^\alpha \text{ as } \omega\to\infty , \quad (6.9)$$

where $3<\alpha<5$. The long high-frequency wings are characteristic of the hard-sphere fluid and reflect the fact that the velocity is a discontinuous function of t.

C. Velocity and Force Autocorrelation Functions

In order that the expression (2.15) for $\rho_1(t)$ satisfy

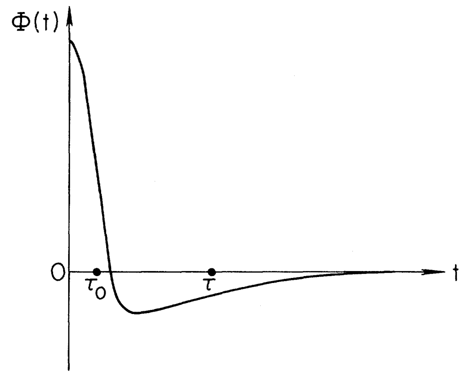

FIG. 2. Force autocorrelation function.

(2.21) it is necessary that[28]

$$\int_0^\infty t^n \Phi(t)\,dt = 0\,, \qquad n=0$$
$$= -3mkT\,, \quad n=1$$
$$= -6m^2D\,, \quad n=2$$
$$= -18m^2C\,, \quad n=3\,. \qquad (6.10)$$

The relations for $n=0$ and 1 also ensure that $\chi(t)\to 0$ as $t\to\infty$, as is evident from (2.14). The simplest form for $\Phi(t)$ consistent with the above relations is that illustrated in Fig. 2, consisting of a positive peak at $t=0$ and a negative tail at large t. The positive peak represents, physically, the intracollisional force correlations and persists for a time of the order of τ_0, the duration of a single collision. In the present context $\tau_0 \sim a/u$ and vanishes in the limit of a hard-sphere fluid. The negative tail, on the other hand, describes the intercollisional correlations among the forces acting on a given atom in successive collisions and persists for a time of the order of τ, the mean time between collisions. Intercollisional correlation effects play an important role in Brownian motion,[5] nuclear electric dipole relaxation,[29] collision-induced infrared absorption[28,30,31] and collision-induced light scattering.[32]

Substitution of the expressions (6.6) into the expansion (4.15) for the force autocorrelation function gives

$$\Phi(t) = \frac{6\eta(kT)^2}{\sigma a}\left[1 - 2\left(\frac{ut}{a}\right)^2 + \frac{10}{3}\left(\frac{ut}{a}\right)^4 - \cdots\right]\,. \qquad (6.11)$$

This expansion clearly describes only the intracollisional part of the force autocorrelation function because it is an expansion in powers of t/τ_0 with density-independent coefficients. It is felt that the asymptotic nature of the above series is not due entirely to the fact that (6.6) gives only the dominant contribution to J_{sp}, but also to the fact that the formal Taylor series expansion (4.15) is itself asymptotic and does not include effects of intercollisional correlations. Equation (6.11) does not satisfy (6.10) but gives instead, in the limit $a\to 0$,

$$\int_0^\infty t^n \Phi(t)\,dt = \tfrac{1}{2}A\,, \quad n=0$$
$$=0\,, \quad n=1, 2, 3, \ldots \qquad (6.12)$$

where

$$A = (12\xi_1\eta/\sigma)(2m)^{1/2}(kT)^{3/2}\,, \qquad (6.13)$$

$$\xi_1 = \int_0^\infty (1 - 2x^2 + \tfrac{10}{3}x^4 - \cdots)\,dx\,. \qquad (6.14)$$

It follows from (6.12) that the intracollisional part of the force autocorrelation function for a hard-sphere fluid is a δ function:

$$\Phi(t) = A\,\delta(t)\,, \qquad (6.15)$$

and hence, from (2.14), that the asymptotic form of the velocity autocorrelation function at small t is given by

$$\chi(t) = 1 - A|t|/6mkT\,. \qquad (6.16)$$

An estimate of ξ_1 can be obtained by expressing (6.14) in the form

$$\xi_1 = \int_0^\infty e^{-2x^2}(1 + \tfrac{4}{3}x^4 + \cdots)\,dx$$
$$= \tfrac{1}{2}(\tfrac{1}{2}\pi)^{1/2} + \tfrac{1}{8}(\tfrac{1}{2}\pi)^{1/2} + \cdots$$
$$= 0.627 + 0.157 + \cdots$$
$$\simeq 0.784\,. \qquad (6.17)$$

This is very near the exact value, $\xi_1 = (2/\pi)^{1/2} = 0.798$, obtained from a direct evaluation of $\dot{\chi}(0^+)$ for the hard-sphere fluid.[5,33] In terms of the exact value for ξ_1 the asymptotic expressions for the velocity and force autocorrelation functions become

$$\chi(t) = 1 - 2|t|/3\tau\,,$$
$$\Phi(t) = (4mkT/\tau)\delta(t)\,, \qquad (6.18)$$

in which τ is the mean time between collisions[18]:

$$\tau = \frac{1}{4\sigma^2\rho\tilde{g}(\sigma)}\left(\frac{m}{\pi kT}\right)^{1/2}\,. \qquad (6.19)$$

D. Cumulant Expansion

On combining (6.18) and (2.15), one finds that

$$\rho_1(t) = u^2(t^2 - 2|t|^3/9\tau)\,, \qquad (6.20)$$

as asserted in (2.17). The corresponding asymptotic expressions for $\rho_2(t)$ and $\rho_3(t)$ can be obtained by arguments similar to those employed in Sec. VIC. Thus, one begins by substituting (6.6) into (4.14), finding that

$$\rho_2(t) = \frac{1}{150}\frac{\eta(ut)^8}{\sigma a^3} - \frac{8}{1575}\frac{\eta(ut)^{10}}{\sigma a^5} + \cdots\,,$$
$$\rho_3(t) = -\frac{2}{6615}\frac{\eta(ut)^{12}}{\sigma a^5} + \cdots\,, \qquad (6.21)$$

from which it follows that, in the limit $a \to 0$,

$$\frac{d^6\rho_2(t)}{dt^6} = \frac{2\xi_2\eta u^5}{\sigma}\,\delta(t)\ ,$$
$$\frac{d^8\rho_3(t)}{dt^8} = \frac{2\xi_3\eta u^7}{\sigma}\,\delta(t)\ , \tag{6.22}$$

where

$$\xi_2 = \int_0^\infty \left(\tfrac{672}{5}x^2 - 768x^4 + \cdots\right)dx\ ,$$
$$\xi_3 = \int_0^\infty \left(-\tfrac{42240}{7}x^4 + \cdots\right)dx\ . \tag{6.23}$$

For $a > 0$, $\rho_2(t)$ and $\rho_3(t)$ satisfy the identities

$$\rho_2(t) = \frac{1}{5!}\int_0^t (t-t')^5 \frac{d^6\rho_2(t')}{dt'^6}\,dt'\ ,$$
$$\rho_3(t) = \frac{1}{7!}\int_0^t (t-t')^7 \frac{d^8\rho_3(t')}{dt'^8}\,dt'\ , \tag{6.24}$$

so that from (6.22) it follows that, in the limit $a \to 0$,

$$\rho_2(t) = (\xi_2\eta/5!\,\sigma)\,|ut|^5\ ,$$
$$\rho_3(t) = (\xi_3\eta/7!\,\sigma)\,|ut|^7\ . \tag{6.25}$$

E. Markovian Approximation

The simplest model for $\chi(t)$, consistent with (6.18) and the requirement that $\chi(t) \to 0$ as $t \to 0$, is that of an exponential decay,

$$\chi(t) = e^{-2|t|/3\tau}\ , \tag{6.26}$$

from which it follows from Sec. II B that

$$\hat{\chi}(\omega) = \frac{3\tau}{2\pi}\,\frac{1}{(\frac{1}{2}3\omega\tau)^2+1}\ , \tag{6.27}$$

$$\Phi(t) = \frac{4mkT}{\tau}\left(\delta(t) - \frac{1}{3\tau}\,e^{-2|t|/3\tau}\right)\ , \tag{6.28}$$

$$\hat{\Phi}(\omega) = \frac{2mkT}{\pi\tau}\,\frac{(\frac{1}{2}3\omega\tau)^2}{(\frac{1}{2}3\omega\tau)^2+1}\ , \tag{6.29}$$

and

$$\rho_1(t) = \frac{9\pi}{32}l^2\left(\frac{2|t|}{3\tau} - 1 + e^{-2|t|/3\tau}\right)\ , \tag{6.30}$$

in which l is the mean free path,[18]

$$l = 1/\sqrt{2}\,\pi\sigma^2 b\tilde{g}(\sigma)\ . \tag{6.31}$$

Also, from (2.21), we have

$$D = \tfrac{3}{16}\pi(l^2/\tau)\ ,\quad C = \tfrac{9}{32}\pi l^2\ . \tag{6.32}$$

The exponential model (6.26) means, physically, that one neglects memory effects and assumes Markovian behavior.[34] From the point of view of the theory of Brownian motion it is equivalent to the assumption that the motion of the atoms is governed by the Langevin equation. The expression (6.23) for D is identical[33] to that obtained from the Enskog theory of transport phenomena in a dense hard-sphere fluid.[18,27]

Molecular dynamics studies of the hard-sphere fluid by Alder and Wainwright[35–37] show that the decay of $\chi(t)$ is in fact exponential to a good approximation at all fluid densities over the time intervals investigated ($|t| \lesssim 8\tau$). The molecular dynamics value for D agrees within 20% with the Enskog value (6.32).

For very large values of t, however, $\chi(t)$ no longer follows an exponential decay but obeys a hydrodynamic $t^{-3/2}$ law.[9–13]

F. Calculation of $\Gamma(\kappa)$ for the Hard-Sphere Fluid

The quantity $\Gamma(\kappa)$, which according to (4.9) measures the narrowing of the classical incoherent scattering function due to final-state interactions, is given for small κ by (4.13). If the Enskog value (6.32) for D is employed in the latter relation, then one finds that

$$\Gamma(\kappa) = 1 - \tfrac{3}{8}(\pi/\ln 2)^{1/2}\kappa l$$
$$= 1 - 0.7984\,\kappa l\ . \tag{6.33}$$

For large values of κ, on the other hand, the series (4.10) provides a useful representation for $\Gamma(\kappa)$. If the coefficients (4.11) are evaluated from (6.6), it follows that

$$\Gamma(\kappa) = \frac{\eta a}{\sigma}\left(\frac{0.38447}{(\kappa a)^2} - \frac{0.070141}{(\kappa a)^4} + \frac{0.010533}{(\kappa a)^6} - \cdots\right)\ . \tag{6.34}$$

Hence, with $\lambda = 1/\kappa$, it is easily seen that, in the limit $a \to 0$,

$$\frac{d^2\Gamma(\lambda)}{d\lambda^2} = \frac{2\xi\eta}{\sigma}\,\delta(\lambda)\ , \tag{6.35}$$

where

$$\xi = \int_0^\infty [(2)(0.38447) - (12)(0.070141)x^2 + (30)(0.010533)x^4 - \cdots]\,dx$$
$$= 0.73496\int_0^\infty e^{-y^2}(1 - 0.15703y^4 + \cdots)\,dy$$
$$= 0.65134 - 0.07671 + \cdots$$
$$\simeq 0.57\ . \tag{6.36}$$

If $a > 0$, $\Gamma(\lambda)$ satisfies the identity

$$\Gamma(\lambda) = \int_0^\lambda (\lambda - \lambda')\,\frac{d^2\Gamma(\lambda')}{d\lambda'^2}\,d\lambda'\ , \tag{6.37}$$

from which it follows with the help of (6.35) that, in the limit $a \to 0$,

$$\Gamma(\lambda) = (\xi\eta/\sigma)\,|\lambda|\ , \tag{6.38}$$

or, from (6.7) and (6.31),

$$\Gamma(\kappa) = \frac{\sqrt{2}\,\xi}{3\kappa l} \simeq \frac{0.27}{\kappa l}\ . \tag{6.39}$$

The asymptotic relations (6.33) and (6.39) indicate that with decreasing κ the change of the scattering function from the Gaussian shape, characteristic of the impulse approximation at large κ, to the Lorentzian shape, characteristic of simple diffusion at small κ, occurs in a hard-sphere fluid when $\kappa l \sim 1$. Since $\kappa \gtrsim 1$ Å^{-1} in most neutron scattering experiments it follows that departures from the impulse approximation are appreciable only if $l \lesssim 1$ Å, i.e., only at typical liquid densities.

APPENDIX: DERIVATION OF EQ. (4.5)

The identity (4.5) can be derived with the help of the binomial theorem by noting first that

$$\delta_{p,0} = \lim_{\epsilon\to 1} \frac{\theta(p)}{p!} (\epsilon - 1)^p$$

$$= \lim_{\epsilon\to 1} \frac{\theta(p)}{p!} \sum_{m=0}^{p} \frac{p!}{(p-m)!m!} \epsilon^m (-)^{p-m}$$

$$= \theta(p) \sum_{m=0}^{p} \frac{(-)^{p-m}}{(p-m)!m!} \quad .$$

Equation (4.5) follows immediately if one replaces p by $p-q$ and puts $n = q + m$.

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

[2]A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. 126, 986 (1962).

[3]P. G. de Gennes, Physica 25, 825 (1959).

[4]P. Schofield, in *Symposium on Inelastic Scattering of Neutrons in Solids and Liquids*, edited by S. Cole (International Atomic Energy Agency, Vienna, 1961), p. 39.

[5]S. A. Rice and P. Gray, *The Statistical Mechanics of Simple Liquids* (Interscience, New York, 1965).

[6]The first two of the relations (2.16) have been obtained previously by Schofield (Ref. 4).

[7]V. F. Sears, Phys. Rev. 185, 200 (1969).

[8]G. H. Vineyard, Phys. Rev. 110, 999 (1958).

[9]B. J. Alder and T. E. Wainwright, Phys. Rev. A 1, 18 (1970).

[10]R. Zwanzig and M. Bixon, Phys. Rev. A 2, 2005 (1970).

[11]K. Kawasaki, Phys. Letters 32A, 379 (1970).

[12]J. R. Dorfman and E. G. D. Cohen, Phys. Rev. Letters 25, 1257 (1970).

[13]M. H. Ernst, E. H. Hauge, and J. M. J. Van Leeuwen, Phys. Rev. Letters 25, 1254 (1970).

[14]M. S. Nelkin and D. E. Parks, Phys. Rev. 119, 1060 (1960).

[15]M. S. Nelkin, in Ref. 4, p. 3.

[16]B. R. A. Nijboer and A. Rahman, Physica 32, 415 (1966).

[17]V. F. Sears, Phys. Rev. A 1, 1699 (1970).

[18]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[19]L. Verlet, Phys. Rev. 165, 201 (1968).

[20]G. H. A. Cole, Repts. Progr. Phys. 31, 419 (1968).

[21]J. S. Rowlinson, Mol. Phys. 6, 517 (1963).

[22]B. J. Alder, Phys. Rev. Letters 12, 317 (1964).

[23]A. Rahman, Phys. Rev. Letters 12, 575 (1964).

[24]G. Dolling and V. F. Sears, Solid State Commun. 8, 2091 (1970).

[25]G. Boato, G. Casanova, and A. Levi, J. Chem. Phys. 37, 201 (1962).

[26]T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), p. 210.

[27]S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge U.P., London, 1939).

[28]V. F. Sears, Can. J. Phys. 46, 2315 (1968).

[29]E. M. Purcell, Phys. Rev. 117, 828 (1960).

[30]J. Van Kranendonk, Can. J. Phys. 46, 1173 (1968).

[31]V. F. Sears, Can. J. Phys. 46, 1163 (1968).

[32]J. C. Lewis and J. Van Kranendonk, Phys. Rev. Letters 24, 802 (1970).

[33]H. C. Longuet-Higgins and J. A. Pople, J. Chem. Phys. 25, 884 (1956).

[34]V. F. Sears, Can. J. Phys. 47, 199 (1969), and references cited therein.

[35]B. J. Alder and T. E. Wainwright, in *Transport Processes in Statistical Mechanics*, edited by I. Prigogine (Interscience, New York, 1958), p. 97.

[36]B. J. Alder and T. E. Wainwright, in *The Many-Body Problem*, edited by J. K. Percus (Interscience, New York, 1963), p. 511.

[37]B. J. Alder and T. E. Wainwright, Phys. Rev. Letters 18, 988 (1967).