

Simple Binary Collision Model for Van Hove's $G_s(r,t)$ †

MARK NELKIN AND AJOY GHATAK*

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

(Received 28 January 1964)

It is noted that the Van Hove self-correlation function $G_s(r,t)$ for a dilute fluid is determined by a linearized Boltzmann equation identical to that occurring in the theory of neutron diffusion. A simple model for the collision integral, in which a molecule emerges from a collision with a Maxwellian distribution, allows some interesting analytic results to be obtained. The double Fourier transform $S_s(\kappa,\omega)$, of $G_s(r,t)$ is expressible in terms of the probability integral for complex arguments. Since $S_s(\kappa,\omega)$ is directly proportional to the Mössbauer line shape, the transition of the line shape from Doppler broadening to simple diffusion broadening is explicitly exhibited as a function of momentum transfer. The spatial moments of $G_s(r,t)$ are calculated as a function of time. The model used gives the same mean-square displacement as does the Langevin equation. The resulting $G_s(r,t)$ is not, however, Gaussian as is shown by the mean fourth power of the displacement which is 25% greater at intermediate times than would be predicted by the Langevin equation. The non-Gaussian effects lead to an appreciable narrowing of $S_s(\kappa,\omega)$ for intermediate values of κ .

I. INTRODUCTION

THE function $G_s(r,t)$ was introduced by Van Hove¹ as the double Fourier transform of the differential energy transfer cross section, $S_s(\kappa,\omega)$ for the incoherent scattering of slow neutrons. It plays a similar role in determining the line shape of the Mössbauer line and of the Doppler broadened neutron absorption resonance line in a fluid.² In the classical limit $G_s(r,t)$ is the probability per unit volume for finding an atom at the position r at time t if the same atom (or more precisely its nucleus) is known to have been at the origin at time zero. Recent work^{3,4} has clarified the relation of this classical limit to the quantum-mechanical process of slow neutron scattering. This work has confirmed the validity of analyzing incoherent neutron scattering from heavy monatomic fluids in terms of the classical $G_s(r,t)$. We consider only this classically defined function and its Fourier transform in the present paper.

A general description of $G_s(r,t)$ in a classical fluid was first given by Vineyard,⁵ who introduced the Gaussian approximation

$$G_s(r,t) \approx [\pi w^2(t)]^{-3/2} \exp[-r^2/w^2(t)] \quad (1)$$

which has been employed in most subsequent work. Non-Gaussian corrections have been considered by Schofield⁶ in the limit of short times, and by Rahman, Singwi, and Sjölander⁷ in the limit of long times, but no quantitative estimates have been given for intermediate times where these corrections are expected to be largest. The Gaussian approximation leads naturally to the consideration of stochastic models for $w(t)$ in analogy to

the theory of Brownian motion. This line of investigation was initiated by Vineyard⁵ and has been most extensively developed by Rahman, Singwi, and Sjölander.⁸ Such descriptions have been useful in obtaining a semiquantitative understanding of slow-neutron scattering data, but it seems appropriate now to shift to a more detailed molecular picture if we are to make most effective use of the more accurate neutron scattering data which are becoming available.

A natural first step is to consider a dilute gas in which the atomic motions are determined by random binary collisions, and the distribution function satisfies the Boltzmann equation. We apply the Boltzmann equation on the microscopic scale associated with localizing an atom at the origin at time zero. The justification for using the Boltzmann equation at this fine a level of description is the demonstration by Grad⁹ "that the Boltzmann equation becomes more nearly valid as the density decreases, and that it is valid for arbitrarily large deviations from equilibrium within a mean free path and arbitrarily rapid fluctuations compared with the mean collision time; the limiting length is the diameter of a molecule and the limiting time is the mean duration of a collision."

Since the disturbance we consider is of microscopically small amplitude, the Boltzmann equation (BE) that we must solve is linear. In addition to $G_s(r,t)$ which satisfies a linear BE analogous to the one occurring in neutron diffusion, there is also a linear BE satisfied by the function $G(r,t)$, which is defined as the probability per unit volume of finding *any* atom at the position r at time t given that an atom was at the origin at time zero. This latter linear BE is the usual linearized BE as it occurs, for example, in the theory of sound propagation in gases.¹⁰ In the BE giving $G_s(r,t)$ momentum and energy

† Work supported in part by the U. S. Atomic Energy Commission.

* Now at Brookhaven National Laboratory, Upton, New York.

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

² M. S. Nelkin and D. E. Parks, Phys. Rev. **119**, 1060 (1960).

³ R. Aamodt, K. M. Case, M. Rosenbaum, and P. F. Zweifel, Phys. Rev. **126**, 1165 (1962).

⁴ A. Rahman, Phys. Rev. **130**, 1334 (1963).

⁵ G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

⁶ P. Schofield, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961).

⁷ A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 986 (1962).

⁸ A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 997 (1962).

⁹ H. Grad, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 12, p. 205.

¹⁰ G. E. Uhlenbeck and G. W. Ford, *Lectures in Statistical Mechanics* (American Mathematical Society, Providence, 1963), Chap. 5.

are transferred between the "test particle" and the other molecules. Thus, an approximation to the transition probability need not accurately satisfy the conservation laws dictated by the kinematics of binary collisions. It is known,¹⁰ however, that energy and momentum conservation must be exactly maintained if the linearized BE for $G(r, t)$ is to properly describe sound propagation. In the present paper we consider only $G_s(r, t)$, for which a very simple kinetic model can be formulated. A calculation of $G(r, t)$ using a kinetic model is necessarily more complicated because of the role of the conservation laws, and will be deferred to a later paper. It should be emphasized that these kinetic models are derivative from the Boltzmann equation, and are thus relevant only for dilute gases and not for liquids. The models are useful, however, in that they demonstrate, in a simple and reasonably accurate manner, the effects of intermolecular collisions on the time-dependent correlation functions.

II. FORMULATION OF THE PROBLEM

The definition of the classical $G_s(r, t)$ corresponds to tagging an atom at a particular time with a marker which does not perturb the system, and then following the subsequent motion of the tagged atom. The function $G_s(r, t)$ describes this motion on the average over a large number of systems. In a dilute gas the motion of the tagged atom is determined entirely by free streaming and by random binary collisions with the untagged atoms of the gas. The appropriate description is thus the *linear* BE describing the diffusion of a dilute gas of type- A atoms in a gas of type- B atoms which is in equilibrium. We can thus neglect A - A collisions as being of negligible frequency, and B - B collisions play no role since the B atoms are in equilibrium. The A atoms differ from the B atoms only by their distinguishability, but are dynamically identical. In neutron scattering, this distinguishability arises from the nuclear spin flip or isotopic incoherence. In the Mössbauer case, it arises from the emission of a γ ray by a particular nucleus. The linear BE describing the average subsequent motion of the tagged atom is of exactly the same form as the governing equation in neutron transport theory. The particular form of the collision integral is quite different, in general, but the analogy to certain primitive models of neutron thermalization is quite close. The active recent study of the latter problem in connection with its applications to reactor technology can thus be exploited in the present context.

The linear BE from which we obtain $G_s(r, t)$ is not an equation for $G_s(r, t)$, but for the density $f(\mathbf{r}, \mathbf{v}, t)$ in phase space. The equation is

$$\left[\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla + \alpha(v) \right] f(\mathbf{r}, \mathbf{v}, t) = \int W(\mathbf{v}', \mathbf{v}) f(\mathbf{r}, \mathbf{v}', t) d^3v', \quad (2)$$

where $W(\mathbf{v}, \mathbf{v}') d^3v'$ is the transition probability per unit time for an atom of velocity \mathbf{v} to make a scattering

collision into the element d^3v' at velocity \mathbf{v}' . The scattering probability per unit time is given by

$$\alpha(v) = \int W(\mathbf{v}, \mathbf{v}') d^3v' \quad (3)$$

so that the number of particles is conserved in a collision. Since we must sample an ensemble of systems at thermal equilibrium to determine $G_s(r, t)$ the appropriate initial condition is

$$f(\mathbf{r}, \mathbf{v}, 0) = f_M(\mathbf{v}) \delta(\mathbf{r}), \quad (4)$$

where

$$f_M(\mathbf{v}) = (m/2\pi kT)^{3/2} \exp(-m\mathbf{v}^2/2kT) \quad (5)$$

is the equilibrium Maxwellian distribution at the gas temperature. The function $G_s(r, t)$ is obtained by integrating over velocity space:

$$G_s(r, t) = \int f(\mathbf{r}, \mathbf{v}, t) d^3v. \quad (6)$$

From Eqs. (2)–(4) we see that $G_s(r, t)$ has the required general properties that

$$G_s(r, 0) = \delta(\mathbf{r}) \quad (7)$$

and

$$\int G_s(r, t) d^3r = 4\pi \int_0^\infty G_s(r, t) r^2 dr = 1. \quad (8)$$

In most problems in neutron scattering it is more convenient to deal with the so-called intermediate scattering function

$$\chi_s(\kappa, t) = \int \exp(i\boldsymbol{\kappa} \cdot \mathbf{r}) G_s(r, t) d^3r, \quad (9)$$

rather than with $G_s(r, t)$ directly. Introducing the spatial Fourier transform of the phase-space density

$$\tilde{f}(\boldsymbol{\kappa}, \mathbf{v}, t) = \int \exp(i\boldsymbol{\kappa} \cdot \mathbf{r}) f(\mathbf{r}, \mathbf{v}, t) d^3r \quad (10)$$

our linear BE becomes

$$\left[\frac{\partial}{\partial t} + i\boldsymbol{\kappa} \cdot \mathbf{v} + \alpha(v) \right] \tilde{f}(\boldsymbol{\kappa}, \mathbf{v}, t) = \int W(\mathbf{v}', \mathbf{v}) \tilde{f}(\boldsymbol{\kappa}, \mathbf{v}', t) d^3v', \quad (11)$$

with the initial condition

$$\tilde{f}(\boldsymbol{\kappa}, \mathbf{v}, 0) = f_M(\mathbf{v}). \quad (12)$$

The intermediate scattering function is related to the phase-space density through

$$\chi_s(\kappa, t) = \int \tilde{f}(\boldsymbol{\kappa}, \mathbf{v}, t) d^3v, \quad (13)$$

and has the general properties

$$\chi_s(\kappa, 0) = \chi_s(0, t) = 1, \quad (14)$$

which follow from (7) and (8). From the isotropy of the system $\chi_s(\kappa, t)$ depends only on the magnitude of κ .

Finally the quantity of direct interest in neutron scattering experiments is

$$S_s(\kappa, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\omega t} \chi_s(\kappa, t) dt. \quad (15)$$

Since $\chi_s(\kappa, t)$ is determined from an initial value problem, we must specify its behavior for negative times in order to completely define $S_s(\kappa, \omega)$. To do this we recall that $S_s(\kappa, \omega)$ is, in general, a real function. For a classical system, $S_s(\kappa, \omega)$ is an even function of ω , and $\chi_s(\kappa, t)$ is a real even function of time. Introducing the Laplace transform for imaginary argument

$$\tilde{f}(\kappa, \mathbf{v}, \omega) = \int_0^{\infty} e^{-i\omega t} \tilde{f}(\kappa, \mathbf{v}, t) dt, \quad (16)$$

and

$$Q(\kappa, \omega) = \int \tilde{f}(\kappa, \mathbf{v}, \omega) d^3v = \int_0^{\infty} e^{-i\omega t} \chi_s(\kappa, t) dt, \quad (17)$$

we have

$$S_s(\kappa, \omega) = (1/2\pi)[Q(\kappa, \omega) + Q^*(\kappa, \omega)], \quad (18)$$

where $\tilde{f}(\kappa, \mathbf{v}, \omega)$ is the solution of

$$\begin{aligned} & [i\omega + i\kappa \cdot \mathbf{v} + \alpha(v)] \tilde{f}(\kappa, \mathbf{v}, \omega) \\ & = \int W(\mathbf{v}', \mathbf{v}) \tilde{f}(\kappa, \mathbf{v}', \omega) d^3v' + f_M(\mathbf{v}). \end{aligned} \quad (19)$$

This completes the formal preliminaries. We turn now to actual calculations using a simple model for $W(\mathbf{v}, \mathbf{v}')$.

III. SIMPLE KINETIC MODEL

The simplest model for $W(\mathbf{v}, \mathbf{v}')$ which conserves particle number and satisfies the "detailed balance" condition

$$W(\mathbf{v}, \mathbf{v}') f_M(\mathbf{v}) = W(\mathbf{v}', \mathbf{v}) f_M(\mathbf{v}') \quad (20)$$

is the single-relaxation-time model

$$W(\mathbf{v}', \mathbf{v}) \approx \alpha f_M(\mathbf{v}). \quad (21)$$

This model was first introduced by Bohm and Gross¹¹ in considering the collisional damping of plasma oscillations. It is a more appropriate model for our present test particle problem because energy and momentum are not conserved even by the correct collision terms in the BE. The same model has been recently used in a mathematically similar context by Corngold *et al.*¹² in the study of neutron thermalization.

Although the approximation (21) cannot hold exactly

¹¹ D. Bohm and E. P. Gross, Phys. Rev. **75**, 1851 (1949).

¹² Noel Corngold, Paul Michael, and Warren Wollman, Nucl. Sci. Eng. **15**, 13 (1963).

for any binary collision kernel, it does not violate any of the basic constraints of the problem. One can think of it as an absorption followed by a re-emission with an equilibrium velocity distribution. In a sense, it corresponds to assigning to a single collision the actual properties of multiple collisions. It is thus appropriate to say that (21) corresponds to the maximum rate of thermalization consistent with a given collision rate α . Since we are interested in quantities like $G_s(r, t)$ which are integrated over all velocities, we might at first sight expect that the results would be insensitive to the thermalization rate. From the closely analogous "diffusion cooling" phenomenon¹³ in the decay of a thermalized neutron pulse, however, we know that this is not quite the case.

If we substitute (21) into (19), divide by $(\alpha + i\omega + i\kappa \cdot \mathbf{v})$, and integrate over all velocities, we find that

$$Q(\kappa, \omega) [1 + \alpha Q(\kappa, \omega)]^{-1} = I(\kappa, \omega), \quad (22)$$

where $I(\kappa, \omega)$ is defined by (18),

$$I(\kappa, \omega) = \pi^{-1/2} \int_{-\infty}^{\infty} e^{-u^2} [\alpha + i\omega + i\kappa v_0 u]^{-1} du, \quad (23)$$

and $v_0 = (2kT/m)^{1/2}$.

Introducing the variables

$$x = -\omega/\kappa v_0, \quad y = \alpha/\kappa v_0, \quad \text{and} \quad z = x + iy, \quad (24)$$

we can write

$$\alpha I(\kappa, \omega) = \pi^{1/2} y w(z) = \pi^{1/2} y [u(x, y) + iv(x, y)], \quad (25)$$

where

$$w(z) = i\pi^{-1} \int_{-\infty}^{\infty} e^{-t^2} (z-t)^{-1} dt \quad (26)$$

is the probability integral for complex argument and is a tabulated function.¹⁴

Finally, we introduce

$$\begin{aligned} U(x, y) &= \pi^{1/2} y u(x, y), \\ V(x, y) &= \pi^{1/2} y v(x, y), \end{aligned} \quad (27)$$

and use (18) to obtain

$$S_s(\kappa, \omega) = \frac{1}{\pi\alpha} \frac{U(1-U) - V^2}{(1-U)^2 + V^2}. \quad (28)$$

It is readily verified that (28) has the correct limiting behavior for both large and small momentum transfer. For large momentum transfer, we can neglect collisions, and let y approach zero. This yields the familiar result

¹³ The phenomenon was first described by G. Von Dardel and A. Sjöstrand, Phys. Rev. **96**, 1245 (1954). The theory is discussed by M. Nelkin, Nucl. Sci. Eng. **7**, 210 (1960).

¹⁴ V. N. Faddeyeva and N. M. Terent'ev, *Tables of the Probability Integral for Complex Arguments* (Pergamon Press, Inc., New York, 1961).

for an ideal gas in the classical limit

$$\lim_{y \rightarrow 0} S_s(\kappa, \omega) = (\kappa v_0 \pi^{1/2})^{-1} \exp[-\omega^2 / \kappa^2 v_0^2]. \quad (29)$$

In the limit of small momentum transfer, we expect to obtain the simple diffusion result first suggested by Vineyard.⁵ To evaluate $S_s(\kappa, \omega)$ in this limit of large y we use the asymptotic expression¹⁴

$$w(z) \approx i\pi^{-1/2} z (z^2 - \frac{1}{2})^{-1} \quad (30)$$

to obtain

$$S_s(\kappa, \omega) \approx \frac{2}{\pi \alpha} \frac{y^2}{1 + 4(y^2 - 1)x^2 + 4x^4} \quad (31)$$

as a good approximation for all values of x , if y is sufficiently large. For $x \lesssim y^{-1}$, where S is appreciable, (31) is accurately given by

$$S_s(\kappa, \omega) \approx \frac{2}{\pi \alpha} \frac{y^2}{1 + 4x^2 y^2}. \quad (32)$$

We see in Sec. IV that the coefficient of self diffusion for this model is given by

$$D = v_0^2 / 2\alpha \quad (33)$$

so that (32) can be expressed in the more familiar form

$$S_s(\kappa, \omega) \approx \frac{1}{\pi} \frac{D\kappa^2}{\omega^2 + (D\kappa^2)^2}. \quad (34)$$

Consider $S_s(\kappa, \omega)$ as the line shape for a Mössbauer line. In this case κ is fixed by the γ -ray energy and the mass of the nucleus, and $\hbar\omega$ is the energy shift of the emitted or absorbed γ ray. In the limit that κ is large we have the familiar Doppler line shape (29). In the opposite limit we have the equally familiar limit of diffusion broadening. The basic result of the present paper is the expression (28) which allows one to calculate the line shape analytically in the intermediate region. This is possible only because we have used the grossly simplified expression (21) for the collision integral in the BE.

The characteristic narrowing of the line shape due to collisions is best seen by plotting

$$R(x, y) = \alpha y^{-1} S_s(\kappa, \omega) \quad (35)$$

as a function of x for fixed y . This function is normalized to unit area when integrated over all x . We plot this result in Fig. 1 for various values of y ranging from zero to one. The approach to the simple diffusion line shape for small κ is best displayed by plotting

$$F(\zeta, y) = \alpha y^{-2} S_s(\kappa, \omega) \quad (36)$$

as a function of

$$\zeta = xy = \omega / 2D\kappa^2 \quad (37)$$

for fixed y . In the limit of large y we have

$$\lim_{y \rightarrow \infty} F(\zeta, y) = \frac{2}{\pi} \frac{1}{1 + 4\zeta^2}. \quad (38)$$

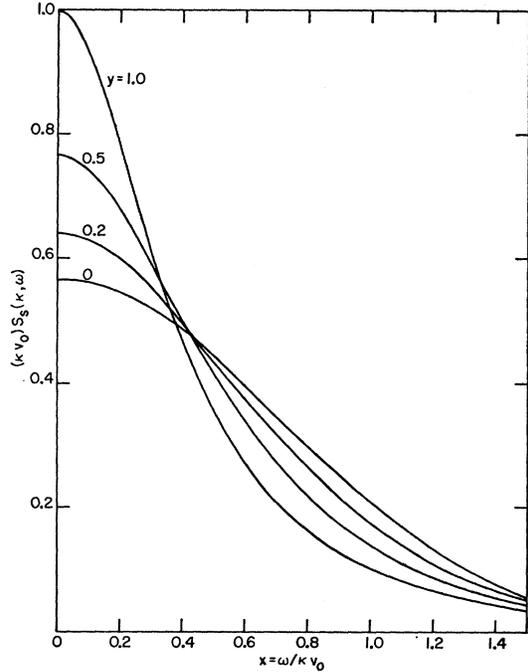


FIG. 1. The deviations from the ideal-gas line shape as the collision rate is increased are exhibited by plotting $\kappa v_0 S_s(\kappa, \omega)$ as a function of $(\omega/\kappa v_0)$ for values of $y = (\alpha/\kappa v_0)$ ranging from 0 to 1. The curve for $y=0$ is the ideal-gas result of Eq. (29).

In Fig. 2 we plot $F(\zeta, y)$ and obtain the characteristic result that the line shape is narrower than the simple diffusion line shape, but approaches it for large y . The result for $y=5$ is almost identical to the limiting result (38). The dashed curves give the results in the Gaussian approximation, and are discussed in Sec. IV.

IV. SPATIAL MOMENTS AND THE GAUSSIAN APPROXIMATION

The kinetic model (21) does not allow an analytic calculation of $\chi_s(\kappa, t)$ or $G_s(r, t)$ as it does for $S_s(\kappa, \omega)$, but it does allow the analytic calculation of the spatial moments of $G_s(r, t)$ as a function of time. To do this calculation we go back to (11), and make the expansion

$$\tilde{f}(\mathbf{r}, \mathbf{v}, t) = \sum_{n=0} \sum_{l=0} f_{nl}(v, t) (i\kappa)^n P_l(\mu), \quad (39)$$

where

$$\mu = (\mathbf{v} \cdot \boldsymbol{\kappa} / \kappa v). \quad (40)$$

Substituting (39) into (11), and using (21) and the spherical harmonics addition theorem, we obtain the set of equations,

$$\left(\alpha + \frac{\partial}{\partial t} \right) f_{nl} = v \left(\frac{l+1}{2l+3} f_{n-1, l+1} + \frac{l}{2l-1} f_{n-1, l-1} \right) + f_M(v) \int f_{nl} v^2 v \delta_{l,0}, \quad (41)$$

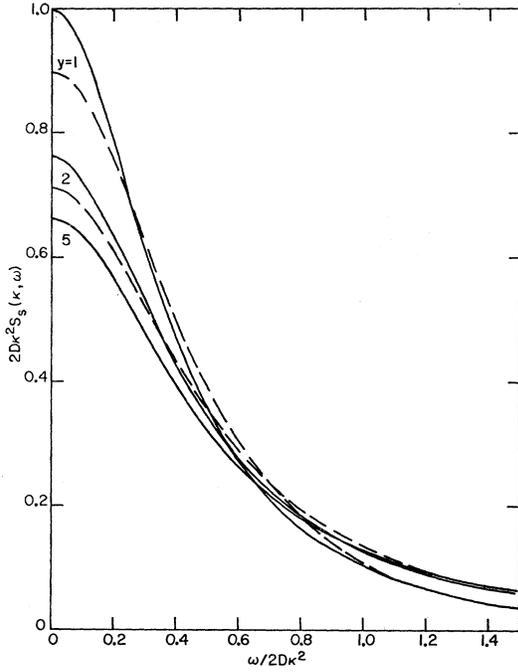


FIG. 2. The deviations from the simple diffusion line shape as the collision rate is decreased are exhibited by plotting $2D\kappa^2 S_s(\kappa, \omega)$ as a function of $(\omega/2D\kappa^2)$ for values of γ ranging from 1 to 5. The curve for $\gamma=5$ is almost identical to the simple diffusion result of Eq. (34) which would apply in the limit as γ approaches infinity. The dashed curves refer to the Gaussian approximation of Eq. (49).

where $f_{nl} \equiv 0$ for $n < 0$. The initial conditions are

$$f_{nl}(v, 0) = f_M(v) \delta_{n,0} \delta_{l,0}. \quad (42)$$

The set of equations (41) is a straightforward generalization of the time-dependent case of the "moments form" of the BE as used in neutron transport theory.¹⁵ The further generalization to an arbitrary $W(\mathbf{v}', \mathbf{v})$ is also straightforward, but will not be used here. With the initial conditions (42) the functions $f_{nl}(v, t)$ are identically zero unless $n+l$ is even and $n \geq l$.

The quantities of greatest physical interest are the spatial moments of $G_s(\mathbf{r}, t)$

$$\langle r^{2n}(t) \rangle = (2n+1)! G_{2n}(t), \quad (43)$$

where

$$G_{2n}(t) \equiv 4\pi \int_0^\infty f_{2n,0}(v, t) v^2 dv. \quad (44)$$

We can integrate the set of equations (41) in an appropriate order, beginning with $f_{11}(v, t)$ to obtain

$$G_{2,0}(t) = (v_0^2/2\alpha^2) [\tau - (1 - e^{-\tau})] \quad (45)$$

and

$$G_{4,0}(t) = (v_0^4/4\alpha^4) \left[\frac{1}{2}\tau^2 + (\tau^2 + 3\tau + 3)e^{-\tau} - 3 \right], \quad (46)$$

where $\tau = \alpha t$.

¹⁵ A. Weinberg and E. P. Wigner, *The Physical Theory of Neutron Chain Reactions* (The University of Chicago Press, Chicago, 1958), pp. 365-367.

The coefficient of self diffusion D is defined by

$$D \equiv \frac{1}{6} \lim_{t \rightarrow \infty} \langle r^2(t) \rangle / t \quad (47)$$

and thus has the value $(v_0^2/2\alpha)$ for our approximate collision integral. The expression (45) gives the same mean-square displacement as is given by a simple Langevin equation¹⁶ with damping constant α . For the Langevin equation, however, $G_s(\mathbf{r}, t)$ is a Gaussian of the form of Eq. (1) so that

$$\langle r^4(t) \rangle / \langle r^2(t) \rangle^2 = 5/3$$

for all times. Examination of Eqs. (45) and (46) shows that (48) holds for our model in the limit of short and long times, but not at intermediate times. In Fig. 3 we plot the ratio

$$\frac{3 \langle r^4(t) \rangle}{5 \langle r^2(t) \rangle^2} = \frac{2G_{4,0}(t)}{[G_{2,0}(t)]^2} \quad (48)$$

as a function of $\tau = \alpha t$. We see that it reaches a maximum of 1.22 at $\tau = 4$.

To compare our analytic calculations of $S_s(\kappa, \omega)$ with the Gaussian approximation, we can use a result of Singwi and Sjölander¹⁷ for the Fourier transform of $\exp[-\kappa^2 G_{2,0}(t)]$ with $G_{2,0}(t)$ given by (45). Their result is given as an infinite series which is rapidly convergent for large values of γ and is thus most directly comparable with Eq. (36). The result is

$$\begin{aligned} F^G(\zeta, \gamma) &= \alpha \gamma^{-2} \pi^{-1} \int_0^\infty \cos \omega t \exp[-\kappa^2 G_{2,0}(t)] dt \\ &= \frac{2}{\pi} \exp\left(\frac{1}{2\gamma^2}\right) \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \\ &\quad \times \left(\frac{1}{2\gamma^2}\right)^n \frac{(1+2n\gamma^2)}{(1+2n\gamma^2)^2 + 4\zeta^2}. \quad (49) \end{aligned}$$

For $\gamma=5$ this is practically identical to the simple diffusion result (38) which is the first term in the series. The results for $\gamma=1$ and $\gamma=2$ are plotted as the dashed lines in Fig. 2. It is seen that the Gaussian approximation gives an appreciably broader line than does the exact solution for this model.

From Eqs. (45) and (46) it follows that the short time behavior of the ratio (48) is given by

$$1 + \frac{2}{15} \alpha t + \dots \quad (50)$$

This disagrees with a general result of Schofield⁶ who

¹⁶ To be more precise we refer to the Langevin equation for a free particle with an initially Maxwellian distribution of velocities. The displacement distribution for this case was shown to be Gaussian by J. L. Doob, *Ann. Math.* **43**, 351 (1942) [reprinted in *Noise and Stochastic Processes*, edited by Nelson Wax (Dover Publications, Inc., New York, 1954)].

¹⁷ K. S. Singwi and A. Sjölander, *Phys. Rev.* **119**, 863 (1960).

proved that departures from the Gaussian approximation for a classical system are of order t^8 at short times. This disagreement comes from our use of a BE rather than from the approximation (21), and reflects the error in replacing the dynamics of the system by random collisions at short times. (Only in the fictitious limiting case of a rigid-sphere fluid would we expect the result from the BE to be preferable to Schofield's result which was derived from general dynamical arguments.) We thus cannot expect our present results to give correctly the Placzek moments,¹⁸

$$\int \omega^{2n} S_s(\kappa, \omega) d\omega, \quad (51)$$

which depend on the analytic behavior of $G_s(r, t)$ at short times. The entire basis of the BE as an approximate description rests on the unimportance of times short compared to the duration of a collision. It is precisely this short time scale, however, which determines the moments (51).

V. DISCUSSION

The calculation of the present paper is applicable to $G_s(r, t)$ in monatomic gases. The parameter α can be chosen to yield the observed diffusion coefficient. Under some circumstances $S_s(\kappa, \omega)$ is directly observable in a gas as the line shape for optical emission where the Doppler broadening is reduced by collisions with a buffer gas.¹⁹ To the authors' knowledge there is no experimental data on the incomplete collisional narrowing that would occur if the number of collisions during the relevant time scale is not large. The present model would apply directly in such circumstances.

The available data for $G_s(r, t)$ come from neutron inelastic scattering²⁰ and the Mössbauer line shape²¹ in liquids. The analysis of these data shows⁸ that a quasicrystalline model is more appropriate than a gas model of the type used here. One feature of the present analysis which is, however, qualitatively in agreement with these experiments is the departure from the Gaussian approximation. From the result plotted in Fig. 3 it follows that $\chi_s(\kappa, t)$ decays less rapidly with increasing κ^2 than does $\exp[-\kappa^2 G_{2,0}(t)]$, and that this effect is most pronounced at intermediate times. These features are

¹⁸ G. Placzek, Phys. Rev. **86**, 377 (1952).

¹⁹ R. H. Dicke, Phys. Rev. **89**, 472 (1953); J. P. Wittke and R. H. Dicke, *ibid.* **103**, 620 (1956).

²⁰ See *Proceedings of the 1962 Chalk River Conference* (International Atomic Energy Agency, Vienna, 1963), Vol. 1.

²¹ P. P. Craig and N. Sutin, Phys. Rev. Letters **11**, 460 (1963).

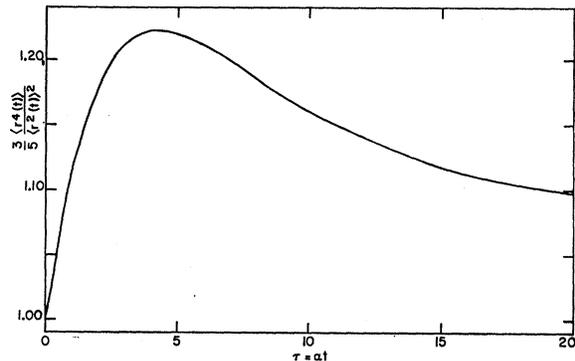


FIG. 3. The non-Gaussian behavior of the present model is illustrated by plotting $3\langle r^4(t) \rangle / 5\langle r^2(t) \rangle^2$ as a function of αt . If $G_s(r, t)$ were Gaussian, this ratio would be one at all times.

present in the analysis of Pope *et al.*,²² but a quantitative comparison is not appropriate.

One can proceed in either of two directions from the present work. One approach is to study the dilute gas with collisions as a model system, and to thoroughly understand the behavior of $G_s(r, t)$ and $G(r, t)$ by accurately solving the BE for physically reasonable interatomic force laws. The present work and its existing extension²³ to $G(r, t)$ can then be considered as illustrative of the kind of results that can be obtained. Work in this direction is certainly feasible, and is desirable to put our understanding of time dependent correlations in fluids on a sounder theoretical basis. It is not likely to lead, however, to any direct comparison between theory and experiment. A more exciting possibility, but one which is both ambiguous and difficult, is to derive or postulate kinetic equations applicable to dense fluids. Such an approach puts the physical problem on the intuitively accessible level of a kinetic equation, and separates the complex but relatively straightforward problem of solving the resulting kinetic equation.

ACKNOWLEDGMENTS

The authors would like to thank S. Ranganathan for performing the computations. They would also like to thank Professor Joel Ferziger and Alan Gibbs for sending them a preprint of a related calculation, and the reviewer for pointing out to them the existence of Eq. (49).

²² N. K. Pope, B. N. Brockhouse, R. H. Johnson, and M. Sakamoto, Bull. Am. Phys. Soc. **7**, 24 (1962). See also Ref. 20, p. 189.

²³ S. Yip and M. Nelkin (unpublished).