Decay of Time Correlations in Two Dimensions

T. E. Wainwright, B. J. Alder, and D. M. Gass

Lawrence Radiation Laboratory, University of California, Livermore, California 94550

(Received 4 January 1971)

Molecular-dynamic studies of the kinetic correlation functions for shear viscosity and heat conductivity of hard disks are consistent with the asymptotic reciprocal time behavior $1/S$ predicted by hydrodynamics. However, this hydrodynamic description, which predicts divergent transport coefficients, must be made self-consistent by introducing time-dependent transport coefficients, leading to a decay of $1/S\sqrt{(\ln S)}$, indistinguishable from the $1/S$ behavior. The hydrodynamic model predicts no such long-time behavior for the potential contributions.

A number of investigators[1-5] have come by a variety of techniques to the conclusion that autocorrelation functions involving kinetic flow behave in a non-Markovian manner indefinitely, leading in two dimensions to divergent transport coefficients. This behavior was suggested by a molecular-dynamics study of the velocity autocorrelation function at fairly long times which could be almost exactly reproduced by a hydrodynamic model.[6] In this hydrodynamic model, the velocity of a small volume element is followed as it slows down in a large body of fluid which is initially at rest and characterized by a viscosity and compressibility. The hydrodynamic flow field developed around the initially moving volume element also agreed nearly exactly for times greater than about 10 mean collision times with the correlations which developed in a molecular-dynamic system in the motion between a molecule and its surrounding molecules.

In this paper the asymptotic form of this hydrodynamic flow field is used to determine the long-time behavior of various other correlation functions occurring in the evaluation of transport coefficients. Comparisons are then made with molecular-dynamic calculations of the same correlation functions for a two-dimensional system of hard disks. The presentation here is confined to two-dimensional systems in order to emphasize how the inconsistency, caused by a hydrodynamic model with finite transport coefficients that predicts divergent ones, can be removed by the use of time-dependent transport coefficients. The introduction of these time-dependent transport coefficients into the Navier-Stokes equations makes it also possible to predict correlation-function behavior at times shorter than those for which the asymptotic form is applicable. The quantitative determination over what time scale such a model is valid awaits numerical solution of the modified hydrodynamic equations.

The calculation of the asymptotic decay of the different correlation functions will first be demonstrated for the shear viscosity, ignoring the self-consistency problem. The shear viscosity is related to the autocorrelation of the stress-tensor elements:

$$J^\eta_{xy} = \sum_i \dot{x}_i \dot{y}_i + \sum_i \ddot{x}_i y_i ,$$

where $\dot{x}_i$ and $\dot{y}_i$ are components of the velocity of molecule i, and $\ddot{x}_i$ is proportional to the x component of the force exerted on molecule i. Since J consists of a sum of a kinetic and a potential term, the autocorrelation function of J consists of three terms which will be discussed separately. The kinetic term requires evaluation of

$$\rho^\eta_K(s) = \left\langle \sum_i \dot{x}_i(t)\, \dot{y}_i(t) \sum_j \dot{x}_j(t+s)\, \dot{y}_j(t+s) \right\rangle , \quad (1)$$

where the bracket indicates an ensemble average which in the molecular-dynamic calculation is accomplished by averaging over the initial times t. Instead of dealing with a finite system of N particles with periodic boundary conditions as required for comparison with molecular dynamics, the formulation, for brevity's sake, is carried out for infinite systems with the understanding that a correction of $1/N$ must be added to the finite $\rho_K(s)$ just as in the diffusion coefficient and for the same reason.[6]

Assuming that the correlated motion of molecule j at time $t+s$ is due to the correlations which have been set up by a molecule p at time t, we have

$$\dot{x}_j(t+s) = [v_\parallel(\vec{r}_{pj}, s)\, \dot{x}_p(t) - v_\perp(\vec{r}_{pj}, s)\, \dot{y}_p(t)] , \quad (2)$$

where $v_\parallel$ and $v_\perp$ are the parallel and perpendicular components of the normalized hydrodynamic flow field set up by a molecule p at a molecule j located at position $\vec{r}_{pj}$ relative to the initial position of molecule p. The minus sign arises from a convention adopted when one rectangular coordinate system is projected onto another one. The hydrodynamic flow field has previously been given[7] in terms of polar coordinates centered at p involving the distance r between particles p and j and the angle θ between the pj direction and the original direction of motion of p:

$$v_\parallel = R(r, s) \cos^2\theta - T(r, s) \sin^2\theta ,$$

$$v_\perp = [R(r,s) + T(r,s)] \sin\theta \cos\theta \ . \qquad (3)$$

Equation (2) is now used to form

$$\sum_j \dot{x}_j \ (t+s) \ \dot{y}_j \ (t+s) = \frac{N}{A} \int \ \sum_p d \, \vec{r}_{pj}$$

$$\times (v_\parallel \ \dot{x}_p - v_\perp \ \dot{y}_p)(v_\parallel \ \dot{y}_p + v_\perp \ \dot{x}_p), \qquad (4)$$

where the summation over j has been replaced by integration over the position $\vec{r}_{pj}$, normalized by the area A of the system of N molecules. When Eq. (3) is substituted in Eq. (4), the subsequent angular integration leads to elimination of the $v_\parallel \times v_\perp$ cross terms, so that the kinetic autocorrelation function given by Eq. (1) can be expressed in terms of its initial value by

$$\rho_K^\eta(s) = \rho_K^\eta(0) \frac{N\pi}{A2} \int_0^\infty dr\, r \ (R-T)^2 \ . \qquad (5)$$

Finally, the hydrodynamic flow field to be substituted into Eq. (5) consists in the late time limit of two well-separated parts.[7] A vortex part centered at the origin and spread over a distance of $(4\nu s)^{1/2}$, where ν is the kinematic shear viscosity equal to $\eta A/mN$, takes the form

$$R - T = (A/4N\pi\nu s) \ e^{-r^2/4\nu s}. \qquad (6)$$

The acoustic part centered at a distance cs, where c is the sound speed, has the form

$$R - T = -\frac{A}{4N\pi^{3/2}r} \frac{\partial}{\partial r} \int_\delta^\infty d\omega$$

$$\times \frac{\omega + \Upsilon}{(\omega^3 - \delta^2\omega)^{1/2}} \ e^{-(\Upsilon-\omega)^2/\omega} \ , \qquad (6')$$

where $\delta = rc/2\nu'$, $\Upsilon = c^2 s/2\nu'$, and ν' is the standard dissipative coefficient which describes the spreading of the acoustic wave

$$Nm\nu'/A = \kappa + \eta + \lambda \ (Nk/C_v - Nk/C_p). \qquad (7)$$

In Eq. (7), κ is the bulk viscosity, λ the thermal conductivity, and C_v and C_p the molar heat capacity at constant volume and pressure, respectively. The integration in Eq. (5) can now be performed, with the result

$$\rho_K^\eta(S)/\rho_K^\eta(0) = \alpha_\eta/S \ ,$$

where S is the average number of collisions per molecule and

$$\alpha_\eta = \left\{ \left(\frac{\eta}{\eta_0}\right)^{-1} + \left[\frac{\eta}{\eta_0} + \frac{\kappa}{\eta_0} + \frac{4\lambda}{\lambda_0} \left(\frac{Nk}{C_v} - \frac{Nk}{C_p}\right)\right]^{-1} \right\} \frac{y}{4\pi}, \qquad (8)$$

in agreement with previous results.[3,4] The transport coefficients are given relative to their low-density limits (zero subscript), and y represents

the equation of state expressed as $pV/NkT - 1$.

The kinetic potential or cross term in the shear-viscosity autocorrelation function,

$$\rho_C^\eta(s) = \langle \sum_i \dot{x}_i \ (t) \ \dot{y}_i \ (t) \sum_j \ddot{x}_j \ (t+s) \ y_j \ (t+s) \rangle , \qquad (9)$$

can be expressed in terms of the hydrodynamic flow field analogous to Eqs. (2) and (4) as

$$\sum_j \ddot{x}_j \ (t+s) \ y_j \ (t+s) = \frac{N}{A} \int \ \sum_p d\,\vec{r}_{pj}$$

$$\times (\dot{v}_\parallel \ \dot{x}_p - \dot{v}_\perp \ \dot{y}_p)[y_p(t) + y_{pj}]. \qquad (10)$$

The terms $\dot{v}_\parallel \ y_{pj}$ and $\dot{v}_\perp(y_p + y_{pj})$ vanish upon angular integration in view of the angular dependence given by Eq. (3). Furthermore, the $\dot{v}_\parallel$ term does not contribute either, because of conservation of momentum, so that the right-hand side of Eq. (10) is zero. The conclusion is that in the hydrodynamic limit the cross term of the autocorrelation function has no $1/S$ tail. Furthermore, since the potential-potential term in the viscosity autocorrelation function involves the same factor as Eq. (10), that term in the long time limit has no $1/S$ behavior either.

The thermal conductivity in the microcanonical ensemble considered here is related to the autocorrelation of an element of the energy-flux vector

$$J_x = \sum_i (\dot{x}_i \ e_i + x_i \ \dot{e}_i) \ ,$$

where

$$e_i = \tfrac{1}{2} m \ u_i^2 + \tfrac{1}{2} \sum_{i \neq j} V_{ij}$$

and V_{ij} is the potential energy of interaction between molecules i and j. Thus the kinetic-kinetic term in the autocorrelation function is

$$\rho_K^\lambda(s) = \langle \sum_i \dot{x}_i(t) \ [\tfrac{1}{2} m \ u_i^2(t)]$$

$$\times \sum_j \dot{x}_j \ (t+s) \ [\tfrac{1}{2} m \ u_j^2(t+s)] \rangle. \qquad (11)$$

The long-time behavior of $\dot{x}_j$ is again determined by the hydrodynamic flow field as given by Eq. (2), but for the kinetic-energy term the cylindrically symmetric pressure wave contributes as well as the flow field given by Eq. (3). This latter flow field has a dipole character and represents the flow of momentum. Thus

$$\tfrac{1}{2} m \sum_j \dot{x}_j \ (t+s) \ u_j^2(t+s)$$

$$= \int \sum_p d\vec{r}_{pj} \ (v_\parallel \ \dot{x}_p - v_\perp \ \dot{y}_p) \ [A_p/N(1+y)] \ , \qquad (12)$$

where $A_p/N(1+y)$ represents the energy of particle j at r_{ps} which is correlated with the energy of particle p at earlier times. Similar considerations[4] have led to the following expression for the kinetic thermal-conductivity autocorrelation function:

$$\rho_K^\lambda(S)/\rho_K^\lambda(0) = \alpha_\lambda/S,$$

where

$$\alpha_\lambda = \left[\left(\frac{\eta C_p}{\eta_0 Nk} + \frac{4\lambda}{\lambda_0}\right)^{-1}\right.$$

$$\left. + \frac{Nk/C_v - Nk/C_p}{\eta/\eta_0 + \kappa/\eta_0 + (4\lambda/\lambda_0)(Nk/C_v - Nk/C_p)}\right]\frac{2y}{\pi}.$$

$$(13)$$

It remains to prove that both the kinetic-potential and potential-potential parts of the thermal-conductivity autocorrelation function do not have a similar term.

Now that it has been shown that the kinetic term of all the transport coefficients, that is the integral of the corresponding autocorrelation function, di-
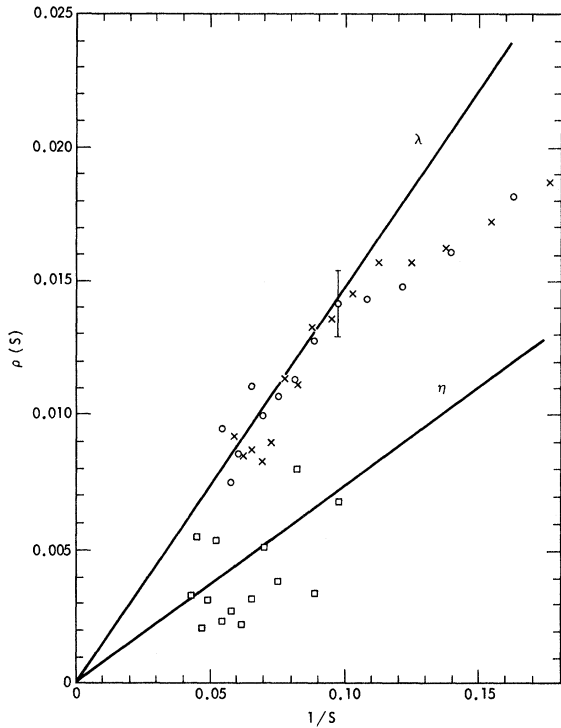

FIG. 1. Comparison of the kinetic autocorrelation function for thermal conductivity λ calculated via molecular dynamics (x, 504; 0, 1672 particles) at long times with the prediction of the hydrodynamic model (solid line) at an area relative to close-packing A/A_0 of 2. Similarly for the viscosity, except only the 1672 particle results are given (□). The vertical bar at S of about 10 mean collision times in the thermal conductivity indicates the typical uncertainty in the run of 10^8 collisions. The errors in the viscosity are larger. The autocorrelation function plotted is the one in excess of the predicted by the exponential decay of the Enskog theory and, furthermore, $1/N$ has been added in order to correct the finite particle result to an infinite system.

TABLE I. Comparison of the cross and potential contribution to the viscosity and thermal conductivity with the Enskog theory[a] at various densities.

A/A_0	λ^c/λ_E^c	λ^P/λ_E^P	η^c/η_E^c	η^P/η_E^P
1.4	1.11	1.13	0.75	1.57
2	1.06	1.06	0.96	1.01
3	1.05	1.05	1.00	1.00
5	1.04	1.05	1.04	1.00

[a] $\lambda_E^c/\lambda_0 = \frac{1}{2}\sqrt{3}\,\pi A/A_0$, $\lambda_E^P/\lambda_0 = (0.872\pi/\sqrt{3})\,(A_0/A)\,y$,

$\eta_E^c/\eta_0 = (\pi/\sqrt{3})\,A/A_0$, $\eta_E^P/\eta_0 = (0.873\pi/\sqrt{3})\,(A_0/A)\,y$, κ/η_0

$= (1.246\pi/\sqrt{3})\,(A_0/A)\,y$.

verge as ln$s$ in the long-time limit, it is necessary to reexamine the hydrodynamic model which originally assumed the existence (finiteness) of these coefficients. It is clear that the usual expressions which consider, for example, the viscosity as the proportionality constant between the shear stress σ and the shear strain rate $\dot\epsilon$ must be generalized. This generalization is taken to be

$$\sigma(s) = \frac{2}{Amu^2}\int_0^s \dot\epsilon\,(t)\,\rho^\eta(s-t)dt$$

$$= \frac{2}{Amu^2}\int_0^s \dot\epsilon\,(s-t)\,\rho^\eta(t)dt.$$

$$(14)$$

The argument then is that at late times the strain rate is slowly varying so that $\dot\epsilon$ can be expanded in a Taylor series about $t = s$. Keeping only the first term in the expansion permits $\sigma(s)$ to be written as
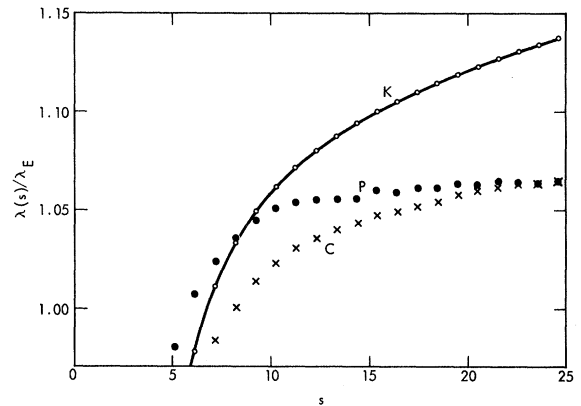

FIG. 2. Integral of the kinetic (K), cross (C), and potential (P) correlation functions for the thermal conductivity as a function of the upper time limit of integration at $A/A_0 = 2$. Results are given relative to the infinite time predictions of the Enskog theory (subscript E). The curve through the points of the kinetic curve is drawn only for contrast.

$\sigma(s) = \dot{\epsilon}(s)\,\eta(s),$ where

$$\eta(s) = \frac{2}{Amu^2} \int_0^s \rho_\eta(t)\,dt \,, \tag{15}$$

which in the infinite limit reduces to the usual expression. The generalization represented by Eq. (14) can be shown to be compatible with the frequently discussed[8-10] frequency-dependent transport coefficients by taking the Fourier transform of the expression. One of the most important properties of this generalization is that it is possible to show that at late times the solution of the hydrodynamic model are the same as the ones obtained above except that the transport coefficients are simply replaced by their time-dependent equivalent. Thus, for the diffusion coefficient I, we have

$$\rho^D(S)/\rho^D(0) = \alpha_D(S)/S,$$

where

$$\alpha_D(S) = \left(\frac{D(S)}{D_0} + \frac{\eta(S)}{\eta_0}\right)^{-1} \frac{y}{\pi} \,. \tag{16}$$

The self-consistent solution of Eqs. (15) and (16) is then that at late times

$$\rho(S) \propto 1/S\,\sqrt{(\ln S)} \,,$$

so that D, or for that matter any of the transport coefficients, behaves as $D = (\text{const} + \ln S)^{1/2}$ compared to the $D = \text{const} + \ln S$ behavior tested previously.[6] In order to distinguish between these two functional dependences on time, it is necessary to have accurate data available over several decades in S beyond where the asymptotic limit becomes valid (about an S value of 10 mean collision times). This seems at best difficult by molecular dynamics, since for 1000 particles, boundary interference distorts the behavior of correlation functions beyond about 30 mean collision times.

Comparison of the theory with molecular dynamics for the thermal conductivity and viscosity presents an additional problem inasmuch as the data is much less precise than for diffusion for a given length run. This is because in a given time step every particle diffuses but that represents only a single change in the state of fluctuation necessary to describe the thermal conductivity or viscosity. Hence, the statistics are reduced by a factor of N for these properties. The molecular-dynamics results, obtained by a previously described method,[11] and their accuracy after a long run, are shown in

Fig. 1 together with the hydrodynamic predictions as given by Eqs. (8) and (13), where the Enskog values for the transport coefficients have been substituted into the equations. Table I indicates that this is sufficiently accurate for present purposes. All that can be said about the comparison carried out at the four different densities, of which Fig. 1 is a typical example, is that the computer experiments are not inconsistent with the theoretical predictions.

For the cross and potential correlation a plot, as given in Fig. 1, would not look substantially different. It thus appears that if one is to believe the theoretical prediction of no tail, it is dangerous to assume that beyond 10 mean collisions the asymptotic decay has been reached. By luck such a short time appears to be sufficient for the kinetic terms. For the cross and potential terms, the behavior between 10 and 25 mean collision times correlates with the deviations from the Enskog theory. These deviations, as given in Table I, are also due to collective effects persisting for long times but not necessarily for the very long times leading to the $1/S$ tail. Indeed, it is this observation that lends encouragement to the idea of using the same hydrodynamic model with time-dependent transport coefficients to explain the behavior of all the correlation functions in this intermediate time regime.

In Fig. 2, the approach of the cross and potential part of the thermal conductivity to their plateau values is compared to that of the kinetic part. Purposely, a case has been shown where the deviations of all terms from the Enskog theory are comparable. It is evident, even though the cross and potential curves are still rising, that they are nearer to reaching constant values than the kinetic curve. If a similar plot had been made at $A/A_0 = 1.4$, especially for the viscosity, where the deviations from the Enskog theory are large (as shown in Table I), the potential part would have had a similar rise to that of the kinetic part; on the other hand, and most significantly, the cross term would have shown a substantial drop. Thus, deviations from the Enskog theory for the cross and potential terms involve many-body correlations of quite long duration, and from the present computer experiments it can not be concluded that they do not lead to a $1/S$ tail. That conclusion can be arrived at only from the hydrodynamic model.

[1]Y. Pomeau, Phys. Letters 27A, 601 (1968); and (private communication).

[2]R. Zwanzig and M. Bixon, Phys. Rev. (to be published).

[3]J. R. Dorfmann and E. G. D. Cohen, Phys. Rev.

Letters 25, 1257 (1970).

[4]M. H. Ernst, F. H. Hauge, and J. M. J. van Leeuwen, Phys. Rev. Letters 25, 1254 (1970).

[5]A. Widom, Phys. Rev. (to be published).

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

[7]T. E. Wainwright and J. A. Viecelli, UCRL Technical Report No. UCRL-72726 (unpublished).

[8]R. Mountain and R. Zwanzig, J. Chem. Phys. 44, 2777 (1966).

[9]B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. 45, 1086 (1966).

[10]P. C. Martin and S. Yip, Phys. Rev. 170, 151 (1968).

[11]B. J. Alder, D. M. Gass, and T. E. Wainwright, J. Chem. Phys. 53, 3813 (1970).

Density Fluctuations in an Interacting Bose Gas[*]

T. H. Cheung and Allan Griffin

Department of Physics, University of Toronto, Toronto 5, Canada

(Received 23 December 1970)

The density fluctuation in a Bose gas interacting via a strong short-range repulsive potential and a weak long-range attractive potential is studied by the methods of quantum-field theory. The density-density correlation function is generated by taking the functional derivative of the single-particle matrix Green's function $G_1(1, 2)$ with respect to an auxiliary scalar field. For $G_1(1, 2)$, we use the Hartree approximation for the attractive potential and the Hartree-Fock approximation for the short-range repulsive potential. We show that the density fluctuation spectrum is identical to the Beliaev approximation for the single-particle excitation spectrum.

I. INTRODUCTION

Beginning with Bogoliubov's classic work in 1947, there have been many studies of an interacting Bose gas using field-theoretic techniques. We mention specifically the important work of Beliaev,[1,2] Hugenholtz and Pines,[3] and Hohenberg and Martin.[4] With few exceptions, these calculations are mainly concerned with the spectrum of the single-particle Green's function $\tilde{G}_1(k, \omega)$. In the present paper, we compute the density-density fluctuation spectrum at finite temperature using the Green's-function method. To be more specific, we study $S(k, \omega)$ for a system of bosons interacting via a strong short-ranged repulsive potential and a weak long-ranged attractive potential in the Hartree-Fock approximation. This model of an interacting Bose gas has been studied by Huang[5] and more recently by Singh and Kumar.[6] However, these authors only considered the single-particle spectrum.

We believe our results give further insight into the general question of the equivalence between elementary excitations and density fluctuations in a condensed Bose system. As is well known, it is this equivalence which is at the center of the phenomenological theories of Landau and Feynman. Moreover, it is this equivalence which makes it possible to study the single-particle excitations (which determine the thermodynamics) by neutron scattering. At the present time, the only rigorous nonperturbative results are those of Gavoret and Nozières.[7] Summing up self-energy contributions to all orders in perturbation theory, they obtained

$(\omega > 0)$

$$S(k, \omega) = 2\pi n k^2 \delta(\omega^2 - c_1^2 k^2) ,$$

$$\mathrm{Im}\,\tilde{G}_{11}(k, \omega) = (\pi n_0/n)\, mc_1^2\, \delta(\omega^2 - c_1^2 k^2) \qquad (1)$$

in the limit $k \to 0$ and 0 °K. The phonon velocity c_1 is given by the usual thermodynamic expression. In their derivation, it was assumed that the Dyson-Beliaev self-energies could be expanded in powers of k and ω.

In Sec. II, we use the *Hartree-Fock* (Girardeau-Arnowitt[8] or GA) approximation to generate the two-particle Green's functions by functional differentiation with respect to an external field. This is an example of a conserving approximation in the sense of Baym and Kadanoff.[9] The two-particle potential is assumed to have a Fourier transform $V(k)$ and is split into a short-range repulsive part $V_R(k) \equiv V_R$ and a long-range attractive part $V_A(k)$. The Hartree self-energy involves $V_R(k) + V_A(k)$ but in the exchange term we only consider $V_R(k)$. The neglect of $V_A(k)$ in the exchange term is justified in one limit discussed in Sec. III.

In Sec. III, we solve the equations of motion obtained in Sec. II using perturbation theory and show that the spectrum of the density-density correlation function is phononlike at very low momentum. This is obtained for zero temperature and is identical to the single-particle spectrum in the Singh-Kumar approximation.[6,2]

In Sec. IV, the equation determining the density fluctuation spectrum for a purely repulsive short-range interaction is shown to be identical to the Beliaev expression for the single-particle spec-