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Molecular Dynamic Results on Transport Properties

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Molecular Dynamic Results on Transport Properties

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Following a broad discussion of generalized hydrodynamics, three examples are given to illustrate how useful this approach is in extending hydrodynamics to nearly the scale of molecular dimensions and the time between collisions, principally by including viscoelastic effects. The three examples concern the behavior of the velocity autocorrelation function, the decay of fluctuations in a resonating system, and the calculation of the dynamic structure factor obtained from neutron scattering. In the latter case the molecular dynamics results are also compared to the predictions of generalized kinetic theory. Finally it is shown how to implement generalized hydrodynamics both on a microscopic and macroscopic level.

Hydrodynamics is unable to account for the long time tails in the velocity autocorrelation functions and the divergent Burnett coefficients observed for the Lorentz gas. Instead, the long time behavior of the Burnett coefficient and the distribution of displacements (the self part of the dynamic structure factor) can be accounted for by a random walk with a waiting time distribution which is chosen to give the correct velocity autocorrelation function. This random walk predicts, in agreement with the observations, that this displacement distribution is Gaussian at long times for the Lorentz gas, while for hard disks it has been found not to be so.

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I GENERAL REMARKS

Before we can speak of generalized hydrodynamics, we must first discuss hydrodynamics. By hydrodynamics we mean the temporal behavior of fluids from the continuum point of view as expressed through the Navier-Stokes equations. These equations consist of the conservation laws supplemented by some empirical subsidiary relations, usually called constitutive laws, that relate the fluxes in the system to the applied gradients. We shall be concerned with two such laws, namely Ficks law of diffusion, where the diffusion coefficient, D , is defined as the proportionality constant between the current and the density gradient or $\frac{\partial F}{\partial t} = D \frac{\partial^2 F}{\partial x^2}$, and the proportionality of the stress, S , to the rate of strain (gradient in velocity), ϵ , that defines the viscosity, η , through $S = \eta \epsilon$. If these laws are valid at all, and we shall see instances where they are not, they are valid only in the limit that the gradients are small in amplitude, are applied over a large distance, and over a long period of time.

It is these restrictions that generalized hydrodynamics tries to remove by generalizing these constitutive relations so that hydrodynamics can be applied with greater accuracy to phenomena on a molecular scale, where gradients may be large but certainly the distances over which they occur range down to molecular diameters and the relevant times are of the order of collision times. The generalization consists of replacing the transport coefficients by transport functions that are functions of space and time. The alternative approach to deal with phenomena at a molecular scale is to use kinetic theory, which in practice means solutions of the Boltzmann

equation or its extension to higher densities, for hard spheres, of the Enskog equation. These equations are valid only in the other extreme of the time scale from hydrodynamics, namely very short times because only in that limit is the molecular chaos or independent binary collision approximation rigorously justifiable, since for short times particles do not have a chance to either recollide or have collisions with a common partner. If one wants to deal by the kinetic theory with phenomena depending on some distance scale, where in the limit of small distances the molecular chaos approximation is again rigorously correct, one must introduce the generalized Enskog equation to which we shall refer later.

Generalized hydrodynamics hence tries to bridge the gap in the description of phenomena on a time and distance scale between the validity of kinetic theory and hydrodynamics. Not so long ago, it was thought that this gap was enormous, but the central result of the computer simulation studies¹ has been that these two stages in the time evolution of a system are intimately coupled. The realization that hydrodynamics is a reasonable description for liquids at a molecular scale brings the hope that generalized hydrodynamics is nearly quantitative. One of the many examples of the accuracy of hydrodynamics is the applicability of the Stokes-Einstein relation to a particle of atomic size diffusing in solvent particles of comparable dimensions.² On the other hand, kinetic theory which is basically a low density gas theory, through neglect of all many-body effects, is a pretty inaccurate description at liquid density except at short times. Improvements in the kinetic or generalized kinetic theory are difficult, involving summation of a class of diagrams called ring diagrams in the graph theoretical development. These

graphs represent, only to lowest order, the effect of correlated collisions, and many more types of graphs must be included before a dense fluid can be effectively dealt with.

Thus, the more practical procedure appears to be to introduce the generalized transport coefficients and then to solve all sorts of hydrodynamic problems of interest. An immediately practical application would be to shock problems in which a steep and large gradient is present for short periods. To be discussed next is the randomization of the translational velocity of a particle in a fluid from which the velocity autocorrelation function and the diffusion constant can be deduced. Although hydrodynamics gives the correct long time behavior of the decay of the velocity,¹ the correct shorter time behavior requires the introduction of a generalized viscosity by means of which, for example, viscoelastic effects can be represented. These are required to reproduce the observed reversal of the velocity at liquid densities, called backscattering. It is in the detailed description of many such relaxation processes at a molecular level, another example being the rotational relaxation of a molecule in a fluid, that generalized hydrodynamics and in particular the generalized viscosity, will be most useful. The generalized viscosity is equivalent to what is often called the transfer function, the response function or the memory function. In its present context, it has the virtue of being theoretically calculable and experimentally measurable, although neither of these aims are as yet fully realized.

II THE VELOCITY AUTOCORRELATION FUNCTION

The molecular dynamics observation that the decay of the velocity autocorrelation function at intermediate densities was non-exponential at long times led to the realization that hydrodynamic modes could be observed at molecular time scales. The fact that a weak positive correlation between the initial velocity of a particle and its velocity some thirty collisions later could be observed meant that some highly collective mode was involved which could only be described by hydrodynamics. An elementary calculation of the decay of the velocity, v , of a sphere moving in a continuum, characterized by a kinematic viscosity, $\nu = \eta/\rho$ and a compressibility, can be obtained from momentum conservation. The momentum of the sphere is either dissipated by sound waves spreading with distance as ct , where c is the sound speed derived from the compressibility and t is time, or as a vortex which spreads as $\sqrt{vt}$, since the vortex obeys a diffusion type of equation, or more elementary, from dimensional considerations. Thus at long times the vortex mode will dominate, and momentum conservation

$$m \int v dr = \text{constant}$$

then leads one to conclude that v is proportional to $(vt)^{-d/2}$ where d is the dimensionality of the system. since the volume element, dr , spreads as $(vt)^{d/2}$. The proportionality constant is also easily determined from the fraction of the momentum that is dissipated in the sound wave relative to that in the vortex mode, namely 1/2 in each in two dimensions.

This hydrodynamic result has been known for many years. What is new is that it is quantitatively applicable at intermediate densities at a molecular scale, beyond about 20 collision times. That time, though long from

the kinetic point of view, is very short from the hydrodynamic point of view, namely about 10^{-13} sec. At that time the vortex has spread only about 3 molecular diameters, as was observed¹ from a detailed molecular dynamics calculation of the velocity field, namely

$$\langle v_1(0) \sum_{j=2}^k v_j(t) \rangle ,$$

where j are the neighboring particles to the centrally located particle 1, whose velocity decay is followed. The observed velocity field after about 20 collisions quantitatively agreed with that deduced from the hydrodynamic calculation, thus establishing the quantitative applicability of hydrodynamics at a remarkably short distance and time scale. At shorter times and distances it is first of all no longer possible to analytically obtain the solution to the hydrodynamic problem because the sound wave and vortex mode are not sufficiently separated. A numerical solution of the hydrodynamic problem, furthermore, failed to be quantitative at earlier times.

The greatest failing of the hydrodynamic picture, however, lies in its inability to reverse the velocity of the moving particle. This reversal occurs at higher densities at short times in the velocity autocorrelation function before the vortex decay mode is dominant. The physical origin of this reversal is clearly the response of the medium to a nearly instantaneous impulse of the moving particle, which can not be characterized by a viscosity that measures the long time response of the medium to a shear wave. If the medium can not readjust sufficiently fast, it acts elastically or viscoelastically, that is as a solid where the particles can only adjust their location in a limited way to any perturbation. In order to remedy the

hydrodynamic picture a time dependent viscosity must be introduced, since a constant viscosity is only able to slow the particle down. This can easily be done by integrating the stress autocorrelation function, $\rho_{\eta}(t)$, only up to a definite time; the viscosity being the long time limit of this integral, that is $\eta(t)$ is proportional to $\int_0^t \rho_{\eta}(s) ds$. Indeed, this time dependent viscosity obtained from molecular dynamics led to a negative velocity autocorrelation function at short time at high density when introduced into the Navier-Stokes equation, but only semiquantitative results were obtained.³ The problem is that this viscosity is still a local quantity and it is hoped that by generalizing it further by including spacial dependences as well, quantitative agreement would be obtained between the velocity autocorrelation function and the hydrodynamic model down to very short times. Encouraging results have been obtained by these means with estimates for the generalized viscosity.⁴ The fact that the time dependent viscosity already introduces the qualitative features of viscoelastic behavior can be seen from the initial value of $\rho_{\eta}(0)$ which can be identified as the bulk elastic modulus.

III FLUCTUATION DRIVEN RESONANCE

This example gives more direct evidence down to what distance scale hydrodynamics is applicable. This is because the observations concern the fluctuations of definite wave lengths that are trapped between two parallel walls. The distance between the walls, which can be made to be only a few molecular diameters in a computer experiment, determines the wave lengths of all the possible ones that naturally arise in the fluid, that is placed between the walls, that can resonate: namely, the ones that are an odd integer fraction of the distance. This condition arises because of the boundary conditions imposed on the system and is entirely analogous to the problem of repeated beating of a drum. The decay of those resonating fluctuations can be analyzed by standard linear fluctuation theory of the Navier-Stokes equation⁵ of Landau and Placzek and compared to the results of molecular dynamics.

The molecular dynamic calculation for a hard sphere system placed between two parallel walls a distance L apart, with periodic boundary conditions in the other two directions parallel to the wall, evaluates the drift or center of mass velocity. This drift velocity or current $\dot{X}_D = \sum_{i=1}^N \dot{X}_i$ is the sum over all particles i of the velocity $\dot{X}_i$ in the X direction perpendicular to the wall. The coherence in the drift velocity is then measured by its autocorrelation function

$$D(t) = \langle \dot{X}_D(0) \dot{X}_D(t) \rangle ,$$

where the brackets indicate, as usual, statistical mechanical averaging over many initial conditions of the drift. Since only the resonating modes lead

to coherence, the drift autocorrelation function can alternatively be written as

$$D(t) = \left(\frac{4}{\pi}\right)^2 \sum_{n=1,3,5}^{\infty} \frac{1}{n^2} \sum_{i,j}^N \langle \dot{x}_i(t) \dot{x}_j(0) \sin\left[\frac{n\pi}{L} x_i(t)\right] \sin\left[\frac{n\pi}{L} x_j(0)\right] \rangle ,$$

consistent with the boundary conditions. The factor n^2 arises because of the amount of momentum carried in each mode and the factor $(4/\pi)^2$ leads to proper normalization. This drift autocorrelation function can furthermore be rewritten as a mode summation over the intermediate longitudinal current autocorrelation function, $C_k(k,t)$, at wave vector k :

$$C_k(k,t) = \sum_{i,j}^N \langle k \dot{x}_i(t) k \dot{x}_j(0) \exp[ik(x_i(t) - x_j(0))] \rangle .$$

Thus

$$D(t) = \frac{1}{2} \left(\frac{4}{\pi}\right)^2 \left(\frac{L}{\pi}\right)^2 \sum_{n=1,3,5}^{\infty} \frac{1}{n^4} C_k\left(\frac{n\pi}{L}, t\right) .$$

The current autocorrelation function is usually calculated for an infinite system and, as we shall see, the difference in boundary conditions is not significant. The temporal Fourier transform of $C_k(k,t)$ is simply related to the familiar Van Hove neutron scattering function $S(k,\omega)$, namely

$$-\omega^2 S(k,\omega) = C_k(k,\omega)$$

although we shall, in the next section for technical reasons, primarily deal with the temporal Fourier transform of $S(k,\omega)$, called the intermediate scattering function, $F(k,t)$.

The comparison given in Fig. 1 between the molecular dynamic results and hydrodynamics for the drift autocorrelation function uses in the hydrodynamic theory values of the thermodynamic and transport properties appropriate to the pressure perpendicular to the wall. This, to first order, takes care of the wall boundary effects. Even though the walls are only about six hard sphere diameters apart, the agreement is remarkable. Only at very short times, less than two mean collision times, shown in the inset, is any discrepancy apparent. The hydrodynamic calculations are made only for the lowest mode and, if the higher modes are included, they improve the agreement even at earlier times. Beyond a few collision times the higher modes make a negligible contribution, partially because they decay much faster and partially because the weight of their contribution is greatly reduced, namely by the factor $1/n^2$. This is more clearly demonstrated in Fig. 2, where the first two modes are separately given for the intermediate longitudinal current autocorrelation function. It is seen there that the hydrodynamic theory fails to be quantitative for the second lowest mode which corresponds to about two molecular diameters. This demonstration of the remarkable validity of hydrodynamics at a distance scale of a few molecular diameters and down to a time scale of a few mean collision times can perhaps be rationalized by the following considerations. First of all, we are dealing with a function which seems remarkably insensitive to the details of the molecular motion, particularly at this intermediate density which is about 30% lower than the solidification density. This will be shown more clearly in the next section, but suffice it to say for the moment that the velocity autocorrelation function at this density has as yet no negative region and the transport coefficients are nearly quantitatively given by the simple

uncorrelated binary collision theory of Enskog. Furthermore, the more relevant parameter by which to measure the validity of hydrodynamics than the distance scale given by the molecular diameter is the mean free path and at these densities the mean free path is a small fraction of a molecular diameter.

IV THE NEUTRON SCATTERING FUNCTION

The intermediate scattering function $F(k,t)$ for hard spheres has been calculated in a straightforward manner from the density autocorrelation function at a couple of densities and a series of k values. At the lower density, even somewhat lower than in the previous section, it is not surprising that hydrodynamics works well at the lowest k value that could be studied in the molecular dynamic system consisting of 500 particles with periodic boundary conditions. This is shown in Fig. 3. Perhaps more surprising is the good agreement with the generalized kinetic theory, also shown, at this relatively high density.

Enskog, in order to make the kinetic theory of Boltzmann applicable for hard spheres at higher density, introduced in front of the collision operator the function χ that takes into account that at higher density the particle size is no longer negligible compared to the distance particles travel between collisions. The factor χ can be determined in many ways, but one way is such that the rigorously known initial slope (short time behavior) of any autocorrelation function is correctly given. For the transport coefficients χ can then be easily shown to be the radial distribution function at contact, that rigorously measures the enhanced collision rate at higher density. For the space or k dependent transport function, a completely analogous procedure can be followed, except now χ is a function of space. Again the initial slope of these transport functions is rigorously known, and is often expressed in terms of the so-called sum rules.⁶ Thus, the generalized kinetic equations that have to be solved are well established⁷ and an accurate solution of them will soon be published. These generalized kinetic equations at long times go over to the hydrodynamic model but

involve the transport properties as given by the Enskog theory. Since, as pointed out earlier, the Enskog theory at this density gives these transport coefficients well, and the known thermodynamic properties and equilibrium structure factors are introduced in the kinetic theory, it is not surprising that good agreement is obtained.

At a density near solidification the generalized kinetic theory shows significant deviations at two different k values, as shown in Figs. 4 and 5. The kinetic theory is, of course, always rigorous at short times, and would also be at sufficiently high k (short wave length), but evidently the higher k value shown, typical of neutron experiments, is not high enough. The ordinary hydrodynamic theory is also not quantitative but by using a crude version of generalized hydrodynamics can be made nearly quantitative. If we introduce into the hydrodynamic theory a crude version of a time dependent viscosity, namely at short times the Enskog viscosity and at longer times the molecular dynamically determined viscosity, which is about twice as large, the hydrodynamic theory gives vastly improved results, as shown in Fig. 4. For neutron diffraction experimentalists it should be pointed out, however, that the deviations of these two extreme theories, namely the kinetic and hydrodynamic theories, from the correct result are quite small, of the order of a few percent, so that these experiments have to be more precise than heretofore if they are to give details of correlated collisions not included in these theories.

Other types of autocorrelation functions that have been calculated at this higher density lead to similar conclusions. The longitudinal current correlation function, here called $J_z(k,t)$ and previously $C_z(k,t)$, disagrees

with both kinetic and hydrodynamic theory at the lowest possible k value, though kinetic theory agreement improves at higher k value, see inset Fig. 6. Again hydrodynamic theory agreement can be extended to much shorter times if instead of the full transport coefficients one uses the Enskog (short time) transport coefficients. The transverse current autocorrelation function, shown in Fig. 7, gives clear evidence at this high density for the need to introduce frequency dependent viscosity. Neither the kinetic nor hydrodynamic theory can predict the negative region of this transverse current, equivalent to the negative feature in the velocity autocorrelation function discussed earlier. Incidentally, this evidence for viscoelastic behavior in hard sphere systems at sufficiently high density and large k values, leads to the conclusion that even in hard sphere fluids shear waves can be propagated.

V GENERALIZED HYDRODYNAMICS

The first objective is to microscopically calculate $\eta(k, \omega)$ or $\eta(r, t)$ so as to introduce it in the generalized relationship

$$S(k, \omega) = \eta(k, \omega) \epsilon(k, \omega)$$

or

$$S(r, t) = \int_{-\infty}^t dt' \int_V dr' \eta(r-r', t-t') \epsilon(r', t').$$

From this representation it can be seen that the generalized viscosity is the response of the system to a perturbation at a point, r' , at a time, t' , as felt at position, r , at some time, t , later. The straight forward calculation starts with the consideration of the ordinary viscosity which can be written,² except for constants, in either the Einstein form as $\eta = \rho \overline{u^2} / 2\tau$ or as the time integral of the stress autocorrelation function $\eta = \int_0^\infty dt \langle G_{xy}(t) \cdot S_{xy}(t) \rangle$, where G is the appropriate dynamical variable, $G_{xy} = m \sum_{i=1}^N \dot{x}_i y_i$ and the time derivative $\dot{G}_{xy} = S_{xy}$, the corresponding current. The symbol S is not to be confused with the neutron scattering function introduced earlier. The generalization starts with the Fourier transform of the momentum density

$$J_x = m \sum_{\ell=1}^N X_{\ell} e^{-ik y_{\ell}} \quad \text{which obeys the conservation law } \dot{J} + \partial S = 0. \quad \text{Thus}$$

$$\eta(k, \omega) = c \int_0^\infty e^{-i\omega t} \langle S_{xy}^k(0) S_{xy}^k(t) \rangle dt,$$

where c is a constant and

$$S_{xy}^k = m \left[\sum_{\ell} \dot{x}_{\ell} y_{\ell} + \sum_{\ell, p} \ddot{x}_{\ell} p_{\ell p}^y \left(\frac{iky_{\ell p} - 1}{iky_{\ell p}} \right) \right] e^{-iky_{\ell}}.$$

The factor in the round brackets is such that at $t = 0$ its value is unity, so that the entire expression reduces to the constant independent expression λ_a at $k = 0$; the bracket then vanishes, so that only the first, the kinetic, term remains, as it should in that limit. This function is readily calculable by molecular dynamics, although the results are not as yet sufficiently digested to be presented here.

Since the function $\eta(r, t)$ is known, it must be introduced in the Navier-Stokes equations and these must in general be solved numerically. One practical suggestion is to fit $\eta(r, t)$ by a sum of exponentials defined by a set of relaxation times, λ_a^{-1} , $\eta(r, t) = \sum_a \eta_a(r) e^{-t/\lambda_a}$. The advantage of this is that the stress now becomes a sum of elements $S(r, t) = \sum_a S_a(r, t)$ such that the time rate of change of $S_a(r, t)$ required to predict the stress for the next time step in such numerical calculations $S_a(r, t + \Delta t) = S_a(r, t) + \Delta t \frac{dS_a(r, t)}{dt}$ can be expressed as

$$\frac{dS_a(r, t)}{dt} = \int_V \eta_a(r-r') \dot{\epsilon}(r', t) dr' - \lambda_a^{-1} S_a(r, t) \quad ,$$

namely a differential equation for $S_a(r, t)$ that requires only the value of $S_a(r, t)$ at the present time step. If such an exponential fit were not made, it would be necessary, in general, to remember $S(r, t)$ many time steps back leading to much larger memory requirements for the computation. Such calculations are still in the future, but the principle has been successfully demonstrated³ with an $\eta(t)$ that was numerically fit by a single exponential.

It is certainly true that the calculation of $\eta(r, t)$ is much more complex than that of the velocity autocorrelation which we are trying to explain by means of the generalized viscosity. One might hence wonder what has been gained. There are two things to be said: One is that with the same function, $\eta(r, t)$, many other hydrodynamic problems can be solved. Secondly, theories

and models can be worked out for this generalized viscosity, for example, by the generalized Eyring theory or more complex kinetic models. Furthermore, this generalized viscosity is subject to direct experimental study. Finally, it should be pointed out that so far we have considered only the linear generalized viscosity and it may very well be that nonlinear effects due to high amplitude gradients may spoil the quantitative applicability of the linear theory to molecular processes, most likely at extremely short times. The nonlinear theory both microscopically and macroscopically is vastly more complex and we shall not go into it here.

VI THE LORENTZ GAS

The Lorentz gas, in which a single particle moves through stationary objects, can clearly not have hydrodynamic modes. Since the single moving particle cannot generate either velocity or spatial correlations in the surrounding medium, the Lorentz gas is easier to analyze theoretically, and can be run by molecular dynamics about ten times faster than the equivalent fluid. Here the dynamical properties of the Lorentz gas have been studied by computer, in the hope that rigorous mathematical analysis will be possible. The Lorentz gas would then be the first nontrivial system for which such properties were rigorously established; however, even this task is difficult. So far only the central-limit theorem,⁸ and the validity of the Fourier law of heat conduction in the Boltzmann-Graßmann limit⁹ appear to have been proven for the Lorentz gas, although a number of mathematicians are actively working in this field, so that there is hope of further exact results.

The nontriviality of the Lorentz gas is indicated by the graph-theoretical result¹⁰ that the velocity autocorrelation function in two dimensions and in the low-density limit is non-Markovian, namely, it decays as α_D/t^2 , where α_D is a constant. These methods also suggest that the next-higher order velocity autocorrelation function, whose time integral leads to the Burnett coefficient, is of the form α_B/t , where α_B is another constant, and hence the Burnett coefficient diverges. If correct, this would imply that the Chapman-Enskog expansion of the Boltzmann equation¹¹ is also not valid for this much simpler case. A version of the Lorentz model has already been studied on the computer, namely, the Ehrenfest wind-tree model, and abnormal diffusion¹² was observed. In this case the moving point-particle is scattered among overlapping squares placed in such a manner that the particle can only travel in the x and y directions.

The slow decay of the velocity autocorrelation function led to a predicted vanishing diffusion coefficient. Another computer study¹³ of the two-dimensional Lorentz gas, where the moving point particle is scattered among overlapping discs, confirmed the theoretical prediction that the diffusion coefficient cannot be simply expanded as a power series in the density. A term logarithmic in the density with a predicted constant coefficient was found to be needed to fit the data.

The disc Lorentz gas is investigated here further, not only at low density but at all densities. The interest is in establishing the percolation density, the transport properties at that density, and the qualitatively different transport properties beyond that density. The percolation point is the lowest density for which the randomly placed discs trap the moving particle, and hence the diffusion coefficient vanishes at that density and higher densities. At the percolation density, the transport properties should show unique behavior, which, unfortunately, is difficult to determine on the computer because of the large statistics required to sample the rare events that could lead the moving particle out of its trapped state. The percolation density has been estimated¹⁴ to be at $n^* = 0.37 \pm 0.02$, where $n^* = nR^2$, the number density multiplied by the square of the radius of the discs.

The versatility of the computer studies allows investigations of the cause of the non-Markovian behavior. For example, by studying the non-overlapping Lorentz gas, the role of the topology of the space in which the particle moves can be studied. The non-overlapping case is experimentally generated by freezing an instantaneous configuration of either a hard-disc fluid or solid and then letting a point particle move in the free space. In this way the percolation problem is avoided and a certain order is created in the scattering centers.

Whether the moving particle is a point and the scatterers are discs or vice versa leads to completely equivalent results. Another variant of the Lorentz model investigates the effects of velocity persistence between successive collisions. That persistence can be removed by diffusive scattering at each collision rather than specular reflection. In diffusive scattering, the particle is scattered randomly in any of the possible directions rather than into the equal-angle direction called for by the dynamics. A further variant is to ignore the velocity and the collisions entirely and let the particle move, by the standard Monte Carlo sampling technique, through the fixed scatterers. In this procedure a random move is accepted or rejected depending on whether it leads to an overlap with one of the fixed scatterers. The displacement of the particle is then recorded as a function of the number of moves and the asymptotic behavior for large numbers of moves can be determined.

VII WAITING-TIME DISTRIBUTION

An attempt will be made to interpret the results of the Lorentz gas in terms of a more general than usual random walk in which, after each random step, the particle waits for a time as sampled from a waiting-time distribution before it makes the next random move.¹⁵ In physical terms the waiting-time distribution can be thought of as corresponding to the different times it might take for the particle to escape from the various nearly-trapping regions it might find itself in. In practical terms the waiting-time distribution has to be introduced since the usual random walk cannot give a power-law decay of the velocity autocorrelation function. In mathematical terms the waiting distribution is, in fact, uniquely determined by the requirement that the experimentally determined velocity autocorrelation function be reproduced. This statement is equivalent to the statement that the waiting-time distribution is such that the second moment of the distribution of displacements is reproduced for all times. The question then is: can this more general random walk give the correct higher moments of the distributions, that is, the distribution itself, from a knowledge of the second moment only, at least at large times? The distribution of displacements for this more general but still random walk must still be Gaussian in the long-time limit. Thus, the limited but important objective is to find whether the random walk with a waiting-time distribution that gives the observed second moment at all times can reproduce at least the rate at which the higher moments approach their long-time Gaussian limit. On that question hinges the long-time behavior of the Burnett coefficients. For example, the first linear super-Burnett coefficient measures the asymptotic rate of the second cumulant of the distribution.

Here, the random walk consists in sampling from a probability density in configuration space, $p(x)$, that a particle makes a jump of length x , and a probability density in time, $\psi(t)$, that the particle makes a jump at time t . Thus, the probability density for the walk to reach the position x when the last transition occurred at time t is simply

$$Q(x,t) = \sum_{n=0}^{\infty} p_n(x) \psi_n(t) \quad ,$$

where the subscripts represent repeated convolutions. To bring the probability density up to the current time, account must be taken of the waiting time after the last jump. Thus the probability density of being at x at time t is

$$F(x,t) = \int_0^t \Psi(t-t') Q(x,t') dt' \quad ,$$

where $\Psi(t) = 1 - \int_0^t \psi(t) dt$ is the probability that the particle remains fixed, after the last jump, for a time t . The Fourier-Laplace transform of $F(x,t)$, indicated by $\tilde{F}(k,s)$, equals

$$\tilde{F}(k,s) = \frac{1-\tilde{\psi}(s)}{s} \tilde{Q}(k,s) \quad ,$$

where

$$\tilde{Q}(k,s) = \sum_{n=0}^{\infty} \lambda^n(k) \tilde{\psi}^n(s) = \frac{1}{1-\lambda(k)\tilde{\psi}(s)}$$

and

$$\lambda(k) = \int_{-\infty}^{\infty} e^{-ikx} p(x) dx \quad .$$

Finally, separating out the initial ($n=0$) term, which locates the particle at the origin, $p_0(x) = \delta(x)$, leads to

$$\tilde{F}(x,s) = \frac{1-\tilde{\psi}(s)}{s} \left[\delta(x) + \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{e^{ikx} \lambda(k) \tilde{\psi}(s) dk}{1-\lambda(k) \tilde{\psi}(s)} \right]$$

The moments of the distribution can be readily determined:

$$\langle \tilde{x}^{2n} \rangle = (-1)^n \frac{\partial^{2n}}{\partial k^{2n}} \tilde{F}(k,s),$$

where the derivatives are to be taken in the $k=0$ limit. Hence,

$$\langle \tilde{x}^2(s) \rangle = \langle \ell^2 \rangle \frac{1}{s} \frac{\tilde{\psi}(s)}{1-\tilde{\psi}(s)}$$

and

$$\langle \tilde{x}^4(s) \rangle = \langle \ell^4 \rangle \frac{1}{s} \frac{\tilde{\psi}(s)}{1-\tilde{\psi}(s)} + 6 \langle \ell^2 \rangle^2 \frac{1}{s} \frac{\tilde{\psi}^2(s)}{(1-\tilde{\psi}(s))^2},$$

where

$$\langle \ell^n \rangle = \int_{-\infty}^{\infty} x^n p(x) dx$$

is the appropriate moment of the step-size distribution for which the odd moments vanish.

The relation between the second moment and the velocity autocorrelation function expressed in Laplace notation is

$$\tilde{p}(s) = s^2 \langle \tilde{x}^2(s) \rangle / 2 \langle \dot{x}^2 \rangle,$$

so that the waiting-time distribution can be determined from a knowledge of the velocity autocorrelation function by

$$s\tilde{\psi}(s) = \frac{2\langle \dot{x}^2 \rangle}{\langle l^2 \rangle} \tilde{\rho}(s) (1 - \tilde{\psi}(s))$$

Practically, the waiting-time distribution was obtained numerically by solving the above equation expressed in actual time, that is,

$$\psi(t) = \int_0^t K(t-t') [1 - \psi(t')] dt'$$

where

$$K(t) = \frac{\langle \dot{x}^2 \rangle}{\langle l^2 \rangle} \int_0^t \rho(t') dt'$$

The analogous formula for the fourth moment

$$\langle x^4(t) \rangle = \frac{\langle \dot{x}^4 \rangle \langle l^2 \rangle}{\langle l^2 \rangle} + 12 \int_0^t D(t-t') \psi(t') dt'$$

where

$$D(t) = \langle \dot{x}^2 \rangle \int_0^t \rho(t') dt'$$

shows that this walk necessarily expresses the higher moments in terms of the second moment. Since the higher moments generally require higher correlations, this expression cannot be expected to be universally valid, except perhaps in the long-time limit, if the higher-order correlations die out sufficiently rapidly.

For the asymptotic analysis¹⁶ to make sense, the velocity autocorrelation function must first of all have a negative tail so that the waiting-time probability distribution is positive. Secondly, the diffusion coefficient must exist, so that if $\rho(t) = -\alpha t^{-\beta}$, β must be greater than one. If β is less than 2,

then the dominant term in $\langle x^4 \rangle$ is the second term in the above equation. Under these circumstances, the choice of the moments of the step-size distribution, $\langle l^n \rangle$, involved in the first term, becomes irrelevant. These moments could, however, be adjusted arbitrarily to fit the early behavior of the fourth moment, or equivalently, the Burnett coefficient. The asymptotic behavior of the Burnett autocorrelation function,¹⁷ that is,

$$\dot{B}(t) = \frac{1}{24} \frac{d^2}{dt^2} [\langle x^4(t) \rangle - 3\langle x^2(t) \rangle^2] \quad ,$$

is then easily shown to be of the form $t^{-\beta+1}$ for $1 < \beta < 2$. Similarly,

$$K_4(t) = \frac{\langle x^4(t) \rangle - 3\langle x^2(t) \rangle^2}{3\langle x^2(t) \rangle^2} \quad , \text{ and all higher dimensionless cumulants}$$

behave asymptotically as $t^{-\beta+1}$. This means that: if the low-density prediction of $\beta=2$ is correct, the Burnett coefficients (the integral of the autocorrelation function) diverge, while the K functions go to zero asymptotically—a necessary condition for the distribution to be Gaussian.

If the diffusion coefficient vanishes, as it does above the percolation limit, the asymptotic analysis differs. The Burnett autocorrelation function then still diverges, as $t^{-2\beta+2}$ if $1 < \beta < 3/2$, and converges for $3/2 < \beta < 2$, as $-t^{-2\beta+2}$. Finally, for a vanishing diffusion coefficient and $\beta > 2$, the Burnett and velocity autocorrelation functions have identical behavior, namely, as $-t^{-\beta}$. In the next section we shall compare these results with the ones found by computer.

VIII RESULTS

The behavior of the low-density velocity autocorrelation function is checked against the prediction¹⁰ of $\rho(s) = -(n^2/\pi)s^{-2}$, as shown in Fig. 8 and Table I. At the lowest feasible densities, the s^{-2} behavior is indeed confirmed within the rather large experimental uncertainty, in spite of the very long runs, after about 10 collision times, s . The figure shows that the two different density runs lead to similar results, indicating that we are in the low-density regime. Furthermore, comparison with the Dutch result,¹⁰ using non-overlapping discs, is also very favorable—a further indication that we are at sufficiently low density. Emphasis is given to these facts, because the experimental results lead to a coefficient of the s^{-2} term about a factor of π higher than the theoretical result, so that $\rho(s) \sim -n^2s^{-2}$. The discrepancy may still be due to the density not being low enough, or the asymptotic time regime not having been reached, but the theoretical result also needs to be checked to determine whether some graphs contributing in lowest order in the density have been omitted.

Figure 9 shows the effect of density on the velocity autocorrelation function. As the density increases, back-scattering becomes more prominent, and the time at which back-scattering is most pronounced occurs later. This indicates that it takes longer for the Lorentz particle to escape its neighborhood the higher the density. Furthermore, as the density is increased, the figure indicates that the velocity autocorrelation function has a stronger negative-tail contribution, until the percolation density is reached. At this density the integral of the velocity autocorrelation becomes zero and, therefore, the stronger earlier back-scattering is compensated by a weaker tail to

to make the sum of the two regions a constant which cancels the contribution, independent of density, of the positive exponential part. As Table I shows, the tail of the velocity autocorrelation function could be represented over the entire density range by $\rho(s) = -\alpha_p t^{-\beta}$ and, as indicated above, the value of β reaches an extreme of about 4/3 at the percolation density ($n^* \sim 0.37$).

Figure 10 illustrates that the tail of the velocity autocorrelation function does not depend on whether the particle scatters diffusively or specularly at a given density. In the diffusive-scattering case, the back-scattering is initially longer and subsequently smaller, while the power-law decay as shown in Table I is, within experimental error, the same. Figure 11 shows that similar slopes are also obtained for the tail of the Burnett coefficient at the same density for diffusive and specular scattering. In addition, Fig. 11 shows that a Monte Carlo walk through the lattice also yields the same slope when the Burnett coefficient is plotted against the number of steps in the Monte Carlo walk. The appropriate numbers can also be found in Table I.

Figure 11 also illustrates that the Burnett coefficient never reaches a plateau value but appears to increase without bound as s increases; that is, it diverges. It is also clear from these results that this divergence, or asymptotic behavior of the autocorrelation function, is a result of the topology of the scattering centers and that the kinematics only affects the early part of the correlation functions. There is also the question of whether the existence of trapped regions is responsible for the long negative tail of the correlation functions of the Lorentz gas. Hence, the fact that the non-overlapping Lorentz gas also shows a tail (see Table I) in agreement with the overlapping case when the density is properly adjusted answers the previous question in the negative, since in the non-overlapping case no trapped regions exist and the

percolation density is approached only in the close-packed limit. Hence, the long tails must be ascribed to a long sequence of back-scattering events that lead to a higher-than-random probability of return of a particle to its starting position. The fact that the velocity autocorrelation function has a negative tail while the Burnett one has a positive tail can be interpreted as being due to those particles that are not back-scattered diffusing for larger distances because of the presence of channels, that is, passages of less-than-average density; the particles which diffuse for larger distances are weighted more heavily in the fourth moment.

In Fig. 12 the waiting-time distribution derived from the specular and diffusive velocity autocorrelation function is demonstrated. The fact that this distribution is negative at intermediate times indicates that it is physically meaningless except perhaps at long times. At long times, the K function, with a slightly different normalization than in the formula given earlier, and hence designated K' , extrapolates smoothly to zero, indicating that the distribution is consistent with a Gaussian distribution (see Fig. 13). The two solid lines refer to different assumptions about the step-size distribution, which as pointed out earlier, do not matter in the asymptotic limit. It is interesting to note that the earlier-time behavior is fitted better by a Gaussian step-size distribution. In contrast, the K_q function at a density beyond the percolation limit does not approach zero, as shown in Fig. 14, and hence the distribution cannot be Gaussian. In fact, it can be shown that in the high-density limit of the overlapping Lorentz gas the distribution is exponential. Another non-Gaussian distribution at long times is indicated in Fig. 15. This is for the two-dimensional hard-disk fluid. In this case the hydrodynamic modes cause the Burnett coefficients to be negative, indicating that the wings of the Gaussian distribution

are reduced.¹⁸ This reduction in the number of particles that diffuse to large distances could be ascribed to the vortex mode which leads particles back to the center.

The cumulant involving the sixth moment, for which the accuracy of the information is very limited, nevertheless also indicates consistency with a Gaussian limiting distribution and an early-time behavior of the Gaussian step-size distribution for the Lorentz gas as shown in Fig. 16. The distribution for a Lorentz gas itself is shown in Fig. 17 relative to a Gaussian of the same half-width, as a function of reduced distance and at three times. It can be seen that the distribution does not change in character with time. The early peak in the distribution at small distances, which is indicative of the trapped particles, gradually disappears as the probability weight of particles in the traps is reduced by the spreading, diffusing particles. The large rise in the far wings of the distribution is also reduced with time, although even at the longest time the situation is still far from being Gaussian. The solid line merely indicates near-consistency of the distribution with that obtained from the Burnett equation where the known diffusion and Burnett coefficients are introduced.

The Burnett equation

$$\frac{\partial F}{\partial t} = D \frac{\partial^2 F}{\partial x^2} + B \frac{\partial^4 F}{\partial x^4}$$

can be solved for F by perturbation methods. To be sure, the expansion does not exist, because B diverges. Nevertheless, a solution can be obtained if we substitute the value of B appropriate to the time the solution of the equation is sought. If B is small compared with D , as it is at these times, an expansion

of $F = F_0 + (B/D)F_1 + \dots$ can be made, where F_0 is the Gaussian distribution function. The solution of the differential equation then becomes, in a straightforward manner

$$F/F_0 = 1 + K_4(3/8 - 3\xi^2/4 + \xi^4/8) \quad ,$$

where $\xi = x^2/2Dt$. The disagreement between the observed and calculated distribution functions is partly due to K_4 not being quite small enough for the perturbation to converge, and partly due to higher moments that have been neglected. These higher moments, however, will not account for the cusp representing trapped particles, near the origin.

For the disc fluid a similar plot, shown in Fig. 18, shows much better agreement with the perturbation solution. This is partly due to a smaller value of the Burnett coefficient and partly due to the absence of trapped particles (and, hence, a cusp) for a diffusing fluid. The change of sign in the Burnett coefficient with time, indicated in Fig. 15, also leads to a change in the character of the distribution with time. The early-time behavior is similar to that of the Lorentz gas. The longest-time behavior gives evidence for fewer particles in the wings than for a Gaussian distribution, as noted earlier. A plot of the distribution for the wings in Fig. 19 contrasts clearly the difference between the Lorentz gas and the disc fluid. In the Lorentz case the distribution in the wings extrapolates to a Gaussian reasonably well, while in the fluid case the extrapolation is to less than the Gaussian value. The figure also gives evidence that the non-Gaussian distribution for the fluid is not due to the finite number of particles used in the computer calculation.

These graphical results indicate that for the Lorentz gas a Gaussian distribution is reached in the long-time limit and the numerical results for the exponents in Table I lead to the conclusion that the rate at which the Gaussian is approached at long times is correctly given by the waiting-time-distribution random walk. In the diffusing region the exponent of the Burnett autocorrelation function $\alpha_B t^{-\beta_B}$ is indeed larger by one than β_D , within experimental error. The exception is near the percolation density and can be ascribed to the limitations of the computer results. At $n^* = 0.318$ and 0.37 the diffusion coefficient, as shown in Table I, vanishes or nearly vanishes when the tail correction is taken into account. The long-time behavior under these circumstances could not be reliably established because of the long time required for the particle to escape from its trapped state; this meant that during that time some particles had diffused to the boundaries of the periodic box used in the molecular-dynamics calculation. This was observed by a change of slope of the Burnett coefficient at long times that depended on the system size used. Hence, only the early-time results at these two densities are reliable and are indicative of the trapped state; that is, the Burnett coefficient is consistent with the $2\beta_D + 2$ prediction of the waiting-time distribution in the nondiffusing case. The waiting-time distribution thus correctly predicts the power of the diverging Burnett coefficient in the entire diffusing region.

In fact, the waiting-time distribution correctly predicts the divergence of the Burnett coefficient even in the nondiffusing region, that is, between the percolation density and an n^* of about 0.477 . Once β_D exceeds $3/2$ in the nondiffusing region, the waiting-time distribution correctly predicts that α_B changes sign and the Burnett coefficient converges. In that region, the Burnett coefficient can be obtained by numerical integration of the autocorrelation

function and, once the tail is added, is found to vanish.

The major conclusion from this is that in the diffusing region the Burnett coefficient diverges for the Lorentz gas, and therefore, the Burnett equation is not the way to expand to obtain k -dependent transport properties. This is also true for the disc and sphere fluids, and in generalized hydrodynamics we completely avoided expanding the transport properties in k . For the Lorentz gas it looks as if the waiting-time distribution leads to the correct long-time behavior of the displacement distribution, so that we can learn how to expand this function so as to avoid the divergent coefficients in the Taylor expansion. This seems the simplest possible extension of a Markovian description and appears to work for one of the simplest nontrivial transport models.

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Table I. The long-time behavior, represented by α^β , of the velocity auto-correlation functions that lead to the diffusion (D) and Burnett (B) coefficients of a two-dimensional Lorentz gas and the diffusion coefficient itself.

$n^*(a)$	$-\alpha_D^{(b)}$	$-\beta_D$	$D/D_0^{(c)}$	$\alpha_B^{(c)}$	$-\beta_B$	$-\beta_B'$
0.736	0.88 ₈	2.1 ₁	0.013 ₂ - 0.014 ₂	-0.6 ₁	1.7 ₃	2.2 ₂
0.654	0.42 ₅	1.7 ₁	0.04 ₁ - 0.06 ₁	-0.14 ₂	1.2 ₁	1.4 ₂
0.654(S)	0.40 ₄	1.7 ₁	0.08 ₁ - 0.09 ₁	-0.4 ₂	1.2 ₁	
0.477	0.19 ₂	1.40 ₄	0.14 ₁ - 0.20 ₄	0	--	
0.370	0.18 ₁	1.34 ₅	0.21 ₁ - 0.25 ₃	(0.06 ₂)	(0.75 ₄)	0.68 ₉
0.318	0.20 ₂	1.40 ₅	0.20 ₁ - 0.16 ₂	(0.11 ₂)	(0.71 ₄)	0.78 ₈
0.260(N)	0.27 ₂	1.6 ₁	0.55 ₁ - 0.07 ₁	0.15 ₅	0.45 ₅	0.6 ₁
0.200	0.23 ₁	1.59 ₅	0.43 ₁ - 0.09 ₁	0.09 ₁	0.60 ₁	0.59 ₅
0.200(S)	0.17 ₄	1.54 ₅	0.36 ₅ - 0.08 ₁	0.08 ₂	0.59 ₅	
0.200(MC)	--	--		--	0.65 ₇	
0.050	0.07 ₁	2.0 ₁	0.81 ₁	0.09 ₃	1.0(d)	1.0 ₁
0.030	0.02 ₁	2.0 ₁	0.87 ₁	0.05 ₂	1.0(d)	1.0 ₁

(a) The first two entries use 90, the last two 1968, and the rest 504 particles.

Runs were 5×10^7 collisions long, except at the lowest two densities where the velocity autocorrelation function results represent 4×10^8 collisions.

Every 10^4 collisions a new random scattering configuration was generated.

The entry marked (S) stands for diffusive scattering, (N) for the no-overlap case, and (MC) for the Monte Carlo run.

(Table I contd)

- (b) The magnitude is determined by normalizing the autocorrelation function initially to unity and by a fit of the data over a range of t from 15 to 50 mean collision times, except at the lowest two densities, where the range is 10 to 20 collisions.
- (c) The magnitude is determined by dividing $d^2(tB)/dt^2$ by D_0^2 ($D_0 = 3v^2/8\Gamma$, where Γ is the collision rate), and by a fit of the data over a range of times comparable to the diffusion data. At densities 0.370 and 0.318 the autocorrelation function changes at late times, of the order of several hundred mean collision times, and this is attributed to boundary-condition effects since the change depends on the number of particles used. Hence, the data that are given correspond to the early-time, trapped-particle region.
- (d) The uncertainty in the last significant number is given in the small number following the entry, except in the case where the Burnett coefficient diverges logarithmically in the range of 10 to 50 mean collision times.
- (e) The second number to be subtracted represents the tail correction.

Figure Captions:

Fig. 1 The drift autocorrelation function $D(s)$ represented by circles, as a function of mean collision time s at an effective v/v_0 of 1.94. The solid curve is the hydrodynamic theory for the lowest mode. The insert shows for short times the difference between the contribution of the lowest mode (solid line intersecting at 1) and that of all modes (solid line intersecting at $\pi^2/8 = 1.23$) calculated hydrodynamically as well as the lowest mode (square) and the sum of the first two modes (triangle) calculated by molecular dynamics by means of the longitudinal current autocorrelation function. Also shown are the initial slope predicted for a system with a wall by kinetic theory (dashed line) and the results of molecular dynamics (circles) from the drift autocorrelation function. The vertical bars indicate the statistical uncertainty of the results.

Fig. 2 The normalized intermediate longitudinal current autocorrelation function, $C_\ell(k, s)$ for a periodic 864 hard sphere system at $v/v_0 = 1.94$ and at two wave numbers, $k\sigma = 0.594$ (circles) and $k\sigma = 1.78$ (triangles), as a function of mean collision time s . The solid curves represent the hydrodynamic theory. The insert shows in greater detail the early time behavior for $k\sigma = 0.594$ as well as the kinetic theory prediction (dashed line). The vertical bars indicate the statistical uncertainty of the results.

Fig. 3 The intermediate scattering function, $S(k, t)$, is shown as a function of time, t , is given in units of Enskog mean collision time $\tau_E = [4\sqrt{\pi} n \sigma_G^2 g(\sigma)]^{-1}$. Computer molecular dynamic results for 500 particles are denoted by open circles. A kinetic model solution of the generalized Enskog equation is denoted by the solid curve. The dashed curve represents calculations based on the linearized equations of hydrodynamics. The arrow indicates the points beyond which the periodic boundary conditions affect the molecular dynamic results.

Fig. 4 As Fig. 3 except for different conditions, namely $n\sigma^3 = 0.884$, $k\sigma = 0.759$ and a different scaling of the time axis. The crosses represent the calculation based on linearized hydrodynamics in which the Enskog values of the transport coefficients were utilized.

Fig. 5 As Fig. 3 except for different conditions namely $n\sigma^3 = 0.884$, $k\sigma = 3.394$ and a different scaling of the time axis.

Fig. 6 The longitudinal current autocorrelation function (as in Fig. 2) as a function of time at $n\sigma^3 = 0.884$ for $k\sigma = 0.759$. Time, t , is given in terms of 6.163 Enskog mean collision times. The various symbols have the same meaning as in Fig. 4. The insert gives the same results at a higher $k\sigma = 2.277$ value.

Fig. 7 The transverse current autocorrelation function as a function of time in the same notation as Fig. 6.

Fig. 8 The low density velocity autocorrelation function for the Lorentz gas as a function of mean collision time, τ . The deviation of the velocity autocorrelation function, $\rho(s)$, normalized so that $\rho(0) = 1$, from an exponential $\rho_0(s) = \exp(-4s/3)$, that is $[\rho_0(s) - \rho(s)]^2/n^*$ is plotted at $n^* = 0.03, 0.05$. The solid circles, represent a run of about 4×10^8 collisions at $n^* = 0.05$. The triangles represent a run of about 5×10^8 collisions at $n^* = 0.03$. Also plotted is a curve for the non-overlapping Lorentz gas at $n^* = 0.05$ which was taken from another paper.¹⁹ The vertical lines represent the estimated uncertainty in the results. The dashed line represents the low density theoretical prediction.

Fig. 9 The deviation of the velocity autocorrelation function for the Lorentz gas from an exponential $\rho_0(s) = \exp(-4/3s)$, for a series of densities as a function of mean collision time, s . The triangles, Δ , are for $n^* = 0.03$; the open squares, $\square$, are for $n^* = 0.16$; the closed squares, $\blacksquare$, are for $n^* = 0.20$; the closed circles, $\bullet$, are for $n^* = 0.37$; and the open circles, $\circ$, are for $n^* = 0.74$.

Fig. 10 The deviation of the velocity autocorrelation function from an exponential $\rho_0(s) = \exp(-4s/3)$, for the Lorentz gas at $n^* = 0.20$. The triangles are for the case in which the Lorentz particle undergoes specular reflection from the scatterers, and the circles are for the diffusive case.

Fig. 11 The reduced Burnett coefficient, B/B_0^2 , as a function of mean collision time s for the Lorentz gas at a reduced density $n^* = 0.20$. The solid circles are for the specular case, the triangles are for the diffusive case and the open circles represent the results of a Monte Carlo walk through the scattering centers. In the latter case s represents the number of steps in the Monte Carlo walk.

Fig. 12 The waiting time distribution as calculated from the velocity autocorrelation function of the overlapping Lorentz gas at $n^* = 0.20$. The hollow circles represent a system in which the Lorentz particle scatters diffusively and the solid circles are for a system in which the Lorentz particle scatters specularly. s is in units of mean collisions.

Fig. 13 A plot of $K'_4 = [\langle \Delta x^4(s) \rangle - 3\langle \Delta x^2(s) \rangle^2] / 3(C_0')^2$ versus $1/s^{0.59}$, where s is time measured in collision times, for the overlapping Lorentz gas at a reduced density of $n^* = 0.20$. The upper solid curve is the prediction of the continuous random walk model if the distribution of step sizes is exponential. The lower solid line is the prediction if the distribution is a Gaussian. The statistical error is no larger than the plotting symbols (triangles) for the molecular dynamics results.

Fig. 14 The fourth cumulant $K_4 = [\langle \Delta x^4(s) \rangle - 3\langle \Delta x^2(s) \rangle^2] / 3 \langle \Delta x^2(s) \rangle^2$ as a function of $1/s$ for a Lorentz gas at a density $n^* = 0.654$.

Fig. 15 The fourth order cumulant $K_4(s) = [\langle \Delta x^4(s) \rangle - 3\langle \Delta x^2(s) \rangle^2] / 3 \langle \Delta x^2(s) \rangle^2$ for a hard disk fluid at $A/A_0 = 3.0$ plotted against $1/s$ where s is in mean particle collision. The statistical error is smaller than the plotting characters.

Fig. 16 The sixth cumulant

$$K_6 = [\langle \Delta x^6(s) \rangle - 30\langle \Delta x^4(s) \rangle \langle \Delta x^2(s) \rangle + 15\langle \Delta x^2(s) \rangle^3] / 15 \langle \Delta x^2(s) \rangle^3$$

as a function of $1/s^{0.59}$ for the Lorentz gas at a density of $n^* = 0.20$. The upper solid curve gives the prediction from the continuous time random walk when the step size distribution is a Gaussian; the lower solid line is if the step size distribution is exponential. The molecular dynamics data is given by the triangles.

Fig. 17 The distribution of displacements for a Lorentz gas at a reduced density $n^* = 0.20$ at three different times as a function of $x / \langle \Delta x^2(s) \rangle^{1/2}$. The distribution, F , has been divided by a Gaussian, F_0 , with the same second moment. The triangles, Δ , are at 8 collisions; the squares, $\square$, are at 48 collisions; and the circles, $\circ$, are at 100 collisions through which a dashed line has also been drawn. The solid line is the prediction from the solution of the Burnett equation solved by perturbation at 100 collisions.

Fig. 18 The distribution of displacements for a disk fluid at $A/A_0 = 3.0$, at three different times as a function of $x/(\Delta x^2(s))^{1/2}$. The distribution, F , has been divided by a Gaussian, F_0 , with the same second moment. The triangles, Δ , are at 3 collisions; the squares, $\square$, are at 36 collisions; and the circles, $\circ$, are at 75 collisions. The solid lines are the prediction for the solution of the Burnett equation solved by perturbation at 3 and 75 collisions.

Fig. 19 Comparison between a system of hard disks and a two dimensional Lorentz gas of the distribution of displacements. The distribution of displacements, normalized by a Gaussian of the same half width, that is the same $\sigma = (\Delta x^2(s))^{1/2}$, in the interval between 3.1σ and 3.3σ plotted against $1/s$. The triangles represent a Lorentz gas at $n^* = 0.1$, while the circles correspond to a disk fluid of 1968 particles and the squares of 4012 particles at an area relative to the close-packed area of $A/A_0 = 3$. The error bars are indicated for the about 10^8 collision runs.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

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Fig. 18

Fig. 19