STUDIES IN MOLECULAR DYNAMICS OF THE FRICTION COEFFICIENT AND THE LORENTZ GAS

William Edward Alley
(Ph.D. Thesis)

June 1, 1979

MASTER

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Studies in Molecular Dynamics of the
Friction Coefficient and the Lorentz Gas

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WILLIAM EDWARD ALLEY
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William Edward Alley
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Abstract

The thesis consists of three hard-sphere molecular dynamics studies. The first describes a modification of Fick's diffusion law, required whenever long-time correlations are present. Due to these persistent correlations, the Burnett coefficients (the rate at which the fourth and higher order cumulants of the spatial distribution of particles approach their asymptotic long-time limit) diverge, since the distribution does not approach its long-time limit as a Gaussian. Thus, Fick's law must be modified, since it describes a Markov process (no persistence) for which the distribution is Gaussian for all time. For the Lorentz gas, the non-Markovian nature of the transport process is shown to correspond to a random walk where, after each step, the particle waits for a time as sampled from a waiting-time distribution before making the next move. The major physical consequence of this stochastic process is that the higher moments can still be expressed in terms of the second moment, but as a time convolution rather than a product as for a Markov process. These convolution expressions lead to convergent Burnett coefficients in which the stochastic process yields explicit expressions for all Burnett coefficients, and hence the time evolution of the entire distribution, in terms of the second moment. Furthermore, the long time behavior of this second moment for the Lorentz gas, as calculated by molecular dynamics, has

been found to be in agreement with the theoretical predictions at low density. Thus, by introducing non-locality in time (memory) into the description of the transport process, the previous theoretical difficulties are removed.

The second study concerns the mass and size dependence of the friction coefficient as well as its dependence on boundary conditions. The study presents a molecular dynamics method which calculates the infinite-mass friction coefficient of finite size hard-sphere particles. The results of the calculations are consistent with Stokes law in the infinite size limit; that is, the calculated friction coefficients extrapolated to very large size for purely specular scattering agree with the one calculated for slip boundary conditions, while the friction coefficients utilizing diffusive scattering agree (when extrapolated) with the one calculated for stick boundary conditions. The friction coefficient of an aggregate particle, made up of infinitely massive hard spheres which are equal in size to the fluid particles, lies between the results for slip and stick boundary conditions. A theory is presented that accounts for the deviation from Stokes law, due to the finite size of the particle, by the introduction of a generalized (wavelength dependent) shear viscosity in the drag coefficient.

The third study presents the applicability of hydrodynamics to describe fluctuations in fluids on the molecular level. This study shows that the fluctuations present in a system of hard spheres when placed between closely spaced parallel hard walls lead to an acoustical resonance for those wavelengths which correspond to the spacing, or integer fractions thereof. The decay of the resonance can be related to the autocorrelation function of the sum over modes of the longitudinal

currents. This relation was verified by a separate calculation of the currents by molecular dynamics. The decay of the resonance can also be analyzed in terms of hydrodynamics and kinetic models, and the regions of the validity of these theories is delineated. These numerical experiments show the remarkable validity of hydrodynamics at a distance scale of a few molecular diameters and a time scale of a few mean collision times.

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I. INTRODUCTION

The purpose of this thesis is to study long-time correlation effects on particle diffusion in fluids. The molecular dynamics method is used to study two of the limiting forms of diffusion: in the first limit the relative mass of the diffusing particle is very small in comparison to the mass of the surrounding particles; in the other limit the mass of the diffusing particle is very large in comparison to the surrounding particles. These two limits represent two extremes of magnitude in long-term hydrodynamic correlation effects. The effects were discovered in 1967 (1), when it was found the rate of decay for the velocity autocorrelation function, which measures the degree of randomization in velocity a representative particle in a fluid undergoes as a function of time, was much slower than expected from a random collision hypothesis.

The physical cause of this slow decay is the development of a velocity correlation in the neighborhood of the diffusing particle (2, 3,4). Even though this flow field occurs on a scale of a few molecular diameters, it can be understood in terms of a hydrodynamic model. In such a model, a fluid is at rest except a small volume element is given an initial velocity. A compression wave develops in front of the region and a rarefaction wave develops to the rear. When the sound waves have separated, the residual flow is in the form of a double vortex in two dimensions, or a vortex ring in three dimensions, which equalizes the pressure difference. Therefore, the medium feeds some of the initial momentum of the moving particle back at a later time, effectively giving it a push. Since the diffusion coefficient is proportional to the infinite time integral of the velocity autocorrelation function, it is

larger in comparison to what is calculated if random collisions are assumed. In two dimensions the long-time tail decays so slowly the time integral is infinite, i.e., the usual diffusion coefficient for two dimensional fluids does not exist.

After it was discovered the velocity autocorrelation of a particle in a fluid decays very slowly at long times, it was recognized the higher order coefficients in the Chapman-Enskog expansion (5) diverge (6,7). The Chapman-Enskog expansion for diffusion is a series expansion of the particle flux in terms of the density gradients. The first term in this series is proportional to the first order gradient and is the constitutive relation known as Fick's first law. All terms in the series are of odd order in the density gradients and linear, that is, there are no terms which are proportional to, say, the square of the density gradient. Therefore, the next term beyond Fick's law is of third order, and the proportionality constant of this term is the first Burnett coefficient for diffusion (sometimes called the super-Burnett coefficient). The cause for the divergence of the Burnett coefficients is the distribution for the positions of the particles as a function of time does not approach its long-time limit as a Gaussian. The long persistent correlations lead to the non-Gaussian approach and also introduce non-locality in time (memory) into the statistical mechanical description of transport theory.

The invalidity of the Chapman-Enskog expansion for fluids brings up the question whether there exists any system in which this expansion exists. A likely candidate is the Lorentz gas, in which a cloud of mutually non-interacting particles diffuses through an array of fixed scatterers. Since the scatterers do not move, no correlated hydrodynamic

fields can influence the diffusing particles. The Lorentz gas is the subject of the next chapter. The emphasis is on long-term correlation effects on the diffusion and Burnett coefficients, and the asymptotic form of the distribution of particle positions as a function of time. This distribution, which measures the probability density as a function of time that a particle is at a certain position, should be Gaussian in the long-time limit, if the steps of the diffusing particle through configuration space are suitably random (8,9). The question is: will the distribution function approach its asymptotic limit in a way that the Chapman-Enskog expansion exists?

For large and massive particles in a fluid, the time scale of the microscopic interactions is very short compared to the hydrodynamic time scale; in the infinite mass and size limit, the Brownian limit, only the slow hydrodynamic responses are important. Chapter III is a study of the opposite limit to the Lorentz gas; namely, the single diffusing particle is of large mass. Because the response of the massive test particle to collisions is negligible compared to the response of the bath particles, it is held fixed; the function which is evaluated in this case is the force autocorrelation function, which describes how the forces on this massive particle are correlated in time. The time integral of the force autocorrelation function is proportional to the force constant, which is the proportionality constant between the drag on a sphere and the slow velocity which it moves through the fluid. If the massive particle is large enough, so the Brownian limit is approached, then the force constant is proportional to the radius of the sphere and the viscosity of the fluid (10). A numerical constant is also predicted (11,12), which depends on whether the fluid sticks or slips on the surface of the sphere.

Chapter III investigates whether this, so called, Stokes law is approached as the size of the massive particle is made larger. In particular, the value of the numerical constant is of interest because of the current theoretical disagreement on its value (13,14,15).

Chapter IV is a direct outgrowth of the technical difficulties associated with the implementation of the molecular dynamics program used for the study of the force constant. When the bath particles strike the central fixed particle, the center of mass motion of the bath particles is changed. The central fixed particle acts as a momentum source which adds increments of momentum in arbitrary directions. At first it was thought this random drift velocity would average out of the calculation of the force constant, but it remains. Long lasting coherent center-of-mass drift velocities are generated which, therefore, violate the equilibrium condition under which the force autocorrelation function must be evaluated. Since the central fixed particle is the source of these drift fluctuations, it was decided to study a limiting form of this situation in which two massive hard spheres of infinite radius are placed with their surfaces a few molecular diameters away from each other. This is equivalent to placing two parallel plates a small distance apart with a fluid between them. The resulting fluctuations are then easier to analyze because of the simpler geometry.

Each chapter to follow is divided into a number of sections and subsections. Each section is labeled alphabetically, and, each subsection is labeled numerically. Important equations are labeled numerically beginning with 1 in each subsection. If an equation is cited in a subsection in which it is defined, then only the equation number is given. However, if an equation is cited that was defined in another

section or subsection, then the equation is cited by section, subsection, and equation number: B3.7 means Eq. 7 in subsection 3, section B.

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II. THE LORENTZ GAS AND A MODIFICATION OF FICK'S LAW

A. Introduction

This chapter consists of a study of the long-term correlation effects on particle diffusion in a simplified model of a gas: the Lorentz gas. In this model, as originally proposed by Lorentz (1,2), the mass of the molecules of one constituent is very great compared to the mass of the others; and the mutual interactions between the light molecules are negligible compared to the interactions with the heavier ones. Also, the range of interaction between the light and heavy molecules is small. The limiting form, where the heavy molecules are immovable hard disks and the light molecules are massless points, is studied here.

The Lorentz gas is of interest because of the simplifying feature that the scatterers, namely the hard disks, are stationary. This eliminates the effects on the moving particle from correlated motion in the surrounding neighborhood, which lead to the slow decay of the velocity autocorrelation function in fluids (3,4,5). Also, analysis is simpler in the Lorentz gas because collisions, which normally depend upon the velocity distribution of both particles in fluids, depend only upon the velocity distribution of the single colliding Lorentz particle. This means the Boltzmann equation, which is an integral differential equation for the probability distribution of a particle, is simpler for the Lorentz gas. The collision term in the Boltzmann equation, which is second order in the distribution function for fluids, is linear in the distribution function for the Lorentz gas (6). This means the Boltzmann equation is easier to solve for the Lorentz gas so certain approximation methods, which are used to approximate the equation for fluids, can be tested.

Although the solution of the Boltzmann equation is important, it does not include, for instance, the many-body effects which lead to the slow decay of the velocity autocorrelation function in fluids. This is because molecules which collide are assumed to be uncorrelated in velocity before the collision occurs. This approximation, called the molecular chaos assumption, is justified only when the gas density is sufficiently low. Then a correlation between their initial velocities is unlikely, because the two molecules originate before the collision at a very large separation. The molecular chaos assumption completely breaks the dynamical many-body correlations.

It is important to remember these statements about the Boltzmann equation when considering the dynamical properties of gases. It has been shown Fourier's law of heat conduction holds for the Lorentz gas in the Grad limit (7). The Grad limit is defined in such a way that the mean-free-path of the Lorentz particle is constant, while the density of scatterers goes to infinity and the radius of the scatterers goes to zero. A similar result no doubt holds for fluids. This constitutes the first time Fourier's law has been shown to be rigorous. However, the Boltzmann equation also rigorously holds in the Grad limit (8,9,10). Thus, the Grad limit removes the dynamical many-body correlations from the distribution function.

Very few other rigorous results have been proven for the Lorentz gas: mathematical analysis has led to proof that the Lorentz gas has good ergodic properties (11,12), and that certain functions obey the central-limit theorem (13). These proofs suggest the probability distribution of the moving particle may be Gaussian after a sufficiently long time.

Some theoretical results, which are valid at low but finite density, have been obtained: a simpler version of the Lorentz gas called the wind-tree model (14), which constrains the particle to move on a plane in only four perpendicular directions, has been used to study the density dependence of the diffusion coefficient (15,16). This work was stimulated by the discovery in fluids of divergences associated with the density expansion of the transport coefficients (17,18). Two versions of the wind-tree model were considered in these theoretical investigations: the first is an overlapping version and the second is a non-overlapping version. In the overlapping version it was found the second moment of displacements does not increase linearly with time at long times, but at a rate which is slower. Thus, the diffusion coefficient, which measures the asymptotic rate of increase of the second moment with time, is zero. Such diffusion is labeled abnormal, to distinguish it from the non-overlapping case, where the second moment increases linearly with time so the diffusion coefficient exists. The zero diffusion result occurs in the overlapping case because of the higher probability of retracing events, where the wind particle retraces its steps partially or totally.

Important multicollision effects are also found in the hard disk and sphere Lorentz gas (19,20). Even though these systems are more general than the wind-tree model, because all directions in velocity are possible, a density expansion of the diffusion coefficient in the Lorentz gas is non-analytic just as in fluids, owing to the high probability of some collision sequences. The most important sequences are the ring collisions in which the moving particles and a scatterer touch initially and finally in the collision sequence; the trajectory forms a closed loop in configuration space.

In fluids, the ring events lead to the slow decay of the velocity autocorrelation function (21,22,23) and justify the physical interpretation in terms of hydrodynamics (5,23). Soon after the discovery of the slow decay of the velocity autocorrelation function in fluids, the divergence of the Burnett coefficients was found (24,25,26). The divergence occurs because the probability distribution function for the positions of the particles as a function of time does not approach its long-time limit as a Gaussian as Fick's law predicts (26). The long persistent correlations in velocity lead to a non-Gaussian approach to the limit. For the Lorentz gas, the ring events also lead to a slow decay of the velocity autocorrelation function (27), but the magnitude of this tail is negative rather than positive, as it is in fluids, owing to the high probability of return paths. By analogy with fluids, these long-term correlations in velocity lead to a non-Gaussian approach of the distribution function to its asymptotic limit, and divergent Burnett coefficients. Since Fick's law is consistent with a Gaussian distribution function at all times, it must be modified to account for the deviation of the distribution function at long, but finite, time.

Many of these multicollision effects have been checked on the computer using molecular dynamics. Because only a finite number of particles (on the order of 10,000) can be handled on the computer, these studies must be carried out at finite density; if the density is too low no collisions will occur and the particles just stream through the system. While the theoretical results for the velocity autocorrelation for fluids apply at all densities, the results for the Lorentz gas are only rigorous at low density. Thus, the approach to the low density limit must be studied.

It was found at finite density for the wind-tree model that the velocity autocorrelation function of the wind particle is negative and decays at a much slower rate than expected at long times (28). In addition, the abnormal diffusion process for the overlapping trees case has been confirmed at finite densities in this model. Similarly, Bruin (29) has made a study of the disk and sphere Lorentz gas. Although he found that the velocity autocorrelation function has negative structure at long time, as in the wind-tree model, he was unable to get quantitative agreement with theory because his statistical accuracy was low. However, in two dimensions, the presence of the logarithmic term in the density expansion of the diffusion coefficient was detected, confirming the non-analytic dependence of this coefficient. Although the existence of a critical density above which the diffusion coefficient is zero is suggested by the tables in Bruin's thesis, this point was never fully investigated. The density, called the percolation point, provides a simple picture of a critical point (30), which is amenable to calculation (31,32). The intermediate and high density dependence of the tail of the velocity autocorrelation function was never investigated by Bruin, nor was the Burnett coefficient or the probability distribution function.

The next section of this chapter discusses the molecular dynamics model in detail. Also discussed are the functions which are evaluated and the configurational averaging techniques which are used. Following this is a section of molecular dynamics results, which opens with a discussion of the effects on accuracy which are not related to statistics. Then the diffusion and Burnett coefficients for the Lorentz gas are presented from the low density regime to a density well above the percolation point where the diffusion coefficient is zero. The section following

this presents a modified Fick's law which agrees quantitatively with the long-time molecular dynamics results for the Lorentz gas distribution function and its moments. This modified Fick's law is necessary because the fixed scatterers in the Lorentz model introduce a memory into the system, which profoundly affects the form of the distribution function. Following this a modified Chapman-Enskog expansion is presented which is free from divergent coefficients. In addition, the idea that the higher order moments can asymptotically be expressed in terms of the lower order moments leads to a simple picture of the Lorentz gas: the particle makes a walk in configuration space in which it waits after each jump for a time, as sampled from a waiting distribution, before it takes another step (33). Finally, these ideas are applied to fluids where it is found that due to the additional hydrodynamic flows, which affect the distribution at long times, the modified Chapman-Enskog expansion is still invalid. What must be done to get convergent coefficients is to account for the diffusion of these hydrodynamic flows away from the origin of coordinates of the diffusing particle.

B. Molecular Dynamics

This section discusses the molecular dynamics method used. In the first subsection, emphasis is placed on techniques used to ensure efficiency and rapidity of the calculation of the dynamics. A detailed discussion of the solution of the dynamical equations can be found elsewhere (34). The next subsection discusses the configurational averaging technique. Emphasis is placed on sampling the configurations for equal time intervals rather than equal collision intervals, otherwise, improper weighting of the configuration results. Following this is a subsection which describes the dynamical variables which are calculated and averaged:

the moments and cumulants together with the distribution function. Also in this subsection a brief discussion of the method used to determine the statistical accuracy of these averages is given.

1. The Dynamics

The computer program for the Lorentz gas calculates the dynamics of a single particle of zero radius, which moves in a square area containing immovable disk scatterers of radius R . A single moving particle can be used because the Lorentz particles do not mutually interact. Thus, the properties of the gas are directly related to the mean motion of a single particle, which is averaged over all possible scattering configurations. The number of scatterers used varies from as few as five to as many as approximately two thousand. The boundary conditions at the edge of the square are periodic; when the moving particle reaches a boundary, it will disappear and reappear on the other side of the square. This is necessary in order to minimize boundary effects in these finite sized systems. The dynamics of the particle is that of hard disks (34), so the Lorentz particle moves in a straight line until it encounters a scattering disk, then the program calculates a new velocity in one of two ways: the first way is by using specular scattering conditions, and the second way is by using diffusive scattering conditions. If the Lorentz particle scatters specularly from the immovable disks, then the program calculates a new velocity from the rule for scattering from smooth surfaces: the angle of incidence is equal to the angle of reflection. If the Lorentz particle scatters diffusively from the immovable disks, then the program calculates a new velocity in a random direction away from the point on the edge of the scattering disk where the Lorentz particle collided. In both the specular and diffusive scattering cases, the absolute value of the velocity of the Lorentz particle is constant; that is, the collisions are elastic.

The key problem the computer program has to solve is: how to efficiently find the time to the next collision and the scatterer which will be hit. To eliminate as many calculations as possible, scatterers which are far removed from the Lorentz particle must be eliminated from the search. This is done by dividing up the large area of scattering disks into many small cells. Then, when the moving particle is in a particular cell, only cells in the immediate vicinity of this cell need to be searched. Since the positions of all the scatterers are fixed, the positions of these scatterers are known relative to every cell in the system. This last fact can be used to simplify the search even further, since it tells the program which scattering centers are likely to be hit when the moving particle is in a particular cell. The number of cells needed for optimum program running speed is on the order of the number of scatterers in the whole system; if the number of cells is too large, then crossing of the cells begins to dominate the molecular dynamics, since cell wall collisions are added to the possible types of collisions that the moving particle can have. This streamlined version of the program can run the Lorentz gas at 20 million collisions per hour on the C.D.C. 7600 computer. This is approximately ten times faster than the disk fluid can be run; the enormous savings in computer time is because the scattering centers are fixed.

2. The Configurations

On the computer the trajectory of a single particle is followed in a particular scattering configuration for a fixed time interval (typically 10^3 to 10^4 mean particle collisions), then a new scattering configuration is generated and the trajectory of the particle is again followed for the same length of time. This process is continued and all

the while the physical properties of the trajectories are measured and averaged for these equal time configurations.

Two types of configurations are generated: a non-overlapping configuration, and an overlapping configuration. In the non-overlapping case, each configuration is generated by a standard molecular dynamics procedure for hard disk fluids, where each scatterer represents an impenetrable disk of radius R . After a few collisions, the configuration is frozen and the movable point particle is placed in the now static configuration of hard disks. In the overlapping case, each configuration is generated by a random placement scheme: the positions of the scatterers of radius R are calculated by a random number generator. Thus, in the overlapping Lorentz gas, the scatterers are allowed to overlap one another.

It is important to emphasize that the configurations must be each sampled for an equal time interval. This has led to some confusion in the past (29), and if not utilized will result in improper configurational averages. For instance, if equal collision sampling is used, that is, each configuration is sampled for the same number of collisions, those configurations in which the local configurations around the Lorentz particle are denser than average will get weighted less than those which are less dense than average. By the ergodic hypothesis each configuration should get equal weight, and the parameter used to measure this should be independent of the configurations chosen: the time. For instance, it is found that when equal collision configurational averages are used (29), the collision rate in the overlapping Lorentz gas disagrees at high densities with the rate which is predicted by low density kinetic theory. Since the scatterers are randomly placed in this system, this theory

should rigorously predict the collision rate. When equal time configurational averages are used, then the collision rate for the overlapping Lorentz gas agrees with the low density kinetic theory.

3. The Averages

A quantity calculated by the molecular dynamics program is the distribution function, $f(x,t)$, which is the probability density of finding the Lorentz particle displaced along the x -axis a distance x in time t . Also calculated are three moments of this distribution: the second moment, $\langle x^2(t) \rangle$; the fourth moment, $\langle x^4(t) \rangle$; and the sixth moment, $\langle x^6(t) \rangle$. These moments are used in the following three cumulants: $C_{2n}(t)$, where $n = 1, 2, 3$ and

$$C_2(t) = \langle x^2(t) \rangle / 2! \quad , \quad (1)$$

$$C_4(t) = [\langle x^4(t) \rangle - 3\langle x^2(t) \rangle^2] / 4! \quad , \quad (2)$$

$$C_6(t) = [\langle x^6(t) \rangle - 15\langle x^4(t) \rangle \langle x^2(t) \rangle + 30\langle x^2(t) \rangle^3] / 6! \quad . \quad (3)$$

These cumulants are different than what is usually defined in the literature because of the division by $(2n)!$ (35,36). Once the cumulants are known, then the diffusion coefficient, D , and the Burnett coefficients B_4 , B_6 , can be evaluated by taking the infinite time limit of the first derivative of these expressions. Thus

$$D = \lim_{t \rightarrow \infty} \dot{C}_2(t) \quad , \quad (4)$$

$$B_4 = \lim_{t \rightarrow \infty} \dot{C}_4(t) \quad , \quad (5)$$

$$B_6 = \lim_{t \rightarrow \infty} \dot{C}_6(t) \quad , \quad (6)$$

where the dot indicates time derivative. The cumulants are evaluated,

together with their first and second time derivatives, as a function of time. Then, at long times the asymptotic behavior of the cumulants, and their time derivatives, can be determined. Once this is done, extrapolation to infinite time is performed.

Equations 4, 5 and 6 can be written in terms of time integrals of velocity correlation functions. However, the moments of the distribution are used to evaluate these coefficients, rather than the physically equivalent velocity correlation functions, because the evaluation of the Burnett coefficients, in terms of the velocity correlation functions, is more complicated. For instance, the velocity correlation function for B_4 is a four point correlation function (35,36), i.e., the velocity of the moving particle is correlated at four different times, rather than two, as for the velocity correlation function which defines the diffusion coefficient. Thus, a multidimensional correlation function must be saved on the computer, which amounts to a large amount of memory storage, because of the accuracy needed to get the transport coefficients in the long-time limit.

The computer program evaluates the moments at uniform time points beginning at $t = 0$, where $C_{2n}(0) = 0$, and steps out in units of Δt , where Δt was typically $\frac{1}{2}$ mean collision time. The transport coefficients then follow from the long-time limit of the time derivative of $C_{2n}(t)$, namely $\dot{C}_{2n}(t)$, which is approximately $\dot{C}_{2n}(t_{p+\frac{1}{2}}) \sim [C_{2n}(t_{p+1}) - C_{2n}(t_p)]/\Delta t$, where $t_p = p\Delta t$ is the value of time at the p^{th} time point. Also evaluated is the second derivative $\ddot{C}_{2n}(t_p) \sim [C_{2n}(t_{p+1}) + C_{2n}(t_{p-1}) - 2C_{2n}(t_p)]/\Delta t^2$, which for $n = 1$ is the usual two point velocity autocorrelation function. These difference approximations are accurate to second order in Δt . For slowly varying functions, as the cumulants are at long times, these difference approximations are very accurate.

The distribution function, $f(x,t)$, is calculated relative to a Gaussian distribution of the same root-mean-square width, $\langle x^2(t) \rangle^{1/2}$. A time dependent width is needed to take into account the spreading of the distribution as a function of time. The Gaussian distribution is used in order to compare the actual distribution with the prediction of simple random walk theory. Therefore, if the distribution is a Gaussian, the ratio computed by the program will be unity.

The number of average collisions run per configuration was typically 10^3 - 10^4 . If the position of the moving particle is saved every $\frac{1}{2}$ mean particle collision and the displacements are wanted for 50 mean collisions, then for 10^4 collisions $10^4 \times 50/.5 = 10^6$ displacement curves are calculated per configuration, because each time point is used as an initial point for another displacement curve. All runs were typically 50×10^6 mean collisions long, except for some low density systems which were run about ten times longer; thus, there were approximately 5000 configurations generated and over 10^9 displacement curves.

Each configuration is independent of all the others. However, since there are many configurations generated for each run, the number of these statistical samples was reduced to facilitate numerical analysis. The procedure is to average the results of these single configurations into larger groups. Typically not more than 10 independent groups resulted from this procedure. The statistical analysis of these groups, or samples, is standard (37): if there are N samples of a particular variable, x_i , then the average of this variable is $\mu(x) = \frac{1}{N} \sum_{i=1}^N x_i$, and the estimated error in $\mu(x)$ is $\sigma = \pm \sqrt{\text{var}(x)/N}$, where $\text{var}(x) = \frac{1}{N-1} \sum_{i=1}^N (x_i - \mu)^2$.

(The estimated error is the one quoted, herein, as the statistical or

experimental error.) The reduction in the number of independent samples in this way does not adversely affect the estimated error in $\mu(x)$ because, as the groups are made larger, the variance of the samples becomes smaller, effectively compensating for the smaller value of N .

C. Molecular Dynamics Results

This section discusses the molecular dynamics results on the cumulants and the distribution of the Lorentz particle. The first subsection is concerned with two effects on the accuracy of the computer results which are not caused by statistical error: the first effect results from computer imprecision, and the second effect is from the use of periodic boundary conditions, which are necessary because of the finite size of the systems. The asymptotic long-time behavior of the velocity autocorrelation function and the Burnett correlation functions is discussed in the following four subsections. These subsections were necessary because of the very different behavior of the cumulants and the distribution function in different density regimes. The first of these four subsections presents the low density results. It is emphasized that these results, although at a low density, are away from the Grad limit so correlated collisions are important and the Boltzmann equation does not apply. A theoretical calculation of the velocity autocorrelation function, which applies in this low but finite density regime, is compared with the molecular dynamics results. The next subsection describes the intermediate density results. This intermediate density is above the low density regime where the theoretical calculations apply and below the percolation point where $D = 0$. The next subsection, then presents the results in the region of the percolation point. And the final subsection presents the results above the percolation point in the high

density regime. The appendix (sec. F1) gives detailed results on selected velocity autocorrelation functions and distribution functions.

1. Preliminary Results and Accuracy

This subsection contains some preliminary results on the moments and cumulants of the overlapping disk Lorentz gas. The emphasis here is on the qualitative behavior of the cumulants and effects on accuracy which are not due to statistics.

In the short time regime, from 0 to 10 collisions, the velocity autocorrelation function behaves qualitatively as expected. The velocity autocorrelation function is proportional to the second time derivative of $C_2(t)$:

$$\rho_D(t) = \ddot{C}_2(t) / \langle \dot{x}^2 \rangle \quad (1)$$

and is equal to unity when $t = 0$. Figure 1 shows the deviation of this function from the Boltzmann result, $\rho_0(t) = \exp(-4t/3)$, for a series of reduced densities, $n^* = nR$, where t is in units of mean particle collisions and n is the number density of scatterers of radius R . The triangles ▲, are for $n^* = 0.03$; the open squares, □, are for $n^* = 0.10$; the closed squares, ■, are for $n^* = 0.20$; the closed circles, ●, are for $n^* = 0.37$; and the open circles, ○, are for $n^* = 0.74$. As the density increases, back-scattering becomes more predominant, and the time at which back-scattering is most pronounced occurs later. This indicates that it takes relatively longer for the Lorentz particle to escape its neighborhood the higher the density. As shown in Fig. 1, the trend in the long-time part of the velocity autocorrelation function beyond 10 collisions is broken at high density. It is later shown the diffusion coefficient is zero at this high density, therefore, the stronger backscattering in the velocity autocorrelation function is compensated by a weaker tail,

Figure 1

The deviation of the velocity autocorrelation function from its low density Boltzmann-Enskog value for the overlapping disk Lorentz gas as a function of mean-particle collisions.

since the total integral of this function must be zero.

At this point, it is of interest to see how the precision of the computer affects the accuracy of the results. As the machine traces out the trajectory of a particle, each interaction introduces errors (due to arithmetical round off) into the calculation. Thus, after a certain number of collisions have elapsed, a given trajectory will not be reversible, that is, if a particle velocity is reversed, so it initially retraces its path, then after, say N_c collisions, the particle will no longer be following its old path but a new one. The number N_c is the reversal number. On the C.D.C. 7600 computer with 14 decimal place precision, the reversal number is 12 for the overlapping specularly scattering Lorentz gas. If we are interested in the asymptotic long-time behavior of the correlation functions, then this result suggests the data will be unreliable beyond a range of about 10 collisions. However, the results show the asymptotic form of the time correlation functions is not affected by the imprecision of the machine. That is, the asymptotic behavior of these functions is completely determined by the topology of the space in which the Lorentz particle moves, and not the detailed dynamics. This conclusion is based on the comparison of three cases: in the first case the moving particle makes specular reflections with the scatterers; in the second case it makes diffusive reflections; and in the third case it makes a random walk through the system of scatterers. The specular and diffusive scattering conditions have been discussed in section B1. In the random walk, the particle is moved through the scattering system consistent with the Monte Carlo method of Metropolis et. al. (38). Each step is counted as a tick of the clock and the step sizes are chosen to be consistent with the mean-free path of the particle in the system. Both the diffusive

scattering Lorentz gas and the random walk Lorentz gas represent systems in which the trajectory reversal number, N_c , is zero. They represent systems in which the imprecision in the velocity direction has been maximized.

Figure 2 shows the deviation of the velocity autocorrelation function, $\rho_D(t)$, from its low density Boltzmann value, $\rho_0(t)$, at an intermediate density. The circles are for diffusive reflections and the triangles are for specular reflections. As the figure shows, the diffusive scattering case yields a greater negative region, due to the elimination of forward velocity correlations, than does the specular case. However, at late times the correlation functions approach the same asymptote. This is illustrated in Fig. 3, where the tail of both of these correlation functions is plotted beyond 10 collisions. The agreement between these two cases is within the statistical error of the data, for these power law tails, although there is a small systematic difference. Fig. 4 shows $\dot{C}_4 \Gamma / D_E^2$ as a function of mean particle collisions for the specular, $\bullet$, diffusive, $\blacktriangle$, and random walk, $\circ$, Lorentz gas, where $\Gamma = 2nR|v|$ is the collision rate and $D_E = 3v^2/8\Gamma$ is the Enskog value for the diffusion coefficient. The random walk Lorentz gas is plotted as a function of Monte Carlo steps. In all these cases, the function $\dot{C}_4$ diverges with the same power law slope. Only the magnitudes of the curves are not the same, because of the difference in initial backscattering. Table 1 gives the asymptotic results of the specular and diffusive Lorentz gases at two densities for the velocity autocorrelation function and the Burnett correlation function. The coefficients $\alpha_D, \beta_D, \alpha_B, \beta_B$ represent a fit of the equation $\rho_D(t) \sim -\alpha_D/t^{\beta_D}$ to the tail of the velocity autocorrelation function, and $\rho_B(t) \sim \alpha_B/t^{\beta_B}$ to the tail of the Burnett correlation

Figure 2

The deviation of the velocity autocorrelation function from its low density Boltzmann-Enskog value for a diffusive scattering and specular scattering overlapping disk Lorentz gas at a reduced density $n^* = 0.20$.

Figure 3

Same as Fig. 2 except beyond 10 mean particle collisions.

Figure 4

The Burnett coefficient for the overlapping disk Lorentz gas.

n^*	$-\alpha_D$	β_D	α_B	β_B
0.654(D)	0.31 ₄	1.60 ₅	-0.10 ₂	1.36 ₄
0.654(s)	0.30 ₃	1.6 ₁	-0.14 ₃	1.2 ₁
0.200(D)	0.19 ₄	1.54 ₅	0.08 ₃	0.61 ₅
0.200(s)	0.23 ₁	1.59 ₅	0.09 ₁	0.60 ₁

Table II-1

The long-time behavior of the velocity autocorrelation function and the Burnett autocorrelation function for diffusion scattering (D) and specular scattering (s) in the two dimensional overlapping Lorentz gas.

function:

$$\rho_B(t) = \bar{C}_u(t)/D_E^2 \quad (2)$$

The total number of scatterers in these systems is 503, and the error in the last figure is indicated by the subscript. These fits were performed between 10 and 30 collisions. As the table shows, the asymptotic tail of the velocity autocorrelation function for the diffusive scattering case is identical to the specular case, within statistical error; the same is true for the Burnett correlation function. Thus, accuracy in the calculation of the direction of the Lorentz particle has no effect on the asymptotic properties of the correlation functions, only the topology of the space in which the particle moves is of importance.

Another effect on the accuracy of the computer results is due to the periodic boundary conditions which are necessary because of the finite size of the system. As long as the diffusing particle is followed in a time interval which is short compared to the time it takes to diffuse across the finite area, called the diffusion time, the results are indistinguishable from those of an infinite system. Figure 5 shows this for the function $K_0 = 2C_u/(D_E t)^2$ as a function of time for a system with 503 scatterers, O, and a system with 1967 scatterers, ●, at an intermediate density. The 503 scatterer system is only plotted when the deviations from the 1967 scatterer system are large. The deviations become noticeable at approximately the diffusion time, which for the 503 system is indicated by the arrow.

Figure 6 shows the velocity autocorrelation function for a small periodic system of only 5 scatterers at an intermediate density. The solid circles, ●, represent the positive power law tail of the velocity autocorrelation function. The open circles, O, represent what happens

Figure 5

The fourth order cumulant for the overlapping disk Lorentz gas.

Figure 6

The velocity autocorrelation function for a small periodic Lorentz gas.

if the configurations in which no collisions occur are excluded. The power law tail is clearly caused by the contributions from those long paths which heavily weight the correlation function. The decay rate is more accurately described by an exponential than a power law as Fig. 6 shows.

2. Low Density Results

The low density results are consistent with the theoretical prediction (27) of a power law decay of $\beta_D = 2$ for the velocity autocorrelation function, but the magnitude of the autocorrelation function, α_D , is not consistent with the prediction; the theoretical result only applies when the density is vanishingly small. This is illustrated in Fig. 7 where the ratio of α_D to the theoretical value of n^*/π is plotted as a function of density. The dashed line represents a least squares fit of the equation $y = mn^* + b$ to the three data points which represent the overlapping disk Lorentz gas, where $m = 55. \pm 2.$ and $b = 1.0 \pm 0.1.$ It is evident from this the theoretical result is valid only in the limit of zero density, i.e., $n^* = 0.$ In this limit the magnitude of the tail will vanish, since it is proportional to $n^*.$

As Fig. 7 shows there is another physical process (other than the ring events which lead to the low density result of n^*/π) that also contributes to the power law decay, $t^{-2}.$ This new physical process is not independent of the topology of the scatterers, as is the low density result. This is illustrated in Fig. 7 by the solid circle which represents a non-overlapping Lorentz gas (39) and Fig. 8, where the difference between the velocity autocorrelation function, $\rho_D(t),$ and its low density Boltzmann approximation, $\rho_0(t),$ is multiplied by $t^2,$ to remove the time dependence, and divided by n^* to remove the density dependence. The solid circles, $\bullet,$ represent a run of 4×10^8 collisions at a density of

Figure 7

The coefficient of the power-law tail of the low-density overlapping and non-overlapping Lorentz gas.

Figure 8

The difference between the velocity autocorrelation function and its low density Boltzmann-Enskog value for an overlapping and non-overlapping disk Lorentz gas at $n^* = 0.05$.

$n^* = 0.05$; the open circles, $\circ$, represent the results of a non-overlapping Lorentz gas at $n^* = 0.05$, which were taken from another paper (39). The dashed line represents the low density theoretical result.

The better agreement of the non-overlapping Lorentz gas with the low-density theory is due to the non-existence of trapping regions in this system. These trapping regions, which are also absent in the low-density theory result in a higher probability of return events for the overlapping Lorentz gas, much as in the overlapping wind-tree model.

Table 2 gives the results of a fit of α_D/t^{β_D} to the tail of the velocity autocorrelation function for the lowest densities in which the power law of the tail could not be distinguished from 2. The fourth column gives the value of D/D_E at the density indicated in the first column. The number to be subtracted from D/D_E at the highest density in Table 2 is the tail correction which is obtained by integration of the fit to the tail beyond 20 collisions. For the lowest two densities studied, this correction is negligible. Also given in the table, in parenthesis, is the theoretical prediction of n^*/π for α_D .

Figure 9 shows a plot of the function $\hat{C}_u(t)\Gamma / D_E^2$ as a function of time for the overlapping Lorentz gas at $n^* = 0.05$. The solid line is a straight line fit to the data. This function diverges logarithmically as time increases so the Burnett coefficient, B_u , does not exist. The logarithmic divergence of $\hat{C}_u$ means the Burnett correlation function, $\hat{C}_u(t)$, decays like t^{-1} as time gets large, which is one power less than the velocity autocorrelation function decays. The coefficient, α_B , of the tail of $\rho_B(t) = \hat{C}_u(t)/D_E^2$ is given in Table 3. It is seen that α_B is positive and increases with the density. These observations suggest it may be possible to relate α_B , β_B to α_D , β_D .

n^*	$-\alpha_D$	D/D_E
0.100	0.20 ₅ (0.031)	0.66 ₁ - 0.01 ₁
0.050	0.060 ₅ (0.016)	0.81 ₁
0.030	0.026 ₅ (0.010)	0.87 ₁

Table II-2

The long-time behavior of the low density velocity autocorrelation function, that leads to the diffusion coefficient, D , of the two dimensional overlapping Lorentz gas and the diffusion coefficient.

n^*	α_B	α_B^M	β_B^M
0.100	0.16 ₂	0.18 ₄	1.0
0.050	0.08 ₂	0.065 ₄	1.0
0.030	0.04 ₂	0.029 ₅	1.0

Table II-3

The long-time behavior of the low density autocorrelation function that leads to the Burnett coefficient of the two dimensional overlapping Lorentz gas and the predictions from the modified Fick's law.

Figure 9

The low-density Burnett coefficient for the overlapping disk Lorentz gas.

3. Intermediate Density

At higher densities the power law of the asymptotic tail of the velocity autocorrelation function, β_D , decreases proportional to the value of D/D_E . This is indicated in Table 4, where it is also seen the coefficient α_D is negative, but insensitive to the density in these systems. The positive coefficient of the Burnett correlation function, α_B , however, is dependent upon the density as is the power law, β_B , as indicated in Table 5. Over the whole density range, represented by Tables 2 through 5, the Burnett coefficient is divergent as seen by integrating the asymptotic tail of the Burnett correlation function, α_B/t^{β_B} , and using the values of the parameters, α_B , β_B , for the given density. Furthermore, the coefficient β_B is very closely equal to β_D-1 , another suggestion that the tail of the Burnett correlation function is related to the tail of the velocity autocorrelation.

In the non-overlapping Lorentz gas, trapping regions in configuration space are absent, although return paths still give a negative power-law tail to the velocity autocorrelation function, as seen in Table 6. Here the area relative to close packing of the scatterers, A/A_0 , is given as well as the reduced density, n^* . In addition, because of the ordering of scatterers, the radial distribution function at contact between the Lorentz particle and a scatterer, $g(R)$, is given. The coefficients α_D , β_D , α_B , β_B and D/D_E are insensitive to the density as $A/A_0 \rightarrow 1$ which is indicative of no trapping regions as seen in Tables 6 and 7. Furthermore, the function $\hat{C}_4(t)$ is divergent as t gets large so the Burnett coefficient, B_4 , does not exist for the overlapping Lorentz gas as well. Table 7 also indicates that $\beta_B \sim \beta_D - 1$ over the density range studied.

n^*	$-\alpha_D$	β_D	D/D_E
0.300	0.26 ₃	1.47 ₅	0.26 ₂ - 0.15 ₂
0.240	0.20 ₂	1.48 ₆	0.38 ₁ - 0.11 ₁
0.200	0.23 ₁	1.59 ₅	0.41 ₁ - 0.07 ₁
0.180	0.20 ₅	1.60 ₅	0.47 ₁ - 0.06 ₁
0.143	0.22 ₅	1.80 ₅	0.54 ₁ - 0.02 ₁

Table II-4

Same as Table 2 except at intermediate densities.

n^*	α_B	β_B	α_B^M	β_B^M
0.300	0.06 ₂	0.53 ₂	0.038 ₁	0.47 ₅
0.240	0.07 ₁	0.50 ₅	0.075 ₁	0.48 ₆
0.200	0.09 ₁	0.60 ₁	0.12 ₁	0.59 ₅
0.180	0.11 ₂	0.62 ₄	0.11 ₃	0.6 ₁
0.143	0.15 ₂	0.87 ₃	0.16 ₃	0.8 ₁

Table II-5

Same as Table 3 except at intermediate densities.

A/A_0	n^*	$g(R)$	$-\alpha_D$	β_D	$D/D_E^{(a)}$
1.10	0.260	5.63 ₁	0.27 ₅	1.6 ₂	0.56 ₁ - 0.08 ₁
1.25	0.228	3.53 ₁	0.24 ₃	1.63 ₅	0.62 ₁ - 0.06 ₁
1.40	0.204	2.78 ₁	0.25 ₅	1.65 ₅	0.54 ₁ - 0.05 ₁
2.00	0.143	1.81 ₁	0.15 ₂	1.7 ₁	0.62 ₁ - 0.02 ₁

(a) The first number corresponds to the value of D/D_E . The last number is the one to be subtracted for the estimated tail correction beyond this point.

Table II-6

The long-time behavior of the velocity autocorrelation function that leads to the diffusion coefficient of the two dimensional non-overlapping Lorentz gas, the radial distribution function at contact, and the diffusion coefficient.

A/A_0	α_B	β_B	α_B^M	β_B^M
1.10	0.15 ₅	0.45 ₅	0.17 ₅	0.6 ₂
1.25	0.18 ₄	0.59 ₅	0.18 ₃	0.63 ₅
1.40	0.13 ₄	0.60 ₅	0.16 ₃	0.65 ₅
2.00	0.08 ₃	0.65 ₅	0.12 ₃	0.7 ₁

Table II-7

The long-time behavior of the autocorrelation function that leads to the Burnett coefficient of the two dimensional non-overlapping Lorentz gas.

Figure 10 shows the time dependence of the distribution function of the overlapping Lorentz gas at an intermediate density as a function of $x/\langle x^2(t) \rangle^{1/2}$. The distribution, f , has been divided by a Gaussian, f_G , 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. It is seen the distribution does not change in character with time. The early peak in the distribution at small distances, which is indicative of trapped particles, gradually disappears as the probability 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. Therefore, Fick's second law, which predicts a Gaussian distribution function, is inadequate as a description of diffusion in the Lorentz gas at these times.

4. Percolation Region

As the density of scatterers is increased in the overlapping disk Lorentz gas, the diffusion coefficient becomes smaller and smaller. Eventually a point is reached where the diffusion coefficient is zero. This density, n_c^* , is called the percolation point. For the overlapping disk Lorentz gas, it has been determined (31) that $n_c^* \sim 0.37 \pm 0.02$ by extrapolation of the virial series associated with the transport process. As Table 8 indicates, the percolation point occurs at or near n_c^* , where the exponent of the velocity autocorrelation function $\beta_D \sim 4/3$. This is shown in Fig. 11a where the exponent β_D is plotted as a function of D/D_E . It is seen that β_D is very nearly linear with respect to D/D_E over the whole range of Table 8. The dashed line represents a least square fit of the equation $y = mx + b$ to all points excluding the three low density ones, where $m \sim 0.71 \pm 0.05$ and $b \sim 1.35 \pm 0.03$.

Figure 10

The distribution function of the overlapping disk Lorentz gas at $n^* = 0.20$. The solid line is drawn for emphasis through the $t_c = 100$ points.

n^*	$-\alpha_D$	β_D	D/D_E
0.477	0.19 ₂	1.40 ₄	0.14 ₁ - 0.20 ₄
0.370	0.18 ₂	1.34 ₅	0.21 ₁ - 0.25 ₃
0.318	0.20 ₂	1.40 ₅	0.21 ₁ - 0.17 ₁

Table II-8

Same as Table 2 except at percolation point.

n^*	α_B	β_B	α_B^M	β_B^M
0.477	0	--	0.06 ₁ (0.00)	0.80 ₈ (0.40 ₄)
0.370	0.06 ₂	0.75 ₄	0.09 ₁ (0.00)	0.7 ₁ (0.34 ₅)
0.318	0.09 ₂	0.70 ₃	0.07 ₁ (0.011 ₁)	0.8 ₁ (0.40 ₅)

Table II-9

Same as 3 except at percolation point.

Figure 11

The exponent of the power-law tail of the velocity autocorrelation function of the overlapping disk Lorentz gas. The left figure shows the exponent as a function of D/D_E , and the right figure shows the exponent above the percolation point as a function of reduced density, n^* .

At the percolation point the function $\tilde{C}_4(t)$ is still divergent. This is shown in Table 9. Here, the coefficient of the tail of $\tilde{C}_4(t)$ is still positive at the percolation point, while at the highest density, Table 9, $\alpha_B = 0$. The power law β_B , however, is not simply related to β_D as at lower densities. This is because in the percolation region the Lorentz particle must sample all of the configuration space in order to find escape paths. Thus, the correlation functions are characteristic of trapped systems, even at the lower density $n^* = 0.318$, where $D/D_E > 0$. Very long times could not be reached, because the Lorentz particle was affected by the periodic boundary conditions, Fig. 5, before it escaped from its trapping configuration.

5. High Density

In the high density regime, above $n^* = 0.477$, the power law of the tail of the velocity autocorrelation function increases in value as the density gets larger. Figure 11b shows a plot of β_D as a function of density from the percolation point, n_C^* , to the high density point at $n^* = 0.734$. A very good fit to the data points is given by the line $\beta_D = 1 + n^*$, which is the dashed line in the figure. There is no reason why the exponent β_D does not increase indefinitely with increasing density, although above the highest density the velocity autocorrelation function was very difficult to measure.

Tables 10 and 11 give the power law tails of the velocity autocorrelation functions, $\rho_D(t)$, and the correlation function, $\rho_B(t)$, for the Burnett coefficient, B_4 . At these high densities, the Burnett coefficient is found to be zero by integration of the negative tail given in Table 9. Above the percolation point the dependence of β_B on β_D is more complicated than below the percolation point. It will be found,

n^*	$-\alpha_D$	β_D	D/D_E
0.736	0.30_5	1.8_1	$0.015_2 - 0.017_2$
0.654	0.30_3	1.6_1	$0.04_1 - 0.06_1$

Table II-10

Same as Table 2 except at high density.

n^*	α_B	β_B	α_B^M	β_B^M
0.736	-0.77_5	1.75_5	-0.68_5	1.6_2
0.654	-0.14_3	1.2_1	-0.15_5	1.2_2

Table II-11

Same as Table 3 except at high density.

however, that simple expressions can be found which relate the Burnett correlation function parameters, α_B and β_B , to the velocity autocorrelation function parameters, α_D and β_D . This is the subject of the next section.

D. Theory

This section discusses the results of the previous section in terms of a more general than usual diffusion theory. The mathematical basis of the theory is the continuous-time random walk in lattices first discussed by Montroll and Weiss (33). The first subsection discusses a simple generalization of this random walk to movement in a continuum rather than in a lattice. The physical basis is the similarity between the jump times in the random walk theory and the time it takes a Lorentz particle to escape a trapping region in configuration space. The next subsection discusses the asymptotic properties of the continuous-time random walk in terms of the results of section C. The emphasis is on long-time properties and the simplifying theory that results. Predictions are made about the correlation functions and the distribution function in the long-time limit. The following subsection presents a more general theory of diffusion suggested by the continuous-time random walk theory. A new Chapman-Enskog expansion is presented in which the coefficients all converge for the Lorentz gas. The last subsection discusses these results in terms of diffusion in fluids. Emphasis is placed on the physical effects which are caused by the hydrodynamic fields present in fluids but absent in the Lorentz gas.

1. Continuous-Time Random Walk

The Lorentz gas can be thought of 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 (33,40,41,42). In physical terms the waiting-time distribution corresponds to the different times it takes for the particle to escape from the various nearly-trapping regions it finds 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-time distribution is determined by the requirement that the experimentally determined velocity autocorrelation be reproduced (43). This statement is equivalent to the statement that the waiting-time distribution is such that the second moment of the distribution of the Lorentz particle is reproduced for all times. The question is: can this more general random walk give the correct higher moments of the distribution, that is, the distribution itself, from a knowledge of the second moment only, at least at large times? 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 limit. On that question hinges the long-time behavior of the Burnett coefficients and the conditions under which the distribution is a Gaussian.

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 particles 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

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

where the subscripts represent repeated convolutions. That is,

$$\psi_n(t) = \int_0^t \psi_{n-1}(t-t') \psi(t') dt' \quad , \quad \text{where } \psi_0(t) = \delta(t) \quad ;$$

$P_n(x) = \int_{-\infty}^{\infty} P_{n-1}(x-x') P(x') dx'$, where $P_0(x) = \delta(x)$, and $\delta(x)$ is the Dirac delta function. 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 a time t is

$$F(x, t) = \int_0^t \psi(t-t') Q(x, t') dt' \quad , \quad (1)$$

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 mathematical analysis becomes much simpler if Eq. 1 is Laplace transformed in time and Fourier transformed in space. This is because the convolutions, $\psi_n(t)$, $P_n(x)$, have simple forms when transformed. The Laplace transform of $\psi(t)$ is $\tilde{\psi}(s) = \int_0^{\infty} e^{-st} \psi(t) dt$ and the Fourier transform of $P(x)$ is $\lambda(k) = \int_{-\infty}^{\infty} e^{-ikx} P(x) dx$. Therefore, the Fourier-Laplace transforms of $F(x, t)$, indicated by $G(k, s)$, is

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

or by summing the series

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

which can be manipulated into the form:

$$G(k,s) = \frac{1}{s + O(k,s)} \quad , \quad (2)$$

where

$$O(k,s) = [1 - \lambda(k)] \frac{s\tilde{\psi}(s)}{1-\tilde{\psi}(s)} \quad . \quad (3)$$

If expression (2) is rearranged: $sG(k,s)-1 = -O(k,s) G(k,s)$, then an integral differential equation for $F(x,t)$ results, when the inverse Fourier and Laplace transforms are performed:

$$\frac{\partial F(x,t)}{\partial t} = - \int_0^t dt' \int_{-\infty}^{\infty} dx' M(x-x', t-t') F(x', t') \quad , \quad (4)$$

where $M(x,t)$ is the inverse Fourier-Laplace transform of $O(k,s)$. The function $M(x,t)$ is a memory function, or transfer function. It shows that the distribution at position x' at time t' affects the rate of of the distribution at position x at time t . For the continuous time random walk, the spatial memory of the system is not connected with the time memory, because the stepsize distribution function, $P(x)$, is independent of time and the waiting time distribution, $\psi(t)$, is independent of position. Thus, the memory function for the continuous-time random walk can be factored into a space part and a time part as Eq. (3) shows.

The moments of the distribution are readily determined:

$$\langle x^{\tilde{2}n}(s) \rangle = (-1)^n \frac{\partial^{2n}}{\partial k^{2n}} G(k,s) \quad , \quad (5)$$

where the derivatives are taken in the $k = 0$ limit, and the tilde, $\sim$, over the even moments means Laplace transform.

Hence,

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

and

$$\langle \tilde{x}^4(s) \rangle = \langle \ell^4 \rangle \frac{1}{s} \frac{\tilde{\psi}(s)}{1 - \tilde{\psi}(s)} + 6 \langle \ell^2 \rangle^2 \frac{1}{s} \frac{\tilde{\psi}(s)^2}{[1 - \tilde{\psi}(s)]^2} \quad , \quad (7)$$

where $\langle \ell^n \rangle = \int_{-\infty}^{\infty} x^n P(x) dx$ is the appropriate moment of the stepsize distribution for which the odd moments vanish.

The relation between the second moment and the velocity autocorrelation function (expressed in Laplace notation) is, from Eq. C1.1,

$$\tilde{\rho}_D(s) = \frac{s^2 \langle \tilde{x}^2(s) \rangle}{2 \langle \dot{x}^2 \rangle} \quad , \quad (8)$$

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

$$s \tilde{\psi}(s) = \frac{2 \langle \dot{x}^2 \rangle}{\langle \ell^2 \rangle} \tilde{\rho}_D(s) [1 - \tilde{\psi}(s)] \quad . \quad (9)$$

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

$$\psi(t) = \int_0^t K(t-t') [\delta(t') - \psi(t')] dt' \quad (10)$$

where

$$K(t) = \frac{2 \langle \dot{x}^2 \rangle}{\langle \ell^2 \rangle} \int_0^t \rho_D(t') dt' \quad . \quad (11)$$

The solution of Eq. 10 leads to negative, and thus physically unacceptable, values for the waiting distribution at intermediate times, Fig. 12. It is only at long times that the waiting distribution is positive and the random walk applies. In the analysis to follow, only long times will be considered.

Figure 12

The waiting-time distribution for the specular, ●, and diffusive, ○, overlapping disk Lorentz gas at $n^* = 0.20$ as a function of mean collision times, t_c .

The formula for the fourth moment can be written in terms of the second moment by substituting Eq. 6 into 7:

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

where

$$D(t) = \langle \dot{x}^2 \rangle \int_0^t \rho_D(t') dt' \quad . \quad (13).$$

As Eq. 12 shows, this walk necessarily expresses the higher moments in terms of the second moment. Since the higher moments generally require higher correlations, Eq. 12 cannot be universally valid, except in the long-time limit if the higher-order correlations die out sufficiently fast.

Since Eq. 12 at most only applies to the Lorentz gas at long times, it is of interest to see how it behaves as time is made large, given the long-time tail of the velocity autocorrelation function. This is easily done by expanding $D(t-t')$ in a power series about t .

$$D(t-t') = D(t) - t' \dot{D}(t) + (t')^2 \ddot{D}(t)/2 - \dots \quad , \quad (14)$$

where the dots over the D 's mean time derivative. Since $\dot{D}(t)$ is proportional to the velocity autocorrelation function, the expansion may be rewritten at long time as

$$D(t-t') \sim D(t) + \frac{A}{t^{\beta-1}} \left(\frac{t'}{t} \right) + \frac{B}{t^{\beta-1}} \left(\frac{t'}{t} \right)^2 + \dots \quad , \quad (15)$$

where the A , B , ... are constant and the power law tail of the velocity autocorrelation, $1/t^\beta$, has been used. Since $\beta > 1$ and $t' \leq t$ in the integral in Eq. 12, the first term in Eq. 15 is the dominant one at long time. Then Eq. 12 becomes

$$\langle x^4(t) \rangle \sim \frac{\langle \ell^4 \rangle}{\langle \ell^2 \rangle} \langle x^2(t) \rangle + 12 D(t) \int_0^t \langle x^2(t') \rangle dt' \quad (16)$$

Since $\langle x^2(t) \rangle \sim 2Dt$ at long times, the integral term in Eq. 16 dominates the expression. An interesting observation to make about Eq. 12 is, if the integral term is subtracted from the fourth moment, given by Eq. 12, then a convergent coefficient results. That is:

$$\lim_{t \rightarrow \infty} \frac{1}{4!} \frac{d}{dt} \left[\langle x^4(t) \rangle - 12 \int_0^t D(t-t') \langle x^2(t') \rangle dt' \right] = \frac{2}{4!} \frac{\langle \ell^4 \rangle}{\langle \ell^2 \rangle} D = D_4, \quad (17)$$

which is finite. This should be contrasted with the definition of the Burnett coefficient, Eq. B3.5. The difference,

$$B_4 - D_4 = \lim_{t \rightarrow \infty} \frac{d}{dt} \left[\frac{1}{2} \int_0^t D(t-t') \langle x^2(t') \rangle dt' - \frac{1}{8} \langle x^2(t) \rangle^2 \right], \quad (18)$$

diverges whenever $1 < \beta_D < 2$, which is seen by substituting Eq. 15 into Eq. 18 after the differentiation has been carried out:

$$B_4 - D_4 = \lim_{t \rightarrow \infty} \frac{D(t)}{t^{\beta_D-1}} \int_0^t D(t') \left[A \frac{t'}{t} + B \frac{(t')^2}{t^2} + \dots \right] dt' \quad (19)$$

In the long-time limit $D(t) \rightarrow D$ and the integral in Eq. 19 can be carried out:

$$B_4 - D_4 = \lim_{t \rightarrow \infty} \text{constant} \cdot t^{1-\beta_B}, \quad (20)$$

where $\beta_B = \beta_D - 1$. This should be compared with the empirical relationship found for the parameters by molecular dynamics (Tables 2 through 5). The appendix (Sec. F2) derives in some detail the coefficients α_B and β_B for the Burnett autocorrelation function, $\rho_B(t)$ (Eq. C1.2). In the long-time limit $\rho_B(t) = \alpha_B/t^{\beta_B}$,

$$\alpha_B = \frac{4}{3} \frac{D}{D_E} \alpha_D \quad , \quad (21)$$

$$\beta_B = \beta_D - 1, \quad (22)$$

where α_D , β_D are the coefficients of the tail of the velocity autocorrelation function, $\rho_D(t) \sim \alpha_D/t^{\beta_D}$, in the long-time limit. The coefficients defined by Eqs. 21 and 22 are given in Tables 2 through 5 with the superscript M. The continuous-time random walk quantitatively predicts the divergence of the fourth order Burnett coefficient, B , over the density range where the diffusion coefficient is non-zero. If the diffusion coefficient is zero then a similar treatment of Eq. 12 yields:

$$\alpha_B = \left(\frac{4}{3}\right)^2 \alpha_D^2 \left[\frac{\Gamma(1-\beta_D)^2}{\Gamma(3-2\beta_D)} - \frac{3-2\beta_D}{(2-\beta_D)(1-\beta_D)^2} \right] \quad , \quad (23)$$

and

$$\beta_B = 2\beta_D - 2 \quad . \quad (24)$$

Tables 9, 10 give the predictions of these coefficients, α_B^M , β_B^M , at the percolation point and in the high density region respectively. The numbers in parenthesis in Table 9 also give the results for $D \neq 0$, Eqs. 21 and 22. Eqs. 23 and 24 agree better with the results at $n^* = 0.318$ where D is small. This is because the rare events which lead the moving particle out of its trapped state are very difficult to sample on the computer. The computer results are characteristic of the trapped state. The high density results above the percolation point agree within experimental error with the predictions of Eqs. 23 and 24, even to the change in sign of α_B at $\beta_D = 1.5$.

With these results at hand, it is of interest to determine the asymptotic differential equation for the distribution function of the continuous-time random walk with the hope it will point the way to a modification of the Chapman-Enskog expansion, which is without divergences. The starting point is the memory function.

2. A Modified Fick's Law and Chapman-Enskog Expansion

The memory function, Eq. D1.3, may be expressed in terms of the velocity autocorrelation function by Eqs. D1.6 and D1.8:

$$\tilde{O}(k,s) = \frac{1-\lambda(k)}{\langle \ell^2 \rangle / 2} \tilde{\phi}_2(s) \quad (1)$$

where $\phi_2(t) = \langle \dot{x}(t)\dot{x}(0) \rangle = \langle \dot{x}^2 \rangle \rho_D(t)$ is the velocity autocorrelation function. The moment theorem of Fourier transforms can be used to obtain an expansion of $\lambda(k)$ in powers of k^2 , since the odd moments vanish:

$$\lambda(k) = 1 - \frac{k^2}{2} \langle \ell^2 \rangle + \frac{k^4}{4!} \langle \ell^4 \rangle - \dots \quad (2)$$

Using 2 in 1 gives:

$$\tilde{O}(k,s) = \tilde{\phi}_2(s) \sum_{n=1}^{\infty} (-k^2)^n D_{2n}/D \quad , \quad (3)$$

where $D_{2n}/D = 2\langle \ell^{2n} \rangle / \langle \ell^2 \rangle (2n)! \cdot$ Using Eq. 3 in Eq. D1.2, an expansion of the diffusion equation which is non-local in time is obtained, after transforming to space and time variables:

$$\frac{\partial f(x,t)}{\partial t} = \sum_{n=1}^{\infty} \frac{D_{2n}}{D} \int_0^t \phi_2(t-t') \frac{\partial^{2n} f(x,t')}{\partial x^{2n}} dt' \quad (4)$$

Since $D_2 = D$, the $n=1$ term is a modified Fick's law,

$$\frac{\partial f(x,t)}{\partial t} = \int_0^t \phi_2(t-t') \frac{\partial^2 f(x,t')}{\partial x^2} dt' \quad , \quad (5)$$

where the kernel, ϕ_2 , is the velocity autocorrelation function. If $\phi_2(t)$ is a very rapidly decaying function, $D\delta(t)$ say, then Eq. 5 reduces to Fick's second law. Eq. 5 is a modification of Fick's law which must be made if long-term velocity correlations exist.

The solution of Fick's second law is a Gaussian distribution for all time, but the solution of Eq. 5 is a Gaussian only in the infinite-time limit. The divergence of the Burnett coefficients for the Lorentz gas is directly related to this fact. This can be seen by taking moments of Eq. 5:

$$\frac{d}{dt} \langle x^{2n} \rangle = \int_0^t \phi_2(t-t') dt' \int_{-\infty}^{\infty} x^{2n} \frac{\partial^2 f(x,t')}{\partial x^2} dx \quad . \quad (6)$$

Eq. 6 is integrated by parts twice:

$$\frac{d}{dt} \langle x^{2n} \rangle = 2n(2n-1) \int_0^t \phi_2(t-t') \langle x^{2n-2}(t') \rangle dt' \quad . \quad (7)$$

When $n=1$, this just repeats the definition of the velocity autocorrelation function:

$$\frac{d}{dt} \langle x^2(t) \rangle = 2 \int_0^t \phi_2(t') dt' \quad . \quad (8)$$

For $n = 2$

$$\frac{d}{dt} \langle x^4(t) \rangle = 12 \frac{d}{dt} \int_0^t D(t-t') \langle x^2(t') \rangle dt' \quad , \quad (9)$$

Where a time derivative has been factored out of the right side of 9.

The Burnett coefficient becomes (Eq. B3.5).

$$B_4 = \lim_{t \rightarrow \infty} \frac{d}{dt} \left[\frac{1}{2} \int_0^t D(t-t') \langle x^2(t') \rangle dt' - \frac{1}{8} \langle x^2(t) \rangle^2 \right], \quad (10)$$

which is divergent by comparison to Eq. D1.18.

Given the asymptotic behavior of the velocity autocorrelation function and the value of the diffusion coefficient, Eq. 5 can be solved at long time by expanding the distribution function about the Gaussian limit. The mathematics are much easier if Eq. 5 is Fourier transformed in space and Laplace transformed in time. Then solving for the distribution:

$$G(k,s) = \frac{1}{s + k^2 \tilde{\phi}_2(s)} \quad (11)$$

It is shown in Appendix F2 that the Laplace transform of the velocity autocorrelation function for small Laplace variable, s , (large time) is

$$\tilde{\phi}_2(s) \rightarrow D - A s^{\beta_D - 1}, \quad (12)$$

where D is the diffusion coefficient and $A = \langle \dot{x}^2 \rangle \alpha_D \Gamma(1 - \beta_D)$. $\Gamma(x)$ is the gamma function (44). With this asymptotic expression for $\phi_2(s)$

$$G(k,s) \rightarrow \frac{1}{s + k^2 D - k^2 A s^{\beta_D - 1}} \quad (13)$$

Eq. 13 is now expanded around the Gaussian distribution:

$$G(k,s) = \sum_{n=0}^{\infty} \frac{(-k^2 A s^{\beta_D - 1})^n}{n!} \frac{d^n}{ds^n} \frac{1}{s + k^2 D} \quad (14)$$

The inverse Laplace and Fourier transform of Eq. 14 is:

$$f(x,t) = f_G(x,t) + \sum_{n=1}^{\infty} \frac{(-At^{1-\beta_D})^n}{n!} \frac{d^n}{d^n} \left\{ f_G(x,t) U\left[n(1-\beta_D), \frac{x^2}{4Dt}\right] \right\}, \quad (15)$$

where $f_G = \exp(-x^2/4Dt)/\sqrt{4\pi Dt}$ and $U(a,b,x)$ is the confluent hypergeometric function of the second kind (44). The derivative in Eq. 15 can be carried out using the recurrence relations of the U's:

$$\frac{f(x,t)}{f_G(x,t)} - 1 = \sum_{n=1}^{\infty} \frac{(-At^{1-\beta_D}/D)^n}{n!} \Lambda_n\left(\beta_D, \frac{x^2}{4Dt}\right), \quad (16)$$

where

$$\Lambda_n(a,z) = \sum_{p=0}^n (-1)^p \binom{n}{p} \frac{\Gamma[n(1-a)+p]}{\Gamma[n(1-a)]} U(p-na, \frac{1}{2}, z)$$

and $\binom{n}{p}$ is the binomial coefficient. The asymptotic series, Eq. 16,

was evaluated on the computer for the Lorentz gas at $n^* = 0.20$. Fig. 13 is a plot of Eq. 16, solid line, compared with the molecular dynamics results plotted with open circles, 0. If the distribution is Gaussian, or Fick's law applies, then the results will lie on the horizontal axis. The deviations of the molecular dynamic results from Eq. 16, as seen in Fig. 13, are small and must be accounted for by higher order corrections to the modified Fick's law, Eq. 5:

$$\frac{\partial f(x,t)}{\partial t} = \int_0^t \phi_2(t-t') \frac{\partial^2 f(x,t')}{\partial x^2} dt' + \int_0^t \phi_4(t-t') \frac{\partial^4 f(x,t')}{\partial x^4} dt', \quad (17)$$

where $\phi_4(t)$ is a higher order memory function, determined by taking the fourth moment of Eq. 17 and integrating over space:

Figure 13

The deviation of the distribution function of the overlapping disk Lorentz gas, Q , relative to a Gaussian, and the deviation of the distribution function from the solution of the modified Fick's law, Δ , relative to a Gaussian of the same root-mean-square width, $\langle \Delta x^2 \rangle^{1/2}$.

$$\phi_4(t) = \frac{1}{4!} \frac{d^2}{dt^2} \left[\langle x^4(t) \rangle - 12 \int_0^t D(t-t') \langle x^2(t') \rangle dt' \right], \quad (18)$$

which should be compared with Eq. D1.17.

The integral of ϕ_4 leads to a convergent coefficient for the two dimensional Lorentz gas, Fig. 14:

$$D_4 = \int_0^\infty \phi_4(t) dt, \quad (19)$$

as Table 12 shows. If these D_4 coefficients are used to correct the distribution function, the small deviations from Eq. 16 are accounted for, as shown in Fig. 13 by the dashed line. As an approximation sufficiently precise for the present purpose, the correction due to D_4 was calculated as a perturbation about a Gaussian distribution rather than the actual one resulting from the solution of the modified Fick's law.

It seems physically plausible the four point correlation function involved in ϕ_4 decays at large times sufficiently fast that it can be expressed in terms of the two point correlation function, ϕ_2 . A successful test of this hypothesis is given in Fig. 15, where it is shown that ϕ_4 decays at long time with the same power law as ϕ_2 , and the proportionality constant is given by $\phi_4(t) = D_4 \phi_2(t)/D$. If the same argument can be made about all the higher coefficients, as is to be expected, the Chapman-Enskog expansion is replaced by Eq. 4, which was derived from the continuous-time random walk. The continuous-time random walk yields expressions for D_{2n} in terms of the $(2n)^{\text{th}}$ moments of the stepsize distribution: $D_{2n}/D = 2 \langle \ell^{2n} \rangle / \langle \ell^2 \rangle (2n)!$. The values of D_4 found are consistent with a Gaussian stepsize distribution whose second moment, $\langle \ell^2 \rangle$, is the mean free path squared, λ^2 . Thus, a quantitative theory for

Figure 14

The newly defined Burnett coefficient, D_4 , as a function of mean particle collisions for the overlapping disk Lorentz gas at a reduced density $n^* = 0.20$.

n^*	$D_4 \Gamma_E / D_E^2$	$D_4 / D \lambda^2$
0.736	0.00 ₅	--
0.318	0.07 ₄	0.7 ₄
0.200	0.26 ₄	0.26 ₄
0.143	0.30 ₄	0.22 ₃
0.050	0.50 ₄	0.23 ₂
0.020	0.57 ₄	0.23 ₂

Table II-12

The generalized Burnett coefficient for the two dimensional overlapping hard-disk Lorentz gas.

Figure 15

The long-time tail of the fourth order correlation function that leads to the newly defined Burnett coefficient, D_4 , for the overlapping disk-Lorentz gas with $n^* = 0.20$.

the Burnett coefficient and the tail of the higher order correlation functions has been established, for example $D_4/D = \lambda^2/4$ (see Table 12).

The relative importance of the D_4 correction to Eq. 5 is measured by the ratio $k^2 D_4/D$, where k is the wave number. From Table 12 it is seen that $D_4/D \sim \lambda^2/4$. D_4 will be an important correction to the distribution function when $k^2 D_4/D > 1$ or $k^2 \lambda^2 > 4$. Thus the wavelength at which D_4 is important is about three mean-free paths, 3λ , otherwise the D_4 correction is small as Fig. 13 indicates.

The sixth order correlation function

$$\phi_6 = \frac{1}{6!} \frac{d^2}{dt^2} \left[\langle x^6(t) \rangle - 60 \int_0^t D(t-t') \langle x^4(t') \rangle dt' + 360 \int_0^t D(t-t') dt' \int_0^{t'} D(t'-t'') \langle x^2(t'') \rangle dt'' \right], \quad (20)$$

whose integral defines $D_6 = \int_0^\infty \phi_6(t) dt$ was calculated for the Lorentz gas at $n^* = 0.20$. Fig. 16 shows that D_6 is at least consistent with a non-diverging coefficient. The dashed line is the prediction of the continuous-time random walk theory for a Gaussian stepsize distribution and $\langle x^2 \rangle = \lambda^2$.

Eq. 5 also makes a prediction about the distribution function when $D = 0$. In this case, if the velocity autocorrelation function decays sufficiently fast, then the second moment,

$$\langle x^2(t) \rangle \rightarrow 2L^2, \quad (21)$$

is bounded for large t . The Laplace transform of Eq. 21 is, therefore, $\langle x^2(s) \rangle = 2L^2/s$ so the Laplace transform of the velocity autocorrelation function is

Figure 16

The newly defined sixth-order Burnett coefficient, D_6 , as a function of mean-particle collisions for the overlapping disk Lorentz gas.

Figure 17

The high density distribution function for the overlapping disk Lorentz gas.

$$\tilde{\phi}_2(s) = sL^2 \quad (22)$$

Using this in Eq. 11 gives:

$$G(k,s) = \frac{1}{s} \frac{1}{1+k^2L^2} \quad (23)$$

The inverse Fourier and Laplace transform of Eq. 23 gives the distribution:

$$f(x,t)dx = \sqrt{2} \exp(-\sqrt{2}\xi)d\xi \quad , \quad (24)$$

where $\xi^2 = x^2/2L^2$. Fig. 17 is a plot of the distribution function for the Lorentz gas at $n^* = 2.5$, Δ ; $n^* = 5.0$, $\bullet$; $n^* = 10.0$, $\circ$. As the density becomes large the data approach Eq. 24.

3. Fluids

When $\phi_4(t)$ was evaluated for the three dimensional fluid, it was found the infinite time integral, D_4 , is divergent, Fig. 18. The divergence is due to the combined effect of diffusion and the hydrodynamic field on the distribution function. "The hydrodynamic flow will not carry the molecule appreciably away from the center; ... in an actual system a molecule has a density dependent probability of diffusing away from the center." (5) In addition, the center of the vortex will diffuse. To account for the diffusing motion, the hydrodynamic field has to be sampled over a spreading Gaussian distribution, $p(x,t)$, which is proportional to:

$$\exp(-x^2/4Dt) \cdot \exp(-x^2/4vt) \quad , \quad (1)$$

where ν is the kinematic viscosity and D is the diffusion coefficient. Eq. 1 accounts for the diffusion of the vortex center and molecule away from the origin. The Gaussian distribution resulting from Eq. 1 spreads

Figure 18

The coefficients D_4 , O, and D_4^h , ●, for the three dimensional hard-sphere fluid at a volume relative to close packing, $V/V_0 = 3.0$. The D_4 data points were evaluated from the molecular dynamics results for the Burnett coefficient given by Wood (26).

with a characteristic diffusion coefficient $D' = Dv/(D+v)$.

If $h(x,t)$ is the distribution resulting from pure hydrodynamics alone, then it must be sampled over $p(x,t)$ to account for the local effects mentioned above:

$$f(x,t) = \int_{-\infty}^{\infty} p(x-x',t)h(x',t)dx' \quad , \quad (2)$$

where $f(x,t)$ is the usual distribution function. D_4 formed from $f(x,t)$ diverges, Fig. 18, due to the diffusive effects of $p(x,t)$. The second moment of the two distributions differ: $\langle x^2 \rangle^h = \langle x^2 \rangle - 2D't$ where the superscript, h , means the average is with respect to $h(x,t)$. This leads to an effective diffusion coefficient in the h -coordinate system of

$D^h = D-D'$ and a Burnett correlation function $\phi_4^h(t) = \phi_4(t) - D't\phi_2(t)$.

Subtraction of these terms in the second and fourth moment leads to

convergent coefficients, Fig. 18, which behave asymptotically as $\phi_4^h(t) =$

$D_4^h\phi_2^h(t)/D^h$, as shown in Fig. 19, where D_4^h is the time integral of ϕ_4^h .

Once the proper coordinate system is used in a fluid, the higher order correlation functions again decay fast enough such that only the second order correlations remain. The distribution, $h(x,t)$ is, therefore, determined from

$$\frac{\partial h(x,t)}{\partial t} = \sum_{n=1}^{\infty} \frac{D_{2n}^h}{D^h} \int_0^t \phi_2^h(t-t') \frac{\partial^{2n} h(x,t')}{\partial x^{2n}} dt' \quad (3)$$

and transformed to $f(x,t)$ by Eq. 2.

Figure 19

The long-time tail of the correlation function that leads to the newly defined Burnett coefficient, D_4^h , for the three dimensional hard-sphere fluid at $V/V_0 = 3.0$.

E. Summary

After the discovery that the velocity autocorrelation function of a particle decays very slowly at long times, it was recognized the higher order coefficients in the Chapman-Enskog expansion diverge. The cause for the divergence of these coefficients, called the Burnett coefficients, is the distribution for the positions of the particles as a function of time does not approach its long-time limit as a Gaussian. The long persistent correlations lead to the non-Gaussian approach and also necessarily introduce non-locality in time (memory) into the description of the transport process. Therefore, Fick's law is only valid in the infinite time limit and only if the distribution is Gaussian in that limit. The latter requirement is by no means assured since in some cases the diffusion coefficient is zero. The diffusion coefficient is divergent in at least one nontrivial case: the two dimensional fluid (5).

Fick's law, consistent with a Markovian random process (no memory), implies the distribution function is Gaussian for all times. The actual non-Markovian nature of the process was shown, by molecular dynamic simulation, to correspond to a random walk where, after each step, the particle waits for a time as sampled from a waiting time distribution before making the next move. The major physical consequence of the validity of this stochastic process is the higher order correlations can be expressed, as they approach their long-time limit, in terms of the lowest one, namely, the velocity autocorrelation function, or equivalently, the waiting-time distribution.

The physical cause of the memory effects differ for different situations. In fluids, persistence is due to slowly decaying hydrodynamic fields. In the Lorentz gas, where a particle moves through stationary

scatterers, the hydrodynamic effects are absent, and the slow decay is related to the higher than random probability of the particle returning to its origin. Restricting discussion to the easier to deal with Lorentz gas, the simplest way to modify Fick's law to take memory into account is by Eq. D2.5. If the velocity autocorrelation decays rapidly enough, then Eq. D2.5 reduces to Fick's second law.

Given the asymptotic behavior of the velocity autocorrelation function, the modified Fick's law, Eq. D2.5, can be solved at long times by expanding the distribution function about the Gaussian limit in terms of a series of confluent hypergeometric functions, Eq. D2.16. The deviations of the molecular dynamic results from the modified Fick's law are small and well accounted for by the higher order corrections given by Eq. D2.17, which defines a new (convergent) Burnett coefficient, D_4 .

The four point correlation function, ϕ_4 , which determines D_4 , decays at large times sufficiently fast that it can be expressed in terms of the two point correlation function, ϕ_2 , which is the velocity autocorrelation function. The proportionality constant is just D_4/D , where D is the diffusion coefficient. If the same argument is made about all the higher coefficients, the Chapman-Enskog expansion is replaced by Eq. D2.4, which is equivalent to a stochastic process where between each step the particle is delayed for a time as sampled from a waiting distribution. The delay can be interpreted physically as the time required for the particle to escape from the various nearly trapping regions. The waiting time distribution is uniquely determined by the requirement that the second moment of the distribution is reproduced for all time. However, it is only for long times that a physically meaningful waiting time distribution can be determined, that is, when the higher order correlations are decomposable.

The stochastic model then yields expressions for D_{2n} in terms of the $(2n)^{\text{th}}$ moments of the stepsize distribution. Thus, a quantitative theory for the Burnett coefficients and the tail of the higher order correlation functions has been established.

For three-dimensional fluids, D_4 was found to be divergent. The divergence is due to the combined effect of diffusion and the hydrodynamic field on the distribution function. To account for the diffusing motion, the hydrodynamic field has to be sampled over a spreading Gaussian distribution, which is proportional to the product of particle diffusion and vorticity diffusion. This results in a total distribution which depends explicitly on the hydrodynamic distribution and the particle and vorticity diffusion at long times.

The hydrodynamic distribution function, $h(x,t)$, which is defined by a transformation, Eq. D3.2, has convergent coefficients, D_{2n}^h . In addition, the fourth-order correlation function, ϕ_4^h , depends only on the two point correlation function at long time; the proportionality constant is D_4^h/D^h . This suggests that the hydrodynamic distribution function satisfies Eq. D3.3 at long times.

F. Appendix

1. Tables

This appendix contains some molecular dynamics results at selected densities for the overlapping disk Lorentz gas. There are four velocity autocorrelation functions: the first two are in the low density range, $n^* = 0.03$ and $n^* = 0.05$; the next is in the intermediate range, $n^* = 0.20$; and the last is above the percolation point at $n^* = 0.74$. The subscript by the first number is the statistical error in the last figure, which must be applied to all points in the column. Also given in this appendix are three distribution functions. The first column in the table is $\xi = x/\langle x^2 \rangle^{1/2}$. The next column gives f/f_G , where f_G is a Gaussian with the width given by $\langle x^2 \rangle$. The last value in these tables, labeled $\xi = \infty$, corresponds to the excess value of f over a Gaussian between the last value of ξ and ∞ . The statistical error for the entries is indicated by the subscript on the first entry in each column.

t	$n^* = 0.03$	$n^* = 0.05$	$n^* = 0.20$	$n^* = 0.74$
0	1.00000 ₃	1.00000 ₆	1.0000 ₁	1.0000 ₆
1	0.23213	0.22340	0.1854	0.1800
2	0.04183	0.02936	-0.0324	-0.0739
3	0.00260	-0.00646	-0.0597	-0.1194
4	-0.00304	-0.00827	-0.0453	-0.1049
5	-0.00262	-0.00551	-0.0297	-0.0760
6	-0.00165	-0.00327	-0.0193	-0.0501
7	-0.00101	-0.00202	-0.0131	-0.0317
8	-0.00065	-0.00129	-0.0091	-0.0196
9	-0.00044	-0.00090	-0.0069	-0.0110
10	-0.00030	-0.00069	-0.0057	-0.0063
11	-0.00021	-0.00056	-0.0051	-0.0040
12	-0.00020	-0.00044	-0.0044	-0.0029
13	-0.00016	-0.00040	-0.0036	-0.0031
14	-0.00016	-0.00027	-0.0032	-0.0030
15	-0.00016	-0.00018	-0.0030	-0.0025
16	-0.00013	-0.00018	-0.0028	-0.0020
17	-0.00009	-0.00019	-0.0027	-0.0020
18	-0.00007	-0.00018	-0.0026	-0.0019
19	-0.00008	-0.00016	-0.0023	-0.0013
20	-0.00005	-0.00019	-0.0020	-0.0010

Table II A-1

The velocity autocorrelation function for the Lorentz gas of overlapping disks as a function of mean particle collisions.

ξ	f/f_G	ξ	f/f_G	ξ	f/f_G
0.05	1.16 ₂	1.25	0.91	2.5061	1.14 ₃
0.15	1.08	1.35	0.91	2.5274	1.15
0.25	1.05	1.45	0.91	2.5593	1.16
0.35	1.03	1.55	0.92	2.5939	1.18
0.45	1.01	1.65	0.92	2.6321	1.20
0.55	0.99	1.75	0.93	2.6745	1.24
0.65	0.98	1.85	0.94	2.7223	1.26
0.75	0.96	1.95	0.96	2.7774	1.29
0.85	0.95	2.05	0.98	2.8426	1.34
0.95	0.94	2.15	1.01	2.9229	1.41
1.05	0.93	2.25	1.04	3.0290	1.50
1.15	0.92	2.35	1.07	3.1904	1.68
		2.45	1.11	∞	2.41

Table II A-2

The distribution for the overlapping disk Lorentz gas at a density $n^* = 0.20$.

ξ	f/f_G	ξ	f/f_G	ξ	f/f_G
0.05	1.97 ₂	1.25	0.58	2.5061	1.24 ₂
0.15	1.63	1.35	0.58	2.5274	1.27
0.25	1.36	1.45	0.59	2.5593	1.32
0.35	1.15	1.55	0.60	2.5939	1.38
0.45	0.99	1.65	0.62	2.6321	1.46
0.55	0.87	1.75	0.64	2.6745	1.55
0.65	0.78	1.85	0.68	2.7223	1.66
0.75	0.71	1.95	0.72	2.7774	1.79
0.85	0.66	2.05	0.77	2.8426	1.99
0.95	0.63	2.15	0.84	2.9229	2.27
1.05	0.60	2.25	0.92	3.0290	2.71
1.15	0.59	2.35	1.02	3.1904	3.63
		2.45	1.15	∞	11.98

Table II A-3

Same as Table A-2 except at $n^* = 0.654$.

f	f/f_G	ξ	f/f_G	ξ	f/f_G
0.05	1.64 ₄	1.25	0.64	2.5061	1.07 ₄
0.15	1.47	1.35	0.63	2.5274	1.11
0.25	1.31	1.45	0.62	2.5593	1.15
0.35	1.18	1.55	0.62	2.5939	1.20
0.45	1.07	1.65	0.63	2.6321	1.26
0.55	0.98	1.75	0.64	2.6745	1.33
0.65	0.90	1.85	0.67	2.7223	1.41
0.75	0.83	1.95	0.70	2.7774	1.53
0.85	0.78	2.05	0.73	2.8426	1.69
0.95	0.73	2.15	0.78	2.9229	1.88
1.05	0.70	2.25	0.84	3.0290	2.23
1.15	0.66	2.35	0.93	3.1904	2.92
		2.45	1.02	∞	8.87

Table II A-4

Same as A-2 except at $n^* = 10.0$.

2. Asymptotic Analysis

Before going into the asymptotic analysis of $\dot{C}_4(t)$, Eqs. B3.2 and B3.5, it will be helpful to discuss how the long-time behavior of the Laplace transform of the velocity autocorrelation function is derived. The molecular dynamics results of section C show the velocity autocorrelation function for the two dimensional Lorentz gas decays in the long-time limit:

$$\rho_D(t) \sim -\alpha_D/t^{\beta_D} \quad , \quad (1)$$

where $\rho_D(t)$ is normalized so $\rho_D(0) = 1$, α_D and $\beta_D > 1$ are dimensionless constants, and the time is in units of mean particle collisions. The Laplace transform of $\rho_D(t)$ is $\tilde{\rho}_D(s) = \int_0^\infty e^{-st} \rho_D(t) dt$ which is rewritten

$$\tilde{\rho}_D(s) = \int_0^\infty \rho_D(t) dt + \int_0^\infty (e^{-st} - 1) \rho_D(t) dt \quad . \quad (2)$$

The first integral is equal to $D/\langle \dot{x}^2 \rangle$, where D is the diffusion coefficient and $\langle \dot{x}^2 \rangle$ is the mean-square velocity. The second integral in Eq. 2 is broken into two integrals: the first integral has limits which go from 0 to t_0 , where t_0 is large enough so the velocity autocorrelation function is given by Eq. 1; the second integral has limits which go from t_0 to ∞ and Eq. 1 is put in place of $\rho_D(t)$ in this integral. Therefore, Eq. 2 becomes

$$\tilde{\rho}_D(s) \sim D/\langle \dot{x}^2 \rangle + \int_0^{t_0} (e^{-st} - 1) \rho_D(t) dt - \alpha_D t_0^{1-\beta_D} \left[E_{\beta_D}(st_0) + \frac{1}{1-\beta_D} \right] \quad , \quad (2)$$

where $E_\beta(z) = \int_1^\infty e^{-zt} \frac{dt}{t^\beta}$ is the exponential integral (44), and the term

added to it, namely $1/(1-\beta_D)$, corresponds to the integral of Eq. 1 between the limits t_0 and ∞ .

The exponential in the remaining integral in Eq. 2 may be expanded in powers of s . The leading order term in this integral is proportional to s . The exponential integral has the following expansion when β is not an integer (44):

$$E_{\beta}(z) = \frac{\Gamma(1-\beta)}{z^{1-\beta}} - \frac{1}{1-\beta} + \frac{z}{1!(2-\beta)} - \frac{z^2}{2!(3-\beta)} + \dots,$$

where $\Gamma(x)$ is the Euler gamma function (44). If β is an integer, then the limit as $\beta \rightarrow \text{integer}$ of this expansion must be taken. For $\beta=2$, the exponential integral has the following expansion (44):

$$\lim_{\beta \rightarrow 2} E_{\beta}(z) \rightarrow 1 + z \ln z + \text{higher order terms.}$$

Using the general expression for $E_{\beta}(z)$ in Eq. 2 yields:

$$\tilde{\phi}_2(s)/\langle \dot{x}^2 \rangle = \tilde{\rho}_D(s) - D/\langle \dot{x}^2 \rangle - \alpha_D \Gamma(1-\beta_D) s^{\beta_D-1}, \quad (3)$$

where terms of order s and higher have been ignored. Therefore, this asymptotic result is only valid for $1 < \beta_D < 2$. For $\beta_D = 2$ the Laplace transform for small s is

$$\tilde{\rho}_D(s) \sim D/\langle \dot{x}^2 \rangle - \alpha_D s \ln s. \quad (4)$$

With these results it is now possible to investigate the asymptotic form of $\tilde{C}_4(t)$. In particular, the asymptotic form of the moments of the distribution function is given by applying Eq. D2.7 recursively. After taking the Laplace transform:

$$\langle \tilde{x}^{2n}(s) \rangle \rightarrow \frac{(2n)!}{s^{1+n}} (D - \alpha_D \langle \dot{x}^2 \rangle \Gamma(1-\beta_D) s^{\beta_D-1})^n, \quad (5)$$

where Eq. 3 is used in place of $\tilde{\phi}_2(s)$.

The case considered here is for $0 < D < \infty$. The results for zero diffusion coefficient are presented in the text. The derivation follows similar lines for the $D \neq 0$ case. The $D = \infty$ case is not considered here.

Since $\beta_D > 1$, D is large in comparison to the second term in Eq. 5 when s is small. After multiplying out the n^{th} order binomial product, Eq. 5 is written to lowest order in s^{β_D-1} as

$$\langle x^{2n}(s) \rangle \sim \frac{(2n)!}{s^{n+1}} (D^n - D^n \alpha_D^{-1} \langle \dot{x}^2 \rangle \Gamma(1-\beta_D) s^{\beta_D-1}) \quad (6)$$

The inverse Laplace transform of Eq. 6 is obtained by applying Eq. 3 in reverse:

$$\langle x^{2n}(t) \rangle \sim \frac{(2n)!}{n!} (Dt)^n - \frac{(2n)! n D^{n-1} \langle \dot{x}^2 \rangle \alpha_D \Gamma(1-\beta_D)}{\Gamma(n+2-\beta_D)} t^{n+1-\beta_D} \quad (7)$$

which is valid for large times. In particular

$$\langle x^2(t) \rangle \sim 2Dt - \frac{2\langle \dot{x}^2 \rangle \alpha_D}{(2-\beta_D)(1-\beta_D)} t^{2-\beta_D} \quad (8a)$$

and

$$\langle x^4(t) \rangle \sim 12(Dt)^2 - \frac{48\langle \dot{x}^2 \rangle D \alpha_D t^{3-\beta_D}}{(3-\beta_D)(2-\beta_D)(1-\beta_D)} \quad (8b)$$

where use has been made of the factorial property of the gamma function:

$\Gamma(1+x) = x\Gamma(x)$. If $\beta_D = 2$, then a similar analysis using Eq. 4 yields

$$\langle x^2(t) \rangle \sim 2Dt + 2\langle \dot{x}^2 \rangle \alpha_D \ln t \quad (9a)$$

$$\text{and } \langle x^4(t) \rangle \sim 12(Dt)^2 + 48\langle \dot{x}^2 \rangle D \alpha_D t \ln t \quad (9b)$$

The asymptotic form of the functions $\dot{C}_1(t)$ and $\dot{C}_u(t)$, whose long-time limits are respectively the diffusion coefficient, D , and the Burnett coefficient, B , are found by using Eqs. 8, 9 in the definitions B3.1 and B3.2:

$$\dot{C}_1(t) = D - \frac{\langle \dot{x}^2 \rangle D t^{-1/2}}{1 - \beta_D} \quad , \quad (10a)$$

and

$$\dot{C}_u(t) = \frac{\langle \dot{x}^2 \rangle D t^{-1/2}}{2 - \beta_D} \quad , \quad (10b)$$

when $1 < \beta_D < 2$. If $\beta_D = 2$, then

$$\dot{C}_1(t) = D - \langle \dot{x}^2 \rangle D / t \quad , \quad (11a)$$

$$\text{and} \quad \dot{C}_u(t) = \langle \dot{x}^2 \rangle D \ln t \quad . \quad (11b)$$

Equations 10 and 11 show $\dot{C}_u(t)$ diverges as t gets large, when $1 < \beta_D < 2$, so the Burnett coefficient, B_u , does not exist for the continuous time random walk, when the velocity autocorrelation function decays slowly enough. The Burnett correlation function, $\rho_B(t)$, is equal to $\dot{C}_u(t)/D_E^2$, where $D_E = 4\langle \dot{x}^2 \rangle / 3$ is the Enskog value of the diffusion coefficient for the Lorentz gas in units of mean particle collisions. From Eqs. 10b, 11b, this is:

$$\rho_B(t) \sim \alpha_B / t^{\beta_B} \quad , \quad (12)$$

where

$$\alpha_B = \frac{4}{3} \frac{D}{D_E} \alpha_D \quad , \quad (13)$$

and

$$\rho_E = \rho_D - 1 \quad (14)$$

The expressions 12 through 14 are valid for $1 < \rho_D < 2$.

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III. THE DEPENDENCE OF THE FRICTION COEFFICIENT ON MASS, SIZE, AND MOLECULAR BOUNDARY CONDITIONS

A. Introduction

The main purpose of this chapter is to determine how the friction coefficient of hard spheres compares to Stokes law when the diffusing particle is of molecular size; and to determine the molecular scattering rules which correspond to the hydrodynamic fluid-particle boundary conditions. The molecular dynamics method is used to directly evaluate the friction coefficient of an infinite-mass hard-sphere particle of molecular size, which has the advantage that it enables a direct study of the molecular interactions on the surface of the test particle.

For a particle which moves with a slow constant velocity through a fluid, the friction coefficient is the absolute value of the ratio of the drag on the particle to its velocity in the fluid (1,2,3,4). Stokes showed (5), for a spherical particle in a continuous fluid, the friction coefficient is proportional to the radius of the particle and the viscosity of the fluid. In this relation, which is known as Stokes law, the value of the proportionality constant varies depending on the fluid-particle boundary conditions: hydrodynamics gives the value as 6π if the fluid sticks to the surface of the sphere, and 4π if the fluid slips perfectly on the surface of the sphere (5,6,7). By the measurement of the diffusion of one species of molecule in a bath of others, it has been found (8,9) the stick boundary condition gives a more accurate friction coefficient for relatively large molecules in fluids, but the slip condition gives a more accurate coefficient for particles which are similar in size to the fluid particles. In particular, for hard-sphere particles of the same size and mass, the Stokes formula was shown by molecular dynamics to give an accurate friction

coefficient if slip boundary conditions are used and the mean-free path is small. This is surprising in view of other results which show both mass and size dependence of the friction coefficient: an expansion of the Liouville equation in the inverse square root of the mass ratio of the test particle and a fluid particle yields the Fokker-Planck equation and a friction coefficient which is equal to the ordinary one plus a correction term proportional to the inverse mass ratio (10,11). The correction term, however, has not been quantitatively evaluated. The size dependence of the friction coefficient has been given in terms of fits to experimental measurements (9,12,13), low density theoretical calculations using the Boltzmann equation (14), and qualitative derivations (15). The experimental results shed little light on the detailed mechanisms responsible for the mass and size dependence of the friction coefficient, because of the uncertainty in the proper boundary conditions to be used, and the uncertainty in the radius of the molecules. Although the calculations using the Boltzmann equation are exact, in that they give the first order correction to the friction coefficient, they only apply in the low density limit. Finally, much more than a qualitative calculation is necessary if the detailed molecular interactions which affect the friction coefficient are to be understood.

1. Mathematical Background

The detailed motion of the test particle in the fluid is described in terms of the so-called extended Langevin equation (16,17):

$$m_1 \frac{d\vec{v}(t)}{dt} = - \int_0^t \phi(t-t') \vec{v}(t') dt' + \vec{R}(t) \quad , \quad (1)$$

where m_1 is the mass of the test particle and the total force on the test

particle is divided into a drag part, represented by the integral, and a fluctuating part, $\vec{R}(t)$. The drag term expresses the fact that the total drag on the test particle depends on the velocity history of the particle. If there is no memory in the system, then $\phi(t) = \gamma\delta(t)$ and Eq. 1 reduces to the ordinary Langevin equation, where γ is the friction coefficient. For a particle moving with constant velocity, $\vec{v}_0$, in the fluid, the drag becomes in the long time limit $-\gamma\vec{v}_0$, where

$$\gamma = \int_0^\infty \phi(t) dt \quad (2)$$

is the friction coefficient. The fluctuating force, $\vec{R}(t)$, is in general not random. In fact, because the drag term and the driving force both result from the same physical process (fluid particle collisions with the test particle), they are related (16,17,18):

$$\langle R_x(t) R_x(0) \rangle = k_B T \phi(t) \quad (3)$$

where k_B is Boltzmann's constant, T is the absolute temperature and the angular brackets mean the correlation of the x-component of the driving force is averaged over all its initial values. Equation 3 results from Eq. 1 by multiplying Eq. 1 by $R_x(0)$ and averaging over the initial values. Finally, by multiplying Eq. 1 by $v(0)$ and averaging over all initial velocities:

$$m_1 \frac{dC(t)}{dt} = - \int_0^t \phi(t-t') C(t') dt' \quad , \quad (4)$$

where $C(t) = \langle \dot{x}(t) \dot{x}(0) \rangle$ is the velocity autocorrelation function and $\langle R_x(t) \dot{x}(0) \rangle = 0$ has been used.

Because of the relationship between the velocity autocorrelation function and the friction coefficient, Eq. 4, the friction coefficient is related to the diffusion coefficient of the test particle. By integrating Eq. 4 and going to the infinite time limit, the friction coefficient and the diffusion coefficient are related in a simple way (if the correlation functions decay sufficiently fast):

$$\gamma D = k_B T \quad , \quad (5)$$

where $D = \int_0^\infty C(t)dt$ is the diffusion coefficient. For large and massive particles, the diffusion coefficients are difficult to obtain by molecular dynamics because the massive particle just streams through the small fluid systems on the computer. An alternate scheme is used, where the massive particle is held fixed and the force on it, due to collisions with the fluid particles, is evaluated. This corresponds to the case where the test particle is of infinite mass.

2. Chapter Outline

The next section discusses the method of calculation of the infinite-mass friction coefficient for hard spheres. The emphasis is on the elimination of streaming of the fluid past the test particle, and finite size effects. The section following this presents the molecular dynamics results. The emphasis is on how the results compare to Stokes law, and the dependence of the friction coefficient upon the molecular boundary conditions. The next section is a summary of the results of the previous sections. The last section contains the Appendices.

B. Molecular Dynamics

This section discusses the molecular dynamics program which calculates the infinite-mass friction coefficient. The first subsection describes the special correlation function which must be evaluated because of the impulsive nature of the hard-sphere forces. This correlation function calculates the integral of the force correlation function which, in the infinite time limit, is the friction coefficient. Also this subsection contains a short discussion of the method of estimating statistical accuracy. The next subsection presents the method used to eliminate streaming effects resulting from the finite size of the system. In the next subsection, the effects on accuracy of the molecular dynamics results due to the finite number of particles in the system is discussed. The last subsection presents two dimensional results which were used to test the molecular dynamics program.

1. Averages

To evaluate the friction coefficient in the infinite mass limit, the test particle is held fixed. The random force is then the total force and

$$\gamma(t) = \frac{1}{k_B T} \int_0^t \langle F_x(t') F_x(0) \rangle dt' \quad , \quad (1)$$

which is equal to the friction coefficient in the infinite time limit. Equation 1 may be put in a form which is suitable for machine calculation by writing the impulsive hard-sphere force in the x-direction

$$F_x(t) = m_2 \sum_c \Delta \dot{x}(t_c) \delta(t - t_c) \quad , \quad (2)$$

where $m_2 \Delta \dot{x}$ is the x-component of the change in momentum of a fluid particle

when it collides with the test particle, $\delta(t)$ is the Dirac delta function, and the sum extends over all fluid-test particle collisions. The angular brackets in Eq. 1 are an average of the initial force over an equilibrium ensemble which is equivalent to a time average in a single system by the ergodic hypothesis. Therefore,

$$\gamma(t) = \lim_{\tau \rightarrow \infty} \frac{m_2^2}{k_B T} \frac{1}{\tau} \int_0^\tau d\tau' \int_0^{\tau'} dt' \sum_{c,c'} \Delta \dot{x}(t_c) \Delta \dot{x}(t_{c'}) \delta(\tau' + t' - t_c) \delta(\tau' - t_{c'}) \quad , \quad (3)$$

where the integral with respect to τ' represents the ergodic time average. After performing the integrations, the delta functions disappear:

$$\frac{\gamma(t_c)}{\gamma_E} = 1 + 2 \sum_{c' > 0}^{t_c} \frac{\langle \Delta \vec{v}(c') \cdot \Delta \vec{v}(0) \rangle_c}{\langle \Delta v^2(0) \rangle_c} \quad , \quad (4)$$

where $\langle \Delta v^2(0) \rangle_c = 8k_B T/m_2$, and $\gamma_E = k_B T/D_E$ is the initial value of the friction coefficient if $\vec{F}(t)$ is completely random, that is, uncorrelated with itself at a later time, and D_E is the Enskog diffusion coefficient. The subscript, c , on the angular brackets in Eq. 4 indicates an average over the initial collisions. Finally, Γ_{12} is the collision rate of the solvent particles of mass m_2 and σ_2 with the infinite mass test particle of diameter σ_1 . The initial value $\langle \Delta v^2(0) \rangle_c$ has been taken out of the above sum to emphasize, relative to it, that the remaining terms have to be twice as large, just as in numerical integration the end points have only half the weight.

To evaluate Eq. 4 on the computer, each momentum change is taken as an initial impulse which is multiplied by the sum up to a time t_c of all the later velocity changes. The process is repeated for each momentum

impulse and the resulting correlations are averaged. The statistical error is estimated by dividing a longer run into smaller ones by taking as initial points equally spaced collision intervals. Since the samples are taken from a continuous collision chain of events, they are not randomly chosen samples; if a long-time correlation exists which spans the sample time interval, then the samples will not be independent. Treating them as independent, the statistical error is calculated in the usual fashion (19).

2. Dynamics

The friction coefficient is calculated from the force on a fixed test particle which is immersed in a fluid of hard spheres (or disks). The boundary conditions at the edge of the volume are periodic; when a moving particle reaches a boundary it will disappear and reappear on the other side of the volume. This is done to minimize surface effects in these finite sized systems. The fluid particles interact via the hard-sphere (or disk) potential. When they strike the test particle, they are reflected in one of two ways: either they are reflected specularly from the test particle, or they are reflected diffusively. If the fluid particles reflect specularly from the test particle, then the angle of reflection from the surface is equal to the angle of incidence. However, if the fluid particles reflect diffusively from the test particle, then the velocity after the collision is chosen in a random direction away from the surface of the test particle. These two boundary conditions are respectively equivalent to the slip and stick boundary conditions used in hydrodynamics to calculate the drag on a large particle in a fluid. In both cases the kinetic energy of the fluid particle after the collision is equal to the kinetic energy before the collision, so the collisions are elastic.

The center-of-mass velocity of the fluid particles is initially zero; however, after each collision with the test particle, the center-of-mass velocity of the fluid changes by an amount equal to the change of momentum of the colliding fluid particle. The reason this does not happen between fluid-fluid particle collisions is the momentum is conserved in these collisions. In a fluid-test particle collision, the test particle is held fixed so it cannot compensate for the change in momentum of the fluid particle. The net result is a center-of-mass drift velocity which fluctuates in time. The average magnitude of the fluctuating drift velocity is $\langle \dot{x}_D^2 \rangle = k_B T / N m_2$, where $\dot{x}_D = \frac{1}{N} \sum_i \dot{x}_i$ is the x-component of the center-of-mass drift velocity and N is the number of fluid particles of mass m_2 . The average lifetime of a drift fluctuation is measured by the drift velocity autocorrelation function,

$$K(t) = \langle \dot{x}_D(t) \dot{x}_D(0) \rangle / \langle \dot{x}_D^2 \rangle \quad (1)$$

This function is plotted in Fig. 1 for a typical systems vs. mean fluid particle collisions. The circles are molecular dynamics and the solid line is the initial slope. The inset shows a much magnified initial region, where it is seen the molecular dynamics data begin to deviate from the initial slope at about two collisions. The initial slope was calculated from the initial value of the derivative of $K(t)$:

$$\dot{K}(0) = \frac{m_2}{N k_B T} \int \dot{x}_2 \Delta \dot{x}_2 d\Gamma_{12} \quad , \quad (2)$$

where $\Delta \dot{x}_2$ is the change in velocity of a fluid particle when it collides with the test particle. The integral is with respect to the differential

Figure 1

The drift velocity autocorrelation function for a typical system.

collision rate between the bath particles and the test particle. The differential collision rate is derived by considering the flux of fluid particles at the surface of the test particle times the differential cross-section for the collision. The result of the integration is

$$\dot{K}(0) = -\gamma_E / Nm_2 \quad , \quad (3)$$

where γ_E is the initial value of the friction coefficient. As seen in Fig. 1, Eq. 3 only holds over a small time range. After this the decay rate decreases; at 100 mean particle collisions Eq. 1 has only decayed 15% of its initial value. Since the decay rate is decreasing at larger time, it takes many hundreds of collisions before the drift vanishes. Figure 2 shows the total center-of-mass drift relative to the thermal speed in two typical systems. The solid circles, ●, represent a system in which the drift velocity is relatively constant over 10^4 mean collisions; the open circles, ○, represent a system in which the drift velocity makes a sudden (on the order of 10^3 collisions) transition to another value. The drift velocity is "locked in" for several thousand mean collisions and then makes a sudden transition, due to a strong fluctuation, to another value. To get an estimate of the amount of computer time involved, suppose the average life time of a drift fluctuation is 10^4 mean collisions and there are 2000 fluid particles in the system. Then it takes $\frac{1}{2} \times 2000 \times 10^4 = 10^7$ total collisions to relax one drift fluctuation. The C.D.C. 7600 runs a molecular dynamics program approximately 2×10^6 collisions per hour. Thus, for a 2000 particle system, approximately 5 hours of computer running time are needed to relax a drift fluctuation.

The stability of the drift velocity is a result of interference of the flow field with its periodic image. Figure 3 is a schematic diagram of

Figure 2

The total center-of-mass drift relative to the thermal speed for two typical systems.

Figure 3

A schematic diagram illustrating the fluid drift in a periodic system.

the central molecular dynamics cell and its nearest neighbor images. In this two dimensional picture, the dashed lines represent the periodic cell boundaries, and the hatched circles represent the fixed test particle and its periodic images. Also represented by the flow lines in the figures is a drift velocity field. The direction of the velocity field is in general arbitrary; any symmetry axis could have been chosen. In this schematic the drift velocity is to the right along the horizontal axis. The circular flow lines are vortices which constructively interfere at the cell boundaries and add momentum to the flow. The fixed test particle in the flow field generates a high pressure region on the side which faces the flow field, and on the opposite side a low pressure region is generated. A vortex ring develops, Fig. 3, which equalizes the pressure difference. In a finite periodic system, the vortex interferes with the periodic image of itself; the velocity components of the vortex and its image add with a resultant which is along the direction of the flow field, Fig. 3. The vortex feeds some of the dissipative momentum back into the flow field, prolonging its existence. This stable flow is similar to what happens when the test particle is not of infinite mass, but is of very large mass. The massive particle streams through the less massive fluid particles. This suggests that the mass dependence of the friction coefficient may be calculated from its dependence on the drift velocity, although the exact relationship is not known at this time.

The infinite-mass friction coefficient must be calculated in a system which is in equilibrium, however, the effect of a coherent drift velocity on the friction coefficient is seen in Fig. 4, where four molecular dynamics curves at liquid density are presented, which correspond to a range of "locked in" drift velocities per particle. It is seen the curves vary as

Figure 4

The effect of the drift velocity on the friction coefficient for a typical system.

much as 30 percent at the extremes between the zero drift case, indicated by Δ , and the case for the ratio of the drift speed, $|\dot{x}_D|$, to the thermal speed, $(k_B T/m)^{1/2}$, equal to 0.01 indicated by the open circles, o. The intermediate curves represent the value of the ratio as 0.0002, indicated by $\bullet$, and 0.001, indicated by $\blacktriangle$.

The non-zero drift cases in Fig. 4 were obtained from separate runs with different stable drift velocities. The case of zero drift is calculated by stopping the molecular dynamics calculation after every test particle collision and zeroing out the drift velocity: the non-zero $\Delta \vec{v}$, which results because of the test particle collision, is divided by the number of other fluid particles in the system. The velocity of every other particle in the system is then reduced by this number, and the total energy of the system is adjusted so it is the same after a collision as before. In this way the system maintains a zero center-of-mass drift velocity.

3. Finite Size Effects

Once the drift velocity is eliminated, there are additional effects on the friction coefficient due to the finite number of particles in the system. Because periodic boundary conditions are used, a sound wave, which is generated by collisions with the test particle, travels out of the molecular dynamics cell and returns to it from an image cell. Also, because a small velocity increment equal to $\Delta v/(N-1)$ is subtracted from all the fluid particle velocities, after each test particle collision, an effect on the order of $1/(N-1)$ will be introduced into the value of the friction coefficient.

The number dependence of the friction coefficient can be related to the number dependence of the velocity autocorrelation function which is known (20,21,22). This is based on the relationship between the velocity

autocorrelation function and the friction coefficient given by Eq. A1.4 and repeated here:

$$m_1 \frac{dC(t)}{dt} = - \int_0^t \phi(t-t') C(t') dt' \quad , \quad (1)$$

where $C(t) = \langle \dot{x}(t) \dot{x}(0) \rangle$ is the velocity autocorrelation function of the test particle of mass m_1 . Equation 1 serves to define the velocity autocorrelation function in terms of the force autocorrelation function $\phi(t)$. Conversely, given $C(t)$, then $\phi(t)$ can be determined. In particular, if $C(t)$ is determined from N-particle molecular dynamics, then $\phi(t)$ can be determined by numerically inverting Eq. 1. However, because of the m_1 dependence on the left side of Eq. 1, this technique cannot be used when the mass of the test particle is very large. However, the long-time tail of $\phi(t)$ can be determined because the tail of $C(t)$ is independent of the mass of the diffusing particle (it only depends on the hydrodynamic variables of the fluid)(23,24,25). To find this relationship integrate Eq. 1 between 0 and t to eliminate the derivative. After changing the order of integration on the right side:

$$m_1 C(0) = m_1 C(t) + \int_0^t \phi(t') D(t-t') dt' \quad , \quad (2)$$

where $D(t) = \int_0^t C(t) dt$. The function $D(t-t')$ is expanded in a Taylor series about t : $D(t-t') = D(t) - t' C(t)/1! + (t')^2 \dot{C}(t)/2! - \dots$.

At long time the velocity autocorrelation function decays as $C(t) \sim A/t^{3/2}$ so $D(t-t') \sim D(t) - At'/t^{3/2}$ as t gets large. Equation 2 becomes

$$m_1 (C(0) - C(t)) \sim \gamma(t) D(t) - At^{-3/2} \int_0^t t' \phi(t') dt' \quad ,$$

where $\gamma(t) = \int_0^t \phi(t') dt'$. Since $\phi(t) \sim t^{-3/2}$ for large t (26,27,28,29),

then the integral is proportional to $t^{1/2}$ for large t , also $C(t) \leq C(0)$ as $t \rightarrow \infty$. Equation 2 becomes:

$$k_B T = D(t) \gamma(t) \quad , \quad (3)$$

where $m_1 C(0) = k_B T$. In the infinite time limit, Eq. 3 reduces to the Einstein relation: $k_B T = D \gamma$, where $D = D(\infty)$, $\gamma = \gamma(\infty)$ are the diffusion and friction coefficients respectively. Equation 3 can be written in a way which explicitly shows the dependence of $\gamma(t)$ on the tail of the velocity autocorrelation function by substituting

$$D(t) = D(\infty) - [D(\infty) - D(t)] = \frac{k_B T}{\gamma(\infty)} - \int_t^\infty C(t') dt' \text{ into 3:}$$

$$\gamma(t) = \frac{\gamma(\infty)}{1 - \frac{\gamma(\infty)}{k_B T} \int_t^\infty C(t') dt'} \quad . \quad (4)$$

Equation 4 is used to extrapolate the molecular dynamics results for $\gamma(t)$ to infinite time given the tail of the velocity autocorrelation function.

The long-time tail of the velocity autocorrelation function is determined from a hydrodynamic model: A fluid is at rest except a small volume element is given an initial velocity. A compression wave develops in front of this region and a rarefaction wave develops to the rear. When the sound waves have separated, the residual flow is in the form of a double vortex in two dimensions, or a vortex ring in three dimensions which serves to equalize the pressure difference. Thus the fluid feeds some of the initial

momentum of the moving particle back at a later time, giving it a push. In an infinite system the sound waves travel away from the diffusing particle and never interact with it again. However, in a periodic system sound waves from the periodic images of the central cell interact with the diffusing particle. In addition, the vortex spreads into the periodic cells and affects the diffusing particle as well.

The long-time tail of the velocity autocorrelation function for finite periodic systems of d -dimensions, volume Ω and mass density ρ can be derived (21,22) by solving the hydrodynamic problem in periodic space:

$$C_N(t) \sim \sum_{\vec{k} \neq 0} [V_N(\vec{k}, t) + S_N(\vec{k}, t)] \frac{k_B T}{\rho} \quad , \quad (5)$$

where $V_N(\vec{k}, t) = (d-1)\exp[-k^2(\nu+D)t]/\Omega d$ is the vortex contribution and $S_N(\vec{k}, t) = \cos(kct)\exp[-k^2(\Gamma+D)t]/\Omega d$ is the sound contribution. The coefficients ν , D , c , Γ are respectively the kinematic viscosity, the diffusion coefficient, the sound speed, and the sound attenuation coefficient. The sum is over all negative and positive $\vec{k}$ -values whose three components are integer multiples of $k_0 = 2\pi/L$ (except $\vec{k} = (0,0,0)k_0$), where L is the length of one of the equal sides of the periodic volume. Equation 5 gives quantitative agreement with finite molecular dynamics calculations of the velocity autocorrelation function if t is larger than approximately 20 collisions (22).

Figure 5 gives $\gamma_N(t)$ for a three dimensional fluid at $V/V_0 = 3.0$, $m_1/m_2 = 1$ when $C_N(t)$, Eq. 5, is substituted for $C(t)$ in Eq. 4. The solid lines in Fig. 5 represent Eq. 4. The upper solid line is for $N = 500$, the middle solid line is for $N = 2000$ and the lower solid line is for $N = \infty$. The arrows pointing to the axis indicate the sound arrival time, $s_c(N)$,

Figure 5

The N -dependent friction coefficient for a three-dimensional fluid at $V/V_0 = 3.0$ as a function of the square-root of the reciprocal of the mean-fluid-particle collision time, t_c .

and the vortex arrival time, $v_c(N)$, for an N -particle system. The reason the curves deviate from the infinite system curve before the sound arrival time is due to the "1/ N effect" on the velocity autocorrelation function in a finite system. Previously (25) it was found that a correction of $1/(N-1)$ needs to be added to the velocity autocorrelation function of a finite system, before sound interference, in order to better approximate the infinite system correlation function at finite times. "This is because whenever a given molecule has a velocity v , the average velocity of the other molecules is $-v/(N-1)$ in a system of N molecules where momentum is conserved." (25) The effect on the friction coefficient can be found by considering Eq. 3. Let $\gamma_N(t)$, $D_N(t)$ be the time dependent friction coefficient and diffusion coefficient for a system of N particles. Then the infinite diffusion coefficient is related to the finite system one by

$$D_\infty(t) = D_N(t) + \frac{k_B T}{m_2} \frac{t}{N-1} \quad (6)$$

Substitute Eq. 6 into Eq. 3 and solve for $\gamma_\infty(t)/\gamma_E$:

$$\frac{\gamma_\infty(t)}{\gamma_E} = \frac{\gamma_N(t)/\gamma_E}{1 + \frac{4}{3} \frac{\Gamma_{12}}{\Gamma_{22}} \frac{\gamma_N(t)}{\gamma_E} \frac{t_c}{N-1}}, \quad (7)$$

where $\gamma_N(t) = k_B T/D_N(t)$ and $\gamma_E = \frac{4}{3} \Gamma_{12} m_2$ has been used. The time, t_c , is in units of fluid-particle collisions. The 1/ N correction is on the order of 10 → 20% for 500-particle systems. For large systems ($N \geq 2000$) the 1/ N correction is small unless the test particle is much larger than the bath particle size. In this case the ratio of collision rates is large, which compensates for the large N in the denominator of Eq. 7.

Appendix E2 lists some selected time dependent friction coefficients.

The $1/N$ correction must be applied to these functions in order to give the infinite system results.

According to the hydrodynamic model for the tail of the velocity autocorrelation function, the mass dependence enters only through the initial velocity of the fluid element. The initial velocity is determined by the equipartition theorem, namely $\sqrt{k_B T/m_2}$, where m_2 is the mass of the fluid particles. Thus, Eq. 5 can also be used in Eq. 4 when the mass of the test particle is infinite. Figure 6 shows three molecular dynamics results for the infinite mass friction coefficient of a particle twice the size of the fluid particles at $V/V_0 = 3.0$. The upper solid line represents Eq. 4 for 500 particles and the lower solid line is Eq. 4 for an infinite system. The open circles, o, are the 500 particle molecular dynamics results; the closed circles ●, are a 2048 system; and the triangles, Δ, represent a 4000 particle system. The periodic interference effects are most noticeable for the 500 particle system. The larger systems, 2048 and 4000, show little difference from the infinite system extrapolation.

Table 1 shows the N -dependence of the infinite-mass friction coefficient at two densities with a size ratio $\sigma_1/\sigma_2 = 2.0$. Since slip boundary conditions are used, the friction coefficient is divided by its hydrodynamic prediction $4\pi\eta\sigma_{12}$, where η is the shear viscosity and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ is the average of the diameters of the test particle and a fluid particle.

Figure 6

The infinite-mass friction coefficient of a particle twice the size of the fluid particles at $V/V_0 = 3.0$.

V/V_0	$\gamma/\gamma_H^{b,c}$	γ/γ_H^d	γ/γ_H^e	γ/γ_H^f	γ/γ_H^g
3.0	0.94 ₃		0.82 ₃	0.82 ₃	0.77 ₄
1.6	0.91 ₂	0.87 ₃			0.79 ₄

Table III-1

The N-dependence of the infinite mass friction coefficient.^a

- a) The total number of fluid particle collisions was 30 million.
- b) $\gamma_H = 4\pi\eta\sigma_{12}$.
- c) For 500 particles.
- d) For 1372 particles.
- e) For 2048 particles.
- f) For 4000 particles.
- g) Extrapolated to infinite systems.

4. Two Dimensions

The two dimensional system is used here as a test for the molecular dynamics evaluation of the friction coefficient. Because the dimensionality is less, a two dimensional system is effectively larger, for a given number of particles, than a three dimensional system; interference between periodic images occurs at later times in the correlation function. Furthermore, the friction coefficient is zero in two dimensions, by the Einstein relation, because the diffusion coefficient is infinite (25,30). Therefore, unlike three dimensions, the asymptotic tail of $\phi(t)$ does not depend upon the extrapolated value $\gamma(\infty)$, as Eq. B3.4 implies by differentiation, but only on the hydrodynamic variables. The validity of hydrodynamics in evaluating the tail of the force autocorrelation function can be easily investigated. In particular, for very long time $\phi(t)$ is independent of the radius of the test particle as seen by substituting the asymptotic form of the diffusion coefficient, $D(t) \sim (k_B T / m_2 \Gamma_{22}) \alpha \ln t_c$, into the time dependent Einstein relation:

$$\gamma(t) \sim k_B T / D(t) \sim \Gamma_{22} m_2 / \alpha \ln t \quad , \quad (1)$$

where Γ_{22} is the collision rate of the fluid particles of mass m_2 and the coefficient α comes from the asymptotic form of the velocity autocorrelation function (25): $C(t) \sim \alpha k_B T / m_2 \Gamma_{22} t$. The tail of the force autocorrelation function, according to hydrodynamics, is evaluated in Appendix E1. The radius in the hydrodynamics solution represents the distance of closest approach of the centers of the fluid particles and the center of the test particle, namely σ_{12} . For a test particle which is infinitely large in comparison to the fluid particles, the distance of closest approach is the radius of the test particle, since $\sigma_{12} \rightarrow \sigma_1/2$ as $\sigma_1/\sigma_2 \rightarrow \infty$.

Figure 7 shows the N-dependence of the two dimensional calculation of the friction coefficient. The solid circles, ●, are for a 504 particle system; the solid triangles, ▲, are for a 986 particle system; and the open circles, ○, are for a 1968 particle system. The density corresponds to an area relative to close packing $A/A_0 = 3.0$ and the ratio of diameters of the test particle and a fluid particle is $\sigma_1/\sigma_2 = 2.0$. The arrows on the axis indicate the travel time, $s_c(N)$, of a sound wave through the periodic system. The vortex interference time, $v_c(N)$ is beyond the range of the horizontal axis even for the 504 particle system. The $1/N$ correction has been applied to these results. The departure times, from the 1968 particle results by the smaller systems, correspond to the sound transit time in these systems.

Figure 8 shows the size dependence of the two dimensional infinite mass friction coefficient at $A/A_0 = 3.0$. The solid circles, ●, are for $\sigma_1/\sigma_2 = 1$; the open circles, ○, are for $\sigma_1/\sigma_2 = 2$; the closed triangles, ▲, are for $\sigma_1/\sigma_2 = 3$; and the open triangles, △, are for $\sigma_1/\sigma_2 = 4$. The sound transit time is indicated by the arrow for these 1968 particle systems. The solid lines are the solutions based on linearized incompressible hydrodynamics (Appendix E1) using for the radius σ_{12} . As the figure shows, the hydrodynamic theory agrees with molecular dynamics at this density when the diameter of the test particle $\sigma_1 > 2\sigma_2$. This corresponds to a mean-free path, $\lambda \leq \sigma_{12}/2$. Thus, the mean-free path must be small compared to the size of the test particle in order for hydrodynamics to give the tail of $\phi(t)$ correctly. The $1/N$ correction has been applied to these points.

Figure 7

The effect of sound wave interference on the friction coefficient in three two-dimensional systems.

Figure 8

The size dependence of the two-dimensional infinite-mass friction coefficient at $A/A_0 = 3.0$.

C. Molecular Dynamics Results

The section discusses the molecular dynamics results for the friction coefficient of an infinite-mass sphere. The first subsection discusses the initial value and slope of the integral of the force autocorrelation function which is used to calculate the friction coefficient. Emphasis is placed on the importance of recollisions on the initial slope. The next subsection presents the molecular dynamics results for the friction coefficient. The emphasis is on how the Stokes or Brownian limit is approached as the size of the massive particle is made larger. Also a simple derivation using generalized hydrodynamics is presented to explain the size dependence. A comparison between slip and stick boundary conditions is made, and a simple model of a molecule with a rough surface is presented which exhibits a roughness midway between perfect slip and perfect stick boundary conditions.

1. Initial Slope

The molecular dynamics evaluation of the initial value of the friction coefficient was found to accurately correspond to the derived result:

$\gamma_E = \frac{4}{3} \Gamma_{12} m_2$. The molecular dynamics method is to average the square of the velocity changes in the fluid-test particle collisions over the collisions (first term of Eq. B1.4).

Another molecular dynamics result, which can be compared to a derived equation, is the initial slope of the friction coefficient. The initial slope of $\gamma(t)$ is found by differentiating Eq. B1.3 by t and taking the limit as $t \rightarrow 0^+$, where 0^+ means the initial collision is not counted. The time average is replaced by an ensemble average which means the Dirac delta functions must be transformed to functions of position rather than

time. Thus $\delta(t-t_c) = \sum_i \delta(r_{1i} - \sigma_{12}) \dot{r}_{1i}$, where r_{1i} is the distance between the test particle and fluid particle i and the dot over the r_{1i} means time derivative. After performing the indicated operations:

$$\begin{aligned} \frac{\dot{\gamma}(0^-)}{\gamma_E} &= \frac{m}{4\Gamma_{12}} \frac{H(N-1)}{2} \int d\vec{r}_2 d\vec{r}_3 d\vec{v}_2 d\vec{v}_3 \rho^{(1,2,3)}(\vec{r}, \vec{v}) \\ &\times \Delta\vec{v}(t_{12}) \cdot \Delta\vec{v}(t_{13}) \frac{r_{12} \cdot \mathbf{v}_{12}}{\sigma_{12}} \frac{r_{13} \cdot \mathbf{v}_{13}}{\sigma_{13}} \\ &\times \delta(r_{12} - \sigma_{12}) \delta(r_{13} - \sigma_{13}) H(-r_{12} \cdot \mathbf{v}_{12}) H(-r_{13} \cdot \mathbf{v}_{13}) \quad , \quad (1) \end{aligned}$$

$$\text{where } \rho^{(1,2,3)}(\vec{r}, \vec{v}) = \left(\frac{m\beta}{2\pi} \right)^3 g_{123}(r_{12}, r_{13}, r_{23}) \exp[-\frac{1}{2}m\beta(v_2^2 + v_3^2)]/\Omega^2$$

is the distribution function for particles 2 and 3 of mass m in volume around the infinite mass test particle and g_{123} is the triplet distribution function. Also $\beta = 1/k_B T$, and $H(x) = 0$ or 1 if $x < 0$ or $x > 0$ respectively.

Performing the integrations leads to

$$\frac{\dot{\gamma}(0^+)}{\gamma_E} = - \frac{\pi}{16} \Gamma_{12} \sin^2 \theta_0 \overline{g_{123}(\theta_0)} \quad , \quad (2)$$

where $\theta_0 = 2 \sin^{-1}[1/(1+\sigma_1/\sigma_2)]$ is the exclusion angle, and $\overline{g_{123}}$ is proportional to the solid angle cosine average of the triplet distribution function at contact with the test particle:

$$\overline{g_{123}(\theta_0)} g_{12}(\sigma_{12}) g_{13}(\sigma_{13}) = \int_{\theta_0}^{\theta_0} g_{123}(\theta_0) \cos\theta d\Omega / \int_{\theta_0}^{\theta_0} \cos\theta d\Omega \quad , \quad (3)$$

where $g_{12}(\sigma_{12})$ is the pair radial distribution function at contact.

Figure 9 shows the molecular dynamics results for the initial slope at two densities, $V/V_0 = 3$ (a) and $V/V_0 = 10$ (b), and a series of hard-sphere test particle sizes: solid circles, $\bullet$, $\sigma_1/\sigma_2 = 1$; open circles, $\circ$, $\sigma_1/\sigma_2 = 2$; triangles, Δ , $\sigma_1/\sigma_2 = 3$. The function $\exp(-\pi\Gamma_{12}t \sin^2\theta_0/16)$ has been subtracted from the molecular dynamics results, which has a slope corresponding to Eq. 2 if $g_{123}(\theta_0) = 1$. The dashed line in the inset of Fig. 9(a) shows the initial slope as calculated from Eq. 2 with $\overline{g_{123}} = 0.89$, which has been calculated (31) using Monte Carlo techniques for the case $V/V_0 = 3.0$ and $\sigma_1/\sigma_2 = 1$ for a finite mass test particle. The distribution $\overline{g_{123}}$ depends only on the interparticle interaction potential, which is independent of the mass, so the finite mass result also applies for infinite mass. Also $\overline{g_{123}}$ was only calculated for the case where all the particles are of the same size, and only for that case is it used. As shown by the dashed line in the inset, the initial slope is still larger by about a factor of 3/2 from that obtained by using the more accurate value of $\overline{g_{123}}(\theta_0)$, namely 0.89, in Eq. 2. The deviation from the kinetic theory slope becomes less when the test particle is made larger or the density is lowered, as Fig. 9 shows; this is due to the lower probability of recollisions, with the test particle, of the original colliding fluid particle discovered previously (32). The recollision effect is reduced as the test particle is made larger, because the probability becomes higher that another fluid particle will collide with it from another direction. As the density is reduced, the recollision effect is less important because fluid particle backscattering decreases.

Figure 9

The initial slope of the friction coefficient at two densities as a function of mean-fluid-particle collisions.

2. Friction Coefficient

Table 2 gives the friction coefficient for hard spheres as a function of mass at two fluid densities, where the size of the test particle of mass m_1 is equal to the size of the fluid particles of mass m_2 . The finite mass friction coefficients were determined from diffusion coefficients available in the literature (20,32,33) by using the Einstein relation $\gamma D = k_B T$. The columns headed by D/D_E give the diffusion coefficient of the test particle relative the Enskog diffusion coefficient $D_E = k_B T / \gamma_E = 3k_B T / 4\mu \Gamma_{12}$, where $\mu = m_1 m_2 / (m_1 + m_2)$ and Γ_{12} is the fluid-test particle collision rate. The columns headed γ/γ_H are the ratio of the friction coefficient to its hydrodynamic prediction for slip boundary conditions, $\gamma_H = 4\pi\eta R$, with R equal to the kinematic radius, that is, the distance of closest approach of the centers of the fluid particles and the test particle, namely, σ_{12} . It has been observed that the Stokes-Einstein law gives excellent agreement with molecular dynamics for particles of equal mass and size when R is equal to the radius of the particles (20), namely, $\sigma_1/2$. This corresponds to multiplying γ/γ_H by 2 in the table. As the table shows, for mass ratios other than $m_1/m_2 = 1$, the agreement is lost. Figure 10 shows γ/γ_H from Table 2 plotted as a function of m_2/m_1 . The circles, $\circ$, are for $V/V_0 = 3.0$ and the triangles, Δ , are for $V/V_0 = 1.6$. The dashed line represents the mass dependence of the initial value of the friction coefficient

$$\gamma_E(m_1/m_2) = 4\mu\Gamma_{12}/3 = \gamma_E(\infty) (\mu/m_2)^{1/2} = \gamma_E(\infty) (1+m_2/m_1)^{-1/2} \quad (1)$$

where $\Gamma_{12} \sim (1/\mu)^{1/2}$ has been used. In order to obtain a better estimate of the mass dependence of the friction coefficient, higher order correlations in the infinite-mass fluctuating force must be calculated (10,11).

m_1/m_2	$V/V_0 = 3.0$		$V/V_0 = 1.6$	
	D/D_E	γ/γ_H^c	D/D_E	γ/γ_H^c
0.01	0.39 ₁	0.26 ₁	0.14 ₁	0.44 ₃
0.10	0.82 ₂	0.37 ₁	0.40 ₂	0.47 ₂
0.25	1.07 ₂	0.42 ₁	0.56 ₂	0.49 ₂
1.00	1.34 ₁	0.53 ₁	0.84 ₁	0.52 ₁
4.00	1.51 ₅	0.57 ₂	0.95 ₃	0.58 ₂
∞	1.66 ₄	0.58 ₄	1.04 ₃	0.60 ₄

Table III-2

The mass dependence of the friction coefficient of a hard-sphere particle of the same size as the fluid particles using slip boundary conditions at two liquid densities.^{a,b}

- a) The first four entries were taken from reference (33), and the fifth entry was taken from reference (32).
- b) The subscripts on the entries indicate the error in the last figure.
- c) $\gamma_H = 4\pi\eta\sigma_{12}$, where η is the shear viscosity.

Figure 10

The friction coefficient relative to $\gamma_H = 4\pi\eta\sigma_{12}$ as a function of the inverse mass ratio at two fluid densities for test particles which are the same size as the fluid particles.

The higher order force correlations take into account streaming of the fluid past the moving finite-mass particle. A further study of these higher order correlations is of interest because they can also account for the effect of the center-of-mass drift velocity on the infinite-mass friction coefficient.

Figure 11 shows the time dependent friction coefficient, $\gamma(t)$, relative to its initial value, γ_E , at $V/V_0 = 3$ and a series of size ratios: circles, $\sigma_1/\sigma_2 = 1$; triangles, $\sigma_1/\sigma_2 = 2$; squares, $\sigma_1/\sigma_2 = 3$. The solid circles and triangles are for 500 particles and the open triangles and squares are for 2048 particles. The molecular boundary conditions are specular except for the crosses in the figure which represent the results of a 500 particle system at the same density using diffusive boundary conditions on the test particle surface with $\sigma_1/\sigma_2 = 2$. The $1/N$ correction has not been applied to these results. A numerical table of these data points can be found in Appendix E2. As Fig. 11 shows, γ/γ_E becomes smaller as the size of the test particle is made larger. This is due to the strong dependence of γ_E on the size of the test particle, rather than a smaller friction coefficient. The effect of diffusive boundary conditions is seen to increase the value of the friction coefficient over the value obtained using specular boundary conditions as seen in the figure.

Table 3 gives the infinite-mass friction coefficient as a function of the size ratio σ_1/σ_2 at two liquid densities. The entries for $\sigma_1/\sigma_2 = \infty$ are the hydrodynamic results. The subscripts s,D on the friction coefficients correspond to the specular (slip) and diffusive (stick) boundary conditions respectively. Table 3 suggests that the size dependence of the friction coefficient is nearly independent of the density. If the hydrodynamic picture is to be maintained, then the deviation from Stokes'

Figure 11

The time dependent friction coefficient relative to its initial value at $V/V_0 = 3.0$ and a series of size ratios.

σ_1/σ_2	$V/V_0 = 3.0$		$V/V_0 = 1.6$	
	$\gamma_S/\gamma_H^{b,c}$	γ_D/γ_S^b	$\gamma_S/\gamma_H^{b,c}$	γ_D/γ_S^b
1	0.58 ₄ (0.10 ₂)		0.60 ₄ (0.06 ₂)	
2	0.65 ₄ (0.23 ₂)	1.23 ₆	0.78 ₄ (0.19 ₂)	1.20 ₅
3	0.75 ₅ (0.30 ₃)	1.40 ₅	0.82 ₄ (0.27 ₂)	1.43 ₉
4			0.87 ₅ (0.57 ₃)	
∞	1	1.5	1	1.5

Table III-3

The size dependence of the infinite-mass friction coefficient of a hard-sphere particle at two fluid densities.^a

- The subscripts on the entries indicate the error in the last figure.
- $\gamma_H = 4\pi\eta\sigma_{12}$, γ_S is the friction coefficient which corresponds to specular scattering, and γ_D is the friction coefficient which corresponds to diffusive scattering.
- The entries in parenthesis are the magnitudes of the hydrodynamic corrections which have been made to the friction coefficients.

law (Table 3) must be accounted for by a wave length dependent viscosity. This leads to a simple picture of the size dependence of the friction coefficient in terms of generalized hydrodynamics, in which the k_z -component of the stress at position $\vec{r}$ at time t is

$$S_k(\vec{r}, t) = \sum_{m,n} \int d^3r' \int_0^t dt' \phi_{k\ell mn}(\vec{r}-\vec{r}', t-t') \dot{e}_{mn}(\vec{r}, t') \quad , \quad (2)$$

where $\phi_{k\ell mn}(r, t)$ is a memory function and $\dot{e}_{mn}(r, t)$ are the components of the strain rate tensor. Equation 2 shows that strain rates at a position $\vec{r}'$ at time t' affect the stress at a later time t at position $\vec{r}$. The memory function is equal to the correlation function of the fluctuating part of the stress tensor:

$$\langle R_{k\ell}(\vec{r}, t) R_{mn}(\vec{r}', t') \rangle = k_B T \phi_{k\ell mn}(\vec{r}-\vec{r}', t-t') \quad , \quad (3)$$

where $R_{k\ell}(\vec{r}, t)$ is the fluctuating component of the stress tensor. If the $R_{k\ell}$ are uncorrelated at different positions and time, then the memory function reduces to (7):

$$\phi(\vec{r}-\vec{r}', t-t') = 2 [\eta(\delta_{km}\delta_{\ell n} + \delta_{kn}\delta_{\ell m}) + (\zeta - 2/3\eta)\delta_{k\ell}\delta_{mn}] \delta(\vec{r}-\vec{r}') \delta(t-t') \quad , \quad (4)$$

where η is the shear viscosity and ζ is the bulk viscosity. Here $\phi_{k\ell mn}$ is defined in such a way that

$$\int d^3\vec{r} \int_{-\infty}^{\infty} dt \phi_{k\ell mn}(\vec{r}, t) = 2\eta(\delta_{km}\delta_{\ell n} + \delta_{kn}\delta_{\ell m}) + 2(\zeta - \frac{2}{3}\eta)\delta_{k\ell}\delta_{mn} \quad (5)$$

If Eq. 4 is substituted into Eq. 2 and the definition of the strain rate is used, Eq. E1.3, then

$$S_{k\ell}(\vec{r}, t) = n[\partial_k v_\ell(\vec{r}, t) + \partial_\ell v_k(\vec{r}, t)] + (c-2/3n)\delta_{k\ell}\nabla\cdot\mathbf{v}(\vec{r}, t) \quad , \quad (6)$$

which is the usual definition of the stress tensor (7).

In general $R_{k\ell}(\vec{r}, t)$ is correlated with itself at another point in space or time on a molecular scale. Equation 2 should, therefore, be used to calculate the drag on a small sphere moving through a fluid rather than Eq. 6. The steady state drag is found by integrating the normal component of the stress tensor over the surface of the sphere and setting $t = \infty$:

$$\begin{aligned} F_k &= \sum_{\ell} \int S_{k\ell}(\vec{r}, \infty) n_{\ell}(\vec{r}) ds \\ &= \sum_{\ell, m, n} \int ds \int d^3\vec{r}' n_{\ell}(\vec{r}) \Omega_{k\ell mn}(\vec{r}-\vec{r}') \dot{e}_{mn}(\vec{r}') \quad , \quad (7) \end{aligned}$$

where $\Omega_{k\ell mn}(\vec{r}) = \int_0^{\infty} \phi_{k\ell mn}(\vec{r}, t) dt$, n_{ℓ} is the ℓ th component of the unit

normal to the surface of the sphere and the surface integral, ds , is over the surface of the sphere. Since a steady state solution is wanted, $\dot{\rho} = 0$ everywhere in the fluid, and the incompressible approximation can be made. This eliminates the dependence of $\Omega_{k\ell mn}$ on the bulk viscosity. Rather than solve the generalized hydrodynamic equations directly, an approximation sufficient for present purposes will be made: choose for the strain rate the angular averaged strain rate which results from the Stokes solution to the drag problem. Along the direction of motion of the sphere, the strain rate (including the pressure term) is (7):

$$\left[\frac{9}{2} \frac{R}{r^2} \cos^2\theta + \frac{3}{2} \frac{R^3}{r^4} (\sin^2\theta - 2 \cos^2\theta) \right] u \quad , \quad (8)$$

where u is the constant velocity of the sphere. The angular average of this expression over the solid angle 4π is

$$\frac{3}{2} \frac{R}{r^2} u \quad (9)$$

Equation 7 is, therefore, replaced by the simpler expression

$$F = \int ds \int d^3\vec{r}' \hat{n}(\vec{r}) \cdot \hat{n}(\vec{r}') \Lambda(\vec{r}-\vec{r}') \frac{2A\sigma_{12}}{r'^2} u \quad (10)$$

where A is a proportionality constant. The function $\Lambda(r)$ gives the spatial dependence of the shear viscosity. In fact $\eta = \int d^3\vec{r} \Lambda(\vec{r})$.

In order to reduce the integral further, the function $\Lambda(r)$ is expanded by a Fourier integral:

$$\Lambda(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3k \eta(\vec{k}) e^{i\vec{k} \cdot \vec{r}} \quad (11)$$

When expression 11 is placed in Eq. 10, the angular integrals can be performed:

$$F = 16A\sigma_{12}^3 \int_0^\infty k^2 dk \int_{\sigma_{12}}^\infty dr' \eta(k) j_1(k\sigma_{12}) j_1(kr') u \quad (12)$$

where the $j_1(x)$ are spherical Bessel functions of the first kind (34).

Performing the r' integration yields:

$$\gamma(\sigma_{12}) = \frac{F}{u} = 8\pi A\sigma_{12} \int_0^\infty j_{3/2}(x) j_{3/2}(x) \eta\left(\frac{x}{\sigma_{12}}\right) dx \quad (13)$$

where the ordinary Bessel functions of fractional order have been substituted for the spherical functions:

$j_n(x) = \sqrt{\frac{\pi}{2x}} J_{n+1/2}(x)$. For $\sigma_{12} = \infty$, the wave number dependent viscosity becomes the ordinary viscosity and factors out of the integral. The remaining integration can be performed with the result: $\gamma = 4\pi A \sigma_{12} \eta(0)$. In order to make contact with the hydrodynamics results, the proportionality constant $A = 1$ for slip and $A = 3/2$ for stick boundary conditions.

For σ_{12} finite, the viscosity can no longer be factored from Eq. 13. A simple assumption about the wave number dependence of the viscosity can be made:

$$\eta(k) = \eta(0)/(1+a^2k^2) \quad , \quad (14)$$

where a is a constant. Substitution of Eq. 14 into Eq. 13, allows the integral to be performed (35):

$$\frac{\gamma(\sigma_{12})}{4\pi A \eta \sigma_{12}} = 1 - \frac{a}{\sigma_{12}} + \left(1 + \frac{a}{\sigma_{12}}\right) \exp\left(-2\frac{\sigma_{12}}{a}\right) \sim 1 - \frac{a}{\sigma_{12}} \quad . \quad (15)$$

Eq. 15 is independent of the boundary conditions at the surface of the sphere because of the simple approximation used for the strain rate, Eq. 9. At present the wave number dependence of the hard sphere viscosity can only be estimated in the Enskog approximation. This is easily done by considering the transverse current correlation function:

$$C_t(k, t) = \sum_{\ell, m=1}^N \langle \vec{k} \times \vec{v}_\ell(t) \cdot \vec{k} \times \vec{v}_m(0) \exp[i\vec{k} \cdot (\vec{r}_\ell(t) - \vec{r}_m(0))] \rangle \quad . \quad (16)$$

The function satisfies a differential equation which is non-local in time (36,37):

$$\frac{\partial C_t(k,t)}{\partial t} = -k^2 \int_0^t \dot{v}(k,t-t') C_t(k,t') dt' \quad (17)$$

The integral of the memory function, $\int_0^\infty \dot{v}(k,t) dt = v(k)$, is the wave dependent kinematic viscosity. As shown before (20), $\dot{v}(k,t)$ has an initial delta function part, $v_1(k)\delta(t)$, and a slowly decaying part, $\dot{v}_2(k,t)$. The initial part may be factored from the integral:

$$\frac{\partial C_t(k,t)}{\partial t} = -k^2 v_1(k) C_t(k,t) - k^2 \int_0^t \dot{v}_2(k,t-t') C_t(k,t') dt' \quad (18)$$

In the limit that $t \rightarrow 0$, Eq. 18 gives:

$$\frac{\dot{C}_t(k,0)}{C_t(k,0)} = -k^2 v_1(k) \quad (19)$$

$v_1(k)$ represents the initial value of the viscosity due to the impulsive change in momentum which hard-sphere particles experience upon collision. As such it may be calculated by kinetic theory. Differentiating Eq. 16 with respect to time, and using the fact that all odd powers of velocity average to zero, the initial slope of $C_t(k,t)$ can be written:

$$\dot{C}_t(k,0) = \sum_{\ell,q} \langle kx \dot{v}_\ell(0) \cdot kx v_q(0) \exp[ik \cdot (r_\ell - r_q)] \rangle \quad (20)$$

After substitution of $\dot{v}_\ell(0) = \sum_{m,c} \Delta v_{\ell m} \delta(t-t_c)$, where $\Delta v_{\ell m}$ is the velocity change of particle ℓ when it colides with particle m and the sum is over all particle collisions, the ensemble average reduces to an average over the collision rate. The result is

$$\frac{\dot{C}_t(k,0)}{C_t(k,0)} = -\frac{\Gamma}{2} \int_{-1}^1 (1-y^2)(1-\cos k\sigma y) dy = -\frac{2}{3} \Gamma \left[1 - 3 \frac{j_1(k\sigma)}{k\sigma} \right], \quad (21)$$

where Γ is the collision rate, σ is the diameter of a fluid particle, and $j_1(k\sigma)$ is the spherical Bessel function of order one. Equation 21 can be written for small $k\sigma$

$$\frac{\dot{C}_t(k,0)}{C_t(k,0)} = -k^2 v_1(k) \sim -k^2 \frac{v_1(0)}{1 + \frac{1}{28} (k\sigma)^2}, \quad (22)$$

where $v_1(0) = \Gamma\sigma^2/15$. As a further approximation, the wave number dependence of the other contributions to the viscosity (eg. the kinetic term) is assumed to be identical to Eq. 22, namely,

$$\eta(k) = \frac{\eta(0)}{1 + \frac{1}{28} (k\sigma)^2}. \quad (23)$$

This gives $a^2 = \sigma_2^2/28$ or $a \sim 0.189 \sigma_2$. Figure 12 shows the results listed in Table 3. The circles are for $V/V_0 = 3.0$ and the triangles are for $V/V_0 = 1.6$. The solid circles and triangles are for slip boundary conditions and the open circles and triangles are for stick boundary conditions. The upper and lower dashed lines were drawn for emphasis from the hydrodynamic solutions (1.0 for slip and 1.5 for stick) through the corresponding data points. The short solid lines, which intersect the ordinate at the hydrodynamic solutions, represent Eq. 15 with $a = 0.189 \sigma_2$. The molecular dynamics results are consistent with a linear dependence on σ_2/σ_{12} , as predicted by Eq. 15, although the coefficient a , which was

Figure 12

The size dependence of the infinite-mass friction coefficient of a hard-sphere particle at two fluid densities and three different boundary conditions.

derived by a simple kinetic argument, is too small. A more accurate determination of this coefficient must await an evaluation of the wave dependent viscosity by molecular dynamics. As seen in Fig. 12, the molecular dynamics results which correspond to specular scattering on the surface of the test particle (a smooth surface) are consistent with the slip hydrodynamic boundary condition, and the diffusive scattering results (a rough surface) are consistent with the stick boundary condition. Therefore, a correspondence between the hydrodynamic boundary conditions and the molecular scattering properties of the surface has been established.

The roughness of the surface of a large molecule is due to the particulate structure of the molecule. The question is: how does the friction coefficient of a large spherical molecule, which is made up of smaller smooth spherical molecules, compare with the friction coefficients of perfectly smooth and perfectly rough hard spheres of the same radius? To answer this question the friction coefficient of a spherical aggregate particle, composed of smaller smooth hard spheres, was calculated. The size of the particles in the aggregate is the same as the size of the fluid particles. The aggregate particle is ~~generated~~ by freezing some particles in a dense fluid whose centers are less than or equal to the distance $\sigma_1/2$ from the origin. Then the friction coefficient is calculated as for the solid hard sphere. In order to average out the irregular shape of the aggregate, periodically a new aggregate is generated and the process is repeated. In this way the average volume of the aggregate is $\frac{4}{3} \pi (\sigma_1/2)^3$ so the average diameter is σ_1 . Table 4 presents the results of three runs in a dense fluid at $V/V_0 = 1.6$ for an aggregate particle. The first column lists the ratio of the average diameter of the aggregate to the diameter of the fluid particles. The second column gives the ratio of

σ_1/σ_2	$\Gamma_{12}^A/\Gamma_{12}^{S^{a,b}}$	$\gamma^A/4\pi\eta\sigma_{12}$
2	1.00 ₁	0.77 ₄
3	1.16 ₁	0.93 ₄
4	1.26 ₁	0.98 ₄

Table III-4

The ratio of collision rate of an aggregate particle and hard-sphere particle of the same average radius at $V/V_0 = 1.16$ for a series of size ratios and the friction coefficient of the aggregate particle.

- a) The superscript "A" denotes the aggregate particle and the superscript "S" denotes the hard sphere.
- b) The estimated error in the last figure is indicated by a subscript.

the collision rate of the aggregate particle with the fluid particles and the collision rate of an equivalent sphere with the fluid particles. As seen in Table 4, the collision rate of the two larger aggregate particles is greater than the collision rate of an equivalent sphere. This is due to the convoluted surface of the aggregate which results in a larger surface area compared to the surface area of an equivalent sphere. As the table shows, the effect becomes larger as the size ratio increases. Figure 13 shows the time dependent friction coefficient, $\gamma(t)$, relative to $4\pi\eta\sigma_{12}$ at a density which corresponds to $V/V_0 = 1.6$ for a smooth hard sphere of diameter $\sigma_1 = 4\sigma_2$ (circles) and an aggregate particle of average diameter equal to σ_1 (triangles). The $1/N$ correction has been applied to these results. As Fig. 13 indicates, the friction coefficient is larger for the aggregate particle than for the smooth particle. The initial values are larger because the collision rate is larger for the aggregate particle. Table 4 lists the results after extrapolation to infinite time based on the hydrodynamic theory. The points are also plotted in Fig. 12 (crosses). As seen in the figure, the friction coefficient for the aggregate particle is midway between the friction coefficients for slip and stick boundary conditions. The middle dashed line in the figure was drawn through the data points and intersects the ordinate (infinite radius) at 1.25 ± 0.10 . This is equivalent to a Stokes proportionality constant of $(5.0 \pm 0.4)\pi$ as compared to 4π for slip or 6π for stick boundary conditions.

Figure 13

The time dependent friction coefficient for a smooth hard sphere of diameter $\sigma_1 = 4\sigma_2$ (circles) and an aggregate particle of average diameter equal to σ_1 (triangles) at a density which corresponds to $V/V_0 = 1.6$.

D. Summary

This chapter presents for the first time a molecular dynamics method for the evaluation of the friction coefficient of hard-sphere particles, which allows a direct study of the size dependence of the friction coefficient and the dependence of the friction coefficient on the molecular boundary conditions. It is found that the Stokes result is valid only in the limit that the fixed test particle is infinite in size. Furthermore, the data are consistent with the hypothesis that the specular scattering molecular boundary condition correspond to the hydrodynamic slip condition at the surface of the sphere, and the diffusive scattering condition corresponds to the hydrodynamic stick condition at the surface of the sphere. More importantly, the friction coefficient of a spherical aggregate particle, which is made up of smooth hard spheres equal in size to the fluid particles, corresponds to the friction coefficient of a hard sphere of the same average radius, but with a surface boundary condition which is midway between the hydrodynamic slip and stick boundary conditions. The molecular boundary conditions of the aggregate particle are somewhere between the specular and diffusive scattering conditions. It is, therefore, of interest to study how the friction coefficient of the aggregate particle is affected if the size of the particles in the aggregate is different than the size of the fluid particles, so the degree of roughness of the surface can be controlled. This experiment is planned in the near future and should lead to a correspondence between the degree of roughness of the surface and the relative size of the particles in the aggregate with those in the fluid. Finally, a simple application of generalized hydrodynamics has shown that the size dependence of the friction coefficient is determined by the wave-length dependence of the shear viscosity. A comparison is

made with the molecular dynamics results using a simple model for the wavelength dependence of the viscosity. It is found to qualitatively explain the size dependence. A more accurate comparison must follow from detailed molecular dynamics evaluations of the wavelength dependence of the viscosity, and a more accurate derivation of the strain rate.

E. Appendix

1. The Time Dependent Friction Coefficient of a Disk

Here the method of induced forces (27,28,29) is used to derive the time dependent friction on a disk moving in an incompressible fluid. The objective is to get an expression for the force on the disk which involves only the parameters $\vec{u}$, R , η , ρ , t , where $\vec{u}$ is the velocity of the disk of radius R in the incompressible fluid of viscosity η and density ρ at time t . This is accomplished by taking averages of the formal solution for the velocity field over the edge of the disk, and over the area of the disk. Then, using these results in the averages of the boundary conditions yields two equations in two unknowns: one unknown is the drag, the other is eliminated. Many of the details of the derivation are left out, since they may be reproduced by following the steps outlined in the literature (27,28,29).

A macroscopic disk of radius R is immersed in a viscous, incompressible two-dimensional fluid. The motion of the fluid is described by the linearized Navier-Stokes equation:

$$\rho \frac{\partial \vec{v}(r,t)}{\partial t} = - \vec{\nabla} \cdot \vec{S} + \vec{F}_{\text{ind}}(r,t) \quad , \quad (1a)$$

together with

$$\vec{\nabla} \cdot \vec{v} = 0 \quad , \quad (1b)$$

where the stress tensor is given by

$$S_{kl} = P \delta_{kl} - 2\eta \dot{e}_{kl} \quad , \quad (2)$$

and

$$\dot{\epsilon}_{k\ell} = \frac{1}{2} \left(\frac{\partial v_k}{\partial x_\ell} + \frac{\partial v_\ell}{\partial x_k} \right) \quad (3)$$

is the strain rate tensor. Finally, $\vec{F}_{\text{ind}}(r, t)$ is the induced force density. This force density allows the fluid fields inside the disk, if the proper conditions are satisfied: the boundary conditions must remain valid if the edge of the disk is approached from outside.

If $\hat{n}$ is the unit normal pointing away from the edge of the disk, and $\vec{u}(t)$ is the velocity of the disk, then the boundary conditions are

$$\hat{n} \cdot \vec{v}(R, t) = \hat{n} \cdot \vec{u}(t) \quad , \quad (4a)$$

that is, the normal component of the fluid velocity is the same as the normal component of the disk's velocity. Also

$$(1 - \hat{n}\hat{n}) \cdot [\vec{v}(R, t) - 2\lambda \vec{e}(R, t) \cdot \hat{n}] = (1 - \hat{n}\hat{n}) \cdot \vec{u}(t) \quad , \quad (4b)$$

where $\lambda = \infty$ for perfect slip and $\lambda = 0$ for perfect stick. When $\lambda = 0$ the stick condition expresses that the tangential component of the fluid velocity is the same as the tangential component of the disk's velocity. When $\lambda = \infty$, Eq. 4b shows that the strain rate tensor is zero, which is the slip condition. A condition on the induced force must be made:

$$\vec{F}_{\text{ind}}(r, t) = 0 \quad , \quad r > R \quad . \quad (5)$$

Thus, the induced force only acts in the interior of the disk.

Equations 1 can be solved formally by Laplace transformation:

$$\nabla^2 \vec{V}(r,s) - q^2 \vec{V}(r,s) = \frac{1}{\eta} \vec{\nabla} P - \frac{1}{\eta} \vec{F}_{ind}(r,s) \quad (6)$$

where $q^2 = s\rho/\eta = s/\nu$ and s is the Laplace variable. Since $\vec{\nabla} \cdot \vec{V} = 0$,

$$\nabla^2 P = \nabla \cdot \vec{F}_{ind} \quad (7)$$

follows from Eq. 6 by taking the divergence.

The method of solution of Eqs. 6,7 is by Green's function. The Green's function satisfies

$$\nabla^2 G(r,s) - q^2 G(r,s) = -\delta(r) \quad (8)$$

The solutions are

$$G(r-r',s) = \frac{1}{2\pi} K_0(qR) \quad , \quad (9a)$$

$$G(r-r',0) = -\frac{1}{2\pi} \ln(R) \quad , \quad (9b)$$

where $R^2 = r^2 + r'^2 - 2rr'\cos(\theta-\theta')$ and $K_0(x)$ is the modified Bessel function of order zero (34).

After some algebra, the solution may be written in the form (27,28,29)

$$\vec{V}(r,s) = \frac{1}{\eta} \int \left\{ G(r-r',s) + \frac{1}{q^2} \vec{\nabla}' \cdot \vec{\nabla}' [G(r-r',0) - G(r-r',s)] \right\} \cdot \vec{F}_{ind}(r',s) d\sigma' \quad , \quad (10)$$

where the integral is over the surface area of the disk. Thus, the induced force completely determines the time dependent velocity field.

The force exerted on the disk by the fluid is

$$\vec{F}_D(t) = - \int_{r \leq R} \vec{S}(r,t) \cdot \hat{n} \, d\ell = - \int_{r \leq R} \vec{v} \cdot \vec{S} \, d\sigma \quad (11)$$

Equation 1a is substituted for the divergence of the stress tensor:

$$\vec{F}_D(t) = \int \left(\rho \frac{\partial \vec{v}}{\partial t} - \vec{F}_{ind} \right) d\sigma \quad (12)$$

By Laplace transforming and by using Gauss's theorem in two dimensions with the boundary condition 4a, there results:

$$\vec{F}_D(s) = \rho s (\pi R^2) \vec{u}(s) - \int \vec{F}_{ind}(r,s) \, d\sigma \quad (13)$$

In order to average the velocity field over the edge and surface of the disk, the edge and surface averages of the Green's functions, Eqs. 9, must be obtained. The following averages are performed:

$$\bar{G}^L = \frac{1}{2\pi} \int_0^{2\pi} G(r-r',s) \, d\theta \quad (14)$$

$$\bar{G}^S = \frac{1}{\pi R^2} \int_0^R r \, dr \int_0^{2\pi} G(r-r',s) \, d\theta = \frac{2}{R^2} \int_0^R \bar{G}^L r \, dr. \quad (15)$$

Using Eqs. 9 the following averages result:

$$2\pi \bar{G}^L(r-r',s) = I_0(qr') K_0(qr) \quad , \quad r' < r \quad (16a)$$

$$2\pi \bar{G}^L(r-r',0) = -\ln r \quad , \quad r' < r \quad (16b)$$

$$\pi R^2 \bar{G}^S(r-r', s) = \frac{1}{q^2} - \frac{R}{q^2} I_0(qr') K_1(qR) \quad , \quad r' < R \quad (16c)$$

$$\pi R^2 \bar{G}^S(r-r', 0) = \frac{1}{4}(R^2 - r'^2) - \frac{1}{2}R^2 \ln R \quad , \quad r' < R \quad , \quad (16d)$$

where $I_n(x)$, $K_n(x)$ are modified Bessel functions of order n (34).

The averages of the velocity field over the edge and surface of the disk can now be performed:

$$2\pi \bar{V}^L(r) = \frac{1}{\eta} K_0(qr) \vec{B}(q, s) \quad , \quad r > R \quad (17a)$$

$$\pi R^2 \bar{V}^S = \frac{1}{2\eta q^2} \int \vec{F}_{ind} d\sigma - \frac{1}{\eta} \frac{R}{q} K_1(qR) \vec{B}(q, s) \quad , \quad (17b)$$

$$\text{where } \vec{B}(q, s) = \int \vec{F}_{ind}(r', s) \cdot \left(\vec{I} - \frac{1}{q^2} \vec{\nabla}' \cdot \vec{\nabla}' \right) I_0(qr') d\sigma' \quad .$$

The next step is to average the boundary conditions over the edge and surface of the disk. Then the results of these averages will be combined with Eqs. 17. The derivation of the averages of the boundary conditions is tedious and will not be produced here. The results follow from the techniques used in the literature for the three dimensional friction coefficient (27,28,29):

$$\overline{v(r, s)}^S = \vec{u}(s) \quad (18a)$$

$$\left(1 + \frac{2\lambda}{R} \right) \bar{v}^L - \lambda \left. \frac{\partial}{\partial r} \overline{v(r)}^L \right|_{r=R} = \left(1 + \frac{2\lambda}{R} \right) \vec{u}(s) \quad . \quad (18b)$$

By combining the averages for the velocity fields, Eqs. 17, with the averages of the boundary conditions, Eqs. 18, two equations result:

$$\pi R^2 \vec{u}(s) = \frac{1}{2\eta q^2} \int \vec{F}_{\text{ind}} d\sigma - \frac{1}{\eta} \frac{R}{q} K_1(qR) \vec{B}(q,s) \quad , \quad (19a)$$

$$2\pi \left(1 + \frac{2\lambda}{R}\right) \vec{u}(s) = \left(1 + \frac{2\lambda}{R}\right) \frac{1}{\eta} K_0(qR) \vec{B}(q,s) + \frac{\lambda}{\eta} q K_1(qR) \vec{B}(q,s) \quad . \quad (19b)$$

The function $\vec{B}(q,s)$ can be eliminated between the two equations. An equation for $\int \vec{F}_{\text{ind}} d\sigma$ results which is used in Eq. 13 for the drag:

$$\vec{F}_D(s) = - \tilde{\phi}(s) \vec{u}(s) \quad , \quad (20)$$

where

$$\tilde{\phi}(s) = (\pi R^2) \rho s + \frac{8\pi \eta x s^{\frac{3}{2}} K_1(2xs^{\frac{1}{2}})}{K_0(2xs^{\frac{1}{2}}) + \alpha x s^{\frac{3}{2}} K_1(2xs^{\frac{1}{2}})} \quad , \quad (21)$$

and $x^2 = R^2/4\nu$, $\alpha = 2\lambda/(R+2\lambda) = 0$ or 1 for stick or slip boundary conditions respectively.

The function $\tilde{\phi}(s)$ is the Laplace transform of the time dependent memory function. In order to obtain the time dependent friction coefficient, $\gamma(t)$, the inverse Laplace transform of $\tilde{\phi}(s)/s$ must be performed:

$$\gamma(t) = \frac{1}{2\pi i} \int_{\epsilon-i\infty}^{\epsilon+i\infty} e^{st} \frac{ds}{s} \tilde{\phi}(s) = (\pi R^2) \rho \delta(t) + \gamma_{>}(t) \quad , \quad (22)$$

where $\gamma_{>}(t)$ is the inverse Laplace transform of the Bessel function part of Eq. 21 divided by s . The inverse Laplace transform may be transformed into a real integral by integration around the contour indicated in Fig. 14.

Figure 14

The contour which is used to convert the inverse Laplace transform into a real integral.

The result:

$$\gamma_z(t) = \frac{8\eta}{\pi} \int_0^{\infty} \frac{e^{-zs}}{s} \frac{ds}{[J_0(2s^{1/2}) + \alpha s^{1/2} J_1(2s^{1/2})]^2 + [\gamma_0(2s^{1/2}) + \alpha s^{1/2} \gamma_1(2s^{1/2})]^2}, \quad (23)$$

where $z = x^2/t = R^2/4vt$ and $J_n(x)$, $\gamma_n(x)$ are the ordinary Bessel functions of order n (34).

Equation 23 was evaluated on the computer numerically using care about the origin, where the integrand has an integrable singularity.

The long-time asymptotic form of Eq. 22 can be determined from the small s asymptotic form of Eq. 21 (38). Using the small argument expansions of the Bessel functions (34), Eq. 21 becomes for small s

$$\tilde{\phi}(s) \sim \frac{-8\pi\eta}{\ln\left(\frac{R^2 s}{4v}\right)}, \quad (24)$$

which may be inverted asymptotically (38) to give for large t

$$\dot{\phi}(t) \sim -\frac{8\pi\eta}{t \ln^2\left(\frac{4vt}{R^2}\right)}. \quad (25)$$

This is seen to be the derivative of

$$\gamma(t) \sim \frac{8\pi\eta}{\ln\left(\frac{4vt}{R^2}\right)}, \quad (26)$$

which should be compared with Eq. B4.1.

The Einstein relation gives:

$$D(t) = k_B T / \gamma(t) \sim \frac{k_B T}{8\pi\eta} \ln\left(\frac{4vt}{R^2}\right). \quad (27)$$

The derivative of Eq. 27 gives the asymptotic velocity autocorrelation function:

$$C(t) = \dot{D}(t) \sim \frac{k_B T}{8\pi\eta t} \quad (28)$$

which agrees with earlier results (23,24,25).

2. Tables

This appendix contains some molecular dynamics results for the time dependent infinite-mass friction coefficient at two fluid densities and various size ratios. The $1/N$ correction has not been made, therefore, Table A-1 gives the ratio of collision rates which are needed in Eq. B3.7. To obtain the correction for the aggregate particle friction coefficients the ratios in Table A-1 must be multiplied by the corresponding entries in Table III-4 before being used in Eq. B3.7.

σ_1/σ_2	$V/V_0 = 3.0$	$V/V_0 = 1.6$
	Γ_{12}/Γ_{22}	Γ_{12}/Γ_{22}
1	$1/\sqrt{2}$	$1/\sqrt{2}$
2	1.83_2	2.05_2
3	3.47_3	4.17_3
4		6.98_3

Table III A-1

The ratio of the collision rate of an infinite mass hard sphere particle of diameter σ_1 and the collision rate of the bath particles of diameter σ_2 as a function of the ratio of diameters at two fluid densities.^a

- a) The error in the last figure is indicated by the subscript on the entry.

t_c	γ_s/γ_E	γ_D/γ_E
0	1.000 ₅	1.000 ₅
1	0.899	0.948
2	0.824	0.896
3	0.758	0.847
4	0.722	0.808
5	0.697	0.787
6	0.665	0.759
7	0.640	0.740
8	0.628	0.720
9	0.628	0.714
10	0.611	0.704
11	0.599	0.691
12	0.595	0.687
13	0.590	0.684
14	0.585	0.675
15	0.587	0.665

Table III A-2

The time dependent friction coefficient at $V/V_0 = 3$ and a size ratio $\sigma_1/\sigma_2 = 2$ for specular, γ_s , and diffusive, γ_D , scattering and 499 fluid particles.^a

- a) The subscript on the first entry indicates the error in the last figure which is to be applied to all entries below it.

t_c	γ_s/γ_E	t_c	γ_s/γ_E
0	1.00 ₂	16	0.55
1	0.88	17	0.55
2	0.80	18	0.55
3	0.73	19	0.55
4	0.69	20	0.55
5	0.66	21	0.55
6	0.64	22	0.55
7	0.63	23	0.55
8	0.61	24	0.53
9	0.59	25	0.54
10	0.58	26	0.54
11	0.58	27	0.54
12	0.58	28	0.54
13	0.57	29	0.54
14	0.57	30	0.54
15	0.56		

Table III A-3

Same as Table A-2 except for 3999 fluid particles and specular scattering only.

N = 2047		N = 1371	
t_c	γ_s/γ_E	t_c	γ_D/γ_E
0	1.00 ₄	0	1.00 ₄
1	0.87	1	0.97
2	0.76	2	0.91
3	0.69	3	0.88
4	0.63	4	0.86
5	0.57	5	0.83
6	0.54	6	0.83
7	0.51	7	0.80
8	0.48	8	0.80
9	0.43	9	0.78
10	0.45	10	0.78
11	0.40	11	0.79
12	0.41	12	0.78
13	0.40	13	0.79
14	0.37	14	0.78
15	0.38	15	0.77
16	0.39	16	0.75
17	0.39	17	0.75
18	0.36	18	0.75
19	0.38	19	0.73

Table III A-4

Same as Table A-2 except for $\sigma_1/\sigma_2 = 3$. The number of fluid particles is indicated above the column heading.

N = 1371		N = 1371		N = 2044	
t_c	γ^S/γ_E	t_c	γ^D/γ_E	t_c	γ^A/γ_E
0	1.00 ₃	0	1.00 ₃	0	1.00 ₂
1	0.94	1	1.01	1	0.95
2	0.91	2	1.02	2	0.92
3	0.89	3	1.02	3	0.90
4	0.86	4	1.01	4	0.89
5	0.85	5	1.02	5	0.89
6	0.84	6	1.03	6	0.88
7	0.83	7	1.04	7	0.88
8	0.83	8	1.04	8	0.88
9	0.84	9	1.06	9	0.88
10	0.85	10	1.05	10	0.89
11	0.85	11	1.05	11	0.89
12	0.85	12	1.05	12	0.89
13	0.86	13	1.06	13	0.91
14	0.86	14	1.04	14	0.90
15	0.87	15	1.05	15	0.90
16	0.87	16	1.06	16	0.90
17	0.88	17	1.07	17	0.90
18	0.89	18	1.06	18	0.91
19	0.88	19	1.08	19	0.90
20	0.88	20	1.06	20	0.89

Table III A-5

The time-dependent friction coefficient at $V/V_0 = 1.6$ and a size ratio $\sigma_1/\sigma_2 = 2$ for specular, γ_S , diffusive, γ_D , and the aggregate particle, γ_A .

t_c	N = 2047	N = 1360
	γ^S/γ_E	γ^A/γ_D
0	1.00 ₁	1.00 ₁
1	0.93	0.93
2	0.88	0.88
3	0.82	0.86
4	0.80	0.83
5	0.79	0.82
6	0.74	0.81
7	0.74	0.81
8	0.74	0.81
9	0.71	0.80
10	0.71	0.80
11	0.70	0.81
12	0.68	0.80
13	0.69	0.82
14	0.68	0.82
15	0.67	0.81
16	0.66	0.82
17	0.63	0.82
18	0.64	0.81
19	0.65	0.81
20	0.64	0.80

Table III A-6

Same as Table A-5 except for $\sigma_1/\sigma_2 = 3$.

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IV. FLUCTUATION DRIVEN RESONANCE

A. Introduction

Using hydrodynamic language, the continuously occurring fluctuations in temperature and density in a fluid can be considered as a source of sound waves of varying wave number and frequency. If such a system is placed in a small enough cavity, so that the sound waves are not absorbed before they reflect many times from the walls, resonance will occur for those sound waves whose wavelengths are commensurate with the cavity dimensions. These resonant modes are fed at the frequency of the generation rate of the fluctuations and dissipated by the viscous damping mechanism of sound absorption. The problem is entirely analogous to the repeated beating of a drum or a whistle driven by a random air flow.

To observe these fluctuations for normal fluids experimentally presents formidable problems since they occur on a microscopic scale. Thus, the cavity dimensions would have to be of the order of a few molecular diameters or the range of the spatial correlation, as given by the pair distribution function. One could, however, imagine measuring the fluctuating current, for example, in a fused salt system or electrolyte solution placed between closely spaced plates of a capacitor.⁽¹⁾ The inductance of the circuit of which the capacitor is a part could then be tuned to measure the resonance. In an uncharged fluid the resonance of the proper wavelengths density fluctuations could be observed by light scattering experiments parallel to a series of equally spaced parallel plates between which the fluid is located.⁽²⁾ Such an experiment might be feasible near the critical point where fluctuations of the order of the wavelength of light become prominent, so that the spacing between plates could be thousands of molecular diameters.

In computer simulation calculations, the small spacing requirement presents no problem, and the present study was undertaken to see what could be learned from such potential experiments about the fluctuation spectrum. Thinking primarily of the current experiment, the total longitudinal current autocorrelation function, consisting of the sum of commensurate modes, which is called here the drift autocorrelation function, is calculated for a small hard sphere system confined between two parallel walls at two different densities. At equivalent densities the individual mode contributions to the longitudinal current autocorrelation function were calculated, also by molecular dynamics using periodic boundary conditions. The sum of those contributions ought to reproduce the cavity results unless boundary effects in these small systems, such as density gradients near the wall, affect the results. These various longitudinal autocorrelation functions are compared to hydrodynamic predictions in order to find out at what short time and distance scale the continuum picture fails. For the prediction of the very short time behavior, the results of kinetic theory are developed. Finally, the results are transformed to the van Hove scattering function relevant to light scattering experiments. (3,4)

B. Analysis

For the 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, the drift or center of mass velocity was calculated. 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. This drift velocity will only fluctuate in magnitude and sign perpendicular to the wall because only in that

direction is momentum not conserved by collisions, namely those with the walls. The coherence in the drift velocity is then measured by its autocorrelation function

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

where the brackets indicate statistical mechanical averaging over many initial conditions of the drift.

Since only certain modes of the current, namely those that lead to resonance, lead to coherence, the drift autocorrelation function can also be written as

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

The sine modes are selected because they obey the vanishing boundary conditions at the wall. Only the odd modes lead to resonance because they are the only ones that carry a net momentum, or mathematically speaking they have the proper symmetry. The n^2 factor arises because of the amount of momentum carried in each mode, or mathematically speaking that factor leads to the proper normalization of each mode as does the $(4/\pi)^2$ factor in front for the total drift. This drift autocorrelation function in mode summation form is expressible in a physically suggestive way in terms of the perhaps familiar intermediate longitudinal current autocorrelation function, $C_\ell(k,t)$ at wave vector k .

$$C_\ell(k,t) = \sum_{i,j=1}^N \left\langle \dot{x}_i(t) \dot{x}_j(0) e^{ik[x_i(t)-x_j(0)]} \right\rangle .$$

Thus

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

The only reservation to these identities is that the drift must be calculated in a system with walls, while the current autocorrelation functions are usually defined for infinite systems. This difference in boundary conditions has been ignored, and is not expected to lead to significantly different physically measurable results, although small differences might appear at high k values, namely those comparable to the distance over which boundary effects propagate into the fluid.

Indeed, the rigorous calculation by kinetic theory of the short time behavior of both $D(t)$ and $C_{\ell}(t)$ shows up such a small difference. The initial slope of $D(t)$, namely

$$\dot{D}(0) = \langle \ddot{x}_D(0) \dot{x}_D(0) \rangle = -4D(0)\Gamma_w/N$$

requires evaluation of the acceleration of the drift. Since that acceleration is due to wall collisions only, the calculation involves averaging the change of velocity upon wall collisions with the rate at which wall collisions, Γ_w , occur.

$$\Gamma_w = \frac{pA}{k_B T} \left(\frac{k_B T}{2\pi m} \right)^{1/2} ,$$

where p is the pressure, A the total area of the walls, m is the mass, $k_B T$ is the Boltzmann constant multiplied by the temperature and $D(0) = Nk_B T/m$.

On the other hand, the initial slope of the longitudinal current autocorrelation function can be written as

$$\dot{C}_{\ell}(k, 0) = \sum_{i,j=1}^N \langle \dot{k} \ddot{x}_i(0) k \ddot{x}_j(0) \cos k(x_i(0) - x_j(0)) \rangle$$

since the other trigonometric terms vanish, being odd in velocity. The acceleration term this time is the velocity change incurred when two particles collide and the averaging must be carried out over the particle collision rate, Γ . This results in

$$\dot{C}_k(k,0) = -\Gamma N \langle \dot{x}^2 \rangle \int_{-1}^1 k^2 y^2 (1 - \cos k\sigma y) dy \quad ,$$

where the 1 arises from having separated the $i = j$ term from the others, and σ is the hard sphere diameter. This expression must now be summed over all odd modes for $k = n\pi/L$, yielding for the periodic system (subscript p)

$$\dot{D}_p(0) = -D(0)\Gamma\sigma/L \quad ,$$

where $\Gamma = \frac{6y}{\sigma} \left(\frac{k_B T}{m} \right)^{1/2}$ and $y = p v / N k_B T - 1$. Relating these two expressions leads to

$$\dot{D}(0) = \frac{2\sqrt{2}}{3} \frac{1+y}{y} \dot{D}_p(0)$$

which for dense fluids, that is large y values, shows that the two boundary conditions lead to nearly the same initial slopes. The comparison of the initial slopes with molecular dynamics results will be carried out in the next section.

For long times the calculation of $D(t)$ by hydrodynamics ought to be quantitative, at least at small k or long wave lengths. The remarkable validity of hydrodynamics down to nearly molecular time scales has previously been established independent of the k value, for example, for the velocity autocorrelation function.⁽⁶⁾ In this calculation, by discriminating on k as well, it will be possible to evaluate the applicability of hydrodynamics for different wave lengths. The hydrodynamic analysis itself follows what is by

now standard linear fluctuation theory of the Navier-Stokes equation except that here the longitudinal current correlation function is evaluated instead of the usual density correlation function.⁽⁷⁾ Furthermore the expressions have not been linearized in k since the full k dependence is of interest here. Thus

$$\frac{C_\ell(k, t)}{C_\ell(k, 0)} = (1 + K) e^{-Qt} \cos Wt + [ak^2 - Q - R + K(Q - R)] e^{-Qt} \sin(Wt)/W - Ke^{-Rt},$$

where

$$C_\ell(k, 0) = Nk^2 \langle x^2 \rangle \text{ and } K = \frac{R(ak^2 - R)}{(Q-R)^2 + W^2}.$$

R and $Q \pm iW$ are the roots of the cubic

$$\omega^3 + i(a+b)k^2\omega^2 - (c_0^2 + abk^2)k^2\omega - iac_0^2k^4/\gamma = 0$$

representing the thermal decay constant R , the viscous decay constant Q , and the resonance frequency W . To first order in k these expressions reduce to the ones given previously^(7,8), namely

$$R = ak^2/\gamma, \quad Q = \frac{1}{2}(b + a(\gamma-1)/\gamma)k^2, \quad \text{and } W = c_0 k,$$

where a is the thermal conductivity divided by ρc_v , b is $(\kappa + 4\eta/3)/\rho$, and where κ is the bulk viscosity, η is the shear viscosity, $\gamma = C_p/C_v$ (the ratio of the heat capacity at constant pressure to constant volume), $c_0^2 = (\partial p/\partial \rho)_s$, (the sound speed squared), and ρ is the density. The intermediate scattering function $F(k, t)$, whose Fourier transform is the van Hove scattering function $S(k, \omega)$, has been previously obtained in the same notation as⁽⁷⁾

$$\frac{F(k, t)}{F(k, 0)} = Le^{-Rt} + (1-L) e^{-Qt} \cos Wt + [(a+b)k^2 - Q - R + L(R-Q)] e^{-Qt} \sin(Wt)/W,$$

where
$$L = \frac{(M-R)^2 + N^2}{(Q-R)^2 + W^2},$$

$$M = \frac{(a + b) k^2}{2} ,$$

$$\text{and } N^2 = \frac{\gamma - 1}{\gamma} (c_0 k)^2 - \left(\frac{a - b}{2} \right)^2 k^4 .$$

$S(k, \omega)$, will be evaluated by Fourier transforming the molecular dynamics calculation on $C_g(k, t)$, through the identity⁽⁵⁾

$$\omega^2 S(k, \omega) = C_g(k, \omega) .$$

The result will be compared to the hydrodynamic formula in the next section.

C. Results

First of all the properties of the small hard sphere system placed between walls must be established. Figure 1 shows the dimensions of the system and the density profile near the wall at the two different densities investigated. The large value of the density at the wall is due to the one-sided collisions which particles experience near the boundary. This effect is analogous to that which causes the large value of the radial distribution function of two hard spheres at contact in a dense system but is considerably enhanced here. It is also clear from Fig. 1 that the spatial correlations extend, at the higher density, over the entire distance between the walls which is about 6 molecular diameters across, but at the lower density the boundary layer is only about one diameter thick.

Because of the different boundary conditions in different directions, the thermodynamic properties are also anisotropic. This can, for example, be seen in Table I where the pressure parallel and perpendicular to the wall is tabulated. The pressure parallel to the wall

Figure 1

The density distribution normalized by the average density near a wall located at A for $V/V_0 = 1.6$ (solid circles) and a wall located at B for $V/V_0 = 3.0$ (open circles). The vertical line C represents the distance of closest approach to the respective walls (half a diameter) by the center of the sphere, and the vertical line D represents the midpoint between the two parallel walls.

corresponds to the value of the reduced volume of $v/v_0 = 1.6$ and 3.0 , respectively for periodic boundary conditions, where v_0 is the close packed volume if the hard spheres were arranged in a face centered cubic lattice. The pressure perpendicular to the wall is lower than the parallel one due to the lower collision rate between particles in that direction. To this lower pressure corresponds, if the system were in a periodic box, a larger value of v/v_0 called in Table I the effective value. The importance of this effective volume lies in comparisons to be made between systems confined to walls and periodic systems for which the longitudinal current autocorrelation function is calculated. The latter properties must be calculated for a periodic system at the effective v/v_0 so that the thermodynamic and transport properties correspond to that of the system with walls. Hence in Table I all the other properties needed for later calculations are tabulated for the periodic system at the effective values of v/v_0 . This includes the ratio of the constant pressure to constant volume heat capacity C_p/C_v , the isothermal compressibility $-p \left(\frac{\partial v}{\partial p} \right)_T / v$, and the various relaxation decay constants, defined earlier, obtained from the known transport coefficients at the effective density, all normalized by the perpendicular collision rate. Finally the value of $k\sigma$ given corresponds to lowest mode that can be accommodated between the walls, whose wave length is $2L$ or about 12σ , as observed earlier.

Unfortunately, due to technical convenience, the periodic system at the same effective v/v_0 was not run at exactly the same $k\sigma$ values as the wall system requires. The periodic system of 864 particles was chosen to be compared to the 108 particle system with walls since the lowest mode is twice as large in the periodic system than the one with fixed boundaries. It then turns out

Table I

Values for the properties of the system of 108 hard spheres contained
between walls at two densities

v/v_0	$(v/v_0)_{\text{eff}}$	$k\sigma$	$\left(\frac{pv}{NkT}\right)_{\perp}$	$\left(\frac{pv}{NkT}\right)_{\parallel}$	$\Gamma_w/\Gamma_{\perp}$	C_p/C_v	$-\frac{p}{v}\left(\frac{\partial v}{\partial p}\right)_T$	$c_0/\Gamma_{\perp}\sigma$	$W/\Gamma_{\perp}$	$Q/\Gamma_{\perp}$	$R/\Gamma_{\perp}$
1.6	1.94	0.633	6.31	7.03	6.10	2.31	0.312	0.381	0.234	0.0824	0.0453
3.0	3.47	0.513	2.57	2.71	6.84	1.84	0.491	0.585	0.291	0.0788	0.0743

Table II

Values for the properties of the hard sphere system with periodic boundary conditions at two densities

v/v_0	$k\sigma^{(a)}$	W/Γ	Q/Γ	R/Γ
1.94	0.594	0.221	0.0724	0.0405
1.94	1.781	0.565	0.730	0.209
3.47	0.489	0.278	0.0713	0.0674

(a) All $k\sigma$ independent properties are the same as those perpendicular to the wall given in Table I.

to be convenient to choose k values in multiples of 2π that coincide with the periodicity of the system. The k values so determined are however close, as Table II shows, and in as much as the relaxation constants do depend on k , their values are slightly different. The quantitative comparison to the hydrodynamic theory involving those constants is not believed to be significantly affected by these small differences in k .

The results of the molecular dynamic calculation for the drift or center of mass autocorrelation function in the walled system are given in Table III at the two densities investigated and graphed in Figs. 2 and 3. The results of the molecular dynamics calculation for the longitudinal current autocorrelation function for the periodic system at the two effective densities and for the first two modes are given in Table IV and graphed at early times in Fig. 2 and the entire function is given in Fig. 4. The runs were typically 10 million particle collisions long leading to acceptably accurate results as shown in the figures.

Comparison of the molecular dynamic drift velocity autocorrelation function with the lowest mode of the hydrodynamic theory using parameters at the effective v/v_0 values (see Tables I and II) are given in Figs. 2 and 3. They show that, except for the first few mean collision times, the lowest mode predictions are for all practical purposes quantitative out to over 50 mean collision times over which the coherence of the drift velocity lasts. This favorable comparison is not surprising in view of the results given in Fig. 4. The hydrodynamic theory for the longitudinal current autocorrelation function is again seen to be nearly quantitative in comparison to the molecular dynamic results for the lowest mode except at very short times. For the next higher mode, however, the hydrodynamic result differs significantly from the molecular

Table III

The normalized drift autocorrelation function at two densities

$s/\Delta s$ (a)	$v/v_O = 1.6$ (b)	$v/v_O = 3.0$ (b)	$s/\Delta s$	$v/v_O = 1.6$	$v/v_O = 3.0$
0	1.000	1.000	26	0.083	0.035
1	0.796	0.770	27	0.079	-0.002
2	0.618	0.570	28	0.072	-0.031
3	0.457	0.382	29	0.060	-0.055
4	0.307	0.201	30	0.047	-0.072
5	0.167	0.028	31	0.032	-0.080
6	0.038	-0.132	32	0.018	-0.081
7	-0.077	-0.265	33	0.005	-0.076
8	-0.173	-0.363	34	-0.006	-0.065
9	-0.249	-0.420	35	-0.015	-0.050
10	-0.302	-0.436	36	-0.023	-0.034
11	-0.333	-0.415	37	-0.027	-0.020
12	-0.342	-0.365	38	-0.029	-0.006
13	-0.333	-0.292	39	-0.030	0.000
14	-0.308	-0.208	40	-0.030	0.017
15	-0.272	-0.119	41	-0.028	0.025
16	-0.227	-0.035	42	-0.025	0.029
17	-0.178	0.039	43	-0.022	0.029
18	-0.127	0.097	44	-0.019	0.027
19	-0.079	0.139	45	-0.016	0.024
20	-0.035	0.162	46	-0.013	0.019
21	0.003	0.167	47	-0.010	0.013
22	0.033	0.158	48	-0.009	0.006
23	0.057	0.136	49	-0.006	-0.001
24	0.072	0.106	50	-0.003	-0.008
25	0.080	0.072	51	-0.003	-0.013

(a) The time interval is given in terms of multiples of $\Delta s = 0.993$ collision times(b) The statistical error is estimated to be ± 0.015

Figure 2

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.

Figure 3

Same as Fig. 2 except at an effective V/V_0 of 3.47.

Table IV

The normalized intermediate longitudinal current autocorrelation function at two densities and two wavelengths (a)

$s/\Delta s$	$v/v_O = 3.47$ $k\sigma = 0.489$ $\Delta s = 1.013$	$v/v_O = 1.94$ $k\sigma = 0.594$ $\Delta s = 1.100$	$v/v_O = 1.94$ $k\sigma = 1.782$ $\Delta s = 0.550$	$s/\Delta s$	$v/v_O = 3.47$ $k\sigma = 0.489$ $\Delta s = 1.013$	$v/v_O = 1.94$ $k\sigma = 0.594$ $\Delta s = 1.100$
0	1.000	1.000	1.000	26	0.045	0.111
1	0.901	0.892	0.703	27	-0.003	0.092
2	0.730	0.738	0.427	28	-0.045	0.069
3	0.514	0.558	0.198	29	-0.080	0.044
4	0.280	0.367	0.029	30	-0.102	0.020
5	0.051	0.178	-0.086	31	-0.113	-0.002
6	-0.156	0.004	-0.154	32	-0.114	-0.020
7	-0.324	-0.148	-0.186	33	-0.106	-0.034
8	-0.447	-0.270	-0.192	34	-0.090	-0.044
9	-0.519	-0.361	-0.181	35	-0.069	-0.050
10	-0.541	-0.418	-0.161	36	-0.046	-0.052
11	-0.519	-0.443	-0.140	37	-0.023	-0.052
12	-0.457	-0.439	-0.119	38	-0.003	-0.050
13	-0.369	-0.412	-0.099	39	0.015	-0.045
14	-0.264	-0.364	-0.083	40	0.028	-0.038
15	-0.153	-0.300	-0.069	41	0.036	-0.031
16	-0.046	-0.228	-0.054	42	0.042	-0.024
17	0.049	-0.153	-0.040	43	0.043	-0.015
18	0.126	-0.081	-0.030	44	0.040	-0.008
19	0.181	-0.017	-0.024	45	0.033	-0.003
20	0.214	0.038	-0.017	46	0.024	0.002
21	0.224	0.080	-0.009	47	0.014	
22	0.212	0.109	-0.005	48	0.004	
23	0.184	0.126				
24	0.143	0.130				
25	0.096	0.125				

(a) The system contained 864 particles and the statistical error is estimated to be ± 0.015 .

Figure 4

The normalized intermediate longitudinal current autocorrelation function $C_\lambda(k, s)$ 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).

dynamic result, but this mode first of all relaxes by an order of magnitude faster and hence contributes only at short times. Furthermore, because of the $1/n^2$ weighting, it contributes only $1/9$ to the intensity of the drift correlation compared to the lowest mode. The quantitative failure of hydrodynamics or continuum models for this higher mode is not unexpected since the wave length corresponds to only about 3σ and thus is of atomic dimensions.

The early time behavior is shown by the insets in Figs. 2-4. The contribution of the sum of all the hydrodynamic modes is to raise the initial value of the drift autocorrelation function to $2(\pi/4)^2 = 1.234$ relative to the contribution of the lowest mode alone. Although the agreement with molecular dynamics is improved when the contribution of all hydrodynamic modes is taken into account compared to only the lowest one, the hydrodynamic theory nevertheless is not quantitative as can be seen at one mean collision time. This is again not unexpected since hydrodynamics fails at short times and in particular fails to quantitatively predict the longitudinal currents, as seen in Fig. 4. It should be pointed out that the larger deviations of the hydrodynamic theory for the drift autocorrelation function shown in Fig. 2, than for the longitudinal current autocorrelation function shown in Fig. 4, is due to the contribution of the higher modes in the drift, since for the lowest mode for the current, hydrodynamics fails only at remarkably short times.

The kinetic theory, as expected, quantitatively predicts the short time behavior in all cases as shown in the inserts in Figs. 2 to 4. The reason the kinetic theory fails at a shorter time for the longitudinal current than for the drift is not understood. The initial behavior should also be correctly predicted by the sum of longitudinal currents as calculated by

molecular dynamics rather than hydrodynamics. The only caveat to that comparison being rigorous is that the boundary conditions are different. As the insert in Fig. 2 shows at $s = 1$ by the square, which represents the lowest mode longitudinal current contribution, and by the triangle, which represents the sum of the first two mode contributions, the contribution of all modes is going to be in close agreement with the molecular dynamics results for the drift.

One might wonder why in spite of the rather large density inhomogeneities near the wall, as shown in Fig. 1, the comparison is nearly quantitative with calculations on uniform density systems such as the molecular dynamic periodic systems or hydrodynamic theories. One way to rationalize this result is to observe that in linearized hydrodynamics density enters only implicitly through the dependence of the sound speed on density, that is, the sound speed squared is the density derivative of the pressure. However, the pressure is independent of the density gradients and hence so must the sound speed. Thus by adjusting the pressure to be the same in the system with walls and the periodic system through the effective value of v/v_0 , the sound speed has been made nearly equal in the two systems and to first order the effect of density inhomogeneities has been taken care of.

The drift autocorrelation function is Fourier transformed to make contact with direct observations on an hypothetical experiment where a conducting fluid is confined between capacitor plates. This is shown in Fig. 5. The resonance frequency $\omega = c_0 k$ (see Table I) is seen to be at 0.29 for the lowest mode showing again that the hydrodynamic sound propagation picture describes the observed phenomena very well. In this picture the bandwidth is given by ω/Q where Q is the amount of coherent energy lost per cycle of oscillation

Figure 5

The Fourier transform of the normalized drift autocorrelation function as a function of ω in radians per collision at an effective $V/V_0 = 3.47$. The molecular dynamics results (circles) are compared to hydrodynamic theory (solid line) with the vertical bar indicating the error estimate.

Figure 6

The Fourier transform of the normalized longitudinal current autocorrelation function as a function of ω in radians per collision at an effective $V/V_0 = 3.47$ and $k\sigma = 0.489$. The molecular dynamics (circles) are compared to hydrodynamic theory (solid line) with the vertical error bar indicating the error estimate.

in the cavity. The Q is about 1.5. The disagreement at large ω reflects the failure of hydrodynamics at short times. For the Fourier transform of the longitudinal current autocorrelation function shown in Fig. 6, the greater accuracy of the hydrodynamic theory for the lowest mode is reflected in the better agreement with molecular dynamics than in Fig. 5.

To make contact with light scattering experiments, the density autocorrelation function is calculated by a double time integration of the current autocorrelation function. Since this is equivalent in Fourier space to $S(k, \omega) = C_\rho(k, \omega)/\omega^2$, the current correlation function was divided by ω^2 and the results are shown in Figs. 7 and 8. Division by ω^2 causes enormous errors at small ω values, but nevertheless the familiar Rayleigh and Brillouin peaks can be recognized, the latter being displaced by the sound speed (0.29) from the origin. For all these Fourier transforms the time autocorrelation functions were continued with the hydrodynamic solution beyond the time (50 collision times) where molecular dynamic data gives out.

These numerical experiments, besides their pedagogical value and suggesting possible experiments, have again shown 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. To be sure, at these densities a few molecular diameters means many mean free paths, the more relevant parameter. Kinetic theory on the other hand holds only up to about one mean collision time. Beyond that time corrections due to correlation beyond binary collisions must be added. Furthermore, these numerical experiments have shown that problems with different boundary conditions can be simply related to each other. These boundary effects are, of course, particularly pronounced for the very small systems studied on the computer.

Figure 7

The van Hove scattering function, $D(\omega)/\omega^2$, as a function of ω , in radians per collision, at an effective $V/V_0 = 3.47$. The molecular dynamics results are given by circles with vertical error bars, and compared to hydrodynamic theory (solid line) for $S(k, \omega)/Nk^2\langle\dot{x}^2\rangle$ for the lowest mode only, and at a slightly smaller (5%) $k\sigma$ value. The error bars indicated in the hydrodynamic result are caused by the uncertainty in the bulk properties.

Figure 8

The van Hove scattering function $S(k, \omega) = C_g(k, \omega)/\omega^2$ as a function of ω in radians per collision, at $V/V_0 = 3.47$ and $k\sigma = 0.489$ from molecular dynamics (circles) compared to hydrodynamic theory for $S(k, \omega)/Nk^2\langle x^2 \rangle$ (solid line).

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