

THE FRICTION COEFFICIENT FORMALISM IN THE STATISTICAL MECHANICS OF TRANSPORT PROCESSES

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Abstract

Kirkwood's theory for the friction coefficient in Brownian motion relates the transport coefficients to the microscopic properties of a system through the time integral of a force autocorrelation function. The expression is useful subject to the validity of certain assumptions on the form of the autocorrelation function. These restrictions and the predicted diffusion coefficients have been examined using the method of molecular dynamics. It is shown that the assumptions are invalid and that when Kirkwood's expression is evaluated exactly it gives negative self-diffusion coefficients. This leads to the conclusion that the friction coefficient approach to transport in simple systems is physically unreasonable and should no longer be used.

I. INTRODUCTION

The problem of calculating the transport coefficients of dense classical fluids is extremely complex. One of the most widely used approaches is to attempt to relate the movement of the particles in the fluid to the theory of Brownian motion. The best known of this type of theory is due to Kirkwood (1946). Kirkwood began by introducing a "coarse graining" procedure into the Liouville equation for the distribution function $f^{(N)}$ of N particles. This led to a set of coupled partial differential equations for the lower order distribution functions $f^{(n)}$, $n \leq N$. These equations have the same form as the Fokker-Planck equation. A similar procedure led to a Langevin equation for the equation of motion of a single particle. By introducing the hypothesis that the integral of the force autocorrelation function reaches a plateau value Kirkwood (1946) obtained an expression relating the friction coefficient to this plateau value. Later Suddaby and Gray (1960), by considering the relations implicit in Brownian motion theory, obtained an expression for the friction coefficient similar in form to Kirkwood's expression. Under certain conditions the expressions are compatible and hence Kirkwood's theory is useful. These conditions, along with a general discussion of the friction coefficient are given by Rice and Gray (1965).

In the present paper the method of molecular dynamics (Rahman 1964) is used to test the assumptions implicit in Kirkwood's (1946) theory. Rahman used his results to calculate the velocity autocorrelation function and compared this with the exponential form predicted by the Langevin equation. In the liquid regime it was found that the machine result gave a negative region, which contradicts the Langevin result. This was evidence for the conclusion that Kirkwood's theory was not exact. However, no test of the range of validity of the assumptions in the friction coefficient theory was carried out and it has generally been assumed that the theory gives good results (see e.g. Cole 1970). We begin in Section II by outlining the

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assumptions inherent in the friction coefficient theory. A brief discussion of the relation between the friction coefficient and the intermolecular forces is also given. The next section gives a short outline of the molecular dynamics calculations, with particular emphasis on the accuracy of the calculations. In Section IV the results of the study are presented, again with some emphasis on possible sources of error. Finally the results are summarized and their implications are discussed.

II. FRICTION COEFFICIENT THEORY

Suppose that the force acting upon a particle can be written as the sum of two terms, the first term being proportional to the momentum of the particle whilst the second term corresponds to a microscopic fluctuating force. Thus we may write

$$F_i = dp_i/dt = -\zeta p_i/M + X_i, \quad (1)$$

where ζ is the friction coefficient and X_i corresponds to the fluctuating force. This is a molecular Langevin equation with p_i the momentum of the i th particle along a given coordinate. In a centre of mass frame, with conservative forces we have at any given time t

$$\langle X_i(t) \rangle = 0,$$

where the angle brackets represent an average over an equilibrium ensemble. The autocorrelation function for the fluctuating term is given by

$$\langle X_1(t) X_1(t+\tau) \rangle_1 = \phi(\tau), \quad (2)$$

where $\langle \rangle_1$ denotes an ensemble average with the initial momentum of particle 1 held fixed. One of the conditions to be satisfied for Kirkwood's (1946) theory to be valid is that $\phi(\tau)$ should be sharply peaked. In particular it should be so sharply peaked at $\tau = 0$ that the integral

$$\int_0^{\tau_2} \phi(\tau) d\tau$$

reaches a value essentially equal to its value when $\tau_2 = \infty$ in a time τ_1 that is sufficiently short to ensure $\tau_1 \ll M/\zeta$. In practice this means that $\phi(\tau)$ must be essentially a δ -function. Provided this condition is met, it then follows (Rice and Gray 1965) that

$$\langle p_1(t) X_1(t+\tau) \rangle_1 = 0 \quad (3)$$

and that

$$\langle X_1(t) p_1(t+\tau) \rangle_1 = 2\zeta kT \exp(-\zeta\tau/M). \quad (4)$$

It can then be shown that the friction coefficient may be calculated from the expression

$$\zeta = (1/kT) \int_0^{\tau_1} \langle F(t) F(t+\tau) \rangle d\tau, \quad (5)$$

where the average is now over a full equilibrium ensemble. Equation (5) is Kirkwood's (1946) expression for the friction coefficient. Provided the conditions on $\phi(\tau)$ are satisfied, Suddaby and Gray (1960) showed that Kirkwood's friction coefficient could

be used to calculate the self-diffusion coefficient through Einstein's equation

$$D = kT/\zeta. \quad (6)$$

The most important concept in the friction coefficient theory is the plateau time τ_1 . Other than to state that it should be microscopically long but macroscopically short, Kirkwood (1946) gave no prescription for calculating it. The condition $\tau_1 \ll M/\zeta$ gives an upper bound, but this cannot be found unless ζ is known. However, we might expect it to be related to the onset of the region of validity of the hydrodynamic equations, in which case τ_1 would be around 10^{-11} s. If the restrictions on $\phi(\tau)$ and τ_1 are met, then it can be shown (Suddaby and Gray 1960) that the force autocorrelation function is given by

$$\langle F(t)F(t+\tau) \rangle = \phi(\tau) - (\zeta^2 kT/M) \exp(-\zeta\tau/M). \quad (7)$$

During the period $\tau < \tau_1$ the function $\phi(\tau)$ is the dominant contributor to the autocorrelation function. However, $\phi(\tau)$ is supposed to be essentially zero when $\tau \sim \tau_1$, and the exponential term will take over. Thus $\langle F(t)F(t+\tau) \rangle$ will reach a minimum value at the plateau time τ_1 and then rise slowly to zero. As the results should be relatively insensitive to τ_1 to be acceptable, again we would expect τ_1 to be of the order of 10^{-11} s.

There exists (in principle) a method of calculating the self-diffusion coefficient corresponding to that measured experimentally. This is the linear response theory of Green (1952) and Kubo (1959). If we assume that the non-equilibrium distribution function can be expanded linearly about its equilibrium value, and define the self-diffusion coefficient as the coefficient of proportionality when writing the mass flux in terms of a chemical potential gradient, then the linear response theory gives

$$D = M^{-2} \int_0^\infty \langle p(t)p(t+\tau) \rangle d\tau, \quad (8)$$

an equation originally derived by Einstein in his theory of Brownian motion. By calculating the momentum autocorrelation function and carrying out the required integration we can obtain D . If Kirkwood's (1946) theory is valid we would expect the D obtained from equation (8) to agree with that obtained from equations (5) and (6). In order to determine D from molecular dynamics calculations we need to truncate the infinite integral in equation (8) at some time τ_D . We might expect that if Kirkwood's theory is valid $\tau_1 \approx \tau_D$. This question is examined again in Section IV.

III. MOLECULAR DYNAMICS CALCULATIONS

Barker, Fisher, and Watts (1971) have recently given a detailed account of calculations of the equilibrium properties of liquid argon. The agreement with experimental data was impressive. Their calculations were carried out using Monte Carlo and molecular dynamics methods for an accurate pair potential for argon. This potential was developed originally by Barker and Pompe (1968) and improved by Barker and Bobetic (1970). In the present investigation two of the molecular dynamics calculations, one near the critical point and the other near the triple point, were used to test Kirkwood's theory.

The Barker–Pompe–Bobetic potential for argon consists of an analytic form for the pair potential,

$$u(r) = \epsilon \left(\exp\{\alpha(1-r)\} \sum_{i=0}^L A_i(r-1)^i - \sum_{i=0}^2 C_{2i+6}/(\delta+r^{2i+6}) \right),$$

together with the Axilrod–Teller triplet potential. Details may be found in the paper by Barker and Pompe (1968). In the results reported here the pair potential was truncated at 2.5σ , where σ is the position of the zero in the potential. It was not possible to perform the calculations with the three-body potential included.

TABLE 1

REDUCED VARIABLES USED

MKS equivalents also shown are for the appropriate reduced variable $R^* = 1$

Reduced variable	Real variable	MKS equivalent ($R^* = 1$)
T^*	$T = (\epsilon/k)T^*$	$1.402 \times 10^2 \text{ K}$
r^*	$r = \sigma r^*$	$3.367 \times 10^{-10} \text{ m}$
v^*	$v = (\epsilon/M)^{1/2} v^*$	$1.716 \times 10^2 \text{ m s}^{-1}$
τ^*	$\tau = (M/\epsilon)^{1/2} \sigma \tau^*$	$1.96 \times 10^{-12} \text{ s}$
F^*	$F = (\epsilon/\sigma) F^*$	$5.746 \times 10^{-12} \text{ N}$
D^*	$D = (\epsilon/M)^{1/2} \sigma D^*$	$5.778 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$
ζ^*	$\zeta = \{(M\epsilon)^{1/2}/\sigma\} \zeta^*$	$3.379 \times 10^{-14} \text{ kg s}^{-1}$

As no satisfactory perturbation theory exists for including such terms no attempt was made to include the long-range and three-body terms. Consequently the results given here are not strictly applicable to argon, although the self-diffusion coefficients are close to the experimental values. However, the truncated potential is at least as realistic as the Lennard–Jones potential, for example, and we believe that our conclusions are generally valid. In order to facilitate the comparisons, the reduced variables given in Table 1 will be used in the rest of this paper.

The molecular dynamics calculations were similar to those described for the Lennard–Jones potential by Rahman (1964) and Verlet (1968). The equations of motion were solved for a system of 108 particles in steps of $\delta\tau^* = 0.00506$ for about 5000 time steps. This corresponds to about $5 \times 10^{-11} \text{ s}$ in real time. During this time the total momentum of, and force on, the system remained essentially zero. The average total energy of the system was constant to about 1% throughout the run. Around 500 time steps were discarded at the beginning of each run to allow the system to reach equilibrium. The agreement with the Monte Carlo results reported earlier (Barker, Fisher, and Watts 1971) along with the good agreement with experiment indicates that equilibrium had been reached.

To show the accuracy of the calculations, in Figure 1 we have compared the values of PV/NkT and U/NkT obtained from the molecular dynamics with the results of the Monte Carlo calculations. The agreement is very satisfactory. It is possible that the diffusion coefficient calculation may depend upon the size of the system. Calculations for the Barker–Bobetic potential using more than 108 particles have

not been performed and consequently we cannot directly test this effect. However, Table 2 includes some values of D that we have calculated. For the liquid-state point the value of 0.026 has been reported by Levesque and Verlet (1970) for 864 particles interacting through the Lennard-Jones (12, 6) potential. The values are in good agreement considering the different potential functions, and so it seems reasonable to suppose that any effect due to the number of particles is small.

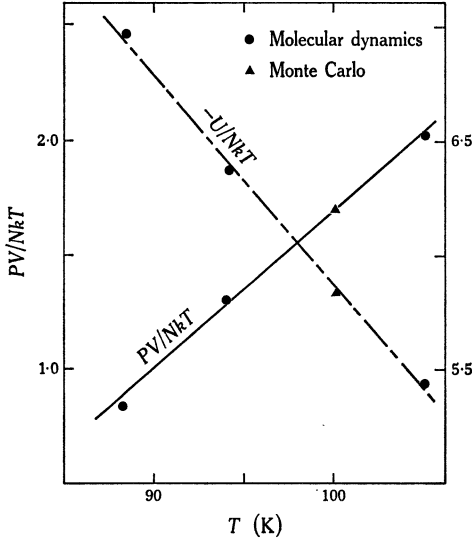


Fig. 1.—Comparison of values for equation of state and internal energy from molecular dynamics and Monte Carlo calculations. The lines give an indication of the agreement obtained.

IV. RESULTS

If we introduce reduced variables into the equations given in Section II we obtain the following results:

Langevin equation

$$F^* = dv^*/d\tau^* = -\zeta^* v^* + X^*; \quad (9)$$

Einstein equation

$$\zeta^* = T^*/D^*; \quad (10)$$

Kirkwood equation

$$\zeta^* = (1/T^*) \int_0^{\tau_1^*} \langle F^*(0) F^*(\tau^*) \rangle d\tau^*. \quad (11)$$

The correlation between the initial momentum and the later fluctuating force becomes

$$\langle v^*(0) X^*(\tau^*) \rangle_1 = \langle v^*(0) X^*(\tau^*) \rangle = 0, \quad (12)$$

while the correlation between the initial fluctuating force and the later momentum is given by

$$\langle X^*(0) v^*(\tau^*) \rangle_1 = \langle X^*(0) v^*(\tau^*) \rangle = 2\zeta^* T^* \exp(-\zeta^* \tau^*). \quad (13)$$

In equations (11)–(13) we have used the fact that the autocorrelation functions depend only upon the difference of time to put $t = 0$. Also, as the results given in equations (3)

and (4) are independent of the initial momentum p_1 we have integrated over this coordinate to get the second parts of equations (12) and (13). Finally, the Kubo-Green equation for the self-diffusion coefficient can be written

$$D^* = \int_0^\infty \langle v^*(0) v^*(\tau) \rangle d\tau^*. \quad (14)$$

All the time-correlation functions reported here were obtained by averaging over all particles at a large number of initial times. For the critical-point results, $T^* = 1.131$ and $\rho^* = 0.25$, 270 initial times were used. The triple-point results, where $T^* = 0.671$ and $\rho^* = 0.85$, were obtained from 700 initial times. To give some indication of the error involved in these averages, the force autocorrelation function for the liquid-state point is given after 350 and 700 initial times in Figure 2(a). Also shown is an independent calculation using 450 initial times for the same state. It is obvious that the results are in very good agreement. Notice that the function vanishes rapidly. This point is considered in more detail below.

Suddaby and Gray (1960) showed that if $\phi^*(\tau)^*$ is sufficiently sharp then, in reduced units,

$$\langle F^*(0) F^*(0) \rangle = \zeta^* T^* / \tau_1^*. \quad (15)$$

In addition this autocorrelation function will reach a minimum at the plateau time τ_1^* , the value of this minimum being $-\zeta^{*2} T^*$. We can now obtain the predicted graph of $\langle F^*(0) F^*(\tau^*) \rangle$. From the molecular dynamics calculations we first obtain $\langle F^*(0) F^*(0) \rangle$, and then using the Kubo-Green equation and Einstein's relation we can evaluate the macroscopic friction coefficient. Rearranging equation (15) gives an estimate of the plateau time τ_1^* . Finally we can write equation (7) in terms of reduced variables to give

$$\langle F^*(0) F^*(\tau^*) \rangle = \phi^*(\tau^*) - \zeta^{*2} T^* \exp(-\zeta^* \tau^*). \quad (16)$$

At times such that $\tau^* < \tau_1^*$, the first term in equation (16) is supposed to be dominant. This conclusion arises from the assumptions that $\phi^*(\tau^*)$ is sharply peaked and that $\zeta^* \tau_1^* \ll 1$.

The curve resulting from equation (16) is also shown in Figure 2(a), together with the function $\phi^*(\tau^*)$. The latter function was calculated by using the Kubo-Green equation together with the Einstein equation to calculate the friction coefficient. After obtaining $X^*(\tau^*)$ from equation (9) the autocorrelation function $\langle X^*(0) X^*(\tau^*) \rangle$ was obtained by averaging over all particles and several hundred initial times.

There are many features of interest in Figure 2(a). Perhaps the most surprising is the time scale over which $\langle F^*(0) F^*(\tau^*) \rangle$ is significant. In comparison with the first peak, the function is small beyond $\tau^* \approx 0.2$; in real time units this interval corresponds to about 4×10^{-13} s. Remembering that Suddaby and Gray (1960) showed the plateau time to be in the region of the minimum, it is obvious that τ_1^* is not microscopically long. In fact the minimum occurs after only two or three molecular collisions. The next most obvious result is that the predicted autocorrelation function, from equation (16), is in very poor agreement with the machine results. The friction coefficient used in the calculation was obtained from the self-diffusion coefficient through Einstein's equation. Notice that the maximum is very high.

For $\tau^* = 0.01$ it was found that the predicted curve had a value greater than 1200. The minimum is far more pronounced than the machine minimum, although it occurs at nearly the same time. It is of interest that the minimum of Suddaby and Gray's conjectured curve, $-\zeta^* \tau^* = -1605$, is very much deeper than that of equation (16). However, it occurs at essentially the same time, $\tau_1^* = 0.18$. The function $\phi^*(\tau^*)$ also shown in Figure 2(a) is definitely sharply peaked, but the minimum in this curve accounts for nearly all the depth in equation (16). It is not, as was conjectured, effectively zero. We can also comment on the restriction $\zeta^* \tau_1^* \ll 1$. If we estimate τ_1^* using the self-diffusion coefficient and $\langle F^*(0)F^*(0) \rangle$ from equation (15) we find $\zeta^* \tau_1^* = 8.92$. Thus the restriction on τ_1^* necessary for Kirkwood's (1946) theory to

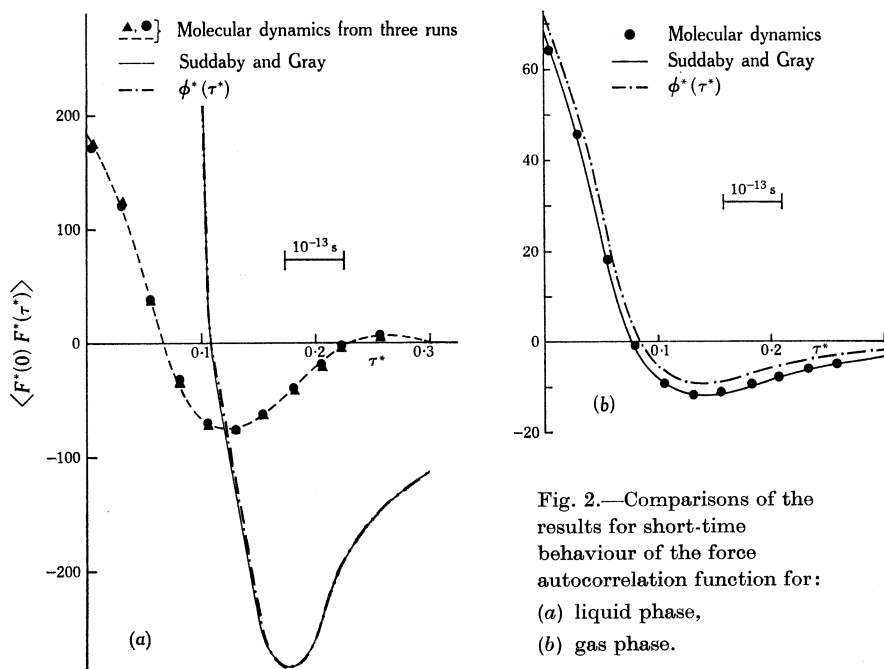


Fig. 2.—Comparisons of the results for short-time behaviour of the force autocorrelation function for: (a) liquid phase, (b) gas phase.

be valid is not satisfied at all. In fact the supposedly sharply peaked function $\phi^*(\tau^*)$ is dominant at all times greater than about $\tau^* = 0.01$. We can conclude from this that at least in the liquid region the concept of a plateau time, in Kirkwood's sense, has no meaning.

There is one other comparison of interest before leaving the liquid-state calculations. We can calculate ζ^* from the self-diffusion coefficient and Einstein's relation, and directly from Kirkwood's equation. The required integrations must be truncated at some point. The resulting coefficients as a function of the upper limit on the integration, are given in Table 2. It is at once obvious that the Kubo-Einstein coefficient is very different from the Kirkwood estimate. In particular the Kirkwood estimate is negative and does not appear to have stabilized. As the negative friction coefficient leads to a negative self-diffusion coefficient, it is obviously not physical.

To test for any evidence of a plateau value in the region of the minimum, the Kirkwood friction coefficient is given for three times near the minimum. Although the results are all positive they are changing rapidly. We can only conclude that at least in the liquid region Kirkwood's theory of the friction coefficient is not valid.

We continue by examining the Kirkwood (1946) theory at a density corresponding to the critical density of argon. The results are given in Figure 2(b). It is at once apparent that the Suddaby-Gray result, equation (16), is in excellent agreement with the machine results. The total disagreement found for the liquid state no longer exists. However, this agreement is about the only satisfactory observation at this density. Again the position of the minimum gives a meaningless plateau time. In addition the function $\phi^*(\tau^*)$ is not particularly sharply peaked, and is obviously the dominant contributor to $\langle F^*(0)F^*(\tau^*) \rangle$ throughout the complete time of interest.

TABLE 2
REDUCED DIFFUSION AND FRICTION COEFFICIENTS

The friction coefficients from the Kubo-Green theory (ζ_E^*) and the Kirkwood theory (ζ_K^*) are compared as functions of the upper limit τ_1^* in the time integration

τ_1^*	Gas phase			Liquid phase		
	D^*	ζ_E^*	ζ_K^*	D^*	ζ_E^*	ζ_K^*
0.11	—	—	2.16	—	—	6.65
0.13	—	—	1.78	—	—	3.74
0.16	—	—	1.51	—	—	1.09
2.08	0.58	1.95	-0.45	0.019	51.6	-2.04
3.09	0.60	1.89	-0.53	0.021	48.6	-1.58
5.02	0.61	1.85	-0.76	0.020	48.9	-2.43

The Suddaby-Gray estimate for the plateau time, equation (15), gives $\tau_1^* = 0.0033$, which is much too small to have any macroscopic interpretation; in fact this is less than the time needed for one collision to take place. Also the Suddaby-Gray estimate of the value of the minimum, $-\zeta^*2T^*$, gives -2.37 , which is too small by a factor of five or six. The value of $\zeta^*\tau^*$ is 0.0061, which is much less than unity, but as τ^* itself is so short this result is of little interest. Finally, we can compare the Kirkwood friction coefficient obtained from equation (11) with that obtained from the Kubo-Green equation and Einstein's relation. The relevant results are presented in Table 2. Again the Kirkwood values are negative and show no real sign of a plateau value existing. Integrating out to the minimum in the autocorrelation function gives results that are close to the macroscopic results, but as with the liquid state results there is no reason to prefer the very short time results over any other. We can only conclude that although the gas phase results are better than those for the liquid phase there is no evidence to suggest that Kirkwood's theory is valid in this region.

V. DISCUSSION

We have seen that the force autocorrelation function approach to the friction coefficient is not valid at dense gas and liquid densities. However, this does not imply that the macroscopic friction coefficient, connecting diffusion with viscosity, is a

meaningless concept. It is well known (see e.g. Edward 1970) that the diffusion coefficients and shear viscosities of simple non-electrolytes are quite strongly correlated through the Einstein equation and the equation

$$\eta = \text{const.} \zeta \rho, \quad (17)$$

where ρ is the density. What must now be questioned is the concept of Brownian motion being the dominating influence on transport phenomena in dense fluids. One of the most popular theories of transport in simple liquids is due to Rice and Allnatt (1961). This theory is essentially an attempt to obtain the friction coefficient from Kirkwood's (1946) equation. In this theory the intermolecular potential is assumed to consist of a rigid core repulsion superimposed on an arbitrary soft potential. On the basis of this separation the forces are treated on two time scales. The hard core

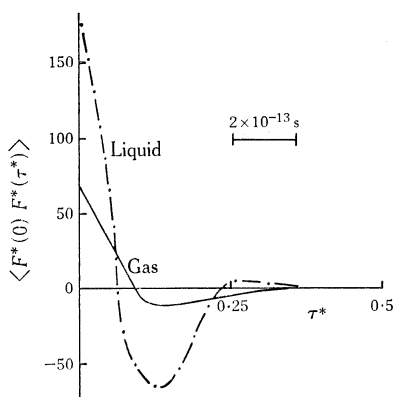


Fig. 3.—Long-time behaviour of the force autocorrelation function for the liquid and gas phases.

collisions are treated using the Enskog approach (Chapman and Cowling 1939) and the soft potential is dealt with using a quasi-Brownian motion approach. Early work on this theory suggested that Rice and Allnatt's approach gave good results for a liquid (Rice and Gray 1965). However, despite its modifications this theory represents an approximate attempt to evaluate the friction coefficient, and consequently there must be some explanation for the apparently good results. The most obvious is that the accumulation of errors was such that accidental agreement with experiment was obtained. In particular, a hard-sphere modified pair potential was used in conjunction with an approximate radial distribution function for that potential (Kirkwood, Lewinson, and Alder 1952). When Monte Carlo calculations using the pair potential were carried out to test the Rice-Allnatt theory, the agreement with experiment was poor, although a positive friction coefficient was found (Collings, Watts, and Woolf 1971). In addition it was shown that the pair potential itself led to very poor predictions of the thermodynamic properties of the inert gases. Obviously there is room for extensive cancellation of errors here. Given the poor agreement between the Rice-Allnatt results for the friction coefficient and the results given here, particularly $\zeta < 0$, it would seem that this theory is not as useful as was first considered.

The Kirkwood (1946) approach to a theory of transport is based on the extension of hydrodynamic equations to microscopic phenomena. This approach would be

acceptable if the fluctuating forces $X(t)$ were small. In fact it would appear that the fluctuating terms are at least as important as the strongly repulsive forces caused by "hard-core" collisions. These "soft" forces appear to swamp the correlations between collisions. This can be seen clearly in Figure 3, where the force autocorrelation functions given in Figures 2(a) and 2(b) are shown over a longer time. It is obvious that the forces acting on a particle become essentially random within about two or three collision times. If the fluctuating terms were small, one would expect the autocorrelation function to be of longer range. Notice that the ratio

$$\langle F^*(0)F^*(0) \rangle / \langle F^*(0)F^*(\tau^*) \rangle_{\min}$$

is greater for the gas than for the liquid. There is also a small positive peak after the minimum on the liquid curve. These observations can be correlated with those of Fehder (1969) on the behaviour of a two-dimensional system of disks. He found that for quite long times a particle tends to stay in a "cage" formed by its neighbours.

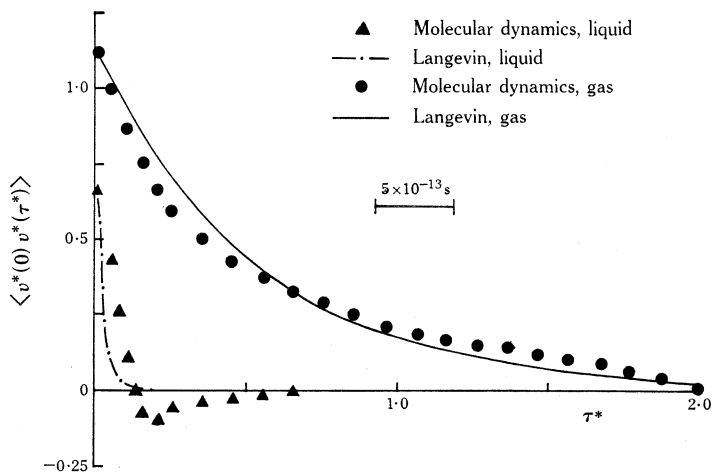


Fig. 4.—Comparison of results for the velocity autocorrelation function.

The force autocorrelation function can be interpreted in a similar way. The strong negative well would represent the particle reaching the end of its cage, and the small positive peak the time at which it returned to the beginning. This effect is not obvious in the more dilute gaseous system.

These effects also show up in the velocity autocorrelation functions given in Figure 4. Here the liquid curve shows the negative regions first observed by Rahman (1964). These regions would correspond to the particle returning along its cage. Also shown in Figure 4 are the Langevin equation results for the autocorrelation function

$$\langle v^*(0)v^*(\tau^*) \rangle = T^* \exp(-T^* \tau^* / D^*).$$

This of course is also the form predicted by Kirkwood's theory. Notice that for the gas the agreement with the present results is good. This is to be expected as Suddaby

and Gray's (1960) conjectured force autocorrelation function agrees with the present results. The Langevin result for the liquid is in poor agreement with the machine results, confirming the findings of Rahman (1964). It is of interest that the gas-phase results are of much longer range than the liquid-phase result. This is in agreement with the much weaker minimum in the gas force autocorrelation function. It would appear that, although after a short time the forces are opposed to the initial forces, this opposition is not sufficient to reverse the velocity of the particle.

VI. CONCLUSIONS

The method of molecular dynamics has been used to examine the friction coefficient approach to transport phenomena. It appears that the concept of a plateau value for the friction coefficient, as proposed by Kirkwood (1946), is invalid. Using the machine results to calculate the plateau time τ_1^* from results due to Suddaby and Gray (1960), it has been found that τ_1^* is less than 2×10^{-13} s, and thus it cannot be termed microscopically long. When the friction coefficient is calculated by integrating the force autocorrelation function to fairly long times it is found to be negative. As this leads to a negative self-diffusion coefficient we conclude that Kirkwood's approach is not useful. Finally, after examining the implications of the present results for the force and velocity autocorrelation functions, we conclude that the behaviour of these functions confirms the findings of Fehder (1969) that particles in liquid systems tend to stay in "cages" formed by their neighbours for quite long times.

VII. ACKNOWLEDGMENT

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