

## Kirkwood Theory of Shear Viscosity in a Simple Dense Fluid

A. F. Collings<sup>A</sup> and Denis J. Evans<sup>B</sup>

<sup>A</sup> Division of Applied Physics, CSIRO,  
P.O. Box 218, Lindfield, N.S.W. 2070.

<sup>B</sup> Research School of Chemistry, Australian National University,  
G.P.O. Box 4, Canberra, A.C.T. 2601.

### Abstract

The molecular theory of momentum transport in dense fluids developed by Kirkwood is examined for the case of the Lennard-Jones (12, 6) fluid. The radial distribution functions and one-particle friction constants used are based on molecular dynamics studies. Shear viscosity coefficients calculated with  $\epsilon/k = 120$  K and  $\sigma = 3.405 \times 10^{-10}$  m vary from one-third to two-thirds of comparable experimental data for argon. The significance of an approximate relationship between the pair friction tensor and the one-particle friction constant is discussed.

### 1. Introduction

While the 1970s witnessed substantial progress in the understanding of the equilibrium properties of dense fluids, advances in the understanding of transport properties have been relatively modest. The development of computer simulation, particularly of nonequilibrium molecular dynamics (NEMD) (Ashurst and Hoover 1973, 1975; Evans 1983), and of the correlation function and linear response formalisms (Green 1954; Kubo 1958; Zwanzig 1964) has been a significant step forward. These latter approaches have had limited practical application because of the difficulty and computational expense in obtaining adequate 'experimental' information about the dynamics of a fluid. Even for the simplest case, the calculation of the self-diffusion coefficient of a model fluid from the velocity autocorrelation function, a large amount of computing time is required for reasonable accuracy. In the view of one experimentalist (Kestin 1983), molecular dynamics has not proved a supplement to measurement as had been hoped, but 'has taken on an independent life of its own'.

In view of these difficulties, workers in the field will continue to seek an understanding or interpretation of the transport properties of dense fluids in terms of empirical models. One major contribution of the correlation function formalism may well be its capacity to demonstrate to the experimentalist why such crude models as those by Eyring *et al.* (1941) and Andrade (1934) have proved successful in some situations and inadequate in others.

Of the older transport models, the friction constant theory of Kirkwood (1946) and its successors (Rice and Gray 1965) have generally been regarded as offering most promise (McLaughlin 1964; Croxton 1974). It is an approach that is still favoured for transport in polymeric liquids (Bird and Curtis 1984). Indeed, the agreement between experimental values for the shear viscosity and thermal conductivity of argon

and data calculated from the Rice–Allnatt theory was exceptional (Rice and Gray 1965). However, the shortcomings of the friction constant model are well known. The various recipes for relating the friction constant to the intermolecular potential and the fluid structure have been shown to be inadequate (Collings 1967; Collings *et al.* 1971). The existence of a plateau value in the friction tensor, a prerequisite for the rigorous application of the Brownian motion analogy has been disproved (Fisher and Watts 1972; Smedley and Woodcock 1974).

In the present work, we study the connection between the statistical mechanical theory of momentum transfer developed by Kirkwood and his colleagues (1949) and the theory of the friction constant (Kirkwood 1946). We assume that an effective friction constant exists, as implied by the general applicability of the Stokes–Einstein relationship in liquids, and that this friction constant may be obtained by computer simulation. However, we emphasise that the relationship between the one-particle friction constant and the pair friction tensor is both complicated and crucial.

We make the first self-consistent test of theory using input data, structures and friction constants which correspond to the pair interaction. The quantities  $D$  and  $g(r)$  have been calculated for the Lennard-Jones (LJ) (12, 6) fluid by the molecular dynamics technique (Verlet 1968; Levesque and Verlet 1970). In previous evaluations of the theory (Zwanzig *et al.* 1953; Rice and Gray 1965; Palyvos and Davis 1967), a hard-sphere modified LJ (12, 6) potential was coupled with LJ (12, 6) parameters, the Born–Green–Yvon approximation for  $g(r)$  (Kirkwood *et al.* 1952) and an experimental estimate of  $D$  for argon. Such a test of the Kirkwood theory was dubious.

Comparison is also made with estimates derived from NEMD simulation (Ashurst and Hoover 1973) for the zero-shear-rate viscosity of liquid argon along the gas–liquid coexistence curve.

## 2. Theory

The friction constant is usually defined by the Einstein equation

$$\zeta = kT/D, \quad (1)$$

where  $D$  is the coefficient of self-diffusion. In the limit of true Brownian motion, i.e. a heavy particle in a bath of light particles, the quantity defined in this way is equivalent to the friction constant in the Langevin equation (Mazo 1961; Resibois and Davis 1964):

$$F(t) = -\zeta v + G(t), \quad (2)$$

where the total instantaneous force on the particle consists of a steady frictional force and a random fluctuating force, the long-time average of which is zero.

The friction constant in the above equations is the single-particle one, whereas the following discussion largely involves the pair friction tensor  $\zeta^{(2)}$ . The relationship between  $\zeta$  and  $\zeta^{(2)}$  will be discussed later.

The procedure used to derive the equations of hydrodynamics from classical statistical mechanics yields an expression for the stress tensor in terms of molecular variables (Kirkwood *et al.* 1949). This consists of two contributions, a Chapman–Enskog type term involving the one-particle distribution function  $f^{(1)}$ , due to the stochastic migration of a ‘faster’ molecule to a slower moving region, and a term involving the two-particle distribution function  $f^{(2)}$ , which arises from energy or

momentum transfer via intermolecular interactions. The latter contribution becomes dominant in dense gases and condensed media (Kirkwood 1946; Kirkwood *et al.* 1949).

The intermolecular contribution to the stress tensor can be expressed in terms of the two-particle distribution function. The Newtonian form of the stress tensor is

$$\sigma = -\{p + (\frac{2}{3}\eta - \phi)\nabla \cdot u\} \vec{1} + 2\eta \vec{\dot{\epsilon}}, \quad (3)$$

where  $\eta$  and  $\phi$  are the coefficients of shear and bulk (volume) viscosity respectively,  $p$  is the equilibrium pressure,  $\vec{\dot{\epsilon}}$  the rate of strain and  $\nabla \cdot u$  the divergence of velocity. In molecular variables, the stress tensor can be expressed as (Rice and Gray 1965)

$$\sigma = \frac{1}{2} \int R_{12} \nabla_{12} u(R_{12}) f^{(2)}(1, 2) dR_{12} dp_1 dp_2, \quad (4)$$

where  $R_i$  and  $p_i$  are the configuration and momentum space coordinates respectively of the molecules. However, the velocity gradient causing momentum flux also perturbs the molecular configuration. It is assumed that, for small rates of strain  $\vec{\dot{\epsilon}}$ , this perturbation can be expressed as an expansion in spherical harmonics,

$$g^{(2)}(R) = g_0^{(2)}(R) \left\{ 1 + \frac{\zeta^{(2)}}{6kT} (\nabla \cdot u) \psi_0(R) + \frac{\zeta^{(2)}}{2kT} \left( \frac{R \cdot \vec{\dot{\epsilon}} \cdot R}{R^2} - \frac{1}{3} \nabla \cdot u \right) \psi_2(R) \right\}, \quad (5)$$

where  $g^{(2)}(R)$  is the non-equilibrium pair distribution function,  $g_0^{(2)}(R)$  is the equilibrium radial distribution function,  $\psi_0(R)$  is the coefficient of the zero-order harmonic arising from the dilational component of the rate of strain and  $\psi_2(R)$  is the second-order coefficient of surface harmonics arising from the shear component.

The combination of equations (3)–(5) leads to the following expressions for the equilibrium fluid pressure  $p$  and the coefficient of shear viscosity  $\eta$ :

$$p = \frac{NkT}{V} - \frac{2\pi N^2}{3V^2} \int_0^\infty R^3 U'(R) g_0^{(2)}(R) dR, \quad (6)$$

$$\eta = \frac{NmkT}{2V\zeta^{(1)}} + \frac{N^2\pi\zeta^{(2)}}{15V^2kT} \int_0^\infty R^3 U'(R) \psi_2(R) g_0^{(2)}(R) dR. \quad (7)$$

The coefficient  $\psi_2(R)$  can be obtained from the equilibrium radial distribution function [which we now write as simply  $g_0(R)$ ] by solving

$$\frac{d}{dR} \left( R^2 g_0(R) \frac{d\psi_2(R)}{dR} \right) - 6g_0(R) \psi_2(R) = R^3 \frac{dg_0(R)}{dR}, \quad (8)$$

using the boundary conditions for the excess probability current density in pair space

$$\lim_{R \rightarrow 0} R^2 g_0(R) \frac{d\psi_2(R)}{dR} = 0, \quad (9)$$

$$\lim_{R \rightarrow \infty} \psi_2(R) = 0. \quad (10)$$

A direct numerical solution of (8)–(10) is possible, but we have used the method proposed by Zwanzig *et al.* (1953) which leads to

$$\psi_2(x) = D(x) - 3A(x)B(x) + 3C(x)$$

$$+ 6A(x) \int_x^\infty g_0(s) \psi_2(s) ds - 6 \int_x^\infty A(s) g_0(s) \psi_2(s) ds, \quad (11)$$

where

$$A(x) = \int_x^\infty \{s^2 g_0(s)\}^{-1} ds, \quad (12)$$

$$B(x) = \int_x^\infty s^2 \{g_0(s) - 1\} ds, \quad (13)$$

$$C(x) = \int_x^\infty s^2 \{g_0(s) - 1\} A(s) ds, \quad (14)$$

$$D(x) = \int_x^\infty s [\{g_0(s)\}^{-1} - 1] ds. \quad (15)$$

Given  $g_0(R)$  for a specific pair potential  $U(R)$ , equations (11)–(15) can be integrated numerically if  $\psi_2(R)$  is known for all  $R > x$ . Since  $g_0(R) \rightarrow 1$  at high  $R$ , the differential equation has the limiting value

$$\psi_2(x) = p/x^3. \quad (16)$$

For any arbitrary value of  $p$ , the function  $\psi_2(x, p)$  can be constructed by analytical integration in the range  $x = R_{\max}$  to  $\infty$  [where  $g_0(R) = 1$  for all  $R > R_{\max}$ ] and then by stepwise numerical integration from  $x = R_{\max}$  to  $x = 0$ . If the correct value of  $p$  is chosen, then  $\psi_2(x, p)$  satisfies the boundary condition at  $x = 0$ , which is

$$\int_0^\infty g_0(s) \psi_2(s) ds = \frac{1}{2} \int_0^\infty s^2 \{g_0(s) - 1\} ds. \quad (17)$$

Since  $\psi_2(x, p)$  is linear in  $p$ , the left-hand side of (17) can be evaluated for two values of  $p$ , and the appropriate value equal to the right-hand side of (17) obtained by interpolation. This value of  $p$  is then confirmed.

### 3. Calculations

Theoretical equilibrium radial distribution functions have been determined for 25 states of an LJ (12, 6) system by the molecular dynamics technique (Verlet 1968). The reduced densities ( $\rho^* = N\sigma^3/V$ ) range from 0.45 to 0.88 and the reduced temperatures ( $T^* = kT/\epsilon$ ) from 0.591 to 3.669. For the present study, the computed distribution functions were interpolated to finer  $R$  space using a sixth-order Lagrangian fit to the functional

$$h(R) = Rg_0(R) \exp\{-U(R)\}. \quad (18)$$

For all save the lowest densities, computed values of the  $g_0(R)$  were still oscillating at the upper limit of  $r/\sigma = 5.0$ . We chose to extrapolate these functions until the amplitude of the oscillations was less than  $1 \times 10^{-6}$ , using the Ornstein–Zernicke

relationship (Green 1960)

$$g_0(R) \propto \exp\{-U(R)\}/R, \quad (19)$$

which was modified by a term  $\cos(kR)$  to reproduce the oscillatory behaviour.

The frequency of oscillations in  $g_0(R)$  for  $R > 5$  was assumed to be the same as for  $R < 5$ , and for each state agreed closely with that predicted from the exact PY solution for hard spheres (Perry and Throop 1972).

Table 1. Viscosity of argon calculated from the Kirkwood theory

Temp. (K)	$V$ ( $10^{-6} \text{ m}^3 \text{ mole}^{-1}$ )	Viscosity ( $10^{-6} \text{ N s m}^{-2}$ )		
		Kinetic	Intermolecular	Total
131.2	27.02	0.018	1.772	1.790
112.1		0.015	1.762	1.776
70.8		0.007	2.096	2.102
346.0		0.064	1.397	1.461
263.8	27.97	0.048	1.460	1.507
152.5		0.026	1.586	1.612
135.0		0.022	1.515	1.537
105.4		0.017	1.641	1.658
94.2	28.86	0.014	1.601	1.616
86.1		0.013	1.643	1.656
78.8		0.011	1.644	1.656
98.2		0.018	1.406	1.424
340.8	31.70	0.079	0.817	0.896
156.2		0.038	0.875	0.913
128.1		0.032	0.887	0.919
99.1		0.025	0.907	0.932
439.5	36.58	0.122	0.426	0.547
218.9		0.065	0.467	0.531
189.8		0.057	0.474	0.531
124.1		0.040	0.470	0.510
107.8	47.55	0.036	0.462	0.498
162.9		0.068	0.160	0.227
351.5		0.145	0.079	0.223
204.9		0.090	0.076	0.166
185.9	52.84	0.083	0.074	0.157

The consistency of solution was subject to the following tests:

- (1) different techniques of integration;
- (2) convergence; and
- (3) insensitivity to the treatment of  $g_0(R)$ , including (i) variation in the cut-off of  $g_0(R)$  and therefore of the remnant oscillation, (ii) modification of the first peak in  $g_0(R)$  and of the net correlation function  $g_0(R) - 1$  by  $\pm 1\%$ , and (iii) an alternative extrapolation procedure in which the oscillations were arbitrarily damped by  $1/R$ .

From these tests we conclude that negligible errors exist in calculations which adopt a step-length in  $r/\sigma$  of 0.01 and a final oscillation in  $g_0(R)$  less than  $10^{-5}$ . The calculations reported here satisfy these requirements.

The friction constants employed here are based on an empirical relationship fitted to self-diffusion coefficients for an LJ (12, 6) fluid calculated by molecular dynamics (Levesque and Verlet 1970):

$$D^* = 0.006423 T^*/\rho^* + 0.0222 - 0.0280\rho^*, \quad (20)$$

where the asterisk implies a reduced parameter. Equation (20) was recommended for use at reduced densities of 0.65 and larger, but we have employed this relationship for the four lowest density points in Table 1 ( $\rho^* = 0.456$ – $0.506$ ) accepting any attendant error which may cause  $D$  to be overestimated by as much as 20%.

#### 4. Discussion

To compare the theoretical results from equation (7) with actual experimental viscosities, the reduced parameters must be transformed into real molecular properties using appropriate LJ (12, 6) values for  $\sigma$  and  $\epsilon/k$ . Since we compare our calculations with experimental values for argon, we have used the recommended values (Hirschfelder *et al.* 1954) of  $\sigma = 3.405 \times 10^{-10}$  m and  $\epsilon/k = 119.8$  K. Values must also be supplied for  $\zeta^{(1)}$ , the singlet friction constant, and  $\zeta^{(2)}$ , but the choice for  $\zeta^{(2)}$  is a matter of contention.

The reduced coefficient of self-diffusion given by (20) is readily converted to an actual coefficient since

$$D = (\epsilon/m)^{\frac{1}{2}} \sigma D^*. \quad (21)$$

Equation (1) is the obvious source for  $\zeta^{(1)}$  because the coefficient of self-diffusion and the mass current density are related to the one-particle distribution function. Three different approximations for relating  $\zeta^{(2)}$  to  $\zeta^{(1)}$  have been proposed. The first evaluation of the Kirkwood theory (Kirkwood *et al.* 1949) assumed that

$$\vec{\zeta}^{(2)} = \zeta \vec{\mathbf{1}}, \quad (22)$$

but in later work (Zwanzig *et al.* 1953, 1954), the preferred approximation was

$$\vec{\zeta}^{(2)} = \zeta \vec{\mathbf{1}}_1 + \zeta \vec{\mathbf{1}}_2, \quad (23)$$

where  $\zeta$  is the scalar one-particle friction constant and  $\vec{\mathbf{1}}_1$  and  $\vec{\mathbf{1}}_2$  are unit dyads in  $r_1, r_2$  space. Equation (23) therefore neglects the dependence of the pair friction tensor on momenta and on the relative configuration of pairs of molecules (Zwanzig *et al.* 1954). Rice and Kirkwood (1959) subsequently proposed that

$$\vec{D}^{(2)} = D \vec{\mathbf{1}}_1 + D \vec{\mathbf{1}}_2, \quad (24)$$

i.e. the pair diffusion tensor was the direct sum of the one-particle diffusion tensors.

When the molecules constituting the pair are well separated, either (23) or (24) is justified. However, at close separations, the assumption of independent movement of the molecules must break down. In any event, in the three evaluations of the shear viscosity coefficient of liquid argon cited above, the form of the pair friction tensor

ultimately employed was

$$\zeta^{(2)} = kT/D_{\text{exp}}, \quad (25)$$

which is compatible only with the use of (22).

We believe that the approximation which is most consistent with the Kirkwood theory is (23). It should be noted that this is our interpretation only, based on a careful reading of the original Kirkwood papers, which are indefinite on this point. In calculating the results in Table 1, we have employed  $\zeta^{(2)} = 2kT/D_{\text{exp}}$ , where  $D_{\text{exp}}$  is based on (20), the self-diffusion coefficient of the LJ (12, 6) fluid. In the range of states corresponding to the real liquid region, the kinetic contribution to momentum transfer predicted by the theory varies from 8% of the intermolecular contribution to less than 0.5% at the most 'solid-like' state. The kinetic contribution reaches a maximum of 65% of the total shear viscosity for  $T^* = 2.934$  and  $\rho^* = 0.450$ , which is well into the dense gas region.

In Fig. 1, the total viscosities (dashed curves) in Table 1 have been compared with experimental data (solid curves) for argon (Michels *et al.* 1954; Hanley *et al.* 1974). The quantitative agreement between theory and experiment is seen to be better at high densities, being of the order of 65% for  $V = 28.0 \times 10^{-6} \text{ m}^3 \text{ mole}^{-1}$ . However, at the lowest density ( $V = 52.8 \times 10^{-6} \text{ m}^3 \text{ mole}^{-1}$ ), the theoretical values are only one-third of the experimental. One can also see that, in the high density region, the predicted temperature dependence is weaker than indicated by experiment.

NEMD simulations of the shear viscosity must employ shear rates which are so high that even liquid argon is non-Newtonian. To afford comparison with experiment or theory, high shear rate viscosities must be extrapolated to zero shear. This process introduces some uncertainty in the comparison of simulated and other values, and emphasises why there are fewer data available for comparison than might be realised. In Fig. 2, simulated (open circles), calculated (squares) and experimental (solid circles) data for the zero-shear-rate viscosity of liquid argon along the gas-liquid coexistence curve are compared. NEMD estimates (Ashurst and Hoover 1973) of the zero-shear-rate viscosity are 10–20% higher than the best experimental data (Haynes 1973). The Kirkwood theory estimates of the viscosity, based on the results in Table 1, are approximately one-half the experimental values.

It can be argued that the comparison with experiment reinforces the point that the Kirkwood theory is specifically applicable to liquids, and not to dense gases where the Brownian analogy is less apt because of the increased mobility of the molecules. It is likely that the temperature dependence and the quantitative agreement would be improved in the liquid region if one could account for the increase in the pair friction tensor at close separations. While there is no correlation of movement between two molecules that are well separated, it is clear that the relative diffusion is much reduced when they are close together. An estimate of the effect of the separation on the pair friction tensor can be obtained by assuming that

$$\zeta^{(2)} = 2\zeta^{(1)}g(r), \quad (26)$$

where we have reasoned that the enhancement of friction will display similar spatial dependence to the radial distribution function. Indeed, the predicted viscosity for the most 'solid-like' case is increased by 30% when this approximation is employed.

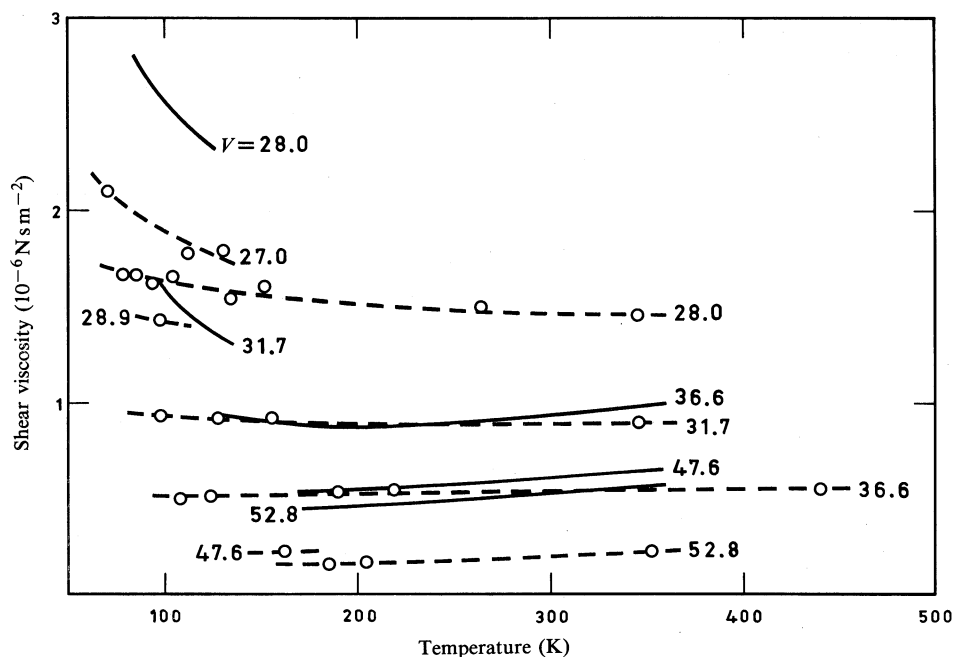


Fig. 1. Temperature dependence of the shear viscosity coefficient for argon at different molar volumes (in  $10^{-6} \text{ m}^3 \text{ mole}^{-1}$ ): solid curves, experimental values (Michels *et al.* 1954; Hanley *et al.* 1974); dashed curves and open circles, calculated values.

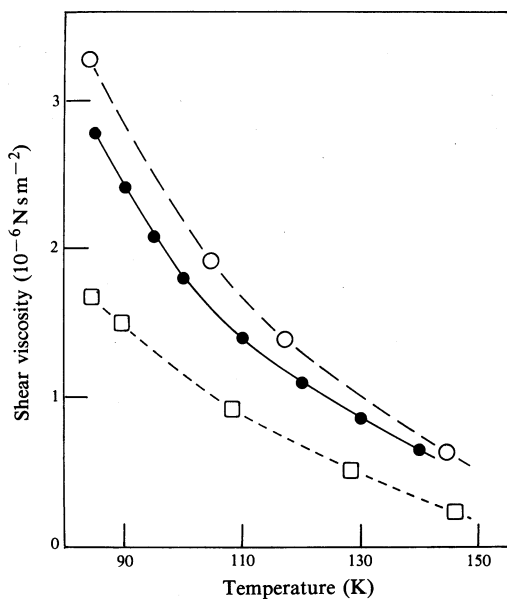


Fig. 2. Comparison of experimental data with Kirkwood and NEMD simulation estimates of the viscosity of liquid argon along the coexistence curve: solid circles, experimental values (Haynes 1973); open circles, NEMD (Ashurst and Hoover 1973); and squares, the Kirkwood theory (present work).



One attempt to quantify the relationship between the singlet and pair diffusion coefficients has been made in a two-dimensional molecular dynamics study by Fehder *et al.* (1971). They estimated that the relative two-dimensional diffusion coefficient at close separations was depressed by about 40%. However, their results also suggest that in the asymptotic limit, equation (24) is more appropriate than (23). The consequence of this result is that the intermolecular contributions to the shear viscosity coefficient in Table 1 for the Kirkwood theory have been overestimated.

Our results do confirm the conclusion of Mazo (1967) that the validation of the Kirkwood and related theories can be achieved only when the relationship between the one- and two-particle friction constants has been determined. This relationship can, in principle, be established by molecular dynamics calculations.

## References

- Andrade, E. N. daC. (1934). *Philos. Mag.* **17**, 497; 698.
- Ashurst, W. T., and Hoover, W. G. (1973). *Phys. Rev. Lett.* **31**, 206.
- Ashurst, W. T., and Hoover, W. G. (1975). *Phys. Rev. A* **11**, 658.
- Bird, R. B., and Curtis, C. F. (1984). *Phys. Today* **37** (No. 1), 36.
- Collings, A. F. (1967). *J. Chem. Phys.* **47**, 1265.
- Collings, A. F., Watts, R. O., and Woolf, L. A. (1971). *Mol. Phys.* **20**, 1121.
- Croxton, C. A. (1974). 'Liquid State Physics—A Statistical Mechanical Introduction' (Cambridge Univ. Press).
- Evans, D. J. (1983). In 'Nonlinear Fluid Behaviour' (Ed. H. J. M. Hanley), p. 51 (North-Holland: Amsterdam).
- Eyring, H., Glasstone, S., and Laidler, K. J. (1941). 'The Theory of Absolute Reaction Rates' (Wiley: New York).
- Fehder, P. L., Emeis, C. A., and Futrelle, R. P. (1971). *J. Chem. Phys.* **54**, 4921.
- Fisher, R. A., and Watts, R. O. (1972). *Aust. J. Phys.* **25**, 21.
- Green, M. S. (1954). *J. Chem. Phys.* **22**, 398.
- Green, M. S. (1960). *J. Chem. Phys.* **33**, 1043.
- Hanley, H. J. M., McCarty, R. D., and Haynes, W. M. (1974). *J. Phys. Chem. Ref. Data* **3**, 979.
- Haynes, W. M. (1973). *Physica* **67**, 440.
- Hirschfelder, J. O., Curtis, C. F., and Bird, R. B. (1954). 'Molecular Theory of Gases and Liquids' (Wiley: New York).
- Kestin, J. (1983). In 'Nonlinear Fluid Behaviour' (Ed. H. J. M. Hanley), p. 421 (North-Holland: Amsterdam).
- Kirkwood, J. G. (1946). *J. Chem. Phys.* **14**, 180.
- Kirkwood, J. G., Buff, F. P., and Green, M. S. (1949). *J. Chem. Phys.* **17**, 988.
- Kirkwood, J. G., Lewinson, V. A., and Alder, B. J. (1952). *J. Chem. Phys.* **20**, 929.
- Kubo, R. (1958). In 'Lectures in Theoretical Physics' Vol. 1 (Eds W. E. Britten and L. G. Dunham), p. 120 (Interscience: New York).
- Levesque, D., and Verlet, L. (1970). *Phys. Rev. A* **2**, 2514.
- McLaughlin, E. (1964). *Chem. Rev.* **65**, 389.
- Mazo, R. M. (1961). *J. Chem. Phys.* **35**, 831.
- Mazo, R. M. (1967). 'Statistical Mechanical Theories of Transport Properties' (Pergamon: Oxford).
- Michels, A., Boltzen, A., and Schuurman, W. (1954). *Physica* **20**, 1141.
- Palyvos, J. A., and Davis, H. T. (1967). *J. Phys. Chem.* **71**, 439.
- Perry, P., and Throop, G. J. (1972). *J. Chem. Phys.* **57**, 1827.
- Resibois, P., and Davis, H. T. (1964). *Physica* **30**, 1077.
- Rice, S. A., and Gray, P. (1965). 'The Statistical Mechanics of Simple Liquids' (Interscience: New York).
- Rice, S. A., and Kirkwood, J. G. (1959). *J. Chem. Phys.* **31**, 901.
- Smedley, S. I., and Woodcock, L. V. (1974). *J. Chem. Soc.* **6**, 955.
- Verlet, L. (1968). *Phys. Rev.* **165**, 201.

Zwanzig, R. (1964). *J. Chem. Phys.* **40**, 2527.

Zwanzig, R., Kirkwood, J. G., Oppenheim, I., and Alder, B. J. (1954). *J. Chem. Phys.* **22**, 783.

Zwanzig, R., Kirkwood, J. G., Stripp, K. F., and Oppenheim, I. (1953). *J. Chem. Phys.* **21**, 2050.

Manuscript received 24 December 1985, accepted 15 July 1986