CALCULATED SELF–DIFFUSION COEFFICIENTS FOR LIQUID ARGON

By R. A. Fisher*† and R. O. Watts*

Abstract

The method of molecular dynamics has been applied with the Barker–Bobetic pair potential for argon interactions to calculate the self-diffusion coefficients of liquid and dense gaseous argon. These self-diffusion coefficients are compared with experimental values and with values obtained from the Lennard–Jones potential. There are significant differences between the calculated and experimental values at high densities.

I. INTRODUCTION

Non-equilibrium statistical mechanics, unlike equilibrium statistical mechanics, still contains a number of conceptual problems. Although many attempts have been made to place it on a rigorous footing (Prigogine 1962), the development of the subject to a stage where reliable numerical estimates of transport coefficients in dense fluids can be made is still in progress. At one time many attempts were made to develop theories based on the BBGKY hierarchy of integral equations for non-equilibrium distribution functions (Irving and Kirkwood 1950; H. S. Green 1952). However, the work of Cohen and others (Ernst, Haines, and Dorfman 1969) has removed much of the interest from this approach. Similarly the work of Kirkwood (1946), who based a theory of transport in dense fluids on concepts derived from Brownian motion theory, has recently been shown to lead to nonphysical results (Fisher and Watts 1972). Another approach to a theory of transport was developed from Kirkwood's theory by Rice and Allnatt (1961) and Allnatt and Rice (1961) and initially this theory appeared to give excellent results (Rice and Gray 1965). However, a number of problems associated with the application of this theory indicated that it was not as good as the initial examinations suggested (Collings 1967) and recent work using exact distribution functions for the hard-sphere modified Lennard–Jones potential has confirmed this (Collings, Watts, and Woolf 1971). The result is that a large number of approaches to a theory of transport in dense fluids have proven to be inadequate.

A more promising approach to a theory of transport is the autocorrelation function method (Kubo 1959). In this method the non-equilibrium distribution function is assumed to be close to its equilibrium value, the deviation from equilibrium being due to a small perturbation on the Hamiltonian of the system. This perturbation may result from the application of external conservative forces (e.g. electrical or magnetic fields) or from internal nonconservative "thermodynamic"

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forces such as the chemical potential gradient responsible for mass diffusion. The non-equilibrium distribution function is then expanded as a power series in the perturbation, and terms beyond those linear in this perturbation are ignored (McLennan 1959). In principle this approach is equivalent to the macroscopic non-equilibrium thermodynamics of Onsager (1931a, 1931b). When the (approximate) non-equilibrium distribution function is used to determine the average value of some microscopic flux, it is found that the first-order term gives the appropriate transport coefficient. In fact, just as in non-equilibrium thermodynamics (Fitts 1962), a linear relation is found between fluxes and their conjugate forces and the appropriate coefficients satisfy the Onsager reciprocal relations (McLennan 1959). This approach was developed by several workers including M. S. Green (1952, 1954), Kubo (1957), and Mori (1958). The end result is that transport coefficients may be related to time integrals of certain autocorrelation functions $C_{ij}(t)$ through

$$\Gamma_{ij} = \int_0^\infty C_{ij}(t)\,\mathrm{d}t = \int_0^\infty \langle \boldsymbol{J}_i(0) \cdot \boldsymbol{J}_j(t) \rangle\,\mathrm{d}t, \qquad (1)$$

where Γ_{ij} is a particular transport coefficient and $\boldsymbol{J}_i(0)$ and $\boldsymbol{J}_j(t)$ are two quantities which can be related to the appropriate fluxes (i) and (j). The average, which is designated by angle brackets, is calculated by using an equilibrium distribution function to determine the positions and momenta.

Although expressions of the form (1) have been given for many different transport coefficients (Zwanzig 1965) only rather limited computations using them have been reported, since the application of these formulae requires a knowledge of the behaviour of the system over some period of time. The positions and momenta of a model system may be generated by solving Newton's equations of motion starting from some convenient initial state, i.e. by the method of molecular dynamics (Wainwright and Alder 1958). After discarding a suitable number of configurations to ensure that the system is in equilibrium, the autocorrelation function $C_{ij}(t)$ is then obtained as a time average over the equilibrium ensemble. The required transport coefficient may then be obtained by numerical integration. This method has previously been used to obtain the self-diffusion coefficient of both the hard-sphere fluid (Alder and Wainwright 1969) and the Lennard–Jones fluid (Rahman 1964; Bruin 1969; Levesque and Verlet 1971). In addition the shear and bulk viscosities have been studied by Wainwright (1964) and Alder, Gass, and Wainwright (1970) for hard-spheres, while Bruin (1969) has also reported the viscosities and thermal conductivity of the Lennard–Jones fluid near the critical region. In the case of the self-diffusion coefficient the Lennard–Jones results were in reasonable agreement with the experimental values for argon in the gaseous phase, and in some regions of the liquid phase. Bruin's results for the viscosities and thermal conductivity were also in reasonable agreement with the corresponding results for argon, whilst the hard-sphere results (Wainwright 1964; Alder, Gass, and Wainwright 1970) were in qualitative agreement with those calculated using the Enskog theory (Chapman and Cowling 1953). However, no extensive calculations of the two viscosities and thermal conductivity have been reported for the liquid region.

The problem of accurately representing the interatomic interactions in a system of argon atoms has been studied for many years. Probably the most accurate representation obtained to date is a combination of a two-body potential and a three-body potential developed during the past few years by Barker and co-workers (Barker and Pompe 1968; Bobetic and Barker 1970; Barker, Fisher, and Watts 1971). This combination was originally used to calculate the second and third virial coefficients and the gas-phase transport data for argon (Barker and Pompe 1968). After being refined so that it reproduced many of the zero-kelvin properties of solid argon (Bobetic and Barker 1970), it was finally adjusted so that one potential function would reproduce all the gas, liquid, and low-temperature solid data of argon (Barker, Fisher, and Watts 1971). As part of this program, extensive molecular dynamics calculations were carried out for the liquid phase by Barker, Fisher, and Watts using the Barker–Bobetic potential (Bobetic and Barker 1970). In the present work the data generated during that study have been used to calculate the transport properties of liquid argon (Mills 1971).

II. Numerical Generation

As stated in the Introduction we have used the Barker–Bobetic potential to model the argon interactions. This potential is a combination of a pair potential involving a number of parameters and the Axilrod–Teller (1943) triplet potential. The pair potential is of the form

$$\phi(r) = \epsilon\left(\exp\{\alpha(1-r)\} \sum_{i=0}^{5} A_i(r-1)^i - \sum_{j=0}^{2} C_{2j+6}/(\delta+r^{2j+6})\right), \qquad (2)$$

where $r = R/R_{\min}$, R being the distance between the centres of the atoms and $R_{\min}$ the separation of the atoms at the minimum in the potential, and the coefficients A_i ($i = 0,\ldots,5$), ϵ, and α are parameters fitted to various experimental properties of the gas and low-temperature solid (Bobetic and Barker 1970). The parameters C_6, C_8, and C_{10} give the first three terms in the long-range multipole expansion of the potential energy (Leonard 1968). This potential has given excellent results for the gas and solid data (Bobetic and Barker 1970; Barker, Bobetic, and Pompe 1971) and good results for the thermodynamic properties of the liquid (Barker, Fisher, and Watts 1971).

The molecular dynamics calculations were carried out for a system of 108 particles in a periodic cubic box using the method described by Verlet (1967, 1968). A total of 10 liquid-state points and 5 points in the critical region were computed, the behaviour of each system being followed for at least 5×10^{-11} seconds. During the course of the calculations the total momentum remained close to zero and the total energy (kinetic plus potential) was constant to four decimal places. The thermodynamic properties obtained from these configurations were in excellent agreement with the Monte Carlo calculations by Barker, Fisher, and Watts (1971), and no sign was observed of the systematic differences found between Verlet's (1967, 1968) molecular dynamics calculations and McDonald and Singer's (1969) Monte Carlo calculations for the Lennard–Jones potential. We conclude from this that our basic

molecular dynamics calculations were accurate. The accuracy of the analysis of the generated data is discussed in Section III.

As stated in the Introduction, the transport coefficients can be calculated as integrals of time autocorrelation functions. In the present case the molecular dynamics calculations were carried out for a set of particles interacting through a two-body potential of the form (2) but truncated at $2 \cdot 5 R_{\min}$ to reduce the amount of computation to a reasonable level, following the precedent set by Rahman (1964) and Verlet (1967, 1968). In principle the results given in Section III should be corrected both for the effects of this truncation and for the neglect of the three-body terms. Such corrections were carried out by Barker, Fisher, and Watts (1971) for the equilibrium results obtained from this potential by using a variant of Zwanzig's (1954) high-temperature perturbation theory. Two simple versions of this theory have been given for transport phenomena, the first by Frisch and Berne (1965) and the second by Watts (1971). Unfortunately both of these theories have subsequently been shown to lead to erroneous results (Harris 1971; Watts 1972) and although Harris (1971) gives the correct form of the theory this does not appear to be computationally viable. Consequently it has not been possible for us to include these correction terms. Although this may have some effect on the results, we believe that these (presumably) small corrections do not substantially alter the following discussion.

III. SELF-DIFFUSION COEFFICIENTS

The expression relating the self-diffusion coefficient to the properties of the particles in a system was first derived using intuitive arguments by Einstein (1905) in his theory of Brownian motion and has since been rederived by many authors (Zwanzig 1965). In the time-integral approach the self-diffusion coefficient D is obtained from the velocity autocorrelation function:

$$D = \tfrac{1}{3} \int_0^\infty \langle \boldsymbol{v}_1(0) \cdot \boldsymbol{v}_1(t) \rangle \, \mathrm{d}t, \tag{3}$$

where $\boldsymbol{v}_1(t)$ is the velocity of particle 1 at time t. In molecular dynamics work, the velocity autocorrelation function C_D is estimated by averaging over all the particles in the system for a large number of initial times:

$$C_D(t) = N^{-1} \sum_{i=1}^N M^{-1} \sum_{k=1}^M \boldsymbol{v}_i(t_k) \cdot \boldsymbol{v}_i(t_k + t), \tag{4}$$

where t_k is the time of the kth step in the molecular dynamics integration, N the number of particles in the system, and M the number of initial times used. For the present work N was 108 and M was chosen to be 1200. The velocity autocorrelation function was calculated for values of t between 0 and 10^{-12} s at intervals of 5×10^{-14} s and between 10^{-12} and 10^{-11} s at intervals of 2×10^{-13} s. Values of the self-diffusion coefficient were then obtained by integrating equation (3) using Simpson's rule. The coefficients calculated in this way from the velocity autocorrelation function have been labelled D_{va} and are listed in Table 1 for corresponding values of molar volume V_M and temperature T. Zwanzig and Ailawadi (1969) have analysed the

errors that occur in calculations of the self-diffusion coefficient using equation (3). Their analysis indicates that the present results for D_{va} could contain errors as large as 10%, mainly due to the difficulty in obtaining good averages for the tail of the autocorrelation function. As this function is small beyond about 2×10^{-12} s for the liquid phase, the errors in the tail can become significant. In principle we have enough information stored on tape to enable these errors to be reduced to about 4% (based on Zwanzig and Ailawadi's formula) but this would require a considerable increase in the amount of computation. Since we cannot at present correct for three-body and truncation effects, which are probably also significant at this higher level of accuracy, we did not attempt the more extensive calculations. As a check on the relative accuracy of the results we found that the velocity autocorrelation functions were similar to those of Rahman (1964) both for the liquid phase, in which negative regions are found, and for the gas phase where the result is close to the
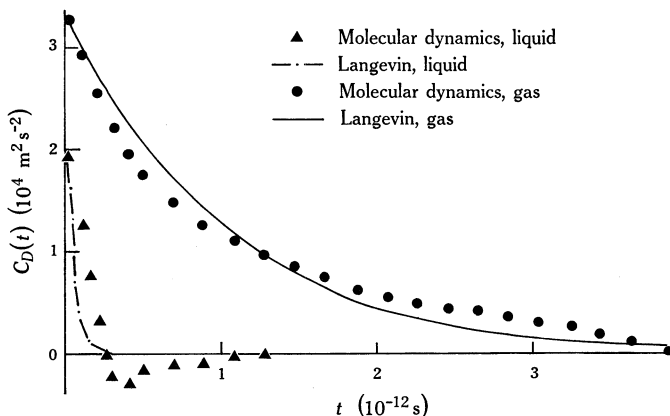

Fig. 1.—Velocity autocorrelation functions $C_D(t)$ for both liquid argon ($V_M = 27 \cdot 04$ cm^3, $T = 94 \cdot 1$ K) and dense gaseous argon ($V_M = 91 \cdot 92$ cm^3, $T = 159 \cdot 1$ K).

exponential decay predicted by the Langevin equation (Rice and Gray 1965). These features are shown in Figure 1, where $C_D(t)$ is compared with the Langevin exponential decay for the liquid phase ($V_M = 27 \cdot 04$ cm^3, $T = 94 \cdot 1$ K) and for the gas phase ($V_M = 91 \cdot 92$ cm^3, $T = 159 \cdot 1$ K).

There is an alternative form of equation (3) in which the self-diffusion co-efficient is related to the mean square displacement of a particle through the formula (Egelstaff 1967)

$$D_{ms} = (1/6t)\langle\{r_1(t) - r_1(0)\}^2\rangle. \tag{5}$$

We estimated D_{ms} from this formula in the following way. The mean square displacement at a particular time was obtained by averaging the displacements of all 108 particles over 167 initial times separated by $1 \cdot 5 \times 10^{-13}$ s. This value was calculated for 400 separate times between $1 \cdot 0 \times 10^{-11}$ and $1 \cdot 4 \times 10^{-11}$ s and the results plotted as a function of time. The slope of a line of least squares fit to these data points was then equal to $6D_{ms}$. The resulting values of D_{ms} for several points in both the gas and liquid phases are also given in Table 1. The accuracy of these values was

checked at two points, one for the liquid phase ($V_M = 27 \cdot 04$ cm^3, $T = 94 \cdot 1$ K) and the other for the gas phase ($V_M = 91 \cdot 92$ cm^3, $T = 159 \cdot 1$ K), by using the same procedure to calculate the mean square displacement at times t between 5×10^{-12} and 9×10^{-12} s. The results are in good agreement (see Table 1), thus suggesting that the onset of hydrodynamic behaviour has occurred by this time. This agrees with the conclusions reached by Rahman (1964) and Levesque and Verlet (1971) who obtained good values of the self-diffusion coefficient from this region. A comparison of D_{va}, D_{ms}, and the two check values of D_{ms} in Table 1 indicates that the numerical errors in D_{ms} are probably smaller than the 10% value assumed for D_{va}.

TABLE 1

SELF-DIFFUSION COEFFICIENTS OF ARGON

All values of the coefficients are expressed in units of 10^{-9} m^2 s^{-1}

V_M (cm^3)	T (K)	D_{va}	D_{ms}	D_{LJ}	D_{exp}
26·26	89·6	0·71	0·80	1·01	0·14
27·04	87·9	1·16	1·28	1·38	0·42
	94·1	1·28	1·37 (1·39)*	1·52	0·28
	105·0	1·46	1·56	1·80	0·19
27·85	83·6	1·78	1·67	1·65	0·93
	89·7	1·64	1·84	1·82	1·12
	103·2	2·08	2·04	2·19	0·53
28·73	91·6	—	2·28	2·30	1·70
	96·5	2·26	—	2·44	1·50
	108·9	2·72	2·76	2·80	1·65
57·45	156·9	21·3	20·4	—	—
65·66	168·9	26·3	27·6	—	—
70·71	159·1	25·9	25·8	—	—
76·60	158·7	27·0	25·6	29·0†	27–30‡
91·92	159·1	33·5	29·6 (26·8)*	—	—

* The values in parentheses were calculated from equation (5) for t in the range 5×10^{-12} to 9×10^{-12} s. They are a check on the accuracy of the D_{ms} values.

† This value was calculated by Bruin (1969) for $V_M = 75 \cdot 3$ cm^3, $T = 150$ K.

‡ This result was given by De Paz (1968) for $V_M = 75 \cdot 3$ cm^3, $T = 150$ K.

Table 1 also includes experimental values of the self-diffusion coefficient for argon (D_{exp}) and the results of calculations for the Lennard–Jones potential (D_{LJ}). The experimental data were obtained from the measurements of Naghizadeh and Rice (1962) for liquid argon. They reported that at a pressure of 135 atm their data were reproduced by the interpolation formula

$$D_{exp} = 0 \cdot 89 \times 10^{-7} \exp(-373/T), \qquad (6)$$

whilst at 12 atm the formula was

$$D_{exp} = 1 \cdot 16 \times 10^{-7} \exp(-352/T). \qquad (7)$$

On the assumption that $\ln D_{\text{exp}}$ is a linear function of the pressure we have extrapolated from these formulae to obtain the values given in Table 1.

Naghizadeh and Rice's (1962) data did not extend to the critical region, and consequently the extrapolation of their formulae cannot be used in this region. The final entry for D_{exp} given in Table 1 was obtained from the work of De Paz (1968) and holds for $V_M = 75 \cdot 3$ cm³, $T = 150$ K. It is possible that the experimental data have quite large error bounds. For example, at $T = 84$ K equation (7) predicts a self-diffusion coefficient of $1 \cdot 74 \times 10^{-9}$ m²s⁻¹ whereas Cini-Castagnoli and Ricci (1960) using the same method for a pressure of $0 \cdot 92$ atm and the same temperature obtained a value of $1 \cdot 53 \times 10^{-9}$ m²s⁻¹ while Zandeveld *et al.* (1970) using inelastic neutron scattering experiments reported a value of $1 \cdot 6 \times 10^{-9}$ m²s⁻¹.

The results for the Lennard–Jones potential included in Table 1 are taken from Levesque and Verlet (1971), who fitted their data to an interpolation formula of the form

$$D_{\text{LJ}} = AT/\rho^2 + B - C\rho, \tag{8}$$

where A, B, and C are constants. This formula also does not hold for the gaseous phase and in addition Levesque and Verlet state that it gives results that are about 5% high for the liquid region. We have allowed for this when calculating D_{LJ} for Table 1.

In an attempt to smooth the results given in Table 1 they were fitted to the interpolation formula (8), which yielded the equation

$$D = (13 \cdot 519 + 2 \cdot 4171 \times 10^{-5} T V_M^2 - 374 \cdot 3/V_M) \times 10^{-9} \text{ m}^2\text{s}^{-1}.$$

From this equation the self-diffusion coefficient at $V_M = 29 \cdot 11$ cm³, $T = 90$ K was calculated to be $2 \cdot 50 \times 10^{-9}$ m²s⁻¹. This should be compared with the experimental value obtained by Naghizadeh and Rice (1962) of $2 \cdot 43 \times 10^{-9}$ m²s⁻¹, which is also the result found by Rahman (1964) for the same molar volume and $T = 94$ K. Although the agreement is satisfactory for $V_M = 29 \cdot 11$ cm³, however, this does not hold for lower molar volumes. From the data in Table 1 it can be seen that at smaller V_M the experimental diffusion coefficients are much less than the corresponding calculated values, despite the differences that exist between the values calculated for the Lennard–Jones potential and our model values calculated for the Barker–Bobetic potential. In particular it appears unlikely that liquid argon would have a self-diffusion coefficient as low as $0 \cdot 28 \times 10^{-9}$ m²s⁻¹ even at a pressure of about 500 atm, which corresponds to $V_M = 27 \cdot 04$ cm³, $T = 94 \cdot 1$ K. Therefore we consider that the experimental extrapolation is incorrect. Either the raw data are not accurate enough for such extrapolations to be made or the assumption that $\ln D_{\text{exp}}$ is a linear function of the pressure does not hold over the whole temperature and density range considered here.

Finally it is worth considering a further qualitative similarity between the present results and those obtained by previous workers. In Figure 2 the self-diffusion coefficient of the particles has been plotted as a function of time. The curve was calculated from equation (5) for the state $V_M = 27 \cdot 04$ cm³, $T = 105$ K. It is seen

that after an initial sharp increase, the function reaches a maximum at about $0\cdot15\times10^{-12}$ s and then slowly decreases to reach a steady value after about 5×10^{-12} s. It was for this reason that the mean square displacement was computed for times greater than 10^{-11} s when calculating D_{ms}. It is of interest that this behaviour was also observed by Alder, Gass, and Wainwright (1970) in their studies of the hard-sphere system. At lower densities it was found that $D(t)$ approached its final value in much the same time as at higher densities, but that it did not exhibit the maximum shown in Figure 2. In addition to this feature of the self-diffusion coefficient calculations, various workers have reported on properties of the velocity autocorrelation function. In particular Alder and Wainwright (1970) have shown that this function decays to zero as $(\eta t)^{-d/2}$, where d is the dimensionality of the system and η the viscosity, while Verlet (1971) has developed various approximate expressions for the function based on the memory function formalism. We did not have enough data to study Alder and Wainwright's (1970) observations for a realistic potential and did not feel that the Barker–Bobetic potential was sufficiently different from the Lennard–Jones potential to enable us to make a significant contribution to the memory function approach.
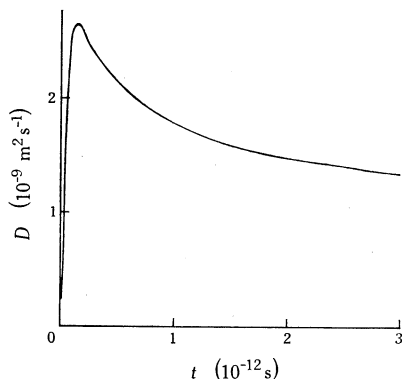

Fig. 2.—Self-diffusion coefficient of argon as a function of time. The curve was calculated from equation (5) for the state $V_M = 27\cdot04$ cm^3, $T = 105$ K.

IV. CONCLUSIONS

Although the self-diffusion coefficients of argon which have been calculated here from the Barker–Bobetic potential are much higher than experimental values for small molar volumes, they are in reasonable agreement with results reported for the Lennard–Jones potential. In addition the coefficients obtained from the mean square displacement of a particle are in acceptable agreement with those obtained by integrating the velocity autocorrelation function. The differences could be reduced by extending the calculations considerably, although this would not seem to be warranted until more accurate experimental data are available. However, the present calculations show, firstly, that it is possible to obtain accurate values of the self-diffusion coefficient from systems of 108 particles and, secondly, that neglect of the long-range and three-body contributions is probably not important at the level of accuracy used here, as indicated by the reasonable agreement with the results of Levesque and Verlet (1971).

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VI. References

ALDER, B. J., GASS, D. M., and WAINWRIGHT, T. E. (1970).—*J. chem. Phys.* **53**, 3813.

ALDER, B. J., and WAINWRIGHT, T. E. (1969).—*J. phys. Soc. Japan* (Suppl. No. 1) **26**, 267.

ALDER, B. J., and WAINWRIGHT, T. E. (1970).—*Phys. Rev.* A **1**, 18.

ALLNATT, A. R., and RICE, S. A. (1961).—*J. chem. Phys.* **34**, 2156.

AXILROD, B. M., and TELLER, E. (1943).—*J. chem. Phys.* **11**, 299.

BARKER, J. A., BOBETIC, M. V., and POMPE, A. (1971).—*Molec. Phys.* **20**, 347.

BARKER, J. A., FISHER, R. A., and WATTS, R. O. (1971).—*Molec. Phys.* **21**, 657.

BARKER, J. A., and POMPE, A. (1968).—*Aust. J. Chem.* **21**, 1683.

BOBETIC, M. V., and BARKER, J. A. (1970).—*Phys. Rev.* B **2**, 4169.

BRUIN, C. (1969).—*Phys. Lett.* A **28**, 777.

CHAPMAN, S., and COWLING, T. G. (1953).—"Mathematical Theory of Non-uniform Gases." (Cambridge Univ. Press.)

CINI-CASTAGNOLI, G., and RICCI, F. P. (1960).—*J. chem. Phys.* **32**, 19.

COLLINGS, A. F. (1967).—*J. chem. Phys.* **47**, 1265.

COLLINGS, A. F., WATTS, R. O., and WOOLF, L. A. (1971).—*Molec. Phys.* **20**, 1121.

DE PAZ, M. (1968).—*Phys. Rev. Lett.* **20**, 183.

EGELSTAFF, P. A. (1967).—"An Introduction to the Liquid State." (Academic Press: London.)

EINSTEIN, A. (1905).—*Annln Phys.* **17**, 549.

ERNST, M. H., HAINES, L. K., and DORFMAN, J. R. (1969).—*Rev. mod. Phys.* **41**, 296.

FISHER, R. A., and WATTS, R. O. (1972).—*Aust. J. Phys.* **25**, 21.

FITTS, D. D. (1962).—"Non-equilibrium Thermodynamics." (McGraw–Hill: London.)

FRISCH, H. L., and BERNE, B. (1965).—*J. chem. Phys.* **43**, 250.

GREEN, H. S. (1952).—"Molecular Theory of Fluids." (Interscience: New York.)

GREEN, M. S. (1952).—*J. chem. Phys.* **20**, 1281.

GREEN, M. S. (1954).—*J. chem. Phys.* **22**, 398.

HARRIS, S. (1971).—*Molec. Phys.* **21**, 933.

IRVING, J. H., and KIRKWOOD, J. G. (1950).—*J. chem. Phys.* **18**, 817.

KIRKWOOD, J. G. (1946).—*J. chem. Phys.* **14**, 180.

KUBO, R. (1957).—*J. phys. Soc. Japan* **12**, 570.

KUBO, R. (1959).—*Lect. theor. Phys. Summer Inst.* **1**, 120.

LEONARD, P. J. (1968).—M.Sc. Thesis, University of Melbourne.

LEVESQUE, D., and VERLET, L. (1971).—*Phys. Rev.* A **2**, 2514.

McDONALD, I. R., and SINGER, K. (1969).—*J. chem. Phys.* **50**, 2308.

McLENNAN, J. A. (1959).—*Phys. Rev.* **115**, 1405.

MILLS, R. (1971).—*Ber. Bunsenges phys. Chem.* **75**, 195.

MORI, H. (1958).—*Phys. Rev.* **111**, 694.

NAGHIZADEH, J., and RICE, S. A. (1962).—*J. chem. Phys.* **36**, 2710.

ONSAGER, L. (1931a).—*Phys. Rev.* **37**, 405.

ONSAGER, L. (1931b).—*Phys. Rev.* **38**, 2265.

PRIGOGINE, I. (1962).—"Non-equilibrium Statistical Mechanics." (Interscience: New York.)

RAHMAN, A. (1964).—*Phys. Rev.* **136**, A405.

RICE, S. A., and ALLNATT, A. R. (1961).—*J. chem. Phys.* **34**, 2144.

RICE, S. A., and GRAY, P. (1965).—"Statistical Mechanics of Simple Liquids." (Interscience: New York.)

VERLET, L. (1967).—*Phys. Rev.* **159**, 98.

VERLET, L. (1968).—*Phys. Rev.* **165**, 201.

VERLET, L. (1971).—*Ber. Bunsenges phys. Chem.* **75**, 389.

WAINWRIGHT, T. E. (1964).—*J. chem. Phys.* **40**, 2932.

WAINWRIGHT, T. E., and ALDER, B. J. (1958).—*Nuovo Cim. Suppl.* **9**(10), 116.

WATTS, R. O. (1971).—*Molec. Phys.* **20**, 765.

WATTS, R. O. (1972).—*J. chem. Phys.* **56**, 3731.

ZANDEVELD, P., ANDRIESSE, L. D., BREGRIAN, J. D., HUSMAN, A., and VANLOF, J. J. (1970).—
    Physica, 's Grav. **50**, 511.

ZWANZIG, R. (1954).—*J. chem. Phys.* **22**, 1420.

ZWANZIG, R. (1965).—*A. Rev. phys. Chem.* **16**, 67.

ZWANZIG, R., and AILAWADI, N. K. (1969).—*Phys. Rev.* **182**, 280.