The Study of Simple Liquids By Computer Simulation

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1 Introduction

The derivation of the physical properties of macroscopic systems from the intermolecular potentials is a major but largely unattained objective of molecular theory. For dilute gases and certain crystalline solids the problem is greatly simplified by the fact that these systems may be satisfactorily represented by models consisting of entities, particles, or oscillators, which are independent of each other. No such simplification is possible in the case of compressed gases, liquids, and solutions and the mathematical difficulties of the many-body problem are obstacles to progress. It is possible to by-pass these difficulties to some extent by making use of powerful computer simulation techniques which have been developed in recent years. Such methods have proved particularly valuable for the study of simple liquids, *i.e.*, liquids composed of molecules obeying the laws of classical mechanics and interacting through potentials which are spherically symmetric and pair-wise additive. The substances which most closely resemble this ideal are the heavier rare gases (A, Kr, Xe) and liquids composed either of certain diatomic molecules (*e.g.*, N_2, O_2, CO) or of polyatomic molecules which are approximately spherical (*e.g.*, CH_4). These systems display the characteristic features of the liquid state without the problems arising from more complicated modes of interaction. Argon is the example most frequently quoted because a wealth of accurate experimental data is available.

This Review is concerned with the application to the study of simple liquids of the techniques of computer simulation known as the Monte Carlo method and the method of molecular dynamics. In each case the properties studied are those of a model system representing a fluid at fixed temperature and density and containing, typically, tens or hundreds of particles. In the Monte Carlo method, devised originally by Metropolis *et al.*[1] and later developed by Wood and his collaborators,[2-4] a set of molecular configurations is generated in the

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[1] Metropolis, Rosenbluth, Rosenbluth, Teller, and Teller, *J. Chem. Phys.*, 1953, **21**, 1087.
[2] W. W. Wood and F. R. Parker, *J. Chem. Phys.*, 1957, **27**, 720.
[3] W. W. Wood, F. R. Parker, and J. D. Jacobson, *Nuovo Cimento, suppl.* X, 1958, **9**, 133.
[4] W. W. Wood, 'Physics of Simple Liquids', ed. H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, North-Holland Publishing Co., Amsterdam 1968.

computer by random displacements of the particles of the model; the configurations are accepted or rejected according to a criterion which ensures that a given configuration occurs with a probability proportional to the Boltzmann factor, exp $(-\beta\Phi)$, for that configuration. (Φ is the total potential energy of the configuration and $\beta \equiv 1/k_BT$.) The equilibrium value of a physical property X may then be found by taking an average value $\langle X \rangle$ over the whole set of configurations. In the method of molecular dynamics developed by Alder and Wainwright[5, 6] the equations of motion of the particles of the model are solved by step-wise numerical integration. The equilibrium properties of the system are calculated from averages taken over a sufficiently long time interval. Time-dependent phenomena may also be studied. The Monte Carlo and molecular dynamics methods therefore provide, respectively, solutions of the many-body problem in classical statistical mechanics and classical kinetic theory. Their success is due to the fact that, at least for homogeneous phases, the average properties per particle of a relatively small model are generally very close to those of the macroscopic system which the model is chosen to represent.

A complete Monte Carlo or molecular dynamics calculation may be regarded as a computer 'experiment' which yields accurate information on the consequences of a given intermolecular force law. The results of such an 'experiment' can be used to test the adequacy of pair potentials proposed for some real system or, conversely, to determine the 'best' pair potential for a real system by comparing measured and computed thermodynamic and transport properties. Statistical mechanical theories may be tested unambiguously by comparing results derived by means of a theory from a given pair potential with those obtained for the same potential in a Monte Carlo or molecular dynamics calculation. It is also possible to obtain data which are experimentally inaccessible or nearly inaccessible. For example the motion of molecules in a simple liquid can be studied in great detail in a molecular dynamics 'experiment'; equilibrium and time-dependent pair distribution functions can be calculated without the considerable errors involved in determining these functions by means of X-ray and neutron diffraction experiments; and for systems of two components, A and B say, the total potential energy and the total radial distribution function can be resolved into contributions from A–A, B–B, and A–B pairs.

At the time of the last review of this subject in these pages[7] the Monte Carlo and molecular dynamics methods had been applied to the study of systems of hard elastic spheres, and a promising beginning had been made with Monte Carlo calculations for a Lennard-Jones 12–6 potential. This early work has also been reviewed elsewhere.[4, 8] Assemblies of hard spheres and other highly idealised systems are of theoretical interest and have continued to receive attention. This review, however, will be mainly concerned with 'realistic' pair

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[5] B. J. Alder and T. W. Wainwright, *J. Chem. Phys.*, 1959, **31**, 459.

[6] B. J. Alder and T. W. Wainwright, 'The Many-Body Problem', ed. J. K. Percus, Interscience, New York, 1963.

[7] M. A. D. Fluendy and E. B. Smith, *Quart Rev.*, 1962, **16**, 241.

[8] I. Z. Fisher, *Soviet Phys. Uspekhi*, 1960, **2**, 783.

potentials such as the 12–6 and exp–6 functions. (These potentials are described in section 3.) Thermodynamic properties, including phase equilibria and the properties of mixtures, structural properties, and time-dependent phenomena are discussed in separate sections.

2 Computational Details

The same basic computer model is used both in Monte Carlo calculations and in molecular dynamics. A system of N particles is confined within a cell, usually a cube, of volume V, and the co-ordinates which define the position of each particle within the cell are stored in the computer. The number of particles in the cell is generally less than a thousand, and in order to simulate as closely as possible the behaviour of a macroscopic system a periodic boundary condition is used: the fundamental cell is surrounded by replicas of itself; each replica contains N particles which occupy the same relative positions as those in the fundamental cell. It is also advantageous to choose N and the shape of the cell in such a way that the periodic boundary condition generates a perfect lattice appropriate to the system under study when the particles in the fundamental cell are arranged in a suitably ordered manner. Argon, for example, crystallises in a face-centred cubic lattice and for this system it is therefore convenient to use a cubic cell and choose $N = 4n^3$, where $n = 1, 2, 3, 4, 5, 6 \ldots$ *i.e.*, $N = 4, 32, 108, 256, 500, 864 \ldots$ The particles are assumed to interact through a pair potential $\phi(r)$; the corresponding pair virial function $\psi(r)$, for potentials without discontinuities, is given by

$$\psi(r) = r(\partial\phi/\partial r) \qquad (1)$$

The total potential energy Φ and total virial Ψ of the model are calculated as the sums of pair terms. Interactions between the particles in the fundamental cell and particles in adjacent cells are included in the sums. The contributions from particles separated by a distance greater than some chosen cut-off value are not calculated explicitly but, usually, by integration over a uniform particle density.

In the Monte Carlo method a particle of the system is chosen, either serially or at random, and given a random displacement. Let the increase in total potential energy of the system be $\Delta\Phi$. If $\Delta\Phi$ is negative the move is accepted and the new configuration replaces the old one. If $\Delta\Phi$ is positive the move is accepted only with the probability $\exp(-\beta\Delta\Phi)$.

Repetition of this procedure generates a chain of configurations which are distributed in phase space with a probability density proportional to the Boltzmann factor $\exp(-\beta\Phi)$. (If a move is rejected the previous configuration is counted again.) The overall chain average of any function of the particle co-ordinates (*e.g.*, Φ, Ψ) therefore converges to the canonical ensemble average of the same quantity as the chain length increases. The molar configurational internal energy $U(V, T)$, where V is the molar volume, is proportional to the average potential energy $\langle\Phi\rangle$ of the computer model and the pressure $P(V, T)$ is calculated from the average virial $\langle\Psi\rangle$ by means of the virial theorem. Thus

$$U = (N_0/N)\langle\Phi\rangle \tag{2}$$

$$PV = N_0k_BT - (N_0/3N)\langle\Psi\rangle \tag{3}$$

where N_0 is the Avogadro number. The radial distribution function and other equilibrium properties may also be determined.

In the method of molecular dynamics the particles are given initial velocities and the subsequent motion of the system is studied by numerical integration of Newton's equations. Equilibrium properties are calculated as time-averages and information is also obtained on time-dependent phenomena and transport coefficients. The total energy of the system remains constant apart from small fluctuations caused by the use of a finite time interval in the numerical integrations. The temperature associated with a particular 'experiment' is calculated from the mean kinetic energy. The particle velocities may be changed in the early stages of a calculation if it is found that the temperature has drifted far from the region of interest. As it is desirable to minimise the fluctuations in temperature the model of a macroscopic system used in a molecular dynamics calculation generally contains a larger number of particles than that used in a Monte Carlo study of the same system. Apart from the choice of initial co-ordinates and velocities the molecular dynamics calculation contains no probabilistic elements.

The great advantage of the method of molecular dynamics is that it allows the study of transport processes. This is not possible with the Monte Carlo method but the latter possesses features which are of value in certain applications. For example the method can be extended to the calculation of average values in other types of statistical mechanical ensemble. The procedure outlined above is one appropriate to the usual Gibbs canonical or *NVT*-ensemble but calculations in the isothermal–isobaric or *NPT*-ensemble have also been reported.[4, 9–11] The fact that the temperature is a fixed parameter in a Monte Carlo calculation makes this method particularly suitable for the study of isothermal processes. The efficiencies of the two methods, measured by the total computing time required to give averages of equal statistical reliability, are much the same. A typical Monte Carlo calculation for a system such as liquid argon requires the generation of *ca.* 300,000 configurations of a model containing 108 particles. An equivalent calculation by molecular dynamics would require the integration of the equations of motion of 864 particles for *ca.* 1500 time intervals of *ca.* 10^{-14} sec. In either case the cut-off distance in the energy summations would be *ca.* 9 Å. The machine requirements are severe. The data given in Table 1 provide some indication of the attainable speeds on a number of computers. These figures can be regarded as only a rough guide because they take no account of different programming practices.

[9] W. W. Wood, *J. Chem. Phys.*, 1968, **48**, 415.

[10] I. R. McDonald, *Chem. Phys. Letters*, 1969, **3**, 241.

[11] I. R. McDonald, 'Proceedings of Culham Conference on Computational Physics', UKAEA Culham Laboratory and IPPS, 1969, Vol. 2, July, paper 38.

Table 1 *Machine time used on various computers in simulation studies of the 12–6 potential at liquid densities*

Column (i): number of time steps per hour in molecular dynamics calculation.

Column (ii): number of Monte Carlo configurations generated per hour.

Computer	N	(i)	(ii)
IBM 704[2]	32		19,000
IBM 704[2]	108		6500
IBM 704[50]	250	90	
CDC 3600[50]	864	75	
CDC 6600[13]	864	1500	
UNIVAC 1107[13]	864	150	
UNIVAC 1108[a]	864		400,000
ICT ATLAS[17]	108		260,000
ICT ATLAS[b]	256		180,000

[a] personal communication from Dr. Levesque; [b] unpublished work.

3 Thermodynamic Properties and Intermolecular Forces

A. One-component Systems.—Computer 'experiments' on systems of hard spheres have confirmed the intuitively plausible proposition that for such systems there exists only a solid and a gas-like phase.[4] In the absence of cohesive forces there is no liquid phase, and a pair potential which allows for both cohesion and repulsion must be used in studies of the liquid state. In an important paper published in 1957 Wood and Parker[2] described the results of a series of calculations by the Monte Carlo method of thermodynamic properties of argon along a supercritical isotherm. They used the 12–6 potential:

$$\phi(r) = 4\epsilon\,[(\sigma/r)^{12} - (\sigma/r)^{6}] \qquad (4)$$

where r is the intermolecular separation, ϵ is the depth of the potential well at the minimum in $\phi(r)$, and σ (the 'collision diameter') is the value of r for which $\phi(r)$ is zero. The values chosen for the interaction parameters ϵ and σ were those deduced by Michels, Wijker, and Wijker[12] from measurements of the second virial coefficients at high temperatures, *viz.*, $\epsilon/k_B = 119{\cdot}8$ K and $\sigma = 3{\cdot}405$ Å. This work represented the first successful application of computer simulation to the study of a real fluid.

Extensive investigations of the thermodynamic properties of the 12–6 fluid have recently been carried out both by molecular dynamics[13] and by the Monte Carlo method.[14–17] There is good agreement between the two sets of

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[12] A. Michels, H. Wijker, and H. Wijker, *Physica*, 1949, **15**, 627.
[13] L. Verlet, *Phys. Rev.*, 1967, **159**, 98.
[14] L. Verlet and D. Levesque, *Physica*, 1967, **36**, 254.
[15] I. R. McDonald and K. Singer, *Discuss. Faraday Soc.*, 1967, **43**, 40.
[16] I. R. McDonald and K. Singer, *J. Chem. Phys.*, 1967, **47**, 4766.
[17] I. R. McDonald and K. Singer, *J. Chem. Phys.*, 1969, **50**, 2308.

results. Attention has been mostly centred on the calculation of pressure and internal energy as a function of density and temperature. Data on other thermodynamic properties, including specific heat, compressibility, and thermal pressure coefficient, have also been reported. The values of these latter quantities are determined by the magnitude of fluctuations in the potential energy and virial and it is sometimes difficult to attain a high accuracy. No serious problems are encountered in the calculation of pressure and internal energy in the liquid range except in the neighbourhood of a phase change. If the computer model contains several hundred or more particles there is a tendency for the system to separate into two phases in the region of the liquid–vapour transition. This leads to large fluctuations in the calculated properties. The isotherms display van der Waals loops and negative pressures are therefore obtained at sufficiently low temperatures and densities. In the melting region the isotherms generally have two distinct branches. One of these branches corresponds to the fluid state and the other corresponds to the solid. Near the critical point there is the additional complication that the small size of the model and the imposition of a periodic boundary condition suppress the large fluctuations in density which characterise the critical region in macroscopic systems. One effect of this is to increase the critical temperature of the 12–6 fluid in the computer model by *ca.* 7%[18] and another is that the specific heat is underestimated.[16]

The results obtained for the 12–6 potential with the parameters of Michels *et al.*[12] are found to agree closely with experimental properties of argon[19] throughout the range between the triple point (83·8 K) and the critical temperature (150·7 K) and also at higher temperatures. Figure 1, for example, shows the excellent agreement between the experimental equation of state and the molecular dynamics calculations of Verlet.[13] There are small systematic discrepancies between the experimental and calculated internal energies but these are removed if the depth of the potential well is reduced by only 2%.[17] The same computer results could be used to assess the adequacy of the 12–6 model for other simple liquids (*e.g.*, Kr, Xe, N_2, O_2, CO, CH_4) by application of the law of corresponding states and it is rather surprising that calculations of this type have not so far been reported.

Levesque and Vieillard-Baron[20] have carried out a series of calculations for other potentials and conclude that the 12–6 function provides the best correlation between computed and measured properties of argon. The success of this potential requires some explanation because it is known that the 12–6 function fails to account satisfactorily for the experimental low-temperature second virial coefficients of argon.[21] Furthermore, the coefficient of the r^{-6}

[18] D. Levesque and L. Verlet, *Phys. Rev.*, 1969, **182**, 307.

[19] (*a*) Clark, Din, Robb, Michels, Wassenaar, and Zwietering, *Physica*, 1951, **17**, 876; (*b*) F. Din, 'Thermodynamic Functions of Gases', vol. 2, Butterworths, London, 1956; (*c*) J. M. H. Levelt, *Physica*, 1960, **26**, 361; (*d*) A. Van Itterbeek, O. Verbeke, and K. Staes, *Physica*, 1963, **29**, 742; (*e*) W. van Witzenburg and J. C. Stryland, *Canad. J. Phys.*, 1968, **46**, 811; (*f*) R. K. Crawford and W. B. Daniels, *Phys. Rev. Letters*, 1968, **21**, 367; (*g*) W. B. Streett and L. A. K. Staveley, *J. Chem. Phys.*, 1969, **50**, 2302.

[20] D. Levesque and J. Vieillard-Baron, *Physica*, 1969, **44**, 345.

[21] Jones, Rowlinson, Saville, and Weir, *Trans. Faraday Soc.*, 1967, **63**, 1320.

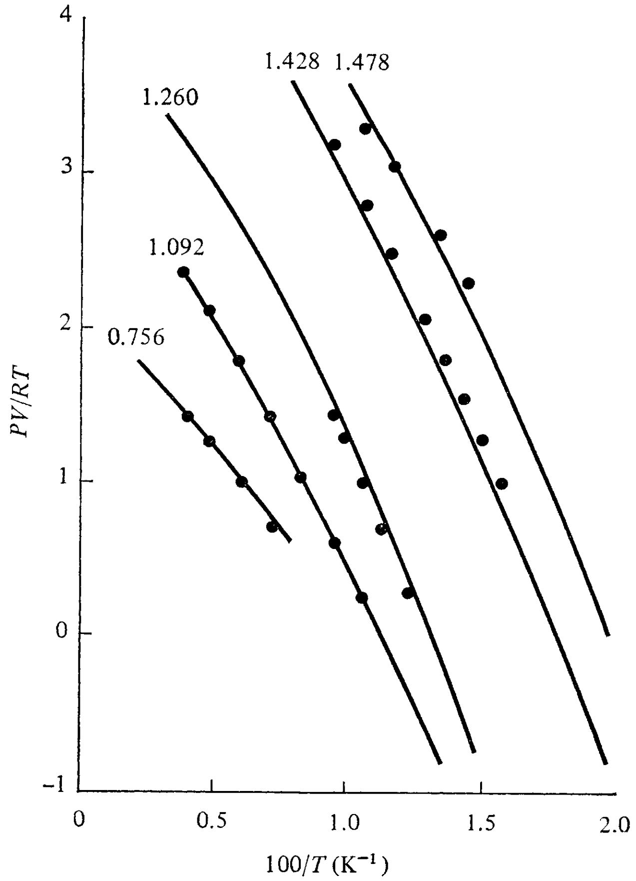

Figure 1 *Compressibility factor of argon as a function of inverse temperature for several isochores. The curves are the results of molecular dynamics calculations (ref.* 13) *based on the* 12–6 *potential with the parameters of Michels* et al. (*ref.* 12). *The curves are labelled with the density in* g cm^{-3}. *The dots are experimental data (refs.* 19*c, d, e)*

term (representing the London dispersion energy) in the empirical potential of Michels *et al.*[12] is larger than that predicted by quantum mechanical calculations by a factor of about two.[22, 23] Careful analysis of the experimental data shows clearly[22] that the true pair potential between argon atoms has a well which is narrower and deeper than that of the 12–6 potential and has a maximum depth of *ca.* 150 k_B K. The simplest proposed representation of the true pair interaction in argon is the Kihara core potential. This resembles the

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[22] J. A. Barker and A. Pompe, *Austral. J. Chem.*, 1968, **21**, 1683.

[23] J. S. Rowlinson, *Quart. Rev.*, 1954, **8**, 168.

12–6 potential except that the intermolecular separation is taken to be the distance between the surfaces of atomic hard cores. A third parameter is therefore introduced to describe the size of the atomic core. A number of more complicated, multi-parameter potentials have also been put forward.[22] Monte Carlo calculations based on the Kihara potential are found to lead to pressures and internal energies which are much lower than the experimental values for liquid argon.[17, 24] It seems plausible to ascribe these differences to the neglect of non-additive, *i.e.*, many-body interactions. On the other hand the 12–6 potential may be used to calculate the properties of argon accurately over a range of temperature and density which includes the solid, liquid, and gaseous states. This suggests that the form of the many body interactions is such as to lead to an effective pair potential which is almost state-independent and approximately of the 12–6 type. It is possible, however, that the calculation of equilibrium thermodynamic properties does not provide a very sensitive test of a proposed potential function and that a number of different functions will give satisfactory results if suitable values are chosen for the parameters.

For simple liquids at normal densities it is thought that the induced dipole–dipole–dipole interaction studied by Axilrod and Teller[25] is the dominant and probably the only important many-body effect. This interaction has a similar physical origin to the London dispersion force between a pair of molecules. Table 2 shows the results of Monte Carlo calculations[24] for liquid argon based on the Kihara potential with parameters derived from measured viscosities and second virial coefficients of the dilute gas.[26] Also shown are the contributions of triple-dipole forces estimated[24] from an analysis of small numbers (*ca.* 50 for each state) of Monte Carlo configurations. The sums of pair and three-body contributions are in very much better agreement with the experimental results than the values obtained from the Kihara potential alone but poorer than that obtained when the 12–6 function is used. The remaining discrepancies may result either from the neglect of other many-body forces or from inaccuracies in the assumed form of the true pair potential. At very

Table 2 *Contribution of triple-dipole forces to thermodynamic properties of argon*[24]

		U/RT					*PV/RT*				
T (K)	ρ (g cm^{-3})	*a*	*b*	*c*	*d*	*e*	*a*	*b*	*c*	*d*	*e*
87·9	1·390	−7·96	−8·53	+0·44	−8·09	−7·96	0·00	−1·99	+1·33	−0·66	−0·04
105·5	1·271	−5·94	−6·32	+0·28	−6·04	−5·92	0·02	−1·31	+0·83	−0·48	0·00
123·1	1·134	−4·45	−4·69	+0·18	−4·51	−4·48	0·05	−0·85	+0·54	−0·31	0·02
140·6	0·934	−3·16	−3·31	+0·10	−3·21	−3·14	0·11	−0·49	+0·30	−0·19	0·08

a, experimental values[19]; *b*, based on Kihara potential of ref. 26; *c*, contribution of triple-dipole forces; *d*, sum of columns *b* and *c*; *e*, based on 12–6 potential of ref. 17.

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[24] I. R. McDonald and L. V. Woodcock, *J. Phys.* (*C*), in the press.

[25] B. M. Axilrod and E. Teller, *J. Chem. Phys.*, 1943, **11**, 299.

[26] J. A. Barker, W. Fock, and F. Smith, *Phys. Fluids*, 1964, **7**, 897.

high densities non-additivity of the repulsive part of the pair potential is likely to be important. Theoretical work suggests[23] that the pair repulsion is more accurately described by an exponential function than by the r^{-12} term which appears in the 12–6 potential. An exp–6 potential, which has an exponential repulsion term and an inverse sixth power attraction term, has been used by Ross and Alder[27] to obtain results for argon by the Monte Carlo method for comparison with shock compression data. They conclude that for liquid argon, compressed two-fold non-additive effects act in such a way as to increase the repulsive part of the effective potential between pairs of molecules by *ca.* 30%. The results obtained from various studies of many-body interactions are by no means conclusive and much work remains to be carried out. Computer simulation may be expected to play an important rôle in such calculations.

B. Liquid Mixtures.—There exists only a limited number of liquid mixtures in which the molecules may be expected to interact according to the 12–6 potential. These are mixtures of the rare gases and of substances obeying the law of corresponding states. Even in such cases there is considerable uncertainty about the values to be used for the parameters which characterise the interaction between unlike molecules. These factors, together with a lack of reliable experimental data on some of the simple mixtures which do exist, have hampered the development of quantitatively satisfactory theories of mixtures. In the case of a mixture of two 12–6 liquids, A and B say, with interaction parameters ϵ_{AA}, σ_{AA} and ϵ_{BB}, σ_{BB} it is usual to assume that the potential between A–B pairs is described by a 12–6 function with parameters defined by the Lorentz-Berthelot rules:

$$\epsilon_{AB} = (\epsilon_{AA}\epsilon_{BB})^{\frac{1}{2}} \; ; \; \sigma_{AB} = \tfrac{1}{2}(\sigma_{AA} + \sigma_{BB}) \qquad (5)$$

The Monte Carlo method may be used to calculate thermodynamic properties of mixtures of 12–6 liquids over an arbitrary range of potential energy parameters. Apart from providing basic information on the properties of such mixtures the results may be used as quasi-experimental data in testing theories of mixtures. Alternatively the comparison of the computer results with measured values of the properties of mixtures should prove to be a reliable method for the determination of ϵ_{AB} and σ_{AB} in real systems.

The changes of pressure and internal energy on mixing at constant volume may be determined from Monte Carlo calculations for the pure components and for the mixture. The method of molecular dynamics is less useful here because the temperature at which a molecular dynamics ‘experiment’ is performed can not be accurately predicted in advance. As the mixtures under consideration are very nearly ideal it is in any case difficult to obtain accurate values of the excess properties. It therefore seems advisable to avoid the additional error which is introduced by uncertainties in the value of the temperature at which mixing takes place. If sufficient Monte Carlo data are obtained the

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[27] M. Ross and B. Alder, *J. Chem. Phys.*, 1967, **46**, 4203.

changes in volume and enthalpy at constant pressure may be determined by extrapolation. In order to calculate the change in free energy the initial and final states of the system are linked by a reversible path along which the potential parameters vary continuously, together with an ideal mixing process at an appropriate point in the path.

The excess Gibbs free energy G_E, enthalpy H_E, and volume V_E have been calculated[28] in this way for a series of liquid mixtures in which $\epsilon_{AA}/\epsilon_{BB}$ and σ_{AA}/σ_{BB} are varied systematically. A selection of the results which have been obtained are shown in Table 3. The cross-interaction parameters are calculated from the Lorentz–Berthelot rules and have the same values in all cases, *viz.*, $\epsilon_{AB}/k_B = 133{\cdot}5$ K and $\sigma_{AB} = 3{\cdot}596$ Å. These are values appropriate to the cross-interaction between molecules of argon and methane. It is possible to make a number of generalisations on the basis of these calculations. Perhaps the most interesting result is that the excess properties of mixtures of molecules which differ only in size (*i.e.*, $\epsilon_{AA}/\epsilon_{BB} = 1$) are very small. This is in agreement with the conclusion reached on different grounds by Leland, Rowlinson, and Sather.[29] The excess energy is positive when the ratios $\epsilon_{AA}/\epsilon_{BB}$ and σ_{AA}/σ_{BB} vary in opposite senses. When they vary in the same sense the excess free energy goes through a negative minimum when plotted as a function of $\epsilon_{AA}/\epsilon_{BB}$. The depth of this minimum becomes greater as the ratio σ_{AA}/σ_{BB} increases. The excess volume is negative in all cases.

Table 3 also shows results of calculations based on the 'one-fluid' (1f) and 'two-fluid' (2f) versions of the Average Potential Model (APM) developed by Prigogine and his collaborators[30, 31] and the recently proposed van der Waals approximation (vdW)[29, 32] In the 'one-fluid' versions of both theories the properties of the mixture are assumed to be those of an imaginary pure liquid characterised by the average potential parameters $\tilde{\epsilon}$, $\tilde{\sigma}$. In the 'two fluid' versions the properties of the mixture are those of an ideal mixture of two imaginary pure components, the molecules of which experience average potentials described by the parameters $\tilde{\epsilon}_1$, $\tilde{\sigma}_1$ and $\tilde{\epsilon}_2$, $\tilde{\sigma}_2$. The two theories differ in the recipe for the determination of the average potential parameters. In the APM theory the averaging is based on the assumption of random mixing whereas in the van der Waals approximation it is carried out in the spirit of the original proposal for the calculation of the van der Waals constants for fluid mixtures. For mixtures of molecules of equal size the two theories are identical and agree well with the Monte Carlo calculations. In other cases the computer results strongly favour the van der Waals theory and, perhaps surprisingly, the 'one fluid' version is somewhat superior to the 'two fluid' model.

The extrapolation to constant pressure of Monte Carlo data obtained at

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[28] K. Singer, *Chem. Phys. Letters*, 1969, **3**, 164. The data in Table 3 differ from the original as it contains errors which will be corrected.

[29] T. W. Leland, J. S. Rowlinson, and G. A. Sather, *Trans. Faraday Soc.*, 1968, **64**, 1447.

[30] I. Prigogine, 'The Molecular Theory of Solutions', North-Holland Publishing Co., Amsterdam, 1957.

[31] A. Bellemans, V. Mathot, and M. Simon, *Adv. Chem. Phys.*, 1967, **11**, 117.

[32] Leland, Rowlinson, Sather, and Watson, *Trans. Faraday Soc.*, 1969, **65**, 2034.

Table 3 *Excess thermodynamic properties of equimolar mixtures of* 12–6 *liquids calculated by a Monte Carlo method.*[28]
$T = 97$ K, $P = 0$; $\epsilon_{AB}/K_B = 133{\cdot}5$ K, $\sigma = 3{\cdot}596$ Å.

σ_{AA}/σ_{BB}		1·000	1·062	1·062	1·062	1·128	1·128	1·128
$\epsilon_{AA}/\epsilon_{BB}$		1·235	0·810	1·000	1·235	0·810	1·000	1·235
G_E	MC	34·7	59·7	−2·4	3·2	83·1	−7·0	−29·0
(J mol^{-1})	APM1f	37·9	139	96	129	410	357	381
	APM2f	34·7	85·5	48	80·6	227	185	211
	vdWlf	37·9	67·7	−1·8	4·0	92·7	0	−34·3
	vdW2f	34·7	49·2	−0·8	17·7	61·3	−4·8	− 2·4
H_E	MC	35	72	6	−11	125	24	−39
(J mol^{-1})	APM1f	31	177	146	175	607	566	582
	APM2f	48	121	73	119	337	286	327
	vdW1f	31	74	0	−12	117	0	−55
	vdW2f	48	68	0	27	90	0	4·8
V_E	MC	−0·13	−0·25	−0·01	−0·09	−0·36	−0·02	− 0·05
(cm^{3}mol^{-1})	APM1f	−0·16	0·03	0·048	0·60	1·24	1·97	2·33
	APM2f	−0·07	−0·04	0·21	0·32	0·44	0·86	1·09
	vdW1f	−0·16	−0·28	−0·04	−0·13	−0·49	−0·18	− 0·19
	vdW2f	−0·07	−0·20	−0·04	−0·04	−0·41	−0·18	− 0·11

Estimated (mean) accuracy of the MC data: G_E : ± 6, H_E : ± 20, V_E : ± 0·08 constant volume may be a source of error if the changes in volume are large. One way of avoiding this difficulty, though it requires more machine time, lies in the use of Monte Carlo calculations in the *NPT*-ensemble. The pressure of mixing is then a fixed parameter. Excess functions for 12–6 mixtures corresponding to some real systems (A + Kr, A + N_2, A + CH_4, CO + CH_4) have been computed by this method.[10, 11] The results again strongly favour the van der Waals approximation. Agreement with experimental values, on the whole, is poor. This is almost certainly due to departures from the Lorentz–Berthelot rules in real systems. Recent work[32] has shown that even in the simplest mixtures the value of ϵ_{AB} is *ca.* 1% less than that given by the geometric mean of ϵ_{AA} and ϵ_{BB}. Such a change would be sufficient to bring the calculated excess properties into agreement with measured values.

C. Phase Equilibria.—Phase equilibria in one-component systems are determined by the equality of the Gibbs free energy per mole of the two phases at a given temperature and pressure. In order to compare the free energies of two fluid phases by means of the usual basic data obtained in a computer experiment, *i.e.*, $U(V, T)$ and $P(V, T)$, it is necessary to link the two states by a reversible path along which the change of A (Helmholtz free energy), and hence of G (Gibbs free energy), can be evaluated by numerical integration. In this way one could, for example, determine the change of G along the stable isochores and isotherms:

$$V_l\,, T \rightarrow V_l\,, T' \rightarrow V_g\,, T' \rightarrow V_g\,, T$$

where T' is a supercritical temperature and the suffixes l and g denote, respectively, liquid and gas. For the computer model there is the additional possibility of integrating along the unstable isotherm $V_l\,, T \rightarrow V_g\,, T$ on which the $P(V, T)$ data exhibit van der Waals loops. This is the method adopted in the Monte Carlo calculations of Hansen and Verlet.[33] (Molecular dynamics is less convenient to use here because changes along an isotherm are required.) Very large pressure fluctuations and slow convergence of the average values were encountered in the unstable part of the isotherm. This difficulty, which arises because of the tendency of the system to separate into two phases, was overcome by the deliberate suppression of large inhomogeneities within the model. Subsequent calculations revealed that this somewhat arbitrary removal of accessible configurations, while greatly improving the statistical convergence, had no effect on the calculated pressures. When the change of G along the isotherm is known, the liquid–vapour coexistence line can be determined because it is then possible to relate the free energy of either phase to that of the dilute gas.

The method described above cannot be used to investigate the solid–vapour and solid–liquid transitions because the lattice arrangement disappears irreversibly on expansion. Hansen and Verlet[33] therefore used an approach

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[33] J. P. Hansen and L. Verlet, *Phys. Rev.*, in the press.

due to Hoover and Ree[34] in which the computer model is expanded in such a way that the particles are constrained to remain within the expanded lattice cells. The pressure is calculated at different volumes and when a density corresponding to the dilute gas is reached the walls of the lattice cells are removed. The only effect of this last step is the appearance of the communal entropy, equal to Nk_B. The changes of A up to and beyond this point are evaluated by the integration of $P(V)\,dV$. By combining these data with the free energies of the fluid phases which were calculated in treating the liquid–vapour

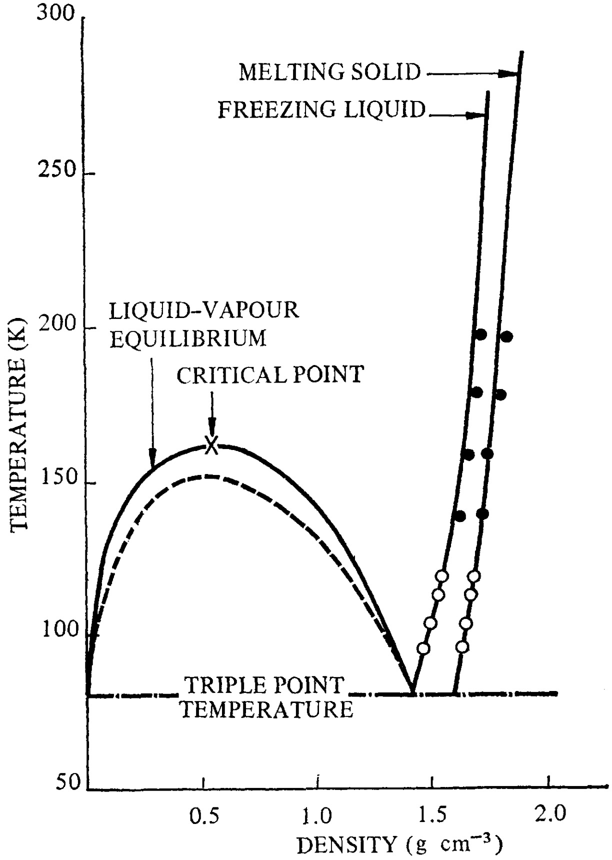

Figure 2 *Solid–liquid–vapour phase diagram for argon. The full curves are the results of Monte Carlo calculations (ref.* 33) *based on the* 12–6 *potential of Michels* et al. *(ref.* 12). *The dashed curve is the experimental liquid–vapour coexistence line (ref* 19*a*). *The open circles and dots are experimental melting data (refs.* 19*e*,*f*)

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[34] W. G. Hoover and F. H. Ree, *J. Chem. Phys.*, 1967, **47**, 4873.

transition it is possible to determine the melting curve. Hoover and Ree[35] have themselves used the cell expansion method to establish the existence of a first-order solid–fluid transition for hard sphere molecules. The solid–liquid–vapour phase diagram for the 12–6 potential of Michels *et al.*[12] is shown in Figure 2. Agreement with experimental data for argon is good except in the critical region where, as has already been remarked, the effect of the suppression of large-scale density fluctuations in the computer model is to raise the critical temperature. This work is important, not only because it supplies additional proof of the surprising excellence of the 12–6 potential for argon, but because it also shows that the quantitative study of phase equilibria by computer simulation is possible.

4 Radial Distribution Function and Liquid Structure

The structure of a simple liquid is usually described in terms of the radial distribution function. Let $n(r)$ be the number of particles situated at a distance between r and $(r + \Delta r)$ from a reference particle. The radial distribution function $g(r)$ is defined as

$$g(r) = (\mathrm{v}/N)\,[n(r)/4\pi r^2 \Delta r] \tag{6}$$

If the intermolecular potential is spherically symmetric and pair-wise additive, then the internal energy, pressure and other thermodynamic properties which can be derived from these may be calculated if $g(r)$ is known as a function of density and temperature. The calculation of the radial distribution function is therefore a fundamental problem in the statistical thermodynamics of simple liquids. Several theories have been proposed in which $g(r)$ is obtained from the intermolecular potential function by solving an integral equation.[36] The most successful of these, at least at high temperatures, is that of Percus and Yevick.[37]

The structure factor $S(\mathbf{k})$ for the liquid is defined in terms of $g(r)$ through a Fourier transform:

$$S(\mathbf{k}) = 1 + \tilde{h}(\mathbf{k}) = 1 + (N/\mathrm{v}) \int_{\mathrm{v}} e^{-i\mathbf{k}\cdot\mathbf{r}}\,[g(r) - 1]\,d\mathbf{r} \tag{7}$$

The importance of $S(\mathbf{k})$ arises from the fact that (for $\mathbf{k} \neq 0$) it is proportional to the differential cross-section for scattering of electromagnetic radiation.[38] The quantity $\mathbf{k}$ is the difference in wave vector between the incident and scattered radiation, though in liquids the structure factor is a function only of the magnitude of $\mathbf{k}$. Neutron and *X*-ray scattering experiments are therefore valuable sources of information on the radial distribution function in liquids. Alternatively, the usual form of the Percus–Yevick or some other integral equation may

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[35] W. G. Hoover and F. H. Ree, *J. Chem. Phys.*, 1968, **49**, 3609.

[36] G. S. Rushbrooke, 'Physics of Simple Liquids', ed. H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, North-Holland Publishing Co., Amsterdam, 1968.

[37] J. K. Percus and G. J. Yevick, *Phys. Rev.*, 1958, **110**, 1.

[38] P. A. Egelstaff, 'An Introduction to the Liquid State', Academic Press, London, 1967.

be inverted to allow the derivation of the pair potential in a liquid from measured scattering intensities. Work of this type has been reported both for argon[39] and for liquid metals.[40] In the latter case the calculation leads to an effective ion–ion interaction potential. Some of the difficulties associated with this potential inversion problem are discussed below.

The radial distribution function for liquid argon shown in Figure 3 is taken from the early work of Wood, Parker, and Jacobson[3] in which the 12-6

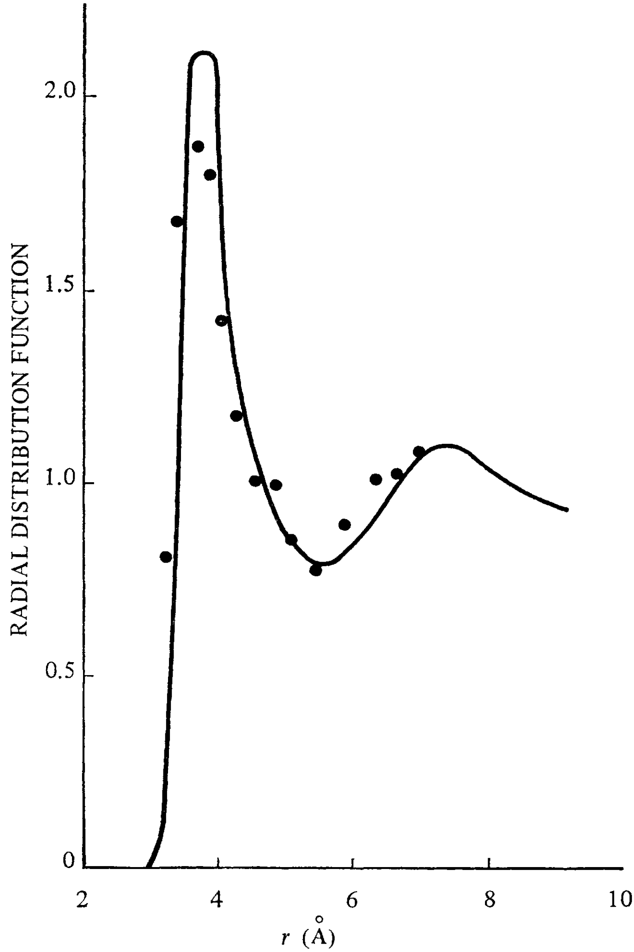

Figure 3 *Radial distribution function for liquid argon at* $T = 126{\cdot}7$ K, $\rho = 1{\cdot}099$ g cm^{-3}. *The curve shows the results of a Monte Carlo calculation* (*ref.* 3) *based on the* 12–6 *potential of Michels* et al. (*ref.* 12). *The dots are results from* X-*ray scattering experiments* (*ref.* 41)

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[39] P. G. Mikolaj and C. J. Pings, *J. Chem. Phys.*, 1967, **46,** 1412.

[40] (*a*) M. D. Johnson, P. Hutchinson, and N. H. March, *Proc. Roy. Soc.*, 1964, *A*, **282,** 283; (*b*) P. Ascarelli, *Phys. Rev.*, 1966, **143,** 36.

potential of Michels *et al.*[12] was used. The main peak in g (r) represents a shell of nearest neighbours and a peak corresponding to a second shell may also be seen. Agreement with the experimental curve derived from X-ray scattering data by Eisenstein and Gingrich[41] is qualitatively good but quantitatively is rather poor. The radial distribution function and structure factor of the 12–6 fluid have since been calculated by Verlet by means of the method of molecular

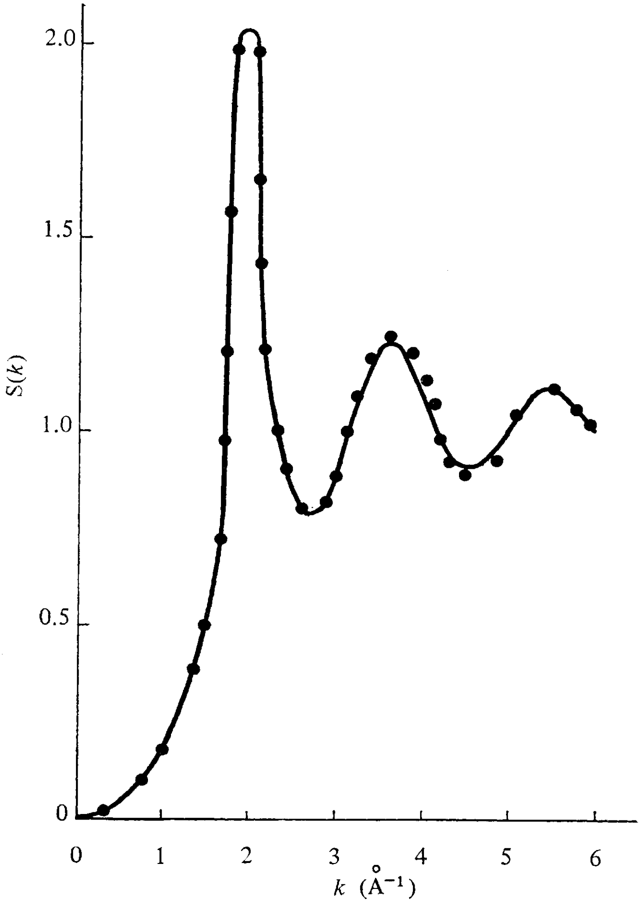

Figure 4 *Structure factor of liquid argon at* $T = 99{\cdot}1$ K, $\rho = 1{\cdot}260$ g cm^{-3}, *obtained from a molecular dynamics calculation (ref.* 42) *based on the* 12–6 *potential with the parameters of Michels* et al. (*ref.* 12). *The dots are the results of neutron scattering experiments* (*ref.* 43) *on liquid krypton in a nearly-corresponding state*

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[41] A. Eisenstein and N. S. Gingrich, *Phys. Rev.*, 1942, **62**, 261.

dynamics.[42] These calculations cover a wide range of density and temperature. At high densities the structure factor has the characteristic shape shown in Figure 4. The curve is dominated by a large peak at $k_0 = 2\pi/r_0$, where r_0 is approximately equal to the value of σ in the 12–6 potential. From the properties of the Fourier transform it follows that the peak in $S(\mathbf{k})$ is responsible for the oscillations in $g(r)$ and that the position of this peak determines the period $r_0 = 2\pi/\mathbf{k}_0$ of the oscillations. The value of r_0, which has the character of a hard core, decreases slowly with increasing density but is almost independent of temperature. Verlet[42] shows that the main features of the structure factor of the 12–6 fluid are accurately reproduced by a hard sphere model in which the only adjustable parameter is the diameter of the hard spheres. These results emphasise the importance of the repulsive part of the potential in determining the form of the radial distribution function and show that the structure of a simple liquid is determined primarily by geometric effects arising from the presence of a hard core.

The adequacy of the Percus–Yevick approximation may be tested by comparing the theoretical radial distribution function with those obtained in computer 'experiments'. A more illuminating test of the theory is provided by solving the potential inversion problem in order to recover the 12–6 potential from the structure factors computed by Verlet. It is found that at densities near the critical point the potential calculated from the Percus–Yevick equation has a bowl which is *ca.* 1% shallower than that of the 12–6 function used in the molecular dynamics 'experiments'. The error increases rapidly as the density rises and it is concluded that the Percus–Yevick theory cannot be used to obtain quantitatively reliable information on the two-body interaction in dense systems.

Figure 4 shows that there is good agreement between the structure factor calculated by computer simulation and the results of neutron scattering experiments on liquid krypton.[43] It is found, in particular, that the neutron data lead to structure factors which display the regular oscillations at high $\mathbf{k}$ values which are a prominent feature of the computer results. The structure factors obtained from *X*-ray scattering experiments[44] show a more erratic behaviour and agreement with the molecular dynamics calculations is not so good. Levesque and Verlet[45] suggest that the available *X*-ray data contain some systematic errors.

The radial distribution function is concerned only with pair correlations and therefore falls some way short of providing a complete description of the structure of the liquid. Multiple correlations can in principle be studied by computer simulation but this requires an extremely large amount of computing time. An alternative method of analysis in terms of Voronoi polyhedra has been developed by Bernal for the study of his random close-packed hard sphere

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[42] L. Verlet, *Phys. Rev.*, 1968, **165**, 201.
[43] G. T. Clayton and L. Heaton, *Phys. Rev.*, 1961, **121**, 649.
[44] P. G. Mikolaj and C. J. Pings, *J. Chem. Phys.*, 1967, **46**, 1401.
[45] D. Levesque and L. Verlet, *Phys. Rev. Letters*, 1968, **20**, 905.

model of the liquid state.[46, 47] It may equally well be applied to the analysis of computer generated configurations. The Voronoi polyhedron for a particle *i* is the smallest closed convex polyhedron surrounding *i* which is formed by the set of planes which bisect the vectors linking *i* to all other particles. A typical two-dimensional 'Voronoi polygon' is shown in Figure 5. The construction is unique and the set of Voronoi polyhedra fill the whole volume occupied by the particles. The structural features of a system may be described in terms of various distributions including the number of faces of the polyhedra, the number of sides of the polygons which form these faces and the volume of the polyhedra. In liquid-type systems it is found[48, 49] that polyhedra with 14 or 15 faces and faces with five sides are dominant. This type of analysis is useful for the pictorial insight into the structure of the liquid which it provides, though it offers no

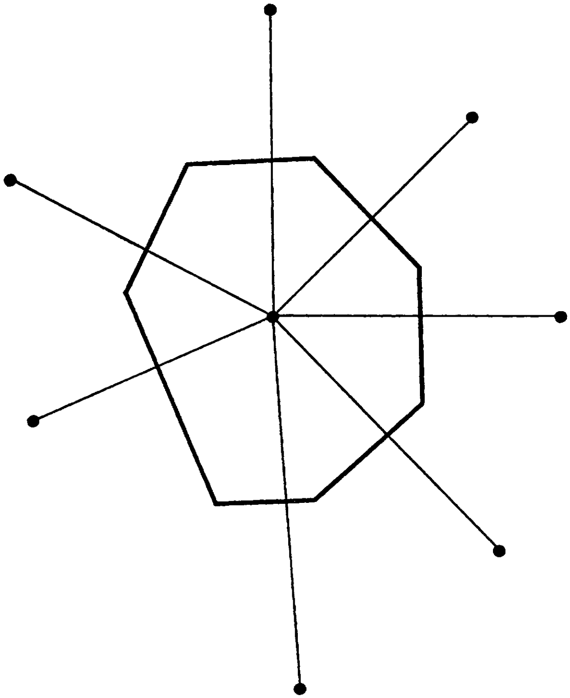

Figure 5 *A typical two-dimensional 'Voronoi polygon'. The dots represent particles of the fluid*

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[46] J. D. Bernal, *Proc. Roy. Soc.*, 1964, *A*, **280**, 299.
[47] J. D. Bernal and J. Finney, *Discuss. Faraday Soc.*, 1967, **43**, 62.
[48] J. Finney, Thesis, University of London, 1968.
[49] A. Rahman, *J. Chem. Phys.*, 1966, **45**, 2585.

obvious route to the calculation of thermodynamic properties. It also proves useful, as later discussion will show, in describing the process of diffusion.

5 Time-dependent Phenomena

The method of molecular dynamics permits the study of microscopic time-dependent phenomena in liquids to a degree of detail which experimental techniques cannot yet approach. In the early work of Alder and Wainwright,[6] for example, much attention was devoted to the problem of the rate at which a system of interacting particles approaches equilibrium starting from some arbitrary non-equilibrium state. The initial condition used most often was one in which the particle velocities are of equal magnitude but have different directions. The results revealed a marked difference between the behaviour of hard spheres and particles interacting through potentials more representative of real systems. For hard spheres the equilibrium Maxwell velocity distribution develops extremely rapidly and is essentially complete after each particle has collided two to four times with its neighbours. This appears to be true at all densities. By contrast, for molecules interacting through a square well potential, a Maxwell distribution again appears after a short time but the mean velocity of this distribution then moves slowly to reach its final equilibrium value after *ca.* 60 collisions per particle. The reason for this difference in behaviour is that the attainment of equilibrium in systems with cohesive potentials requires the interchange of kinetic and potential energy. This is a relatively slow process. At equilibrium, the total energy being constant in a molecular dynamics calculation, the mean square fluctuations in kinetic and potential energy are equal.

The motion of particles in a system at equilibrium may be described in a variety of ways. Consider a particle i which at time $t = 0$ is located at a position $\mathbf{r}_i(0)$ and has a velocity $\mathbf{v}_i(0)$. The mean square displacement at a time t is defined as

$$\langle r^2 \rangle = (1/N) \left\langle \sum_{i=1}^{N} [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \right\rangle \tag{8}$$

and the velocity autocorrelation function Z (t) is defined as

$$Z(t) = (1/N) \left\langle \sum_{i=1}^{N} \mathbf{v}_i(0) \,.\, \mathbf{v}_i(t) \right\rangle \tag{9}$$

The form of the velocity autocorrelation function is determined by the rate at which the velocities of the particles change as a result of interactions with other particles. The angular brackets in equations (8) and (9) denote averages over an equilibrium ensemble of initial conditions. The two functions may also be defined in terms of a time average and in practice, in the molecular dynamics 'experiment', the averages are calculated by considering a number of different time origins.

Both the mean square displacement and the velocity autocorrelation function are related to the process of diffusion in the liquid. Thus the coefficient of self-diffusion D may be expressed in terms of $Z(t)$ by the equation

$$D = \int_0^\infty Z(t)\,dt \tag{10}$$

The function $Z(t)$ is equal to one at $t = 0$ and decays to zero as time advances and the memory of the initial conditions is lost. Figure 6 shows the velocity

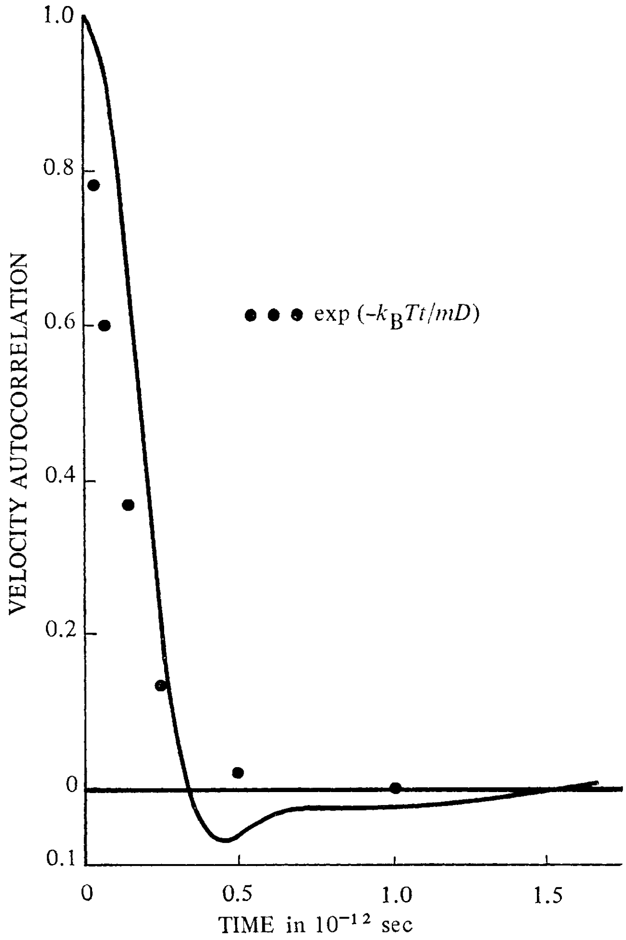

Figure 6 *Velocity autocorrelation function for liquid argon at* $T = 94{\cdot}4$ K, $\rho = 1{\cdot}374$ g cm^{-3}, *obtained from a molecular dynamics calculation (ref. 50) based on a 12–6 potential (see text). The dots show the Langevin type of velocity autocorrelation* (m *is the atomic mass*)

autocorrelation for liquid argon calculated by Rahman[50] from a 12–6 potential ($\epsilon/k_B = 120$ K, $\sigma = 3{\cdot}4$ Å) by the method of molecular dynamics. The autocorrelation decays to zero in *ca.* 2×10^{-12} sec but the most striking feature of the curve is that $Z(t)$ becomes negative after $0{\cdot}33 \times 10^{-12}$ sec and remains essentially negative as the decay goes to zero. The physical significance of a negative autocorrelation is that it represents 'back scattering' of particles.[6] At sufficiently high densities a particle is trapped for a time within a cage formed by its neighbours. The motion of the particle is therefore characterised by frequent reversals of velocity within a narrow range of angles. This results in a negative correlation or anti-correlation of velocity. In the extreme case of an harmonic oscillator $Z(t)$ is a cosine curve. It is clear that simple oscillation does not contribute to self-diffusion and inspection of equation (10) confirms that the effect of negative regions in $Z(t)$ is to reduce the value of D.

The behaviour of $\langle r^2 \rangle$ as a function of time for the system studied by Rahman[50] is shown in Figure 7. The slope of the linear portion of the graph is proportional to the coefficient of self-diffusion. Thus D may be calculated by means of the equation

$$\mathop{\mathrm{Lt}}_{t \to \infty} \langle r^2 \rangle = 6Dt + C \tag{11}$$

where C is a constant. Figure 7 shows that this asymptotic behaviour is already reached at 10^{-12} sec. The calculated value of D is $2{\cdot}43 \times 10^{-5}$ cm^2 sec^{-1}, which is *ca.* 15% lower than the experimental value for argon at the same temperature and density. Agreement with experiment is improved when an exp–6 potential is used.[49] It may also be seen from Figure 7 that the root mean square displacement after $2{\cdot}5 \times 10^{-12}$ sec [by which time $Z(t)$ is effectively zero] is only 1·9 Å. This is approximately one-half the nearest neighbour distance in the liquid. The persistence of short range order which is suggested by this result may be described more precisely by means of a time-dependent pair correlation function $G_d(r, t)$. Let $n(r, t)$ be the number of particles situated at time t at a distance between r and $(r + \Delta r)$ from the position occupied by a reference particle at $t = 0$. Then $G_d(r, t)$ is defined as

$$G_d(r, t) = (v/N)\,[n(r, t)/4\pi r^2 \Delta r] \tag{12}$$

The subscript d (symbolising 'distinct') indicates that the reference particle is not included in the number $n(r, t)$. The function $G_d(r, 0)$ is equivalent to the radial distribution function $g(r)$. Rahman[50] finds that the height of the first peak in $G_d(r, t)$ for liquid argon at 94·4 K at $t = 0$, 1, and $2{\cdot}5 \times 10^{-12}$ sec is, respectively, 2·8, 1·5, and 1·1. Remnants of the first shell of neighbours therefore persist for at least $2{\cdot}5 \times 10^{-12}$ sec.

Fluctuations in short range order are closely related to the phenomenon of self-diffusion. Rahman[49] shows that for liquid argon near the triple point the decay time τ of the fluctuations in the shape of the Voronoi polyhedra is *ca.* $0{\cdot}5 \times 10^{-12}$ sec. In this time interval the particle tends to 'slip' along the

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[50] A. Rahman, *Phys. Rev.*, 1964, **136**, A405.

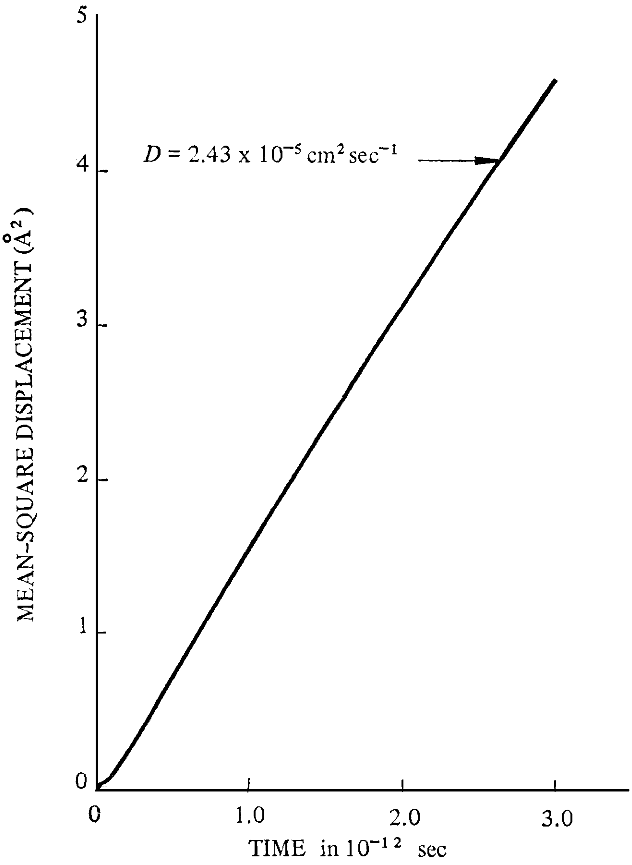

Figure 7 *Mean-square displacement of atoms in liquid argon (ref. 50). For details of the calculation see caption to Figure 6*

direction corresponding to the elongation in the polyhedron to which the fluctuations give rise. As these fluctuations result from the correlated motion of many particles it is clear that this description is one truly appropriate to the liquid state and does not rely on concepts borrowed from the study of gases or solids. The direction along which a particle moves in the decay time τ may be used to resolve the total velocity autocorrelation into two parts corresponding to 'slipping' and 'rattling' motion of the particles. Thus

$$Z(t) = S_\tau(t) + R_\tau(t) \tag{13}$$

where $S_\tau(t)$ (the 'slipping' part) is the autocorrelation of the component of velocity parallel to the direction of displacement in the time τ and $R_\tau(t)$ (the 'rattling' part) is the autocorrelation of the velocity component perpendicular to this direction. The function $S_\tau(t)$ may be further resolved into two parts, $S_\tau^+(t)$ and $S_\tau^-(t)$, which represent the contributions of particles which at $t = 0$ are moving, respectively, with a positive velocity component along the direction of displacement in the time interval τ and with a positive velocity component in the opposite direction. Both $S_\tau^-(t)$ and $R_\tau(t)$ represent an oscillatory type of motion. Figure 8 shows this resolution for a system representing argon at 85·5 K. The sum $[R_\tau(t) + S_\tau^-(t)]$ decays to zero in *ca.* 10^{-12} sec after passing through a deep negative minimum. The motion described by these components of the total velocity autocorrelation contributes little to the process of self-diffusion and is analagous to the vibrations of atoms

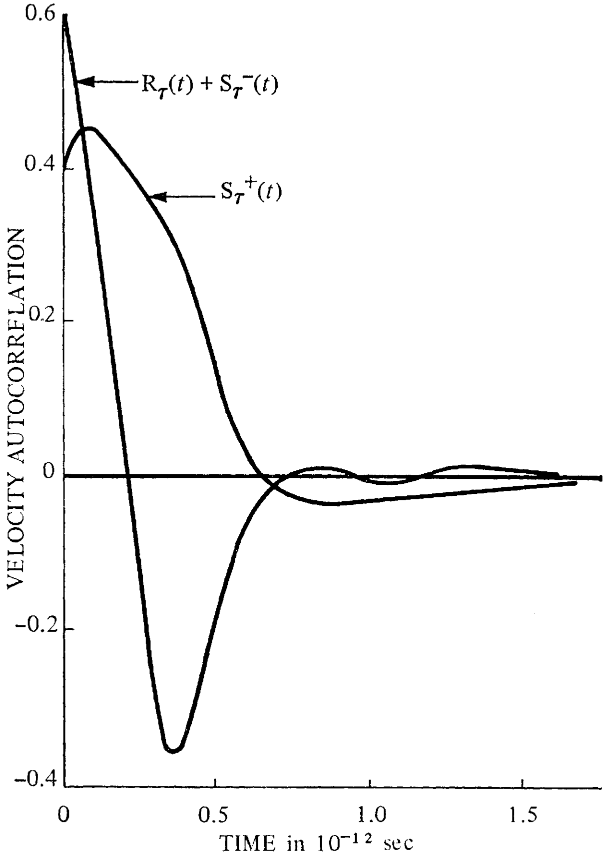

Figure 8 *Components of the velocity autocorrelation function for liquid argon corresponding to 'slipping' and 'rattling' motion of the atoms. The curves are obtained from a molecular dynamics calculation (ref.* 49) *at* $T = 85·5$ K, $\rho = 1·407$ g cm^{-3}, *based on an* exp–6 *potential*

in an anharmonic solid. The function $S_T^+(t)$ decays more slowly and becomes only weakly negative. The major contribution to D comes from this component of $Z(t)$.

Other transport properties, including viscosity and thermal conductivity, may be expressed in terms of appropriate time-correlation functions.[51] These could be calculated in a molecular dynamics 'experiment'. The tumbling motion of diatomic molecules may also be characterised by various correlation functions. Harp and Berne have recently calculated the angular momentum autocorrelation function for liquid carbon monoxide by molecular dynamics.[52] The autocorrelation has an oscillatory behaviour but the detailed structure of the function is dependent on the strength of the non-central part of the pair potential used in the calculations. The angular momentum autocorrelation is important in determining the shape of n.m.r. signals in liquids. Similarly, the i.r. and Raman spectra for diatomic molecules are related to the form of the autocorrelation functions which describe the rotation of the molecular axis.[53] The importance of time-correlation functions in statistical mechanics makes it certain that more work of this type will be carried out.

6 Final Remarks

Computer simulation has also been used in studies of a number of other systems. Monte Carlo calculations of thermodynamic properties of liquid water,[54] based on a rather simple pair potential, and of liquid potassium chloride,[55] based on potentials which are the sums of an exp–6 function and a Coulomb term, have been briefly reported. Systems of hard ellipsoidal particles,[56] which can serve to simulate the properties of liquid crystals, and the pair correlation function in liquid metals[57] have also been studied. The equilibrium number of lattice defects in solid argon has been determined[58] by a method which could be generalised to yield absolute chemical potentials in liquids and liquid mixtures.

Work on increasingly complex systems including, for example, ionic solutions will no doubt be carried out in the near future; and it is probable that what has been achieved for the system of 12–6 molecules, *i.e.*, a knowledge of the thermodynamic properties including the phase diagram, will also be achieved for systems in which less simple pair potentials are operative (*e.g.*, polar molecules). It is reasonable to hope that systematic work of this kind will lead to a thorough understanding of the relationship between the bulk properties of a system and the form of the intermolecular pair potentials. By contrast, the study of systems in which many-body forces cannot be treated as small

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[51] R. Zwanzig, *Ann. Rev. Phys. Chem.*, 1965, **16,** 67.

[52] G. D. Harp and B. J. Berne, *J. Chem. Phys.*, 1968, **49,** 1249.

[53] R. G. Gordon, *Adv. Magnetic Resonance*, 1968, **3,** 1.

[54] J. A. Barker and R. O. Watts, *Chem. Phys. Letters*, 1969, **3,** 144.

[55] L. V. Woodcock and K. Singer, 'Proceedings of the Culham Conference on Computational Physics', UKAEA Culham Laboratory and IPPS, 1969, Vol. 2, July, paper 25.

[56] D. Levesque, D. Schiff, and J. Vieilland-Baron, *J. Chem. Phys.*, 1969, **51,** 3625.

[57] A. Paskin and A. Rahman, *Phys. Rev. Letters*, 1966, **16,** 300.

[58] D. R. Squire and W. G. Hoover, *J. Chem. Phys.*, 1969, **50,** 701.

would make computational demands which, for some time to come, will be prohibitive. The same is true of time-dependent phenomena characterised by a relaxation time greater than, say, 10^{-8} sec.

No general method has as yet been devised for the computer simulation of non-classical systems. This is the most fundamental and, from the chemist's point of view, the most frustrating limitation. If this problem were to be solved it would be possible to examine in great detail all kinds of elementary chemical processes.